1D and 2D molecular nanoarchitectures: electronic insights from SIESTA simulations

carbon-based

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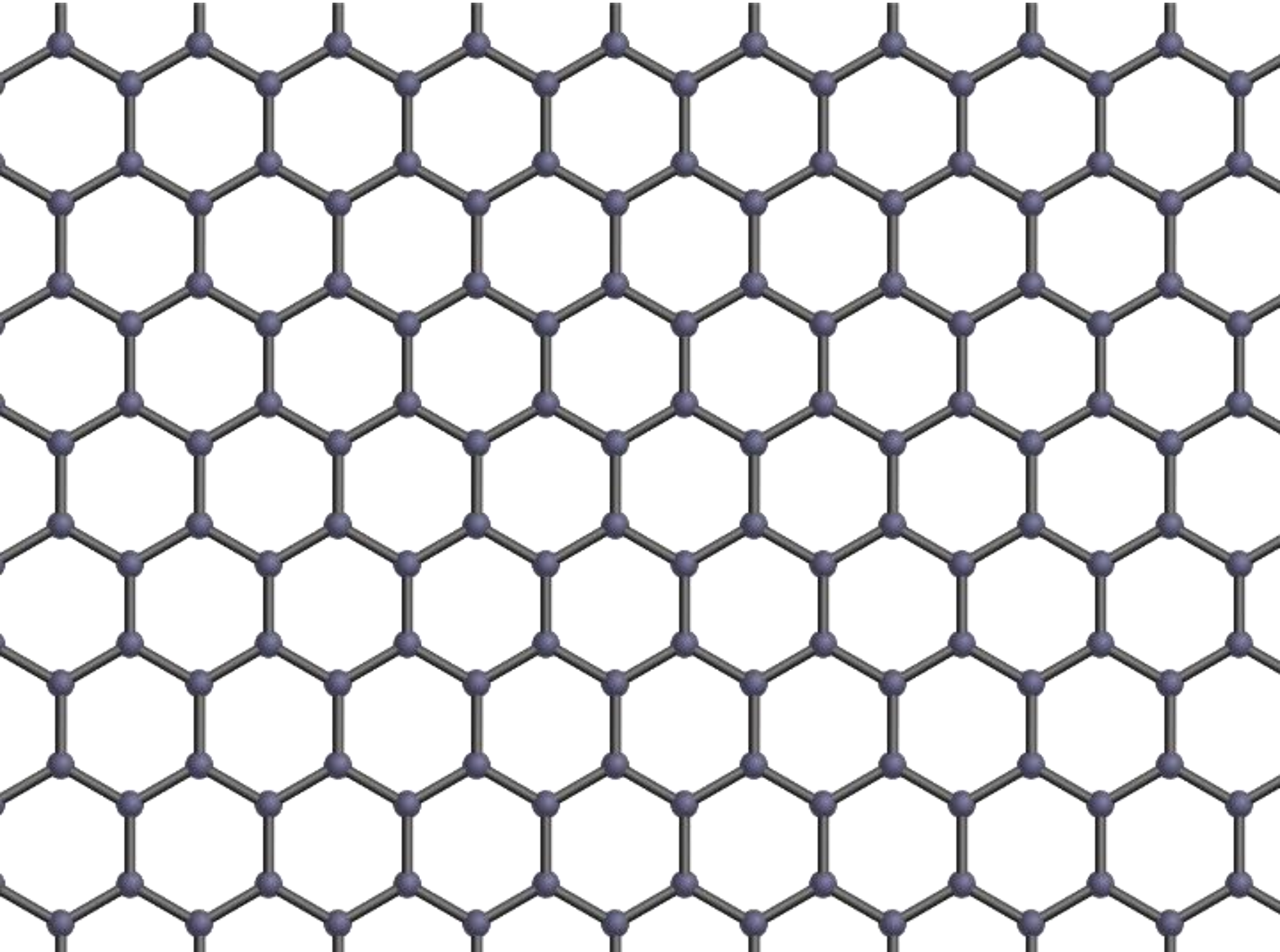
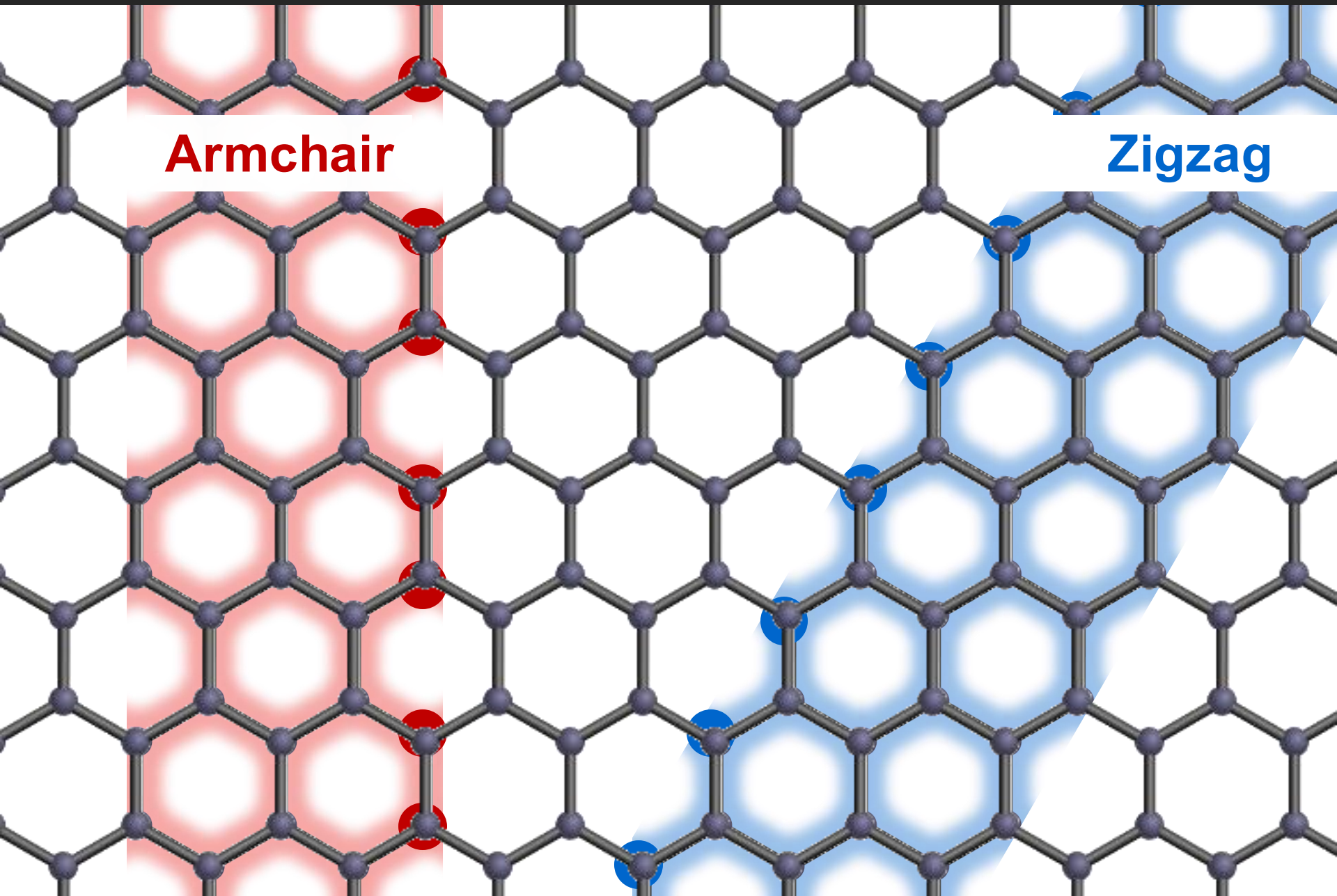
Basque Foundation for Science

Advanced SIESTA Workshop 2025

DIPC



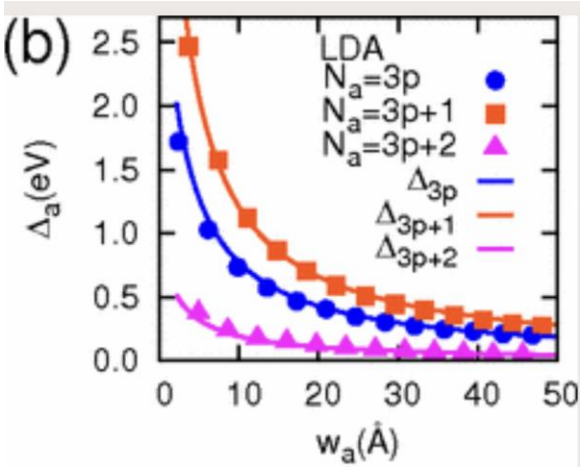
Graphene Nanoribbons (GNRs)



Graphene Nanoribbons (GNRs)

Armchair

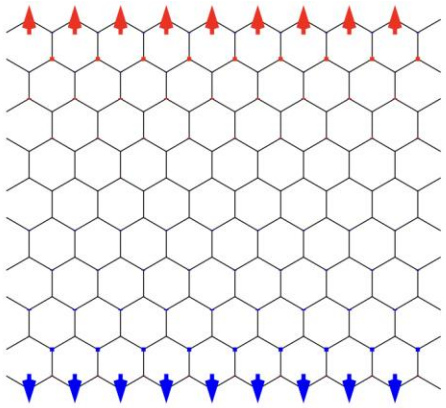
Semiconducting



Son et al., PRL97, 216803 (2006)

Zigzag

Magnetic edge states



Nakada et al., PRB 54, 17054 (1996)

Wakabayashi et al., Sci. Tech. Adv. Mater. 11, 054504 (2010)

