Karlsruhe Institute of Technology

Functionalization of Graphitic Carbon Materials and Control: Ab-inito Study

Velimir Meded

11 September 2013

Institute of Nanotechnology, Campus North, KIT

Team at KIT

- Institute of Nanotechnology (INT)

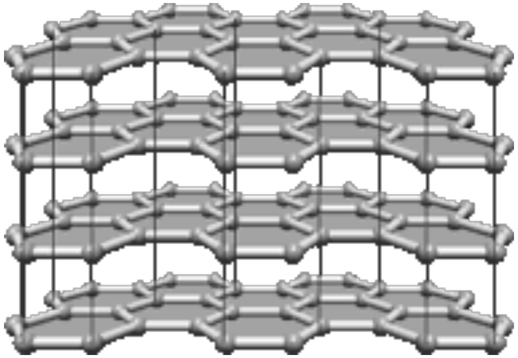
Pascal Friederich	OLED, Shredder Code
Paul Kleine	OLED, Shredder Code
Franz Symalla	**Intercalation of twisted graphene bilayers**
Tobias Neumann	Morphologies, DEPOSIT Code
Igor Beljakov	**Graphene based devices (*e.g.* Quantum Dots)**
Simon Widmaier	OLED, Morphologies
Denis Danilov	Morphologies, Organic Interfaces
Wolfgang Wenzel	

- Steinbuch Centre for Computing (SCC)

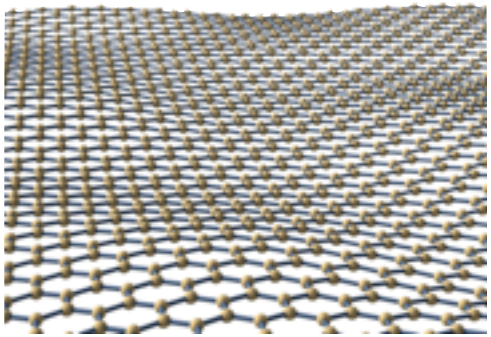
Angela Poschlad	**Polymer Wrapping of CNT, OLED**
Stefan Bozic	Workflow Generation, Grid-Beans
Ivan Kondov	Workflow, UNICORE, HTC

Introduction: Graphitic Carbon Materials

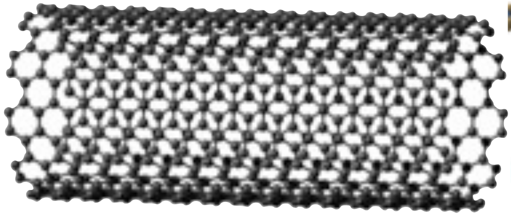
- *sp*^{2} carbon based structures can exist in 0 - 3 dimensions:
  - 3D – Graphite:



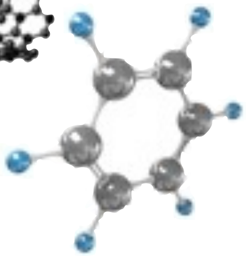
  - 2D – Graphene (Gr):

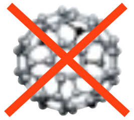


  - 1D – Carbon Nanotube (CNT):



  - 0D – Benzene Ring (~~Fullerenes~~):



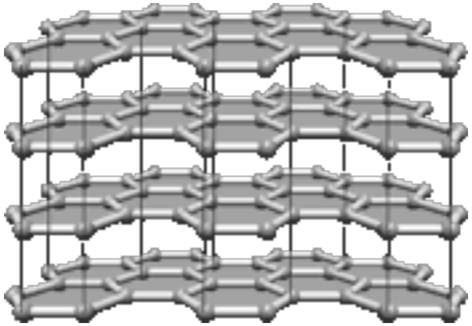


'off-topic'

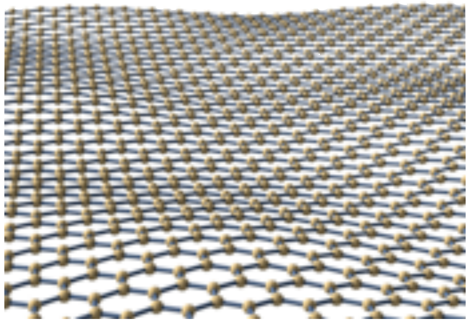
- And nearly infinite possibilities to combine them!

Outline: Design Possibilities

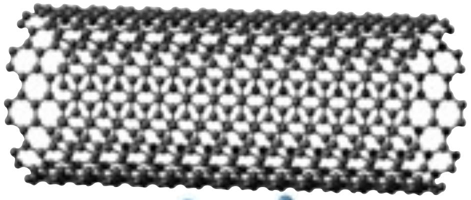
3D



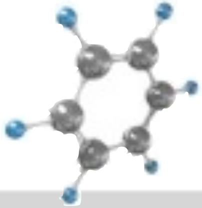
2D



1D

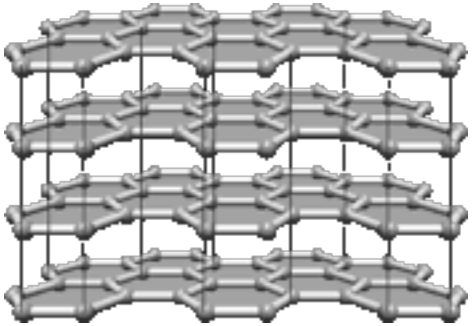


0D

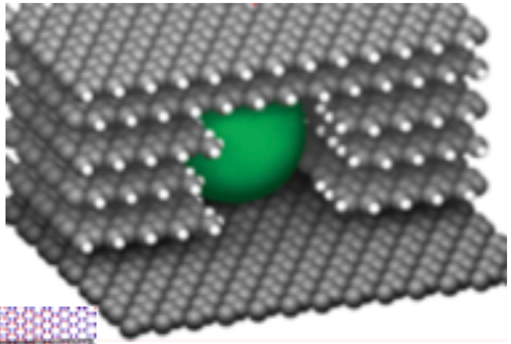


Outline: Design Possibilities

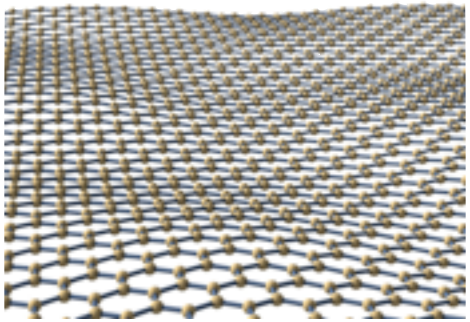
3D



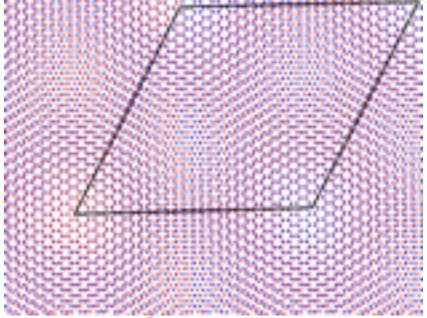
Nano-particle Etching of *Tunnels* in Graphite

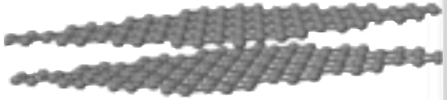


2D



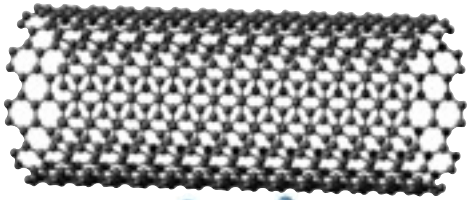
(Intercalated) Twisted Gr bilayer



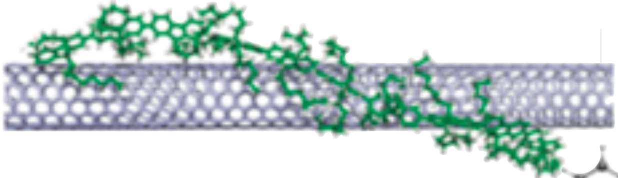


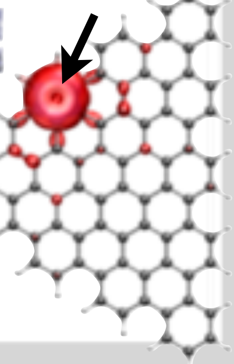
Moiré pattern

1D



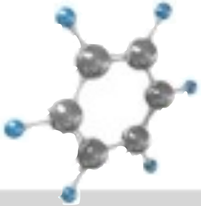
Selective Polymer Wrapping of CNT’s





Ru Adatom

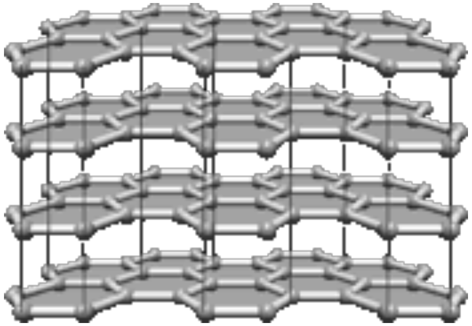
0D



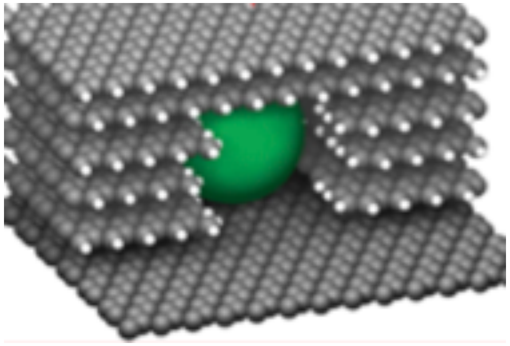
(Decorated) Graphene Flakes (Quantum Dots)