Bottom-up fabrication of graphene nanostructures

On-surface synthesis

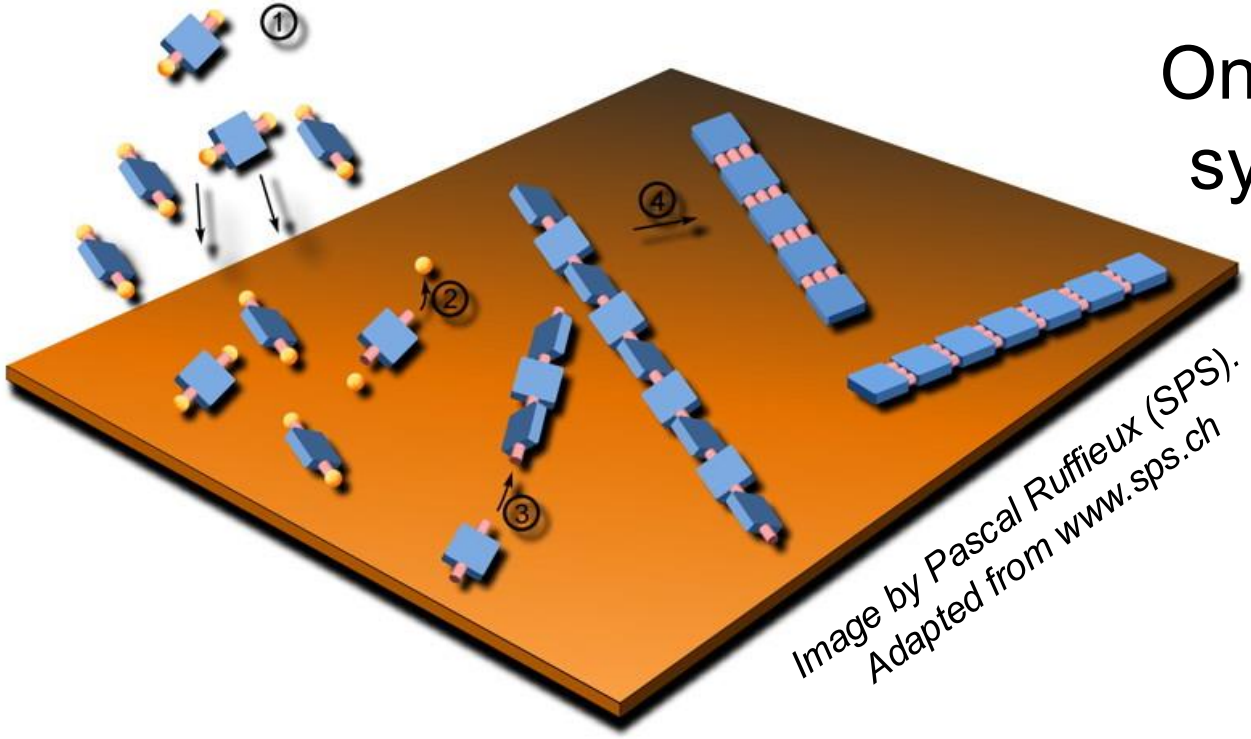
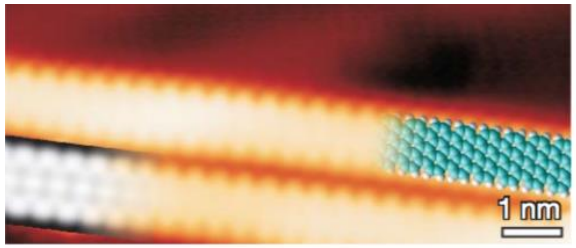


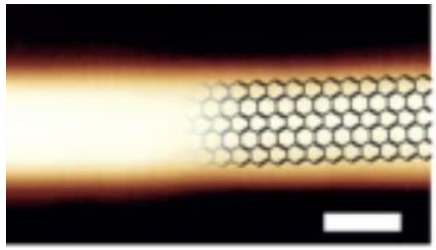
Image by Pascal Ruffieux (SPS). Adapted from www.sps.ch

Armchair graphene nanoribbons (AGNR)



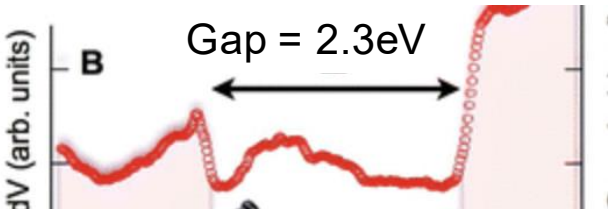
Cai et al., Nature 466, 470 (2010)

Zigzag graphene nanoribbons (ZGNR)

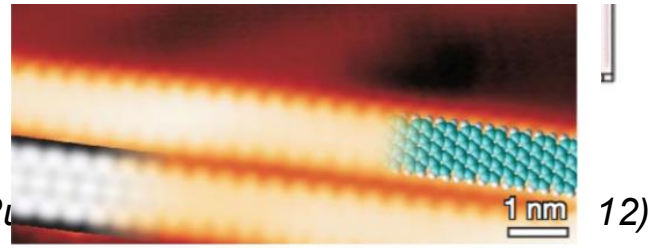


Ruffieux et al., Nature 531, 489 (2016)

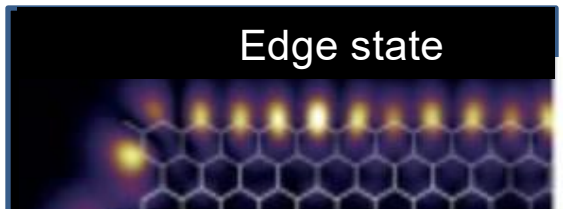
Atomically precise graphene nanoribbons



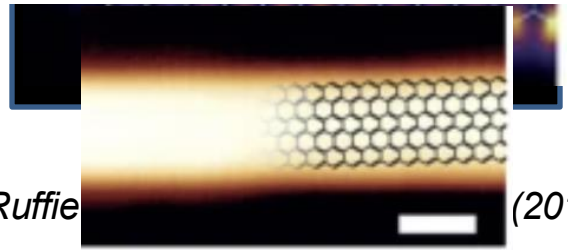
Armchair graphene nanoribbons (AGNR)



Cai et al., Nature 466, 470 (2010)



Zigzag graphene nanoribbons (ZGNR)

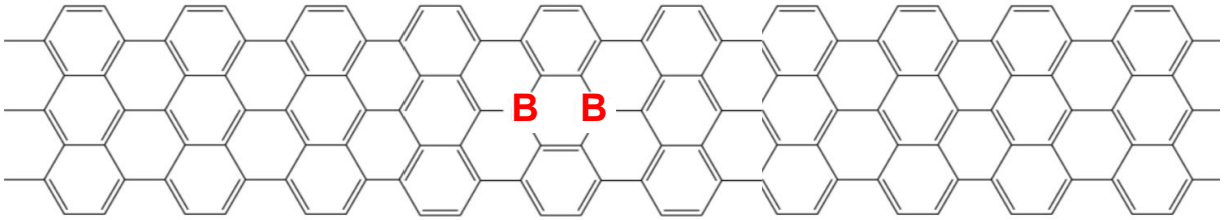


Ruffieux et al., Nature 531, 489 (2016)

Atomically precise graphene nanoribbons

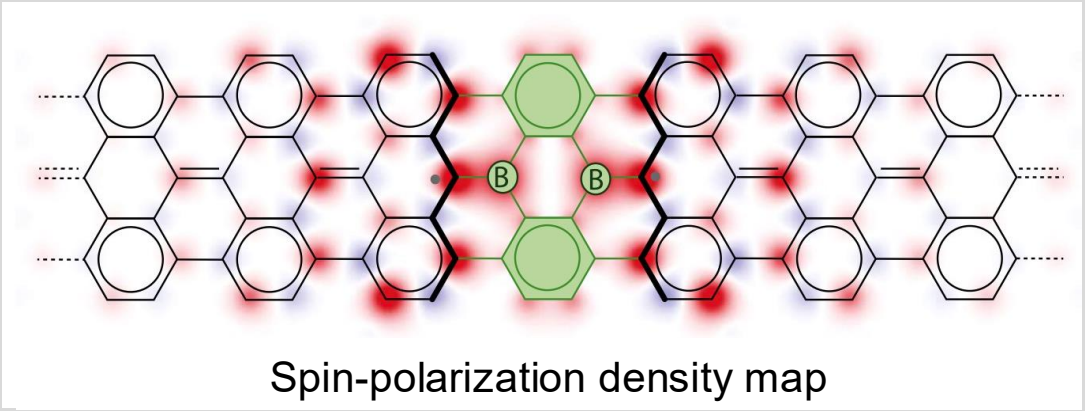
Chemical doping

Chemical substitution in GNRs



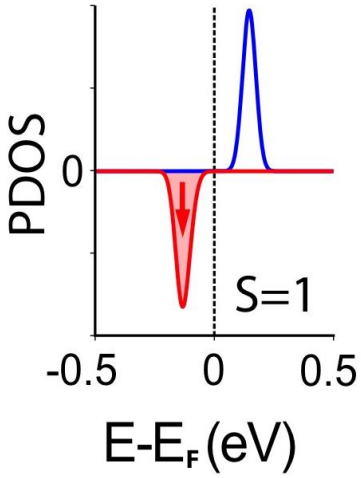
2B-units in the backbone of 7-armchair GNRs (2B-7AGNR)