Subsurface etching of nanoscale channels in graphite

3D

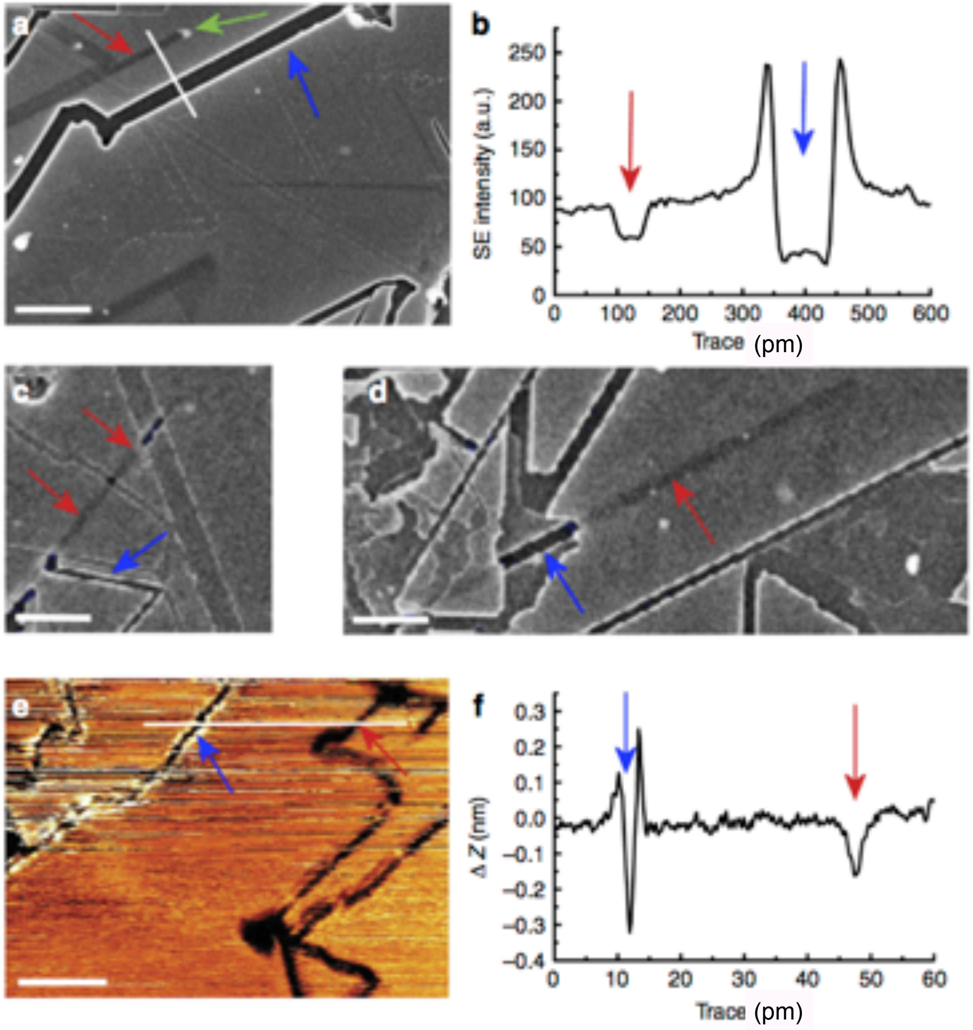


Nano-particle Etching of *Tunnels* in Graphite



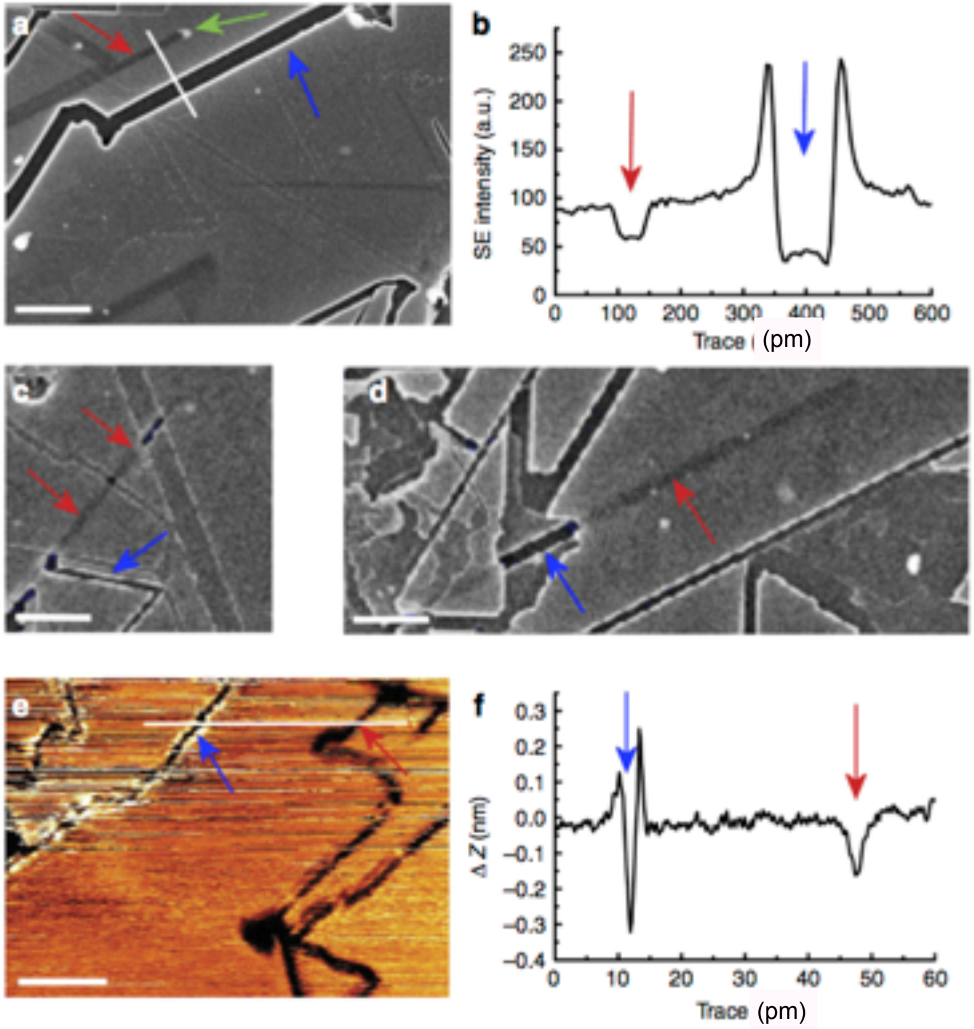
Subsurface etching of nanoscale channels in graphite

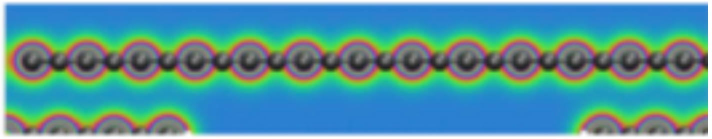
- Experimental evidence of nanoparticle ***tunnel*** etching in HOPG



Subsurface etching of nanoscale channels in graphite

- Experimental evidence of nanoparticle ***tunnel*** etching in HOPG

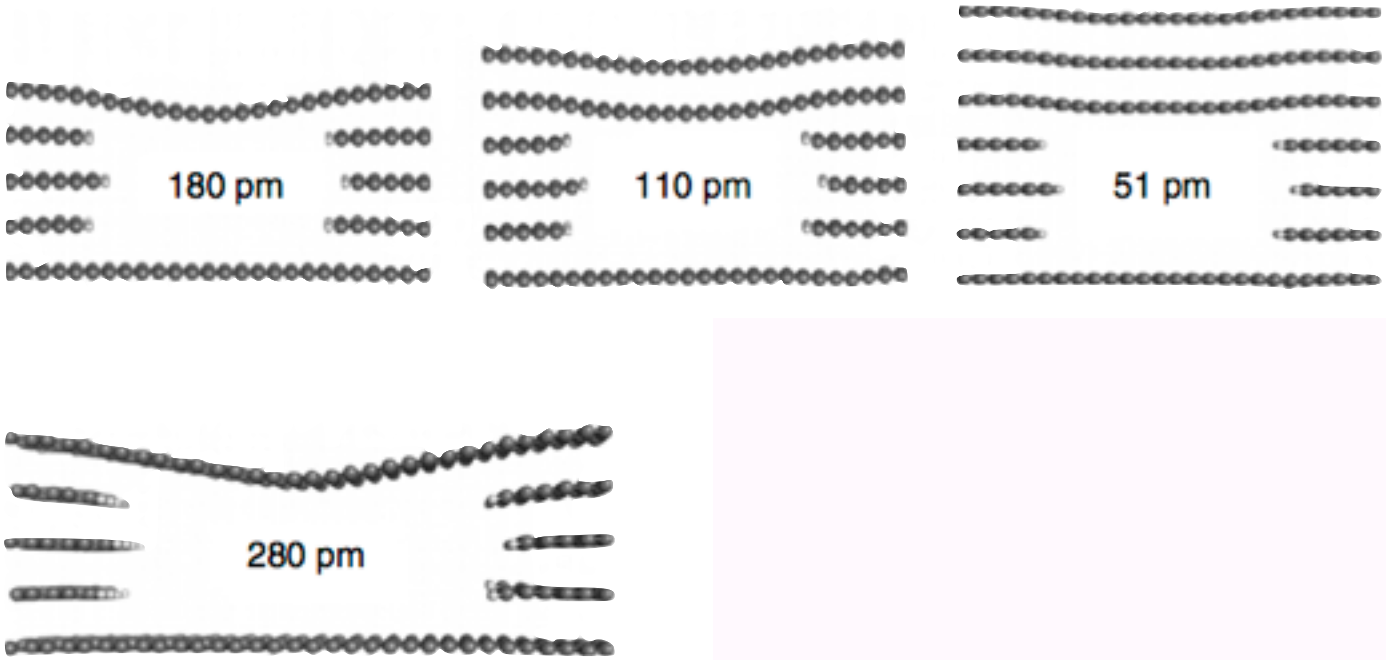




Uniform DFT electron density on the top layer

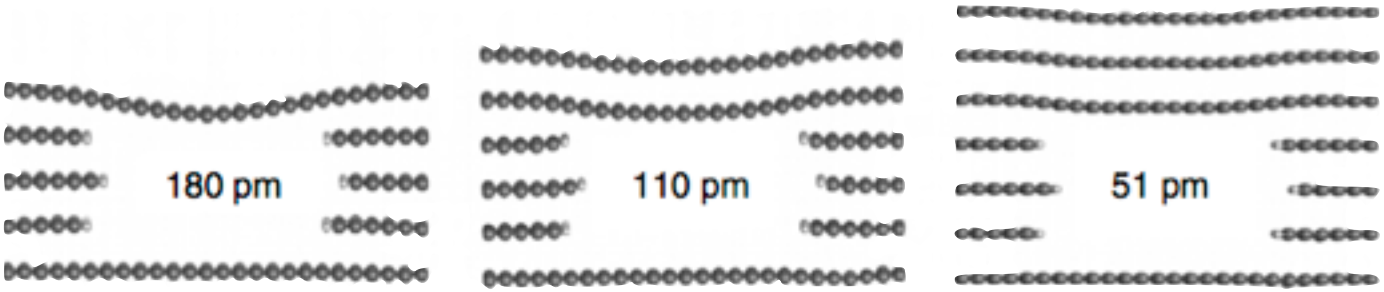
Subsurface etching of nanoscale channels in graphite

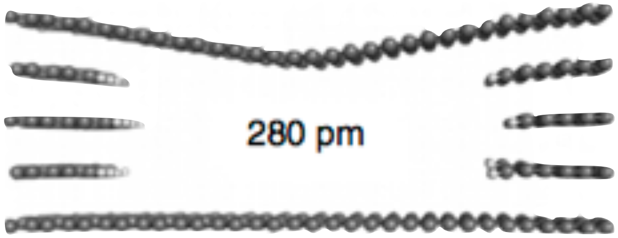
- Origin of the ‘smooth’ depression?
- Semi-empirical quantum chemical calculations point in direction of geometry relaxation.

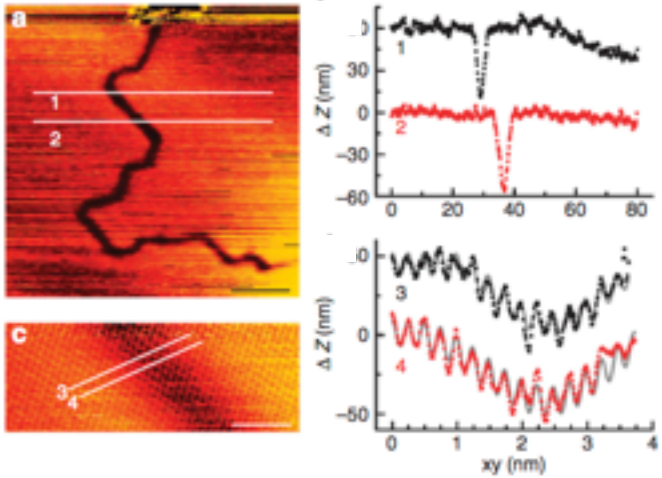


Subsurface etching of nanoscale channels in graphite

- Origin of the ‘smooth’ depression?
- Semi-empirical quantum chemical calculations point in direction of geometry relaxation.



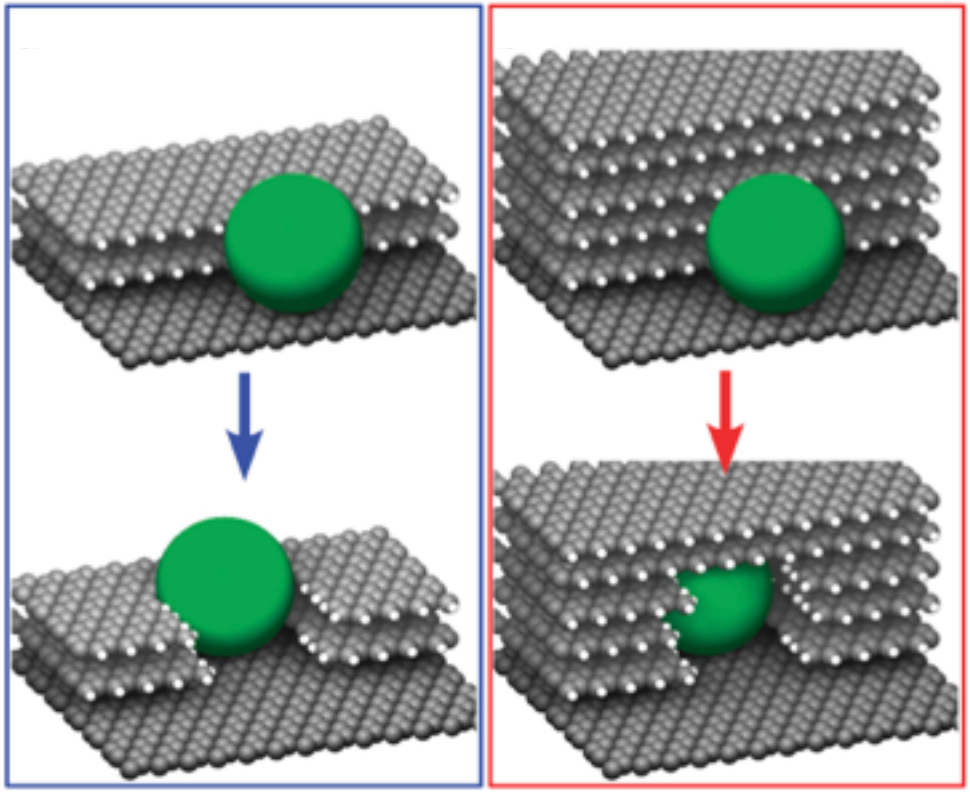




- Agrees very well with the STM images

Subsurface etching of nanoscale channels in graphite

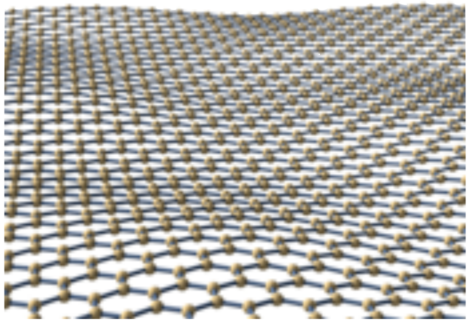
- The mechanism:



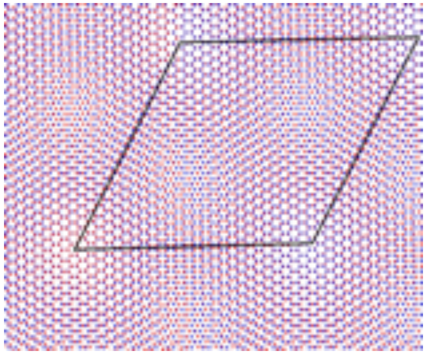
Nature Comm. **4**,1379 (2013)

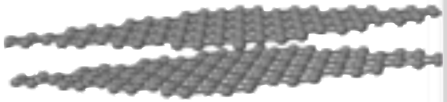
Bandgap Engeneering in twisted Graphene bilayers

2D



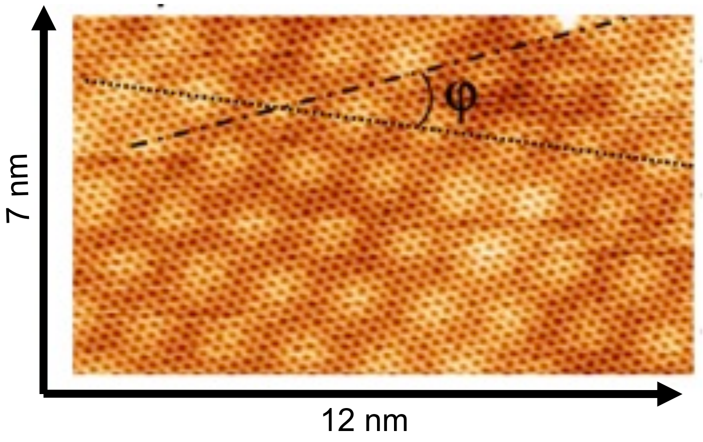
(Intercalated)
Twisted Gr bilayer



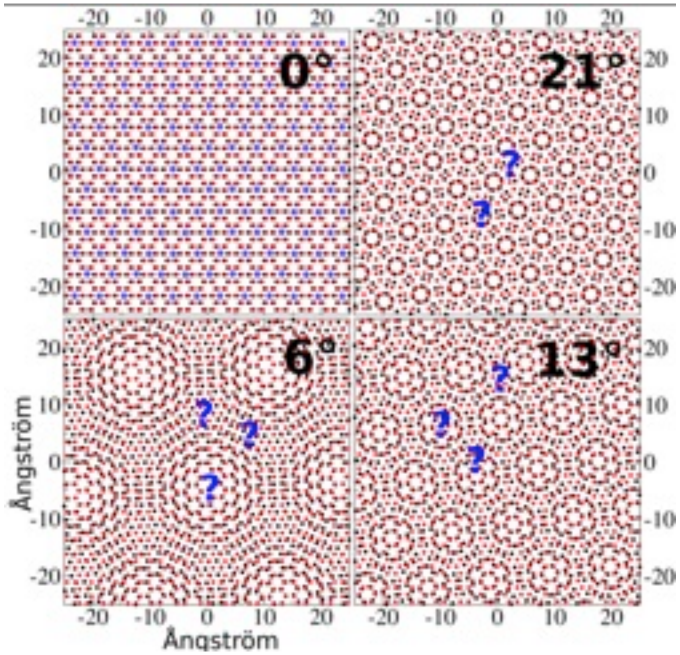


Moiré pattern

Bandgap Engeneering in twisted Graphene bilayers



- What happens if we epitaxially grow few Gr layer systems? – Azimuthal rotations create superlattice patterns