DFT-SIESTA simulations



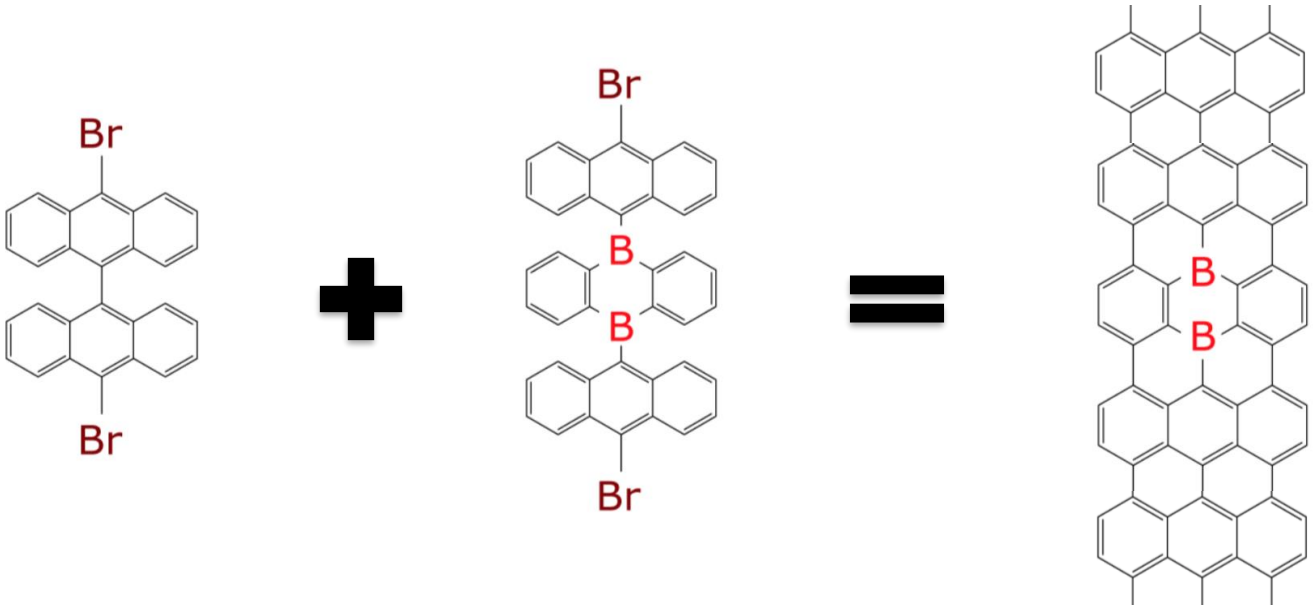
Spin-polarization density map

The 2B-units induce a net magnetic moment of $2\mu_B$

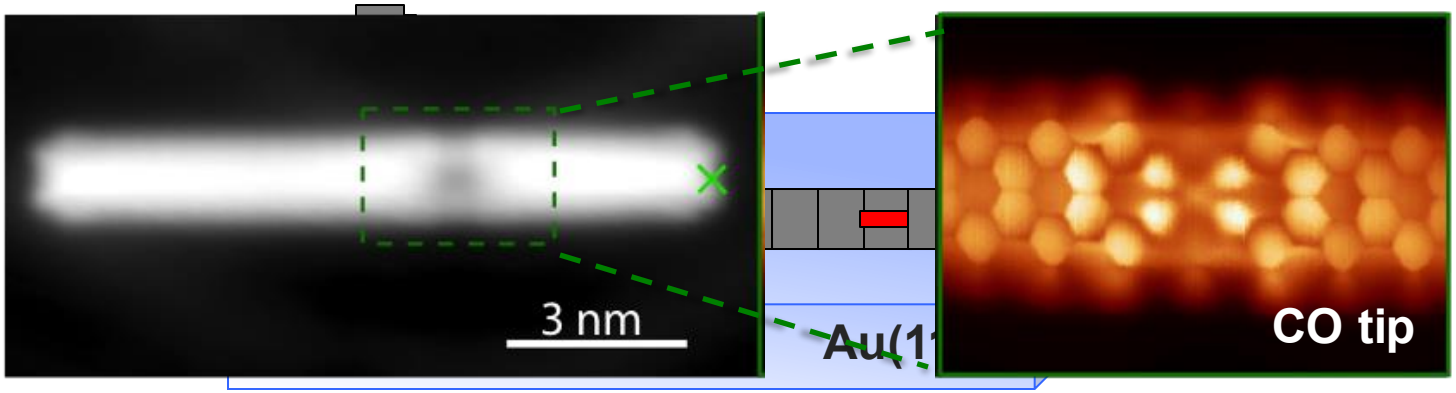


DOS projected
over C atoms around 2B

Synthesis of borylated 7AGNRs

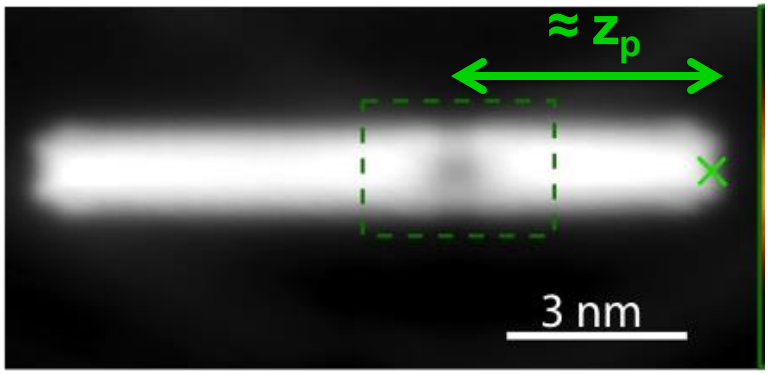


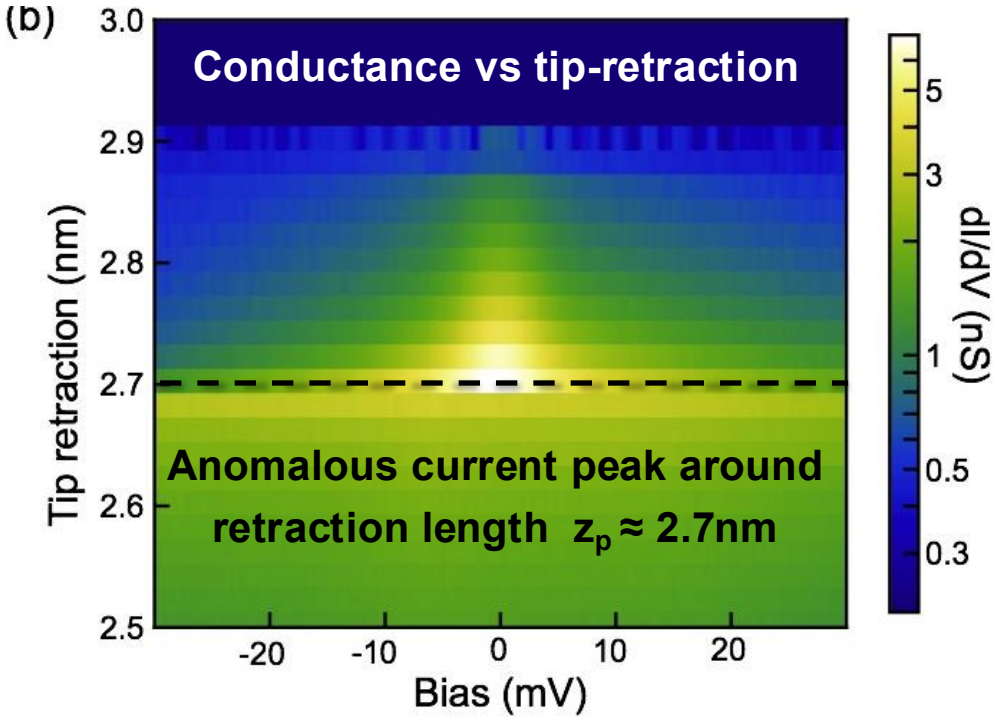
Scanning Tunneling Microscopy (STM)

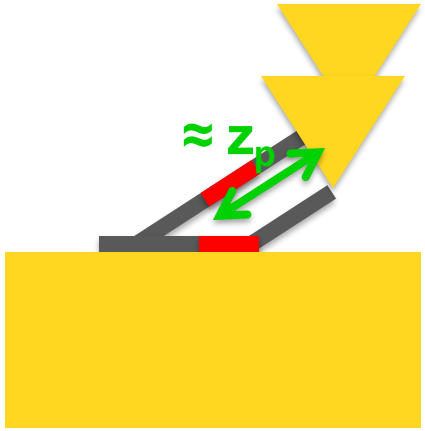


Experiments by J.I. Pascual's group (Nanogune, San Sebastian)

Experimental characterization of 2B-7AGNRs







Kondo resonance

Signature of magnetism

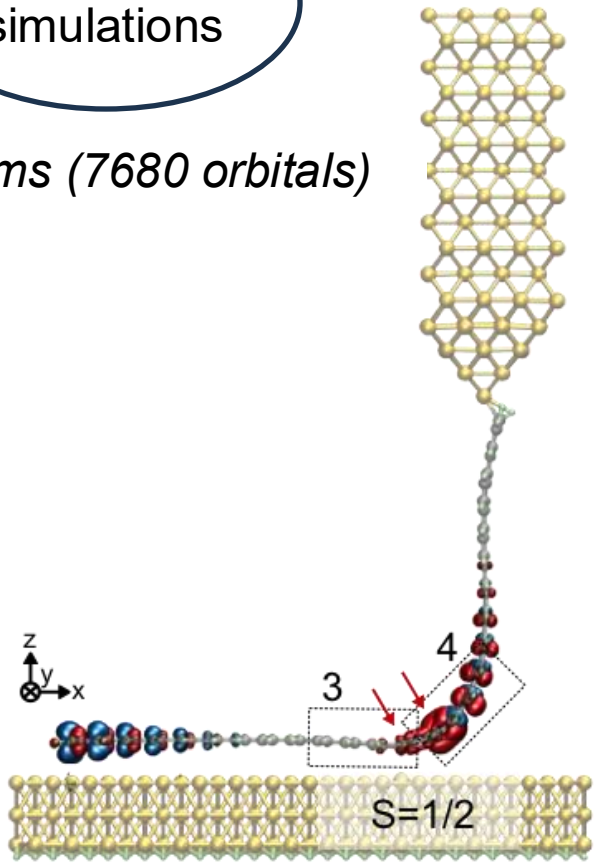
N. Friedrich, AGL et al.

Phys. Rev. Lett. 125, 146801 (2020)

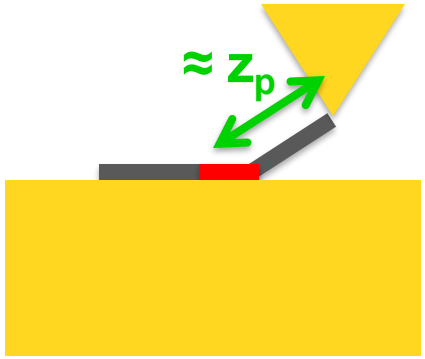
Experimental characterization of 2B-7AGNRs

SIESTA simulations

640 atoms (7680 orbitals)



Only of the B atoms detached, S = 1/2



Kondo resonance

Signature of magnetism

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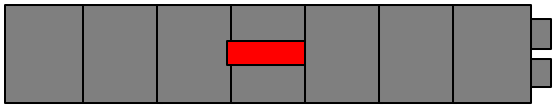
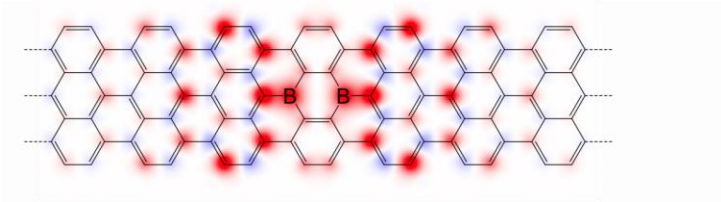
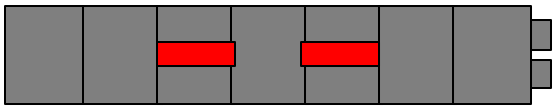
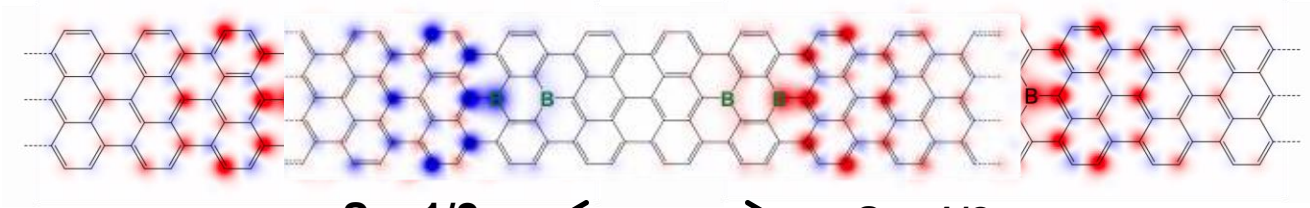
Periodically borylated 7AGNRs