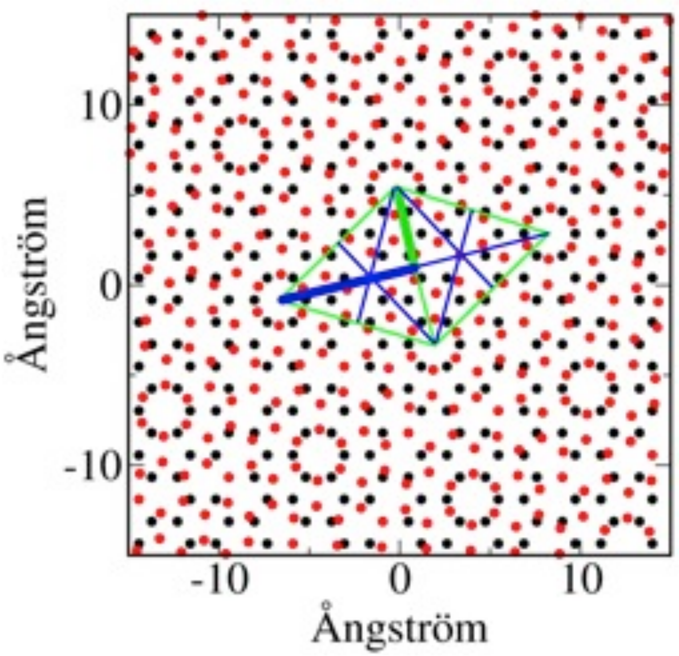


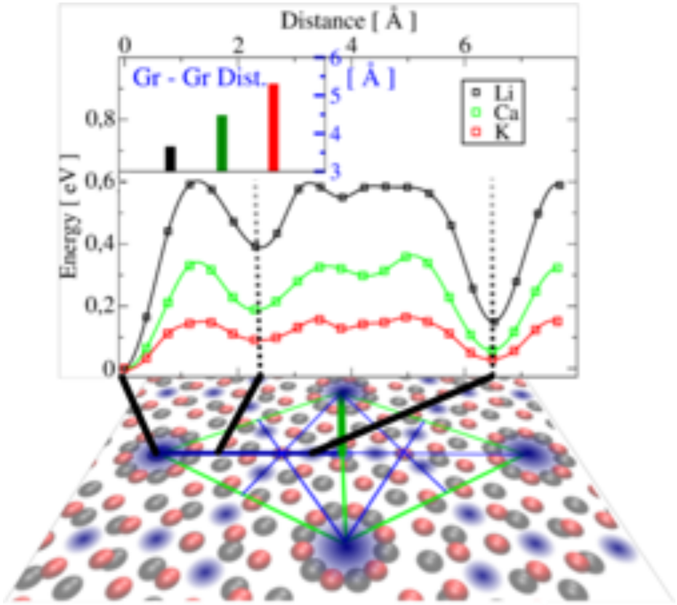
- Different twist angle – different size superlattices (moiré patterns)

- Use moiré pattern (the superlattice) to control the functionalization of graphene (selective intercalation)

Varchon et al.,Phys. Rev. B **77**, 165415 (2008)

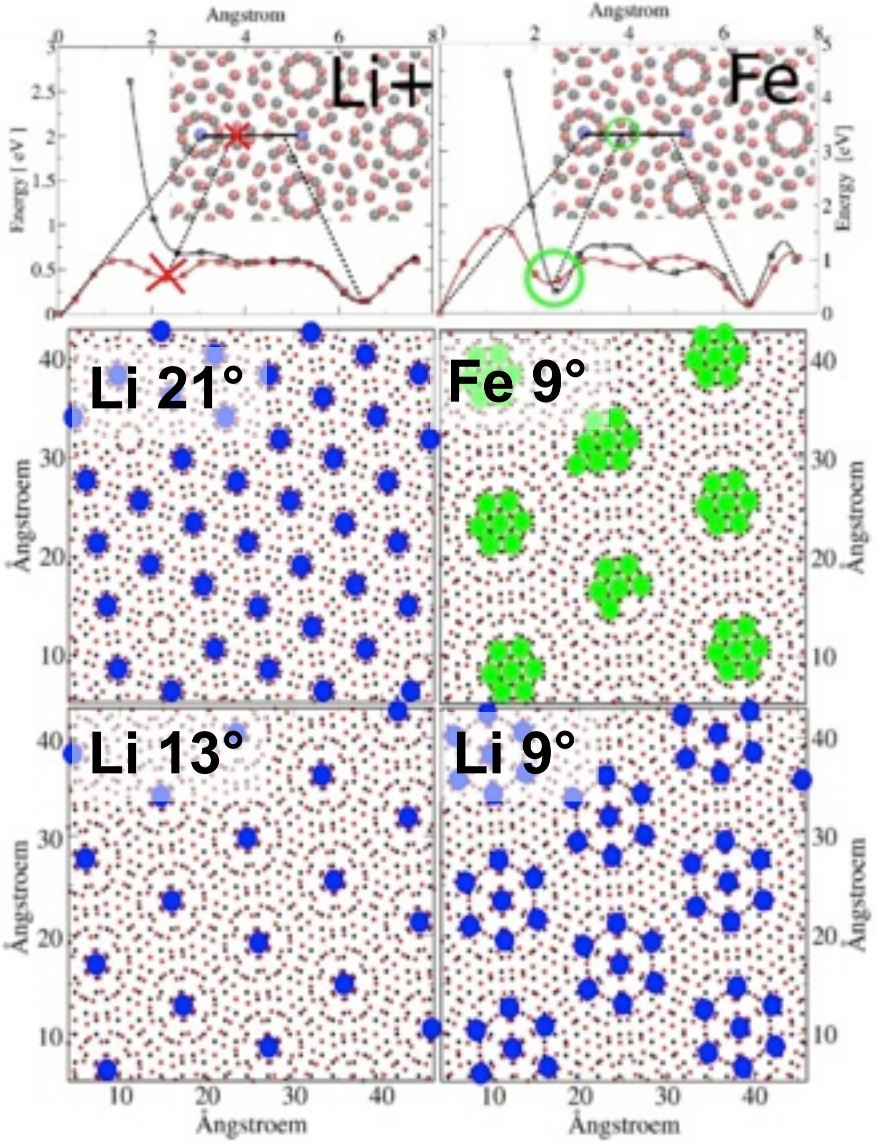
Intercalation Landscape





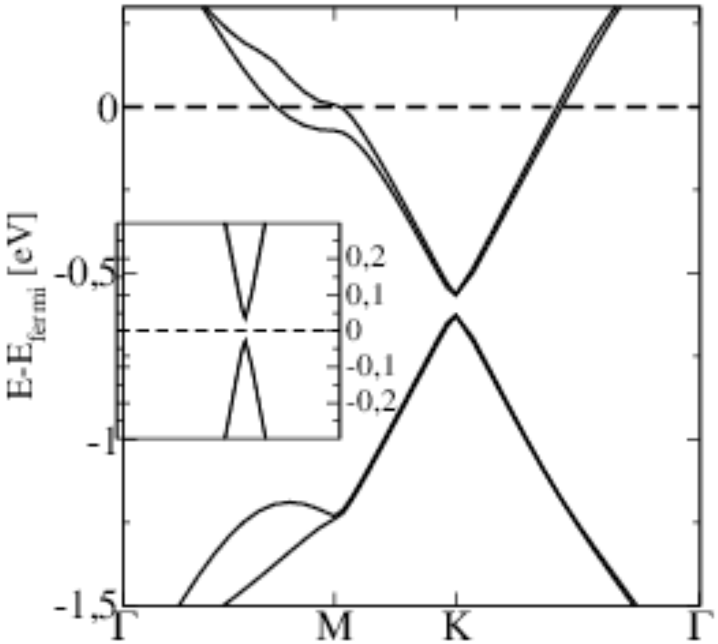
- Superlattice of a twisted bilayer creates intercalation *landscape* (breaking of the symmetry)
- Preferred intercalation sites at sites of matching carbon rings (AA)
- Twist angle defines multitude of intercalation templates

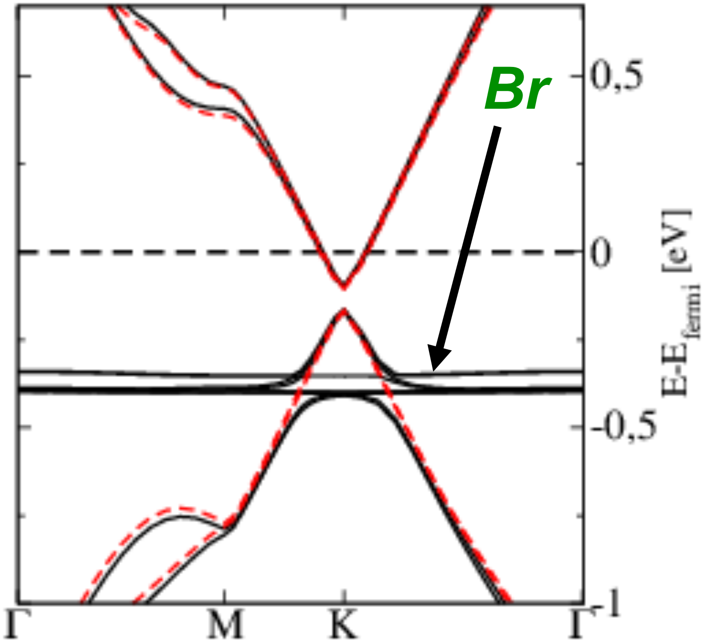
Intercalant Interactions



- The angle *and* the intercalant form the pattern (concentration too)
- Example: Coulomb repulsion between alkali (earth) atoms forbids neighboring sites occupation (blue)
- Iron atoms are weakly attracted, forming clusters (green)

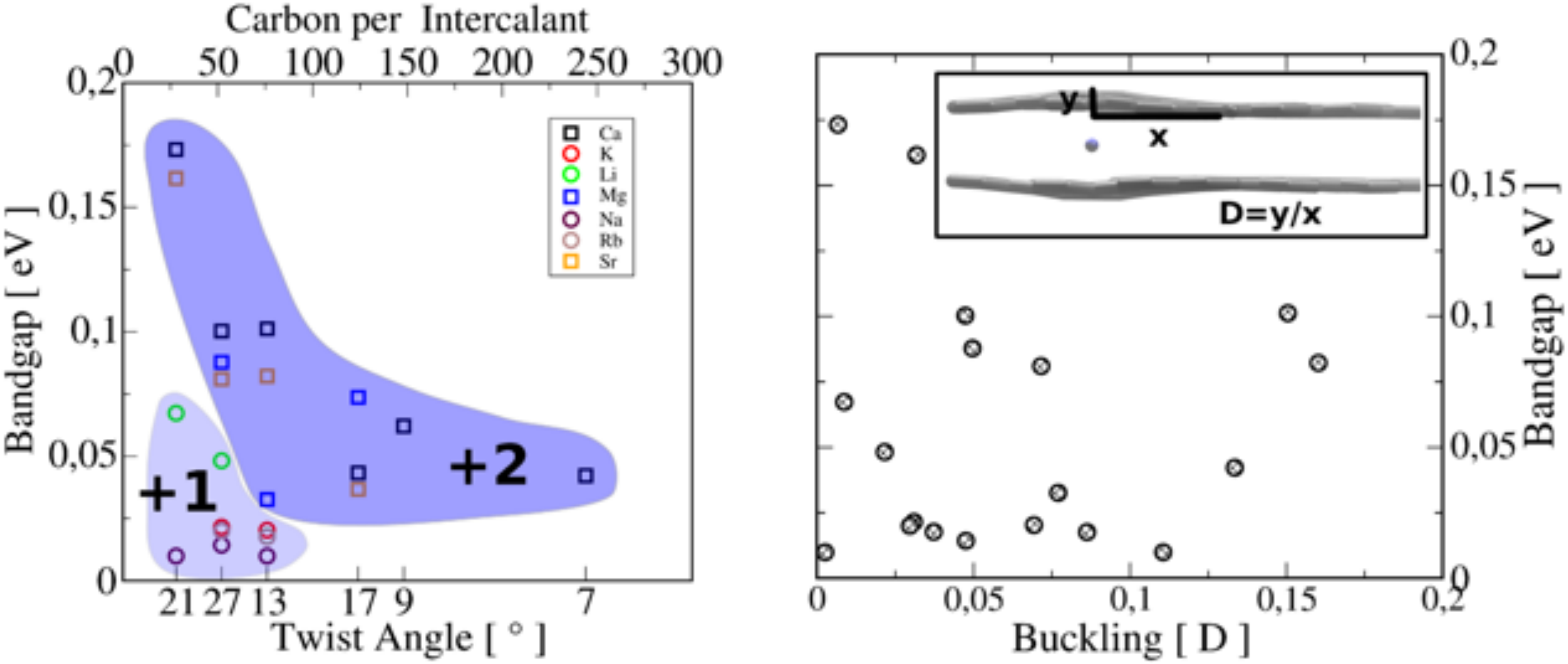
Bandgap opening in Intercalated Bilayers





- Alkali (earth) intercalants open band gap (up to 180 meV) and shift E_F due to electron donation (*e.g.* Li → Li^+)
- Inset: the donated charge removal restores E_F *without* closing of the gap
- System periodic → the band structure preserved (the degenerate Dirac cones)
- *Br* adsorbtion shifts the E_F level back to the Dirac-point (flat *Br* band below E_F)

Ionized intercalants open band gap (E-field)

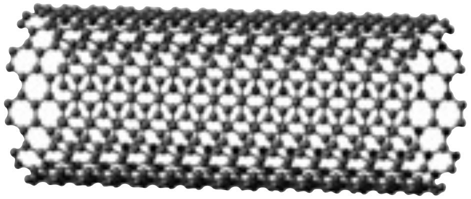


- The gap proportional to the donated charge and concentration
- *No correlation* between structural buckling and bandgap
- Ionized intercalants are source of periodic inhomogeneous external potential

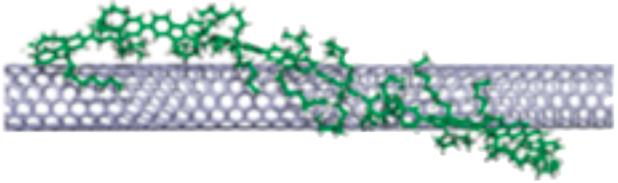
Manuscript in preparation

Sorting CNT by selective polymer wrapping

1D

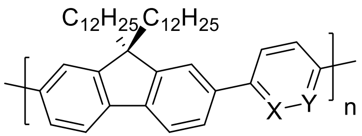


Selective Polymer Wrapping of CNT’s



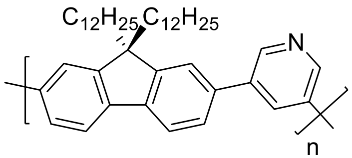
Sorting CNT by selective polymer wrapping

- Four different polymers

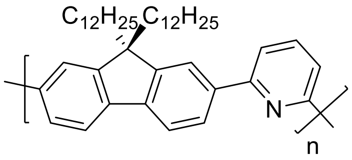


X=N, Y=CH or X=CH, Y=N

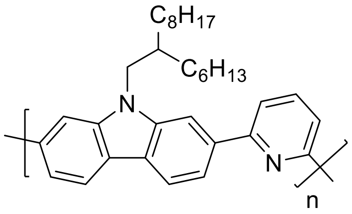
P1



P2

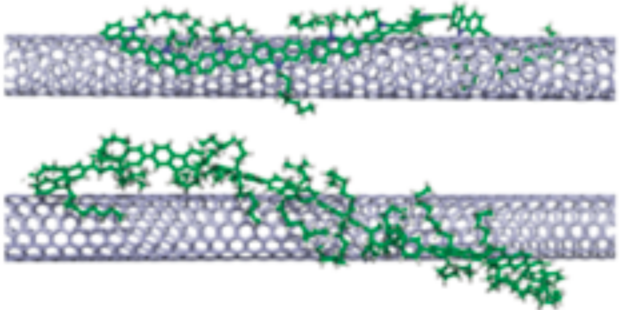


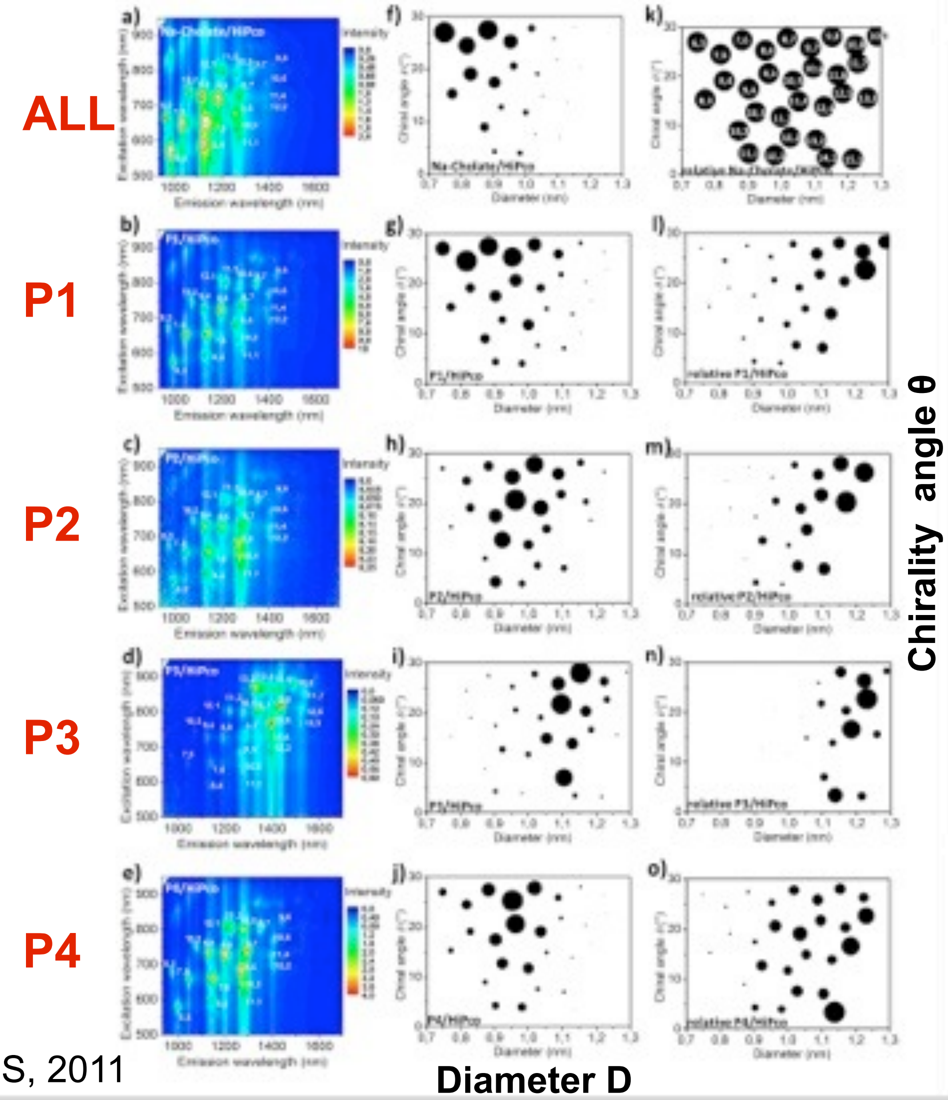
P3



P4

- Selectivity not fully understood
- MD inefficient to wrap the NTs
- No design principles