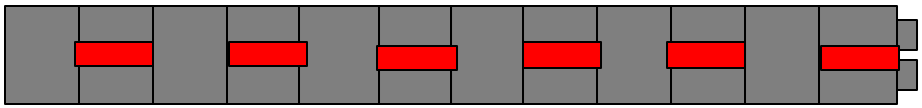
S = 1





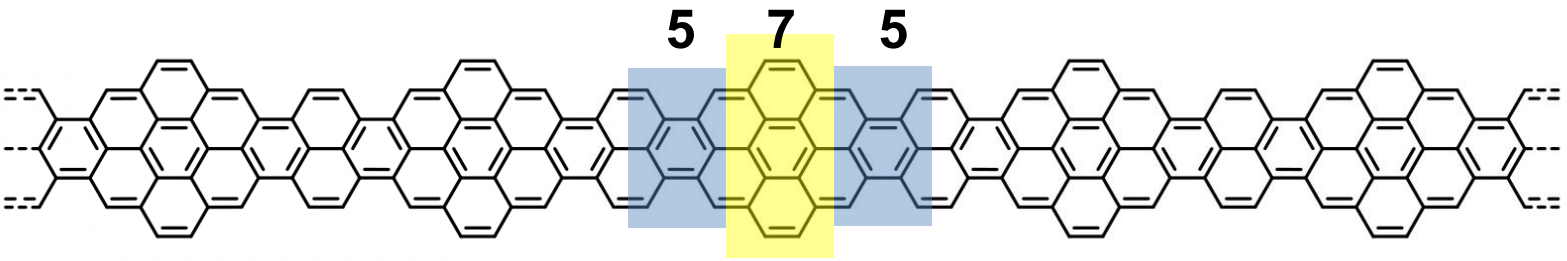
S = 1 S = 1/2 S = 1/2 S = 1

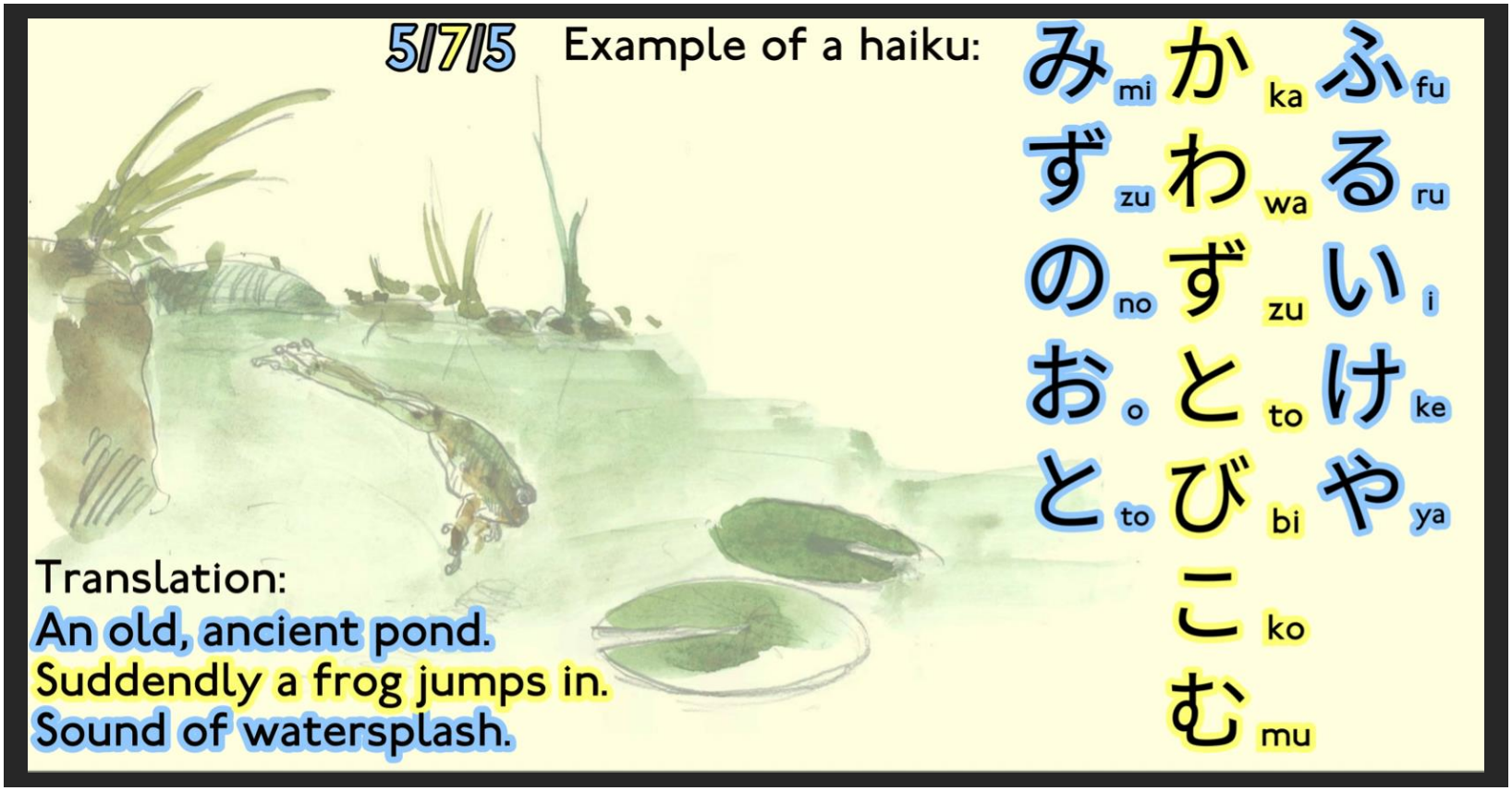
Spin polarization vanishes



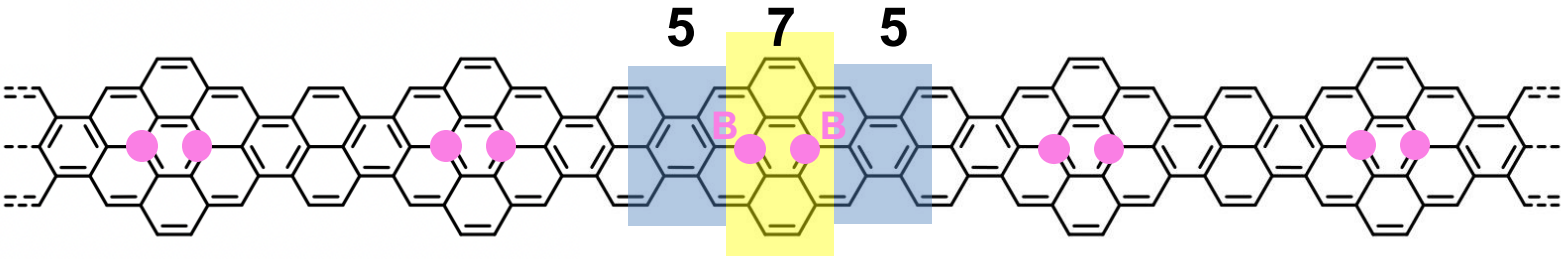
Fully borylated 7-AGNR is non-magnetic

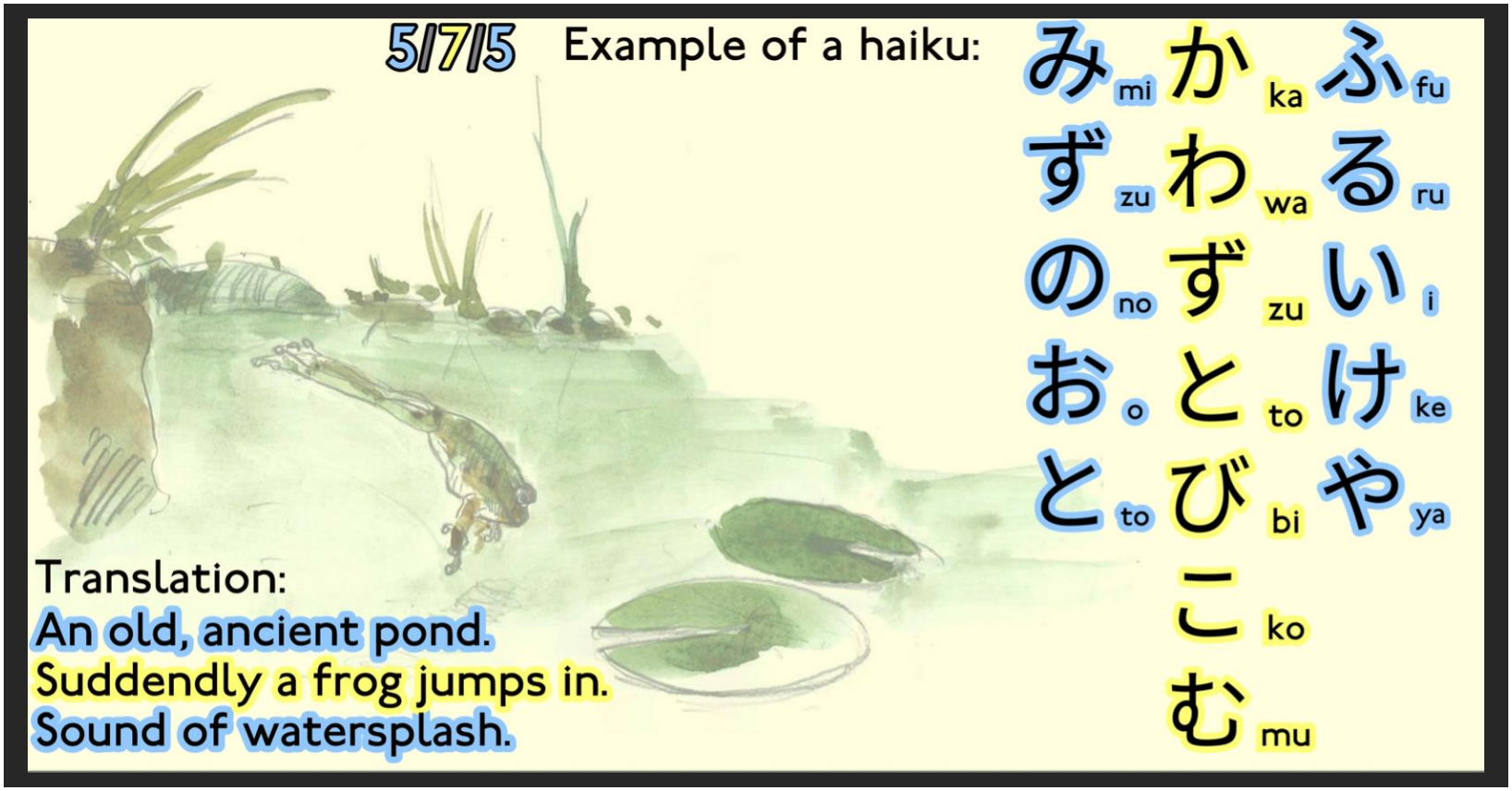
Haiku graphene nanoribbons



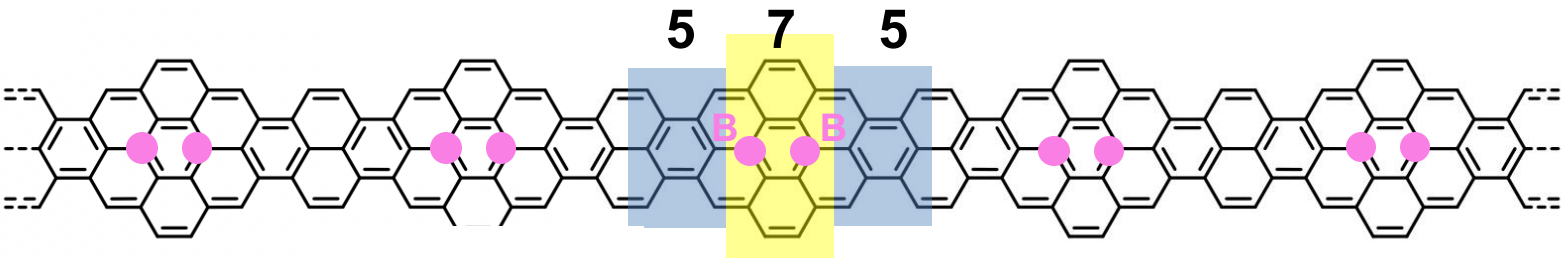


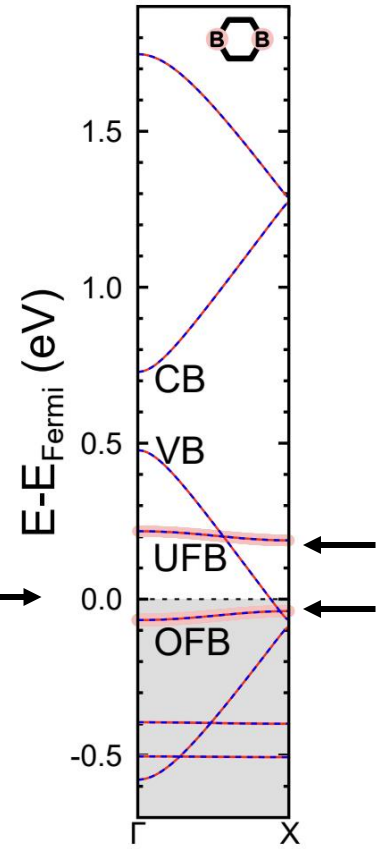
Haiku graphene nanoribbons





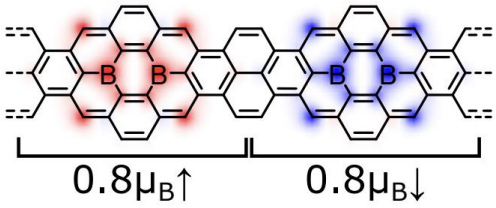
Haiku graphene nanoribbons





Metallic →

Spin-polarized DFT simulations (SIESTA)

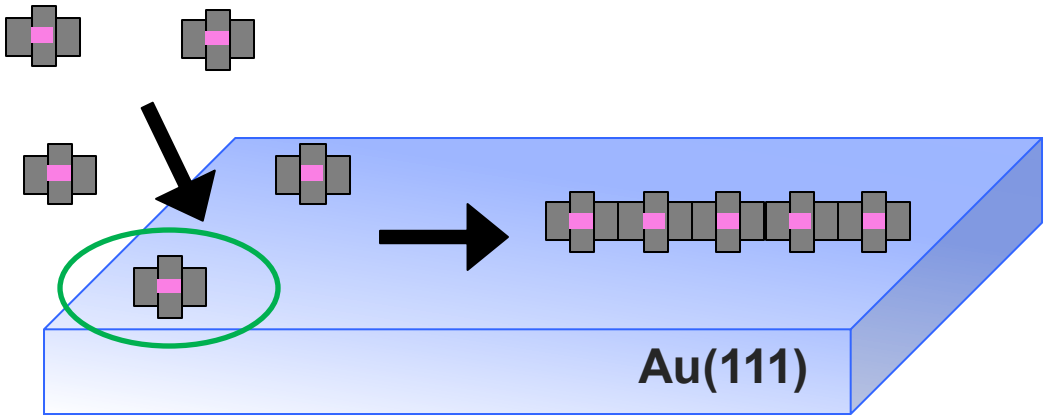


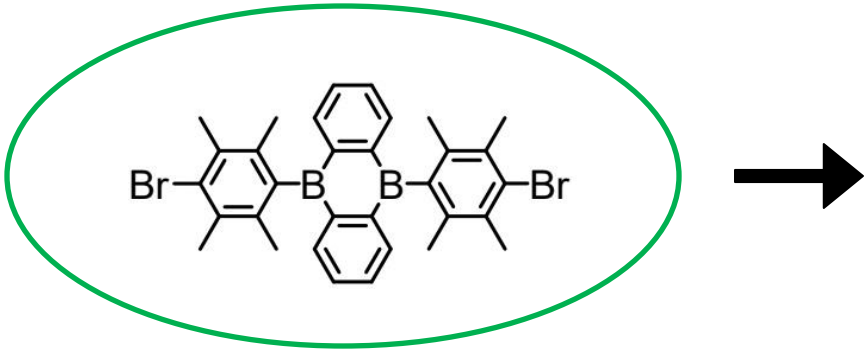
S = 1/2 **S = 1/2**

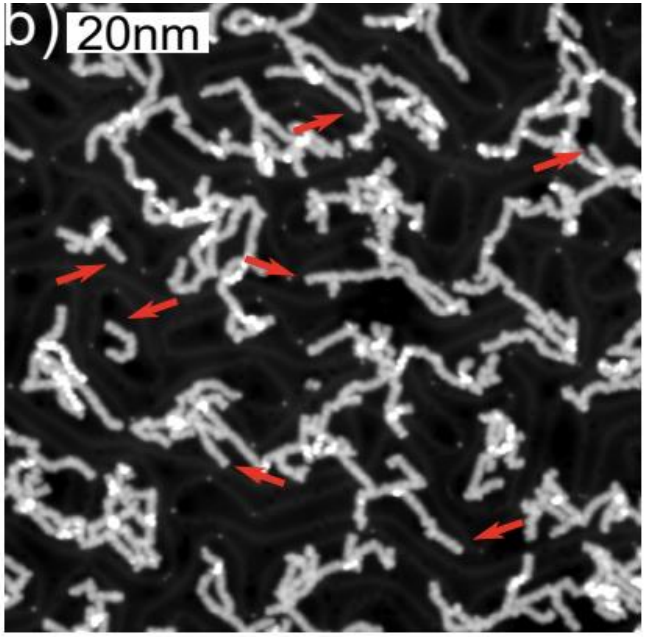
← Localized bands with strong B character