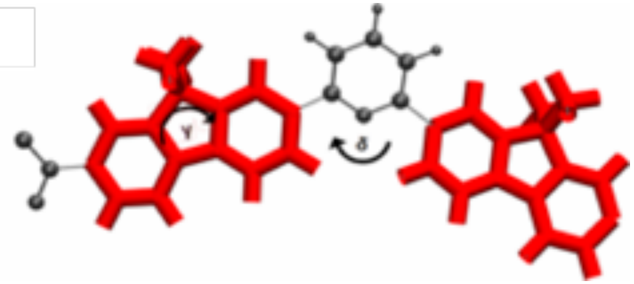


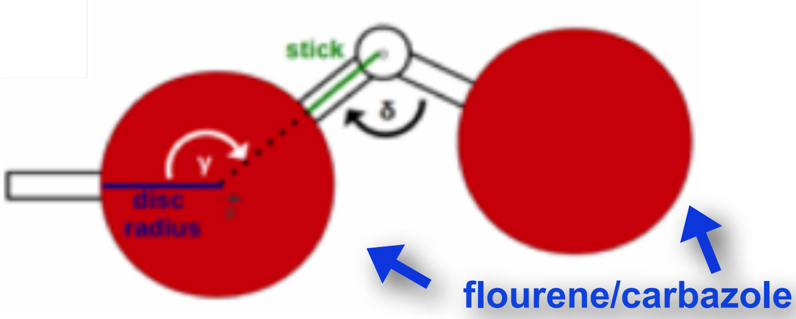


F. Lemasson, *et al*, JACS, 2011

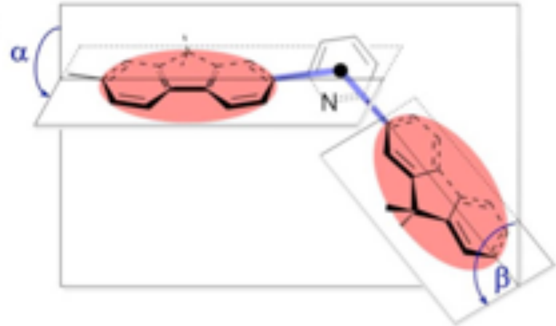
Coarse-grained model for conformational search

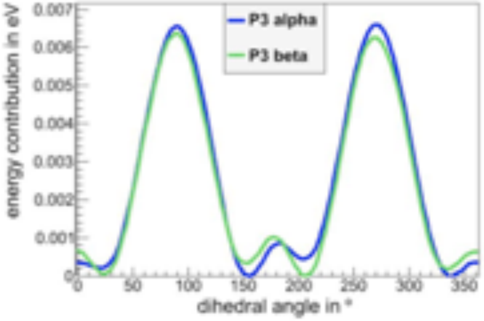
- MD inefficient
- Construct a geometrical coarse-grained model
  - Disk-joint model
  - Parametrisation of shapes and chemically constrained angles δ and γ to polymer specific values by DFT

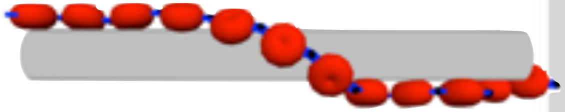




  - Polymer specific model for the internal energy (DFT): use dihedrals α and β as free parameters.

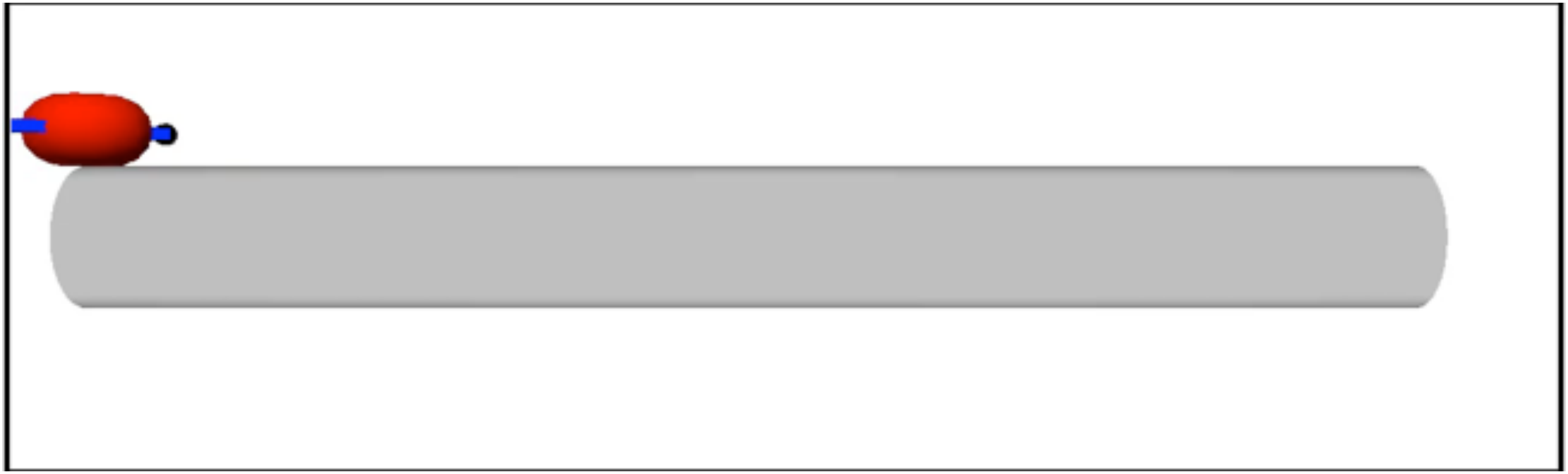




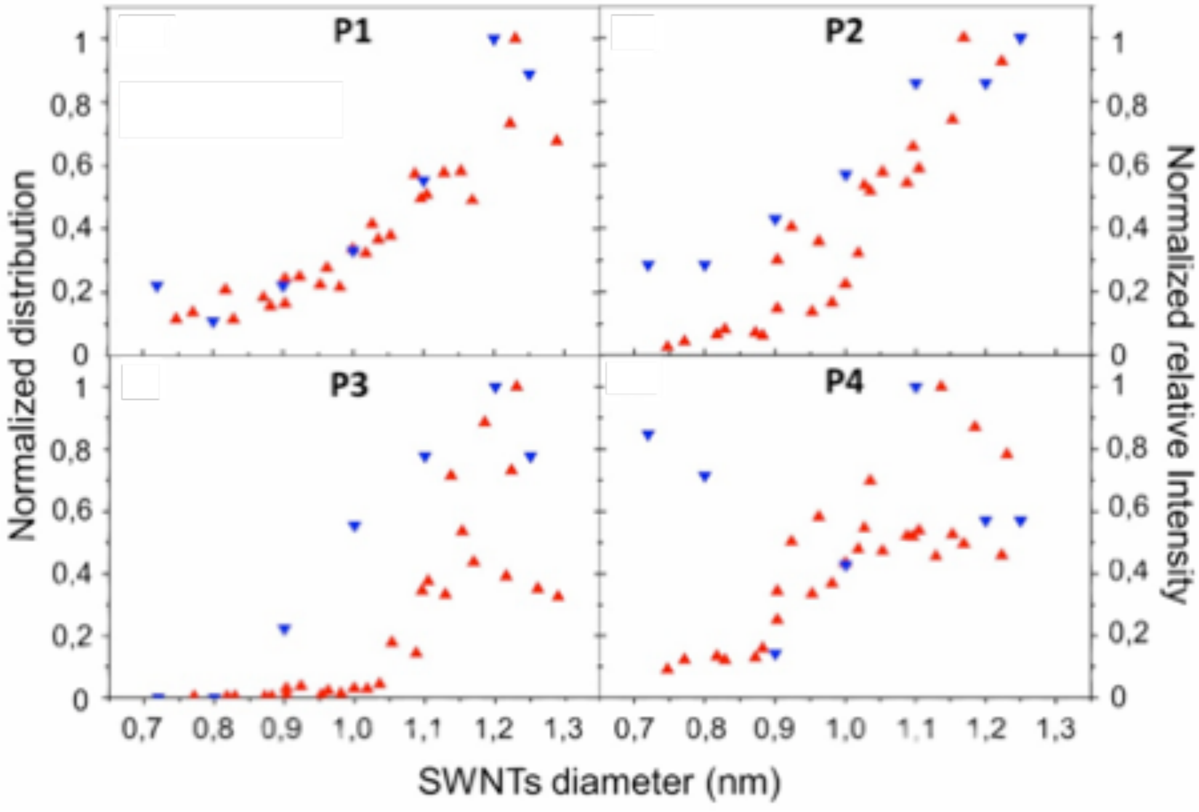


Construction of conformational ensemble by recursive exhaustive sampling

- Construct *all conformations* of polymers with length n=12 links, such that all polymer units (red discs) are in contact with the tube of a given diameter D
- For many diameters/polymer combinations no solutions exist!
- Optimise the total internal energy: compute fraction of conformations with lowest internal energy