Magnetic metallic GNR

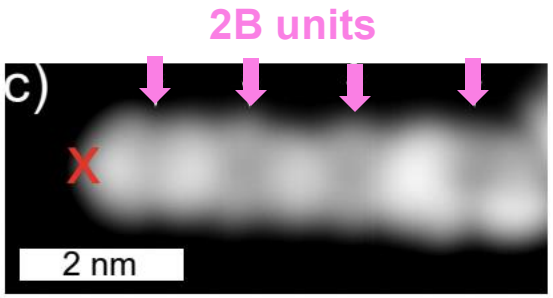
2B-Haiku GNRs: on-surface synthesis

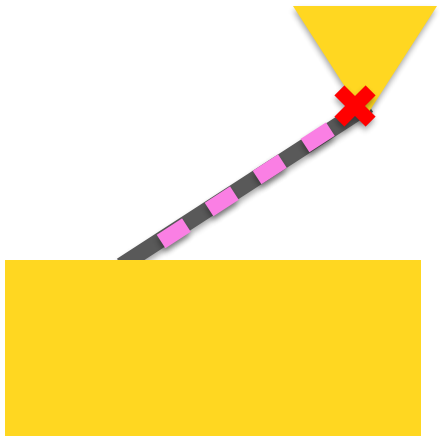


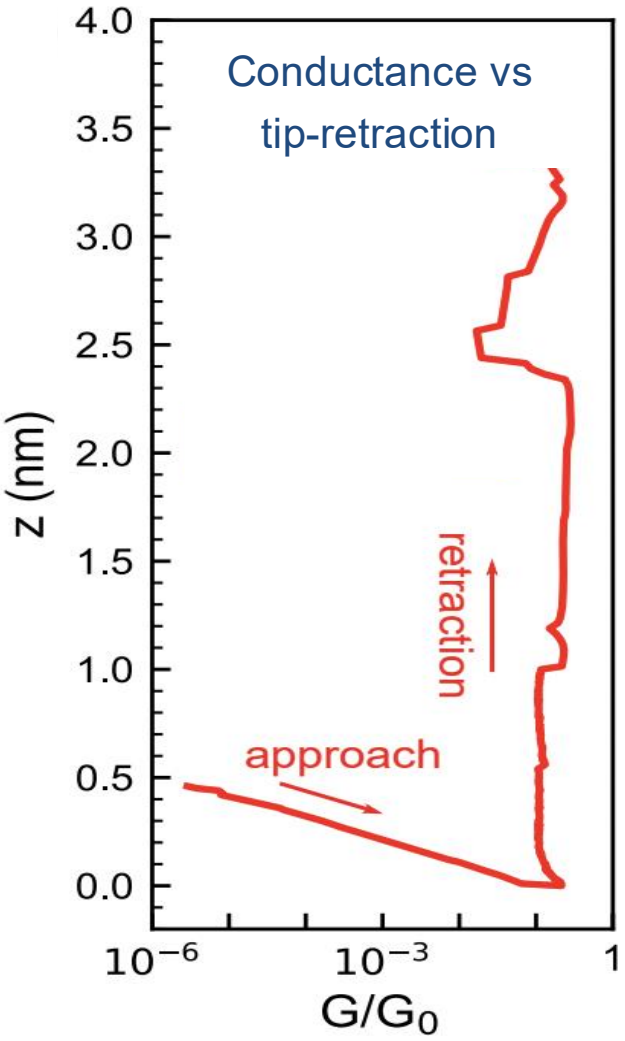




2B-Haiku GNRs: STM characterization



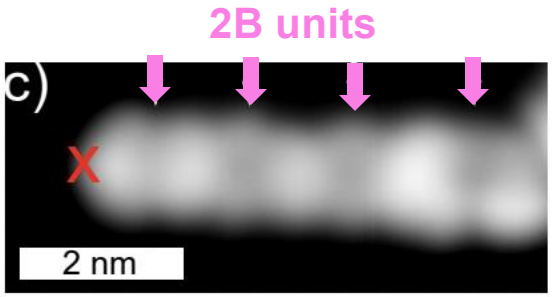


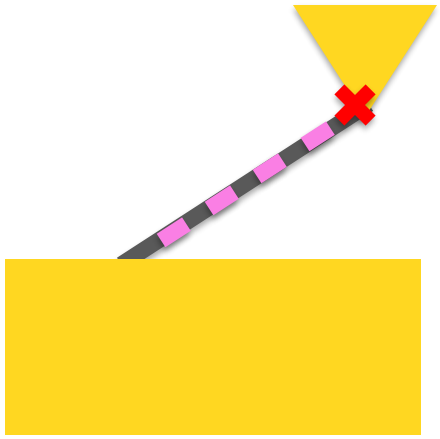


≈ constant transmission

Ballistic electron transport

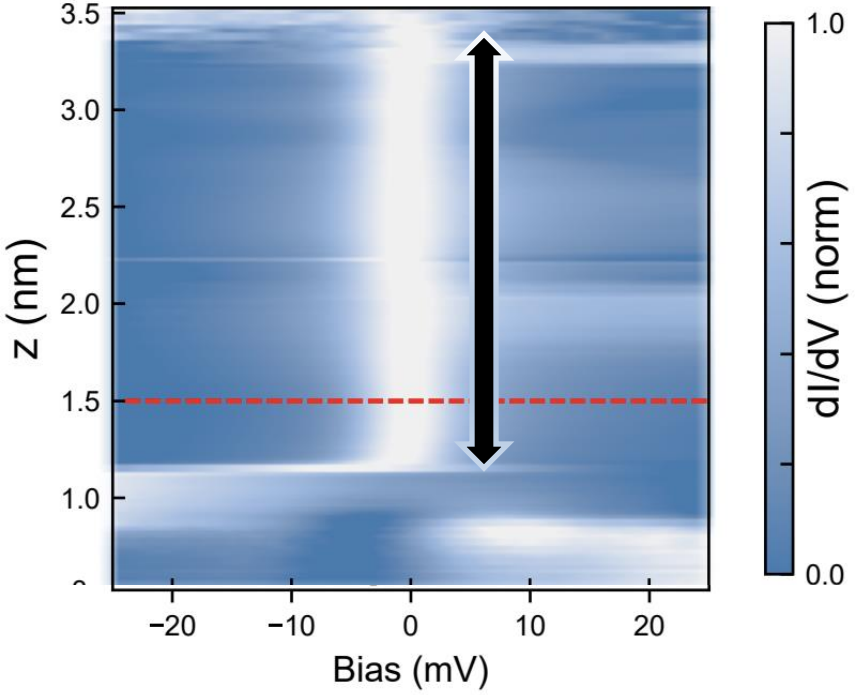
2B-Haiku GNRs: STM characterization





N. Friedrich, AGL et al.
ACS Nano 16, 14819 (2022)

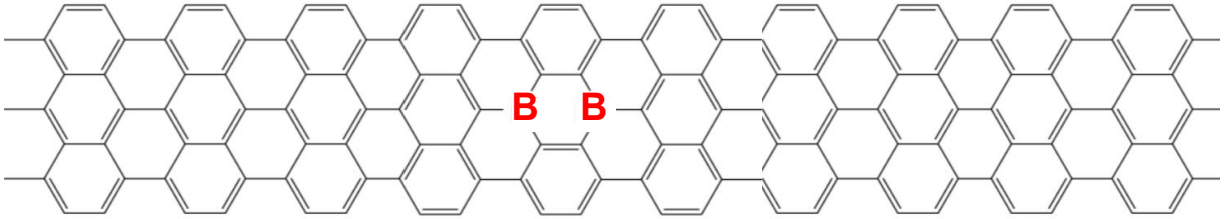
dI/dV vs tip-retraction



Kondo resonance

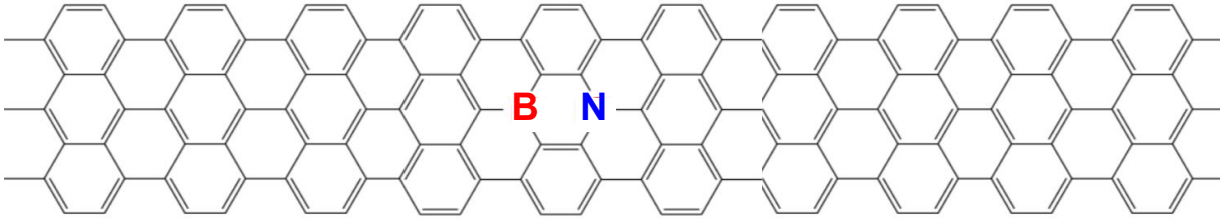
Screening of the localized magnetic moments by the metallic band

Chemical substitution in GNRs

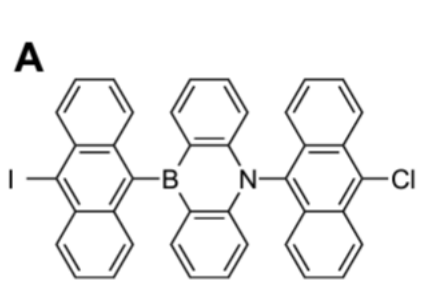


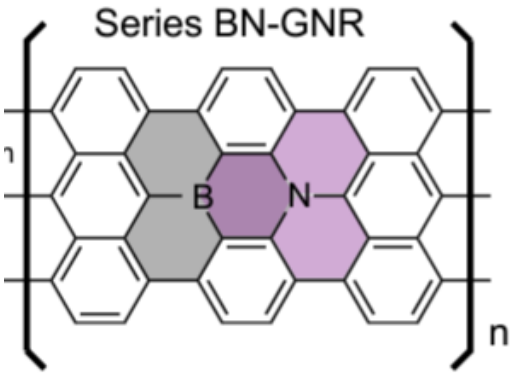
2B-units in the backbone of 7-armchair GNRs (BN-7AGNR)

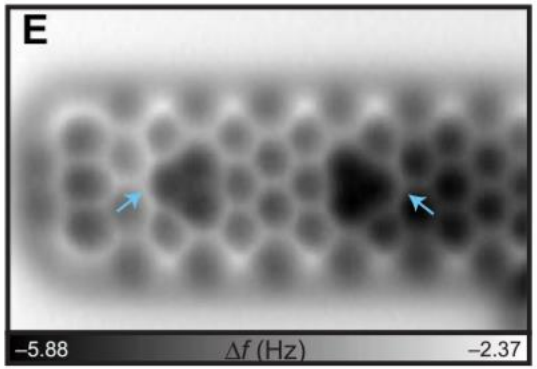
Chemical substitution in GNRs



BN-units in the backbone of 7-armchair GNRs (2B-7AGNR)

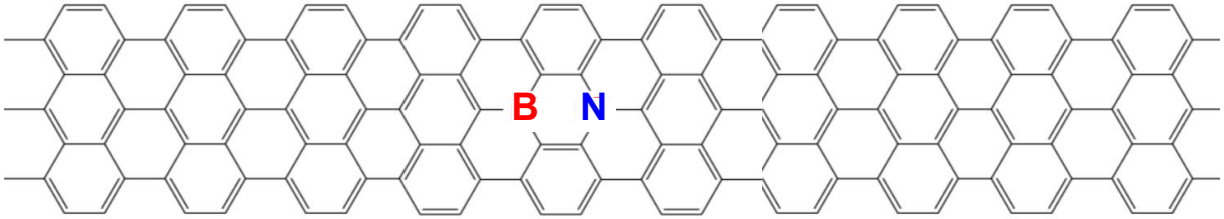




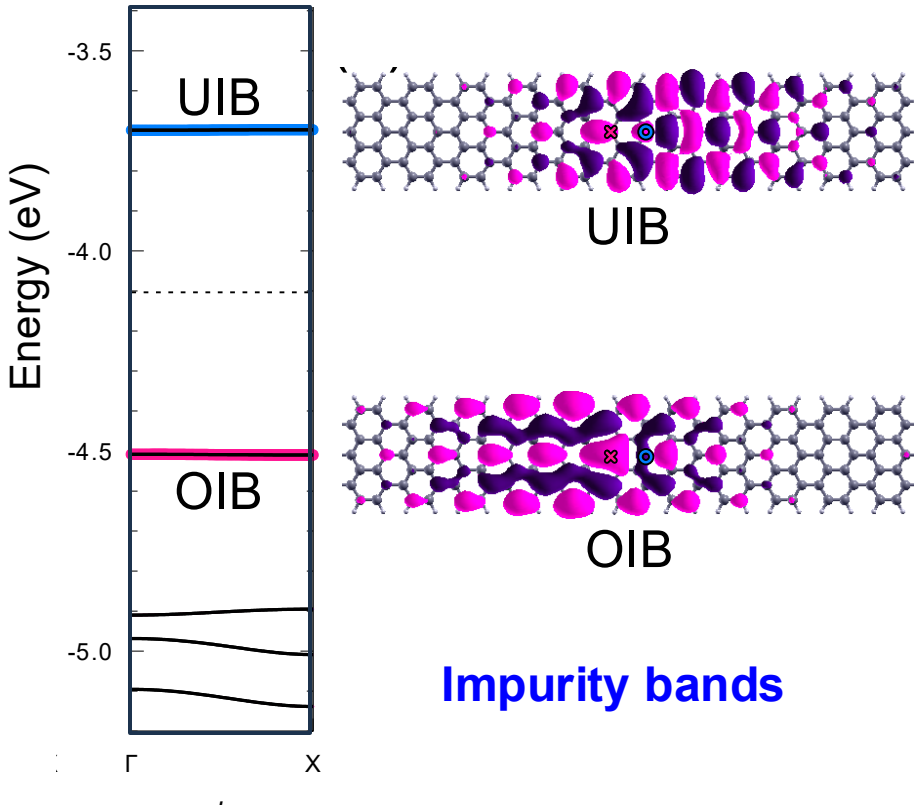


Kawai et al., Sci. Adv. 4, eaar7181 (2018)

Chemical substitution in GNRs



DFT/SIESTA simulations



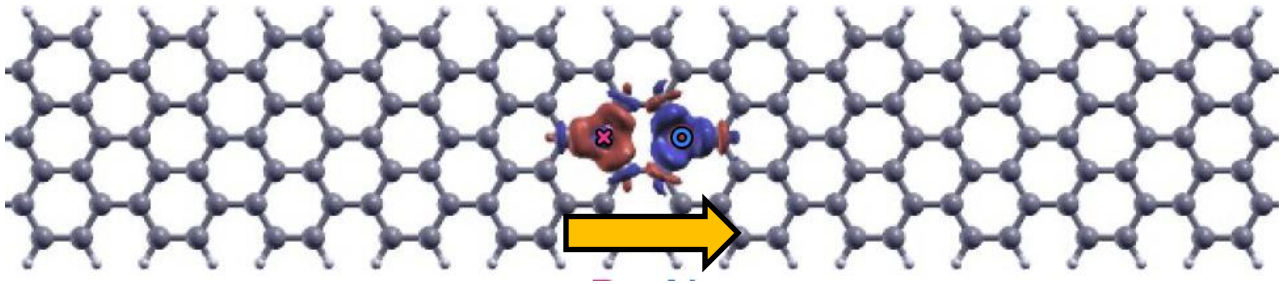
UIB

OIB

Impurity bands

R. Menchon, AGL et al., Electron. Struct. 5, 045103 (2023)

Chemical substitution in GNRs



Dipolar moment

RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 47, NUMBER 3 15 JANUARY 1993-I

Theory of polarization of crystalline solids

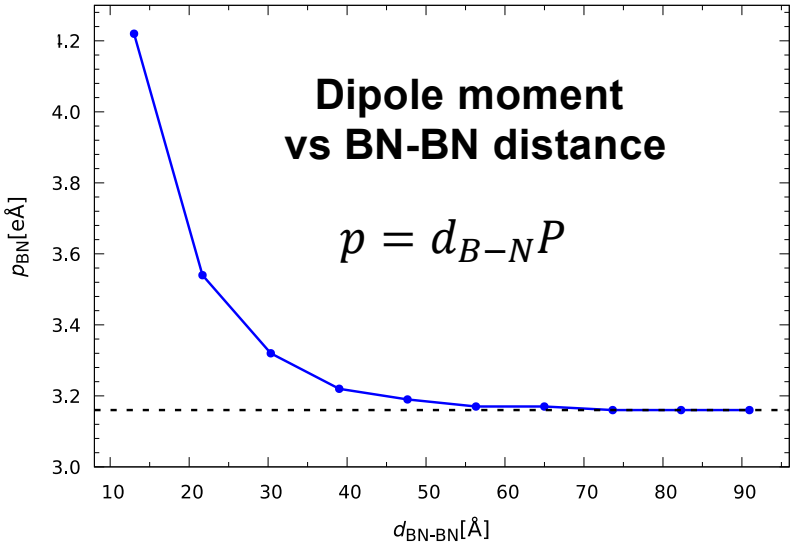
R. D. King-Smith and David Vanderbilt
Department of Physics and Astronomy, Rutgers University, P. O. Box 849, Piscataway, New Jersey 08855-0849
(Received 10 June 1992)

Electronic polarization as a Berry phase

$$P = \frac{e}{2\pi}\int_{BZ} i\langle u_k|\partial u_k\rangle dk$$

Berry curvature

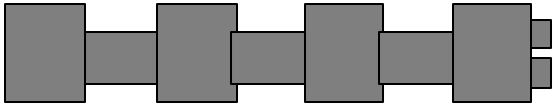
DFT/SIESTA simulations



R. Menchon, AGL et al., Electron. Struct. 5, 045103 (2023)

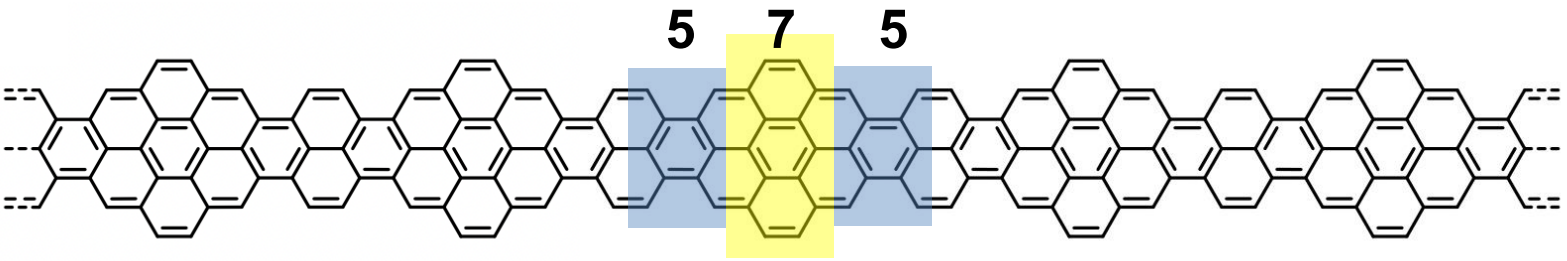
Chemical doping

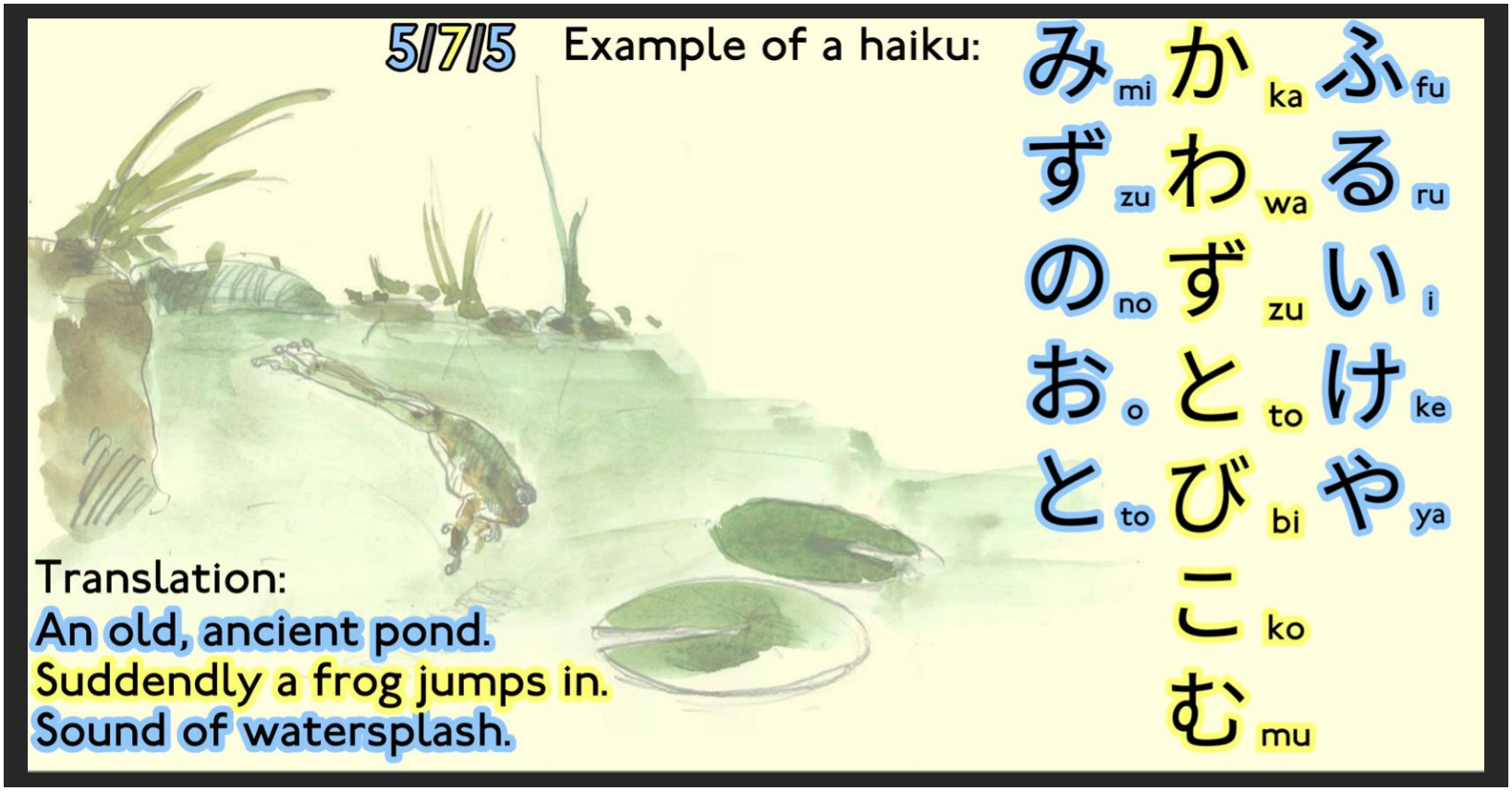
Topological properties



Atomically precise graphene nanoarchitectures

Haiku graphene nanoribbons

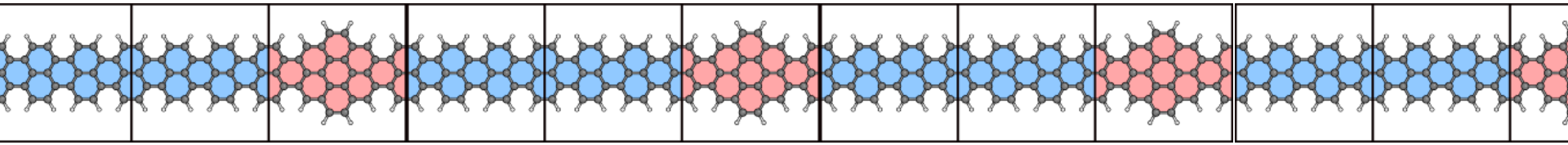




Hybrid Haiku GNRs: theoretical experiment

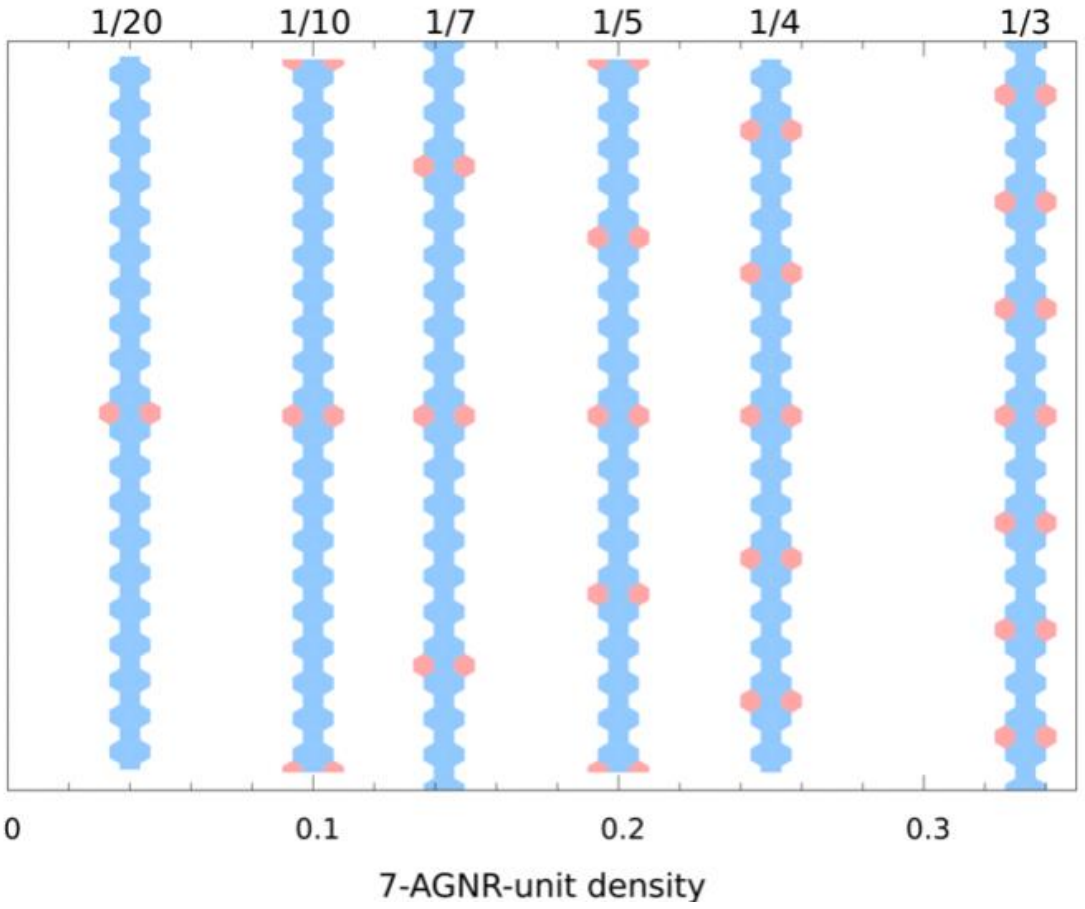
Precursor for 5-AGNR

Precursor for Haiku-AGNR



Tunable topology in hybrid Haiku-GNRs

Haiku-AGNR