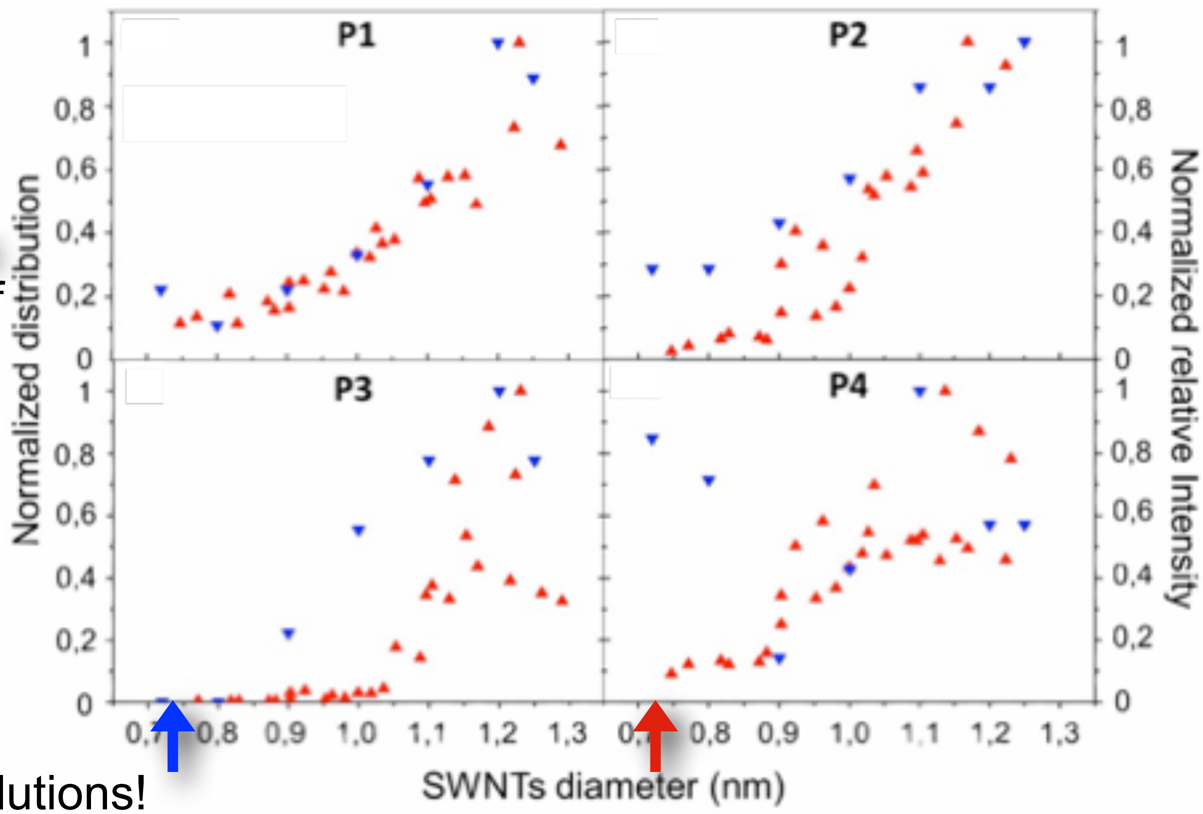


Selective polymer wrapping of SW-CNT



▲ Normalised relative intensity, exp.
▼ Fraction of low energy solutions, theo.

Selective polymer wrapping of SW-CNT



P1 & P2: Fraction of solutions correlates with measured relative intensity!

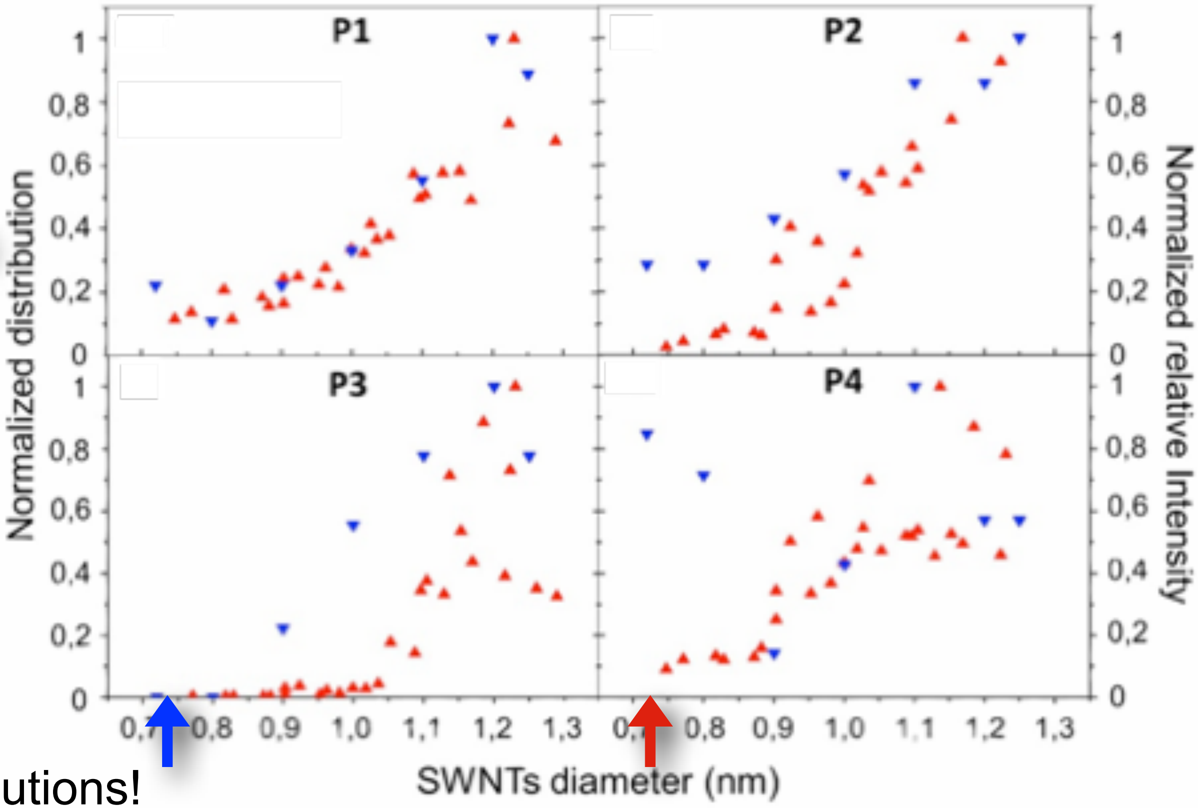
No solutions!
P3 does not wrap small tubes!

Many solutions for small radii

▲ Normalised relative intensity, exp.
▼ Fraction of low energy solutions, theo.

Selective polymer wrapping of SW-CNT

P1 & P2: Fraction of solutions correlates with measured relative intensity!



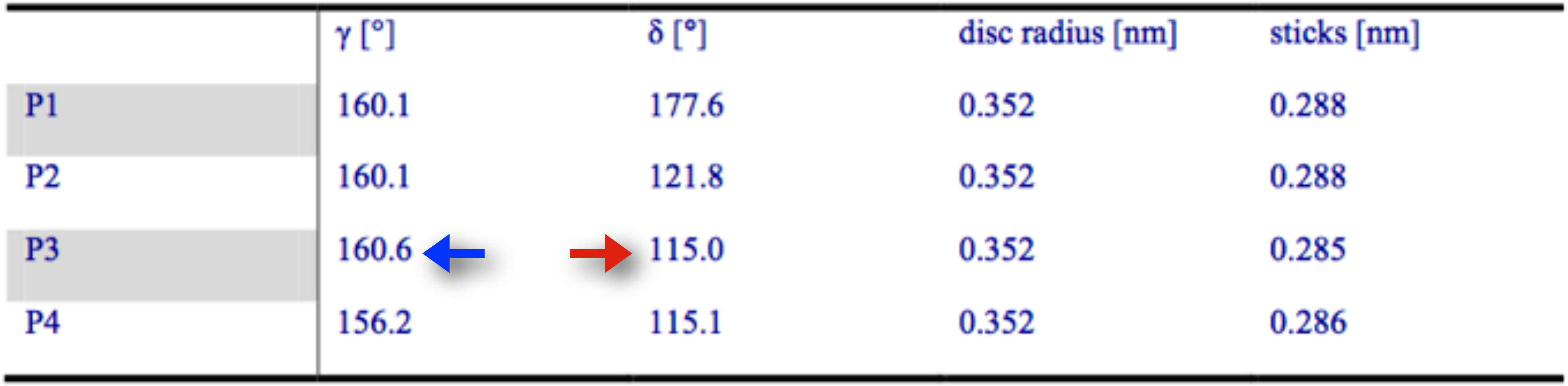
No solutions!
P3 does not wrap small tubes!

Many solutions for small radii: **multiscale modelling required!**

To do: refine the coarse-grained model with MD

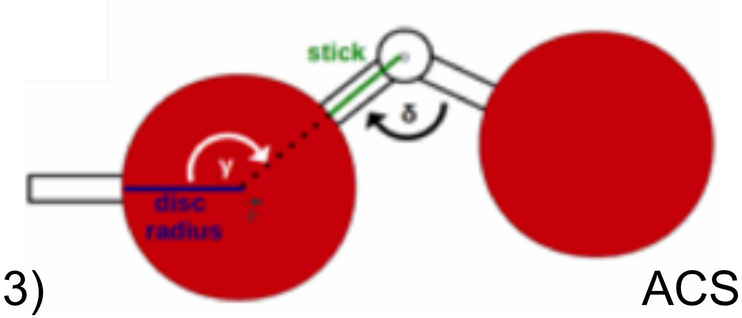
▲ Normalised relative intensity, exp.
▼ Fraction of low energy solutions, theo.

Selective polymer wrapping of SW-CNT



	γ [°]	δ [°]	disc radius [nm]	sticks [nm]
P1	160.1	177.6	0.352	0.288
P2	160.1	121.8	0.352	0.288
P3	160.6	115.0	0.352	0.285
P4	156.2	115.1	0.352	0.286

P3 has greatest γ fixed angle and smallest δ which seems to result in selection of widest CNTs

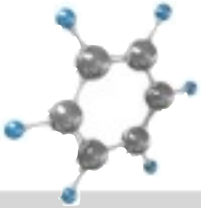


SMALL, accepted (2013)

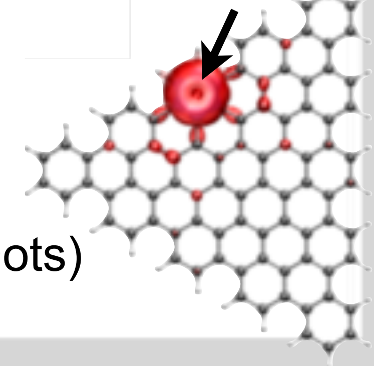
ACS Macro Letters (submitted)

Magnetic Anisotropy of Ru Adatom Decorated Gr Flakes

0D



(Decorated) Graphene Flakes (Quantum Dots)



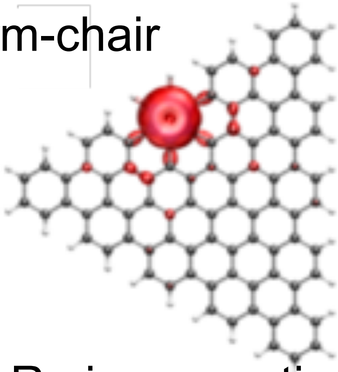
Magnetic Anisotropy of Ru Adatom Decorated Gr Flakes

- Creation of graphene based magnetic storage devices by magnetic transition metal adsorbtion has been proposed.
- The studied systems are either graphene, graphene ribbon, or benzene ring based.

H. Zhang, *et al*. PRL (2012)

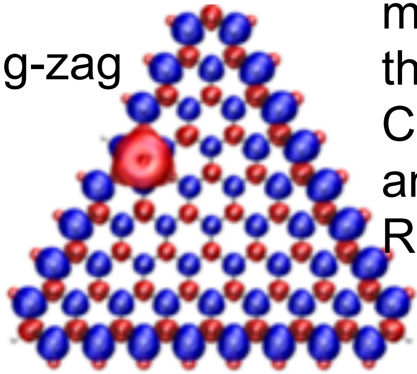
- Introducing something finite but larger than a benzene ring!
- Triangulines (simplest form with unique edge type)

arm-chair



Only Ru is magnetic.

zig-zag



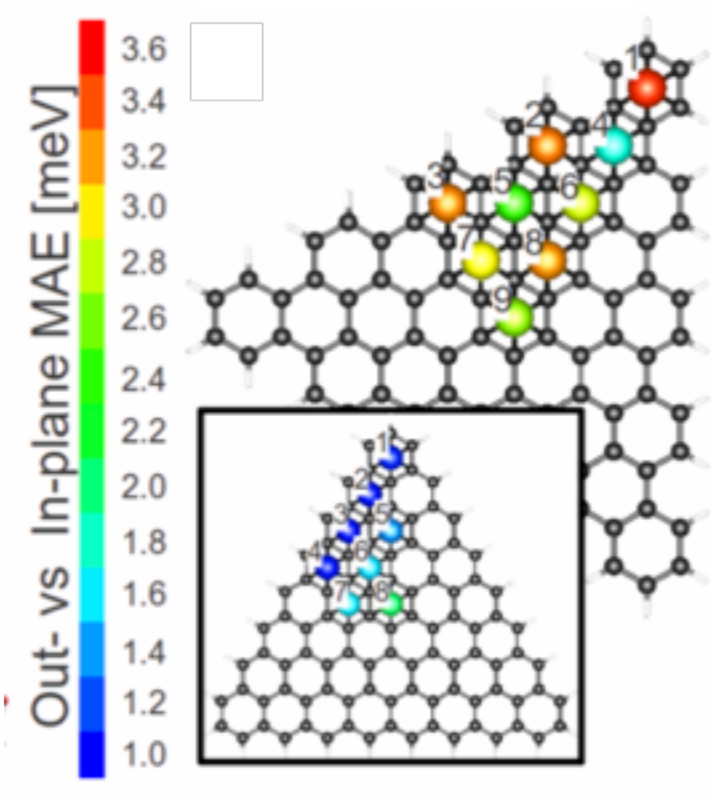
The flake magnetic with manetism strongest at the edge.
Couples antiferromagnetically to Ru adatom.

L. Chen, *et al.*
Angew. Chem. Int. Ed. (2012)

Magnetic Anisotropy (MAE), Ru on Gr Flake

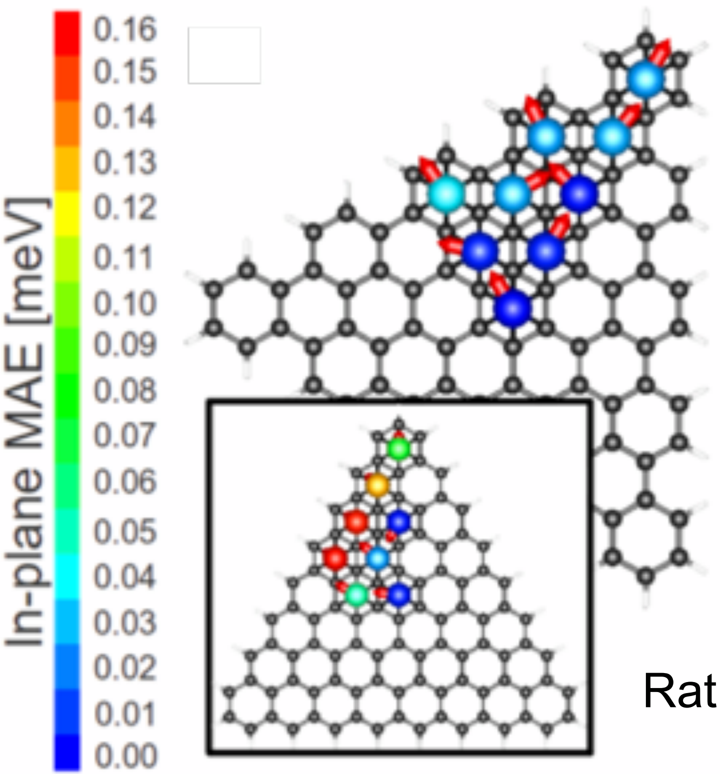
In-out-of plane

$$E_{\mathrm{IO}} = E_{\perp} - E_{||,\min},$$



In plane

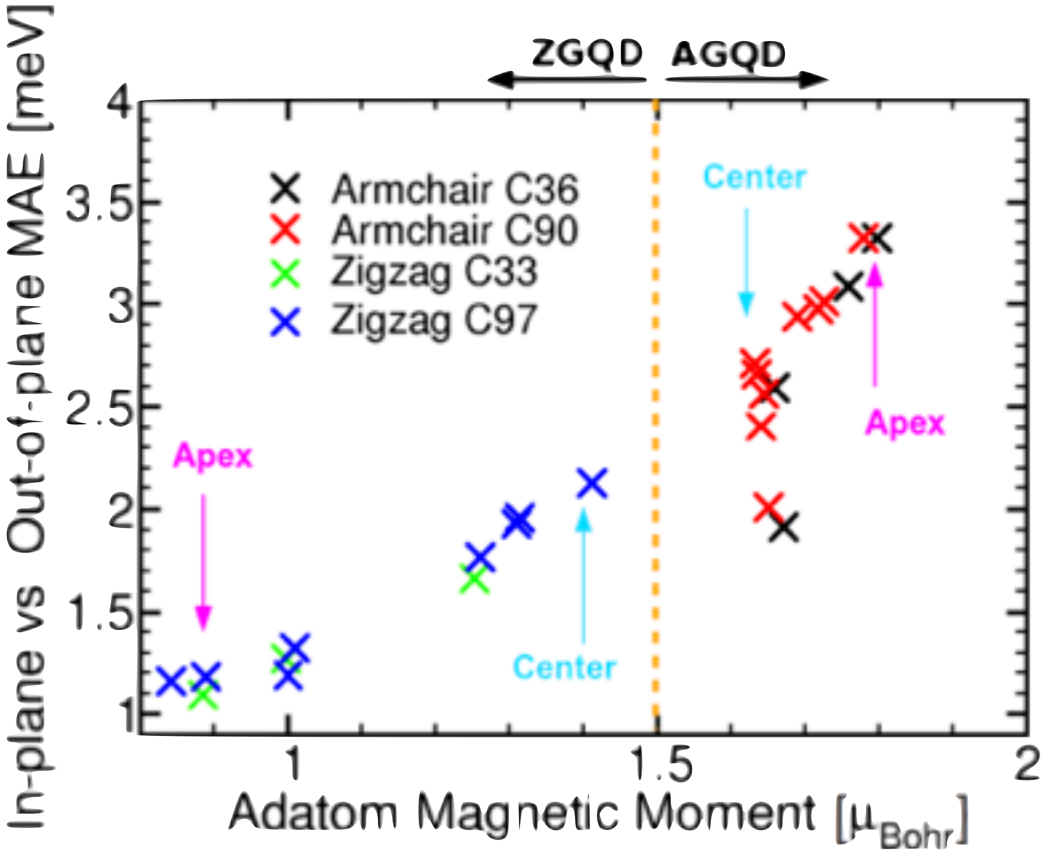
$$E_{\mathrm{IP}} = E_{||,\max} - E_{||,\min}.$$



Rather small!

5d much larger, in preparation

In-out-plane MAE as function of the Ru mag. moment



Beilstein J. Nanotechnol. **4,** 441 (2013)

- Arm-chair (zig-zag) edge leads to incresead (decreased) magnetic moment, as well as, increased (decreased) E_{IO}.
- The zig-zag is magnetic and couples antiferromagnetically to Ru.

Conclusions and Outlook

- Graphitic materials open great possibility for fine-tuning the properties and, thus, broad application field in nanotechnology.
- Understanding the often non-trivial underlying mechanisms which govern the physical properties is crucial for device deployment.
- Continue to identify interesting problems together with our experimentalist colleagues.
- For more realistic simulations in future, combinations of techniques established on various scales must be interconnected in scale-bridging models.
- Where applicable the corresponding multiscale workflows are already in development.

THANK YOU!

- Industrial partners:

PHILIPS
sense and simplicity

BASF
The Chemical Company

SONY
make.believe

- Funding from EC:

CAPACITIES

e-infrastructure

- Partner projects, supporting infrastructures and software

PRACE

NOMTOR
Metal Insulator Organic

D-GRID

NGI-DE

UNICORE