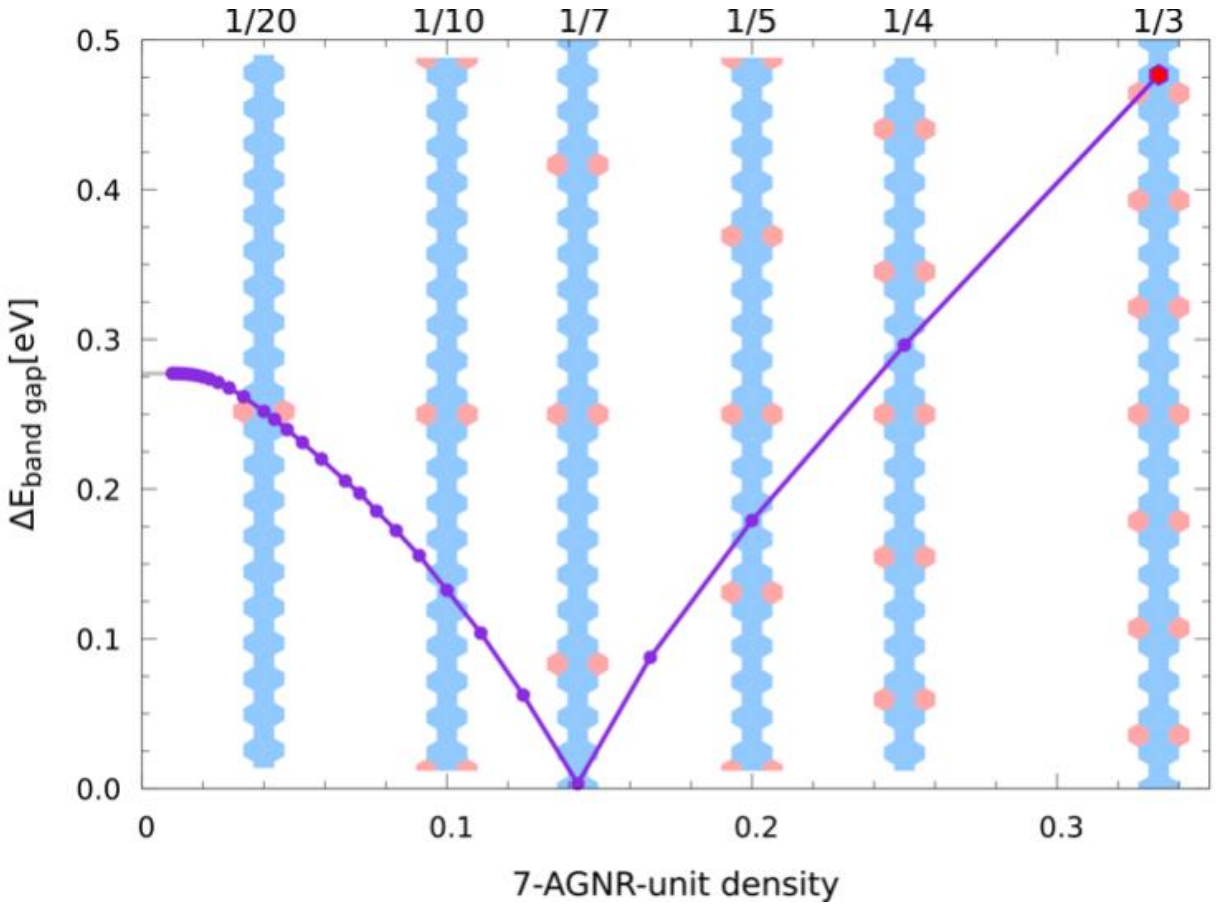


Tunable topology in hybrid Haiku-GNRs

DFT / SIESTA simulations

$$P = \frac{e}{2\pi}\Phi_{Zak} mod(e) \longrightarrow Z_2 = \frac{\Phi_{Zak}}{\pi} mod(2)$$

Haiku-AGNR



Tunable topology in hybrid Haiku-GNRs

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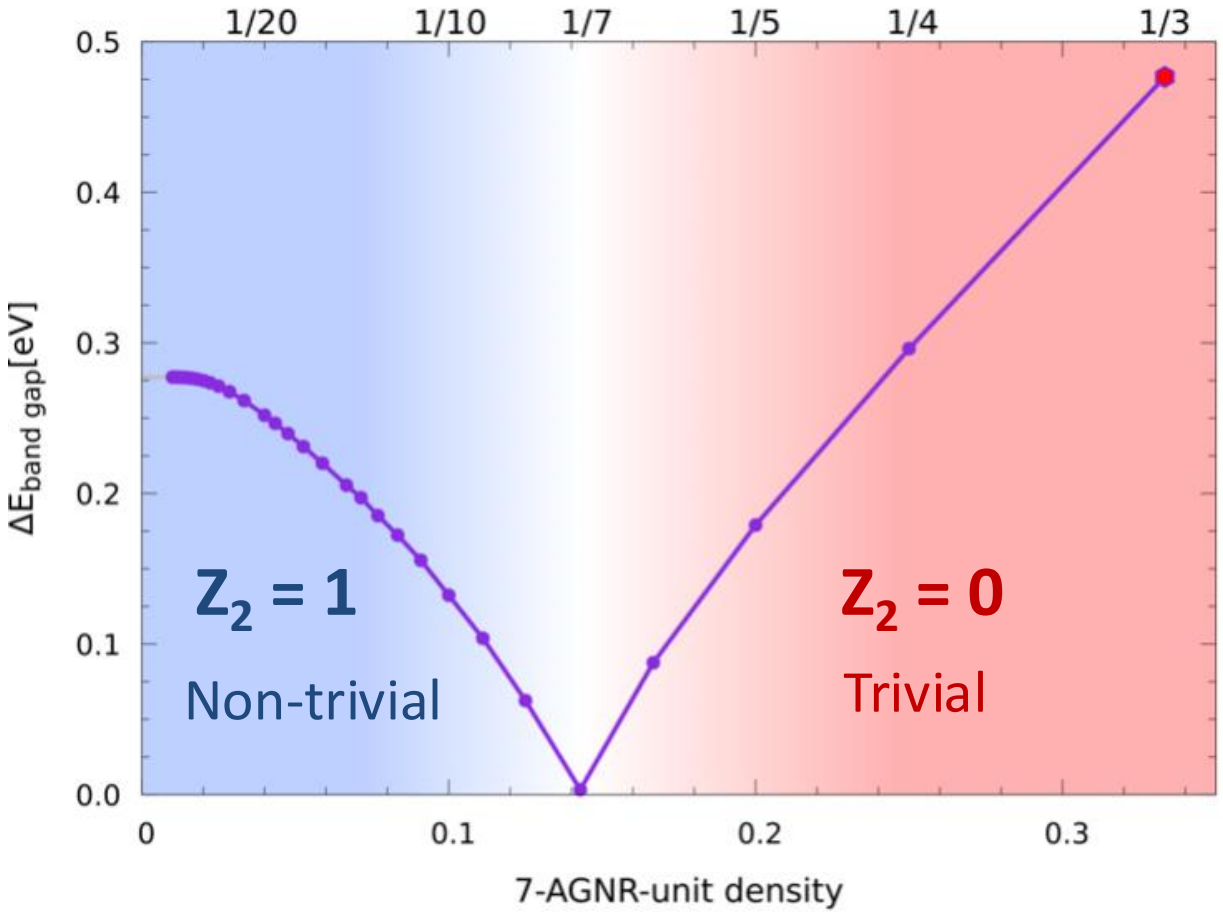
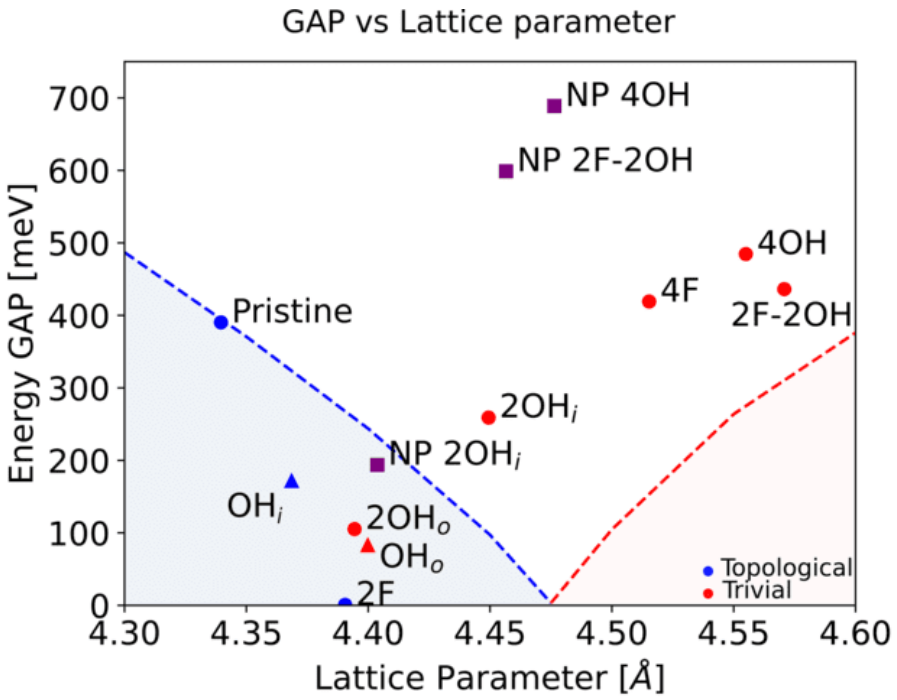
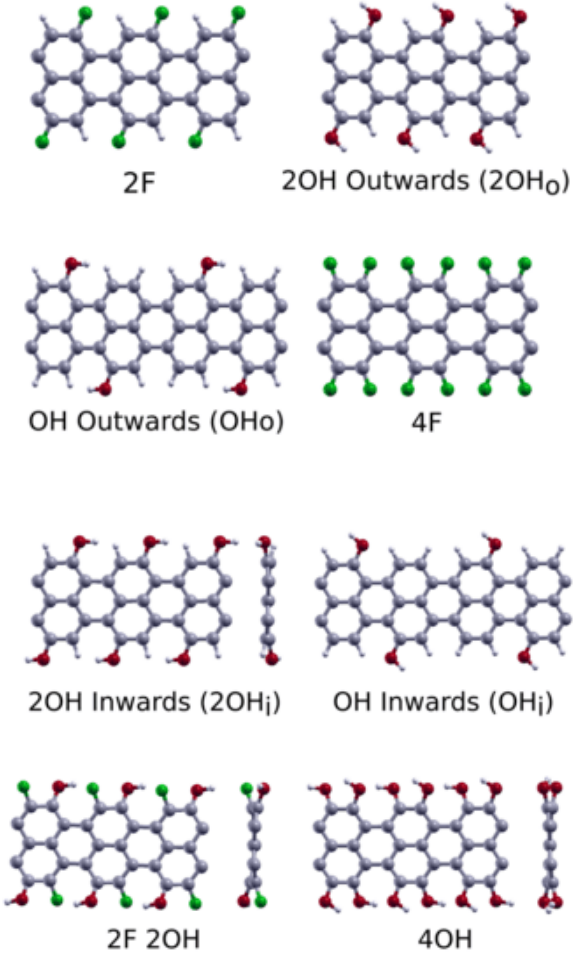
$$P = \frac{e}{2\pi}\Phi_{Zak} mod(e) \longrightarrow Z_2 = \frac{\Phi_{Zak}}{\pi} mod(2)$$



R. Menchón, AGL et al. (submitted)

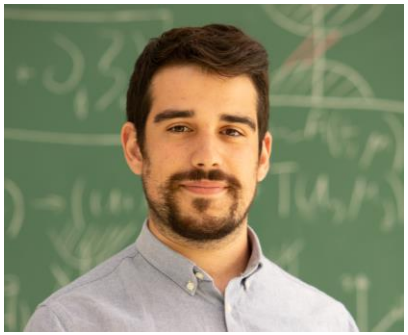
Topology of functionalized 5AGNR





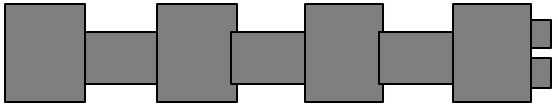
POSTER:

Daniel Garcia-Pina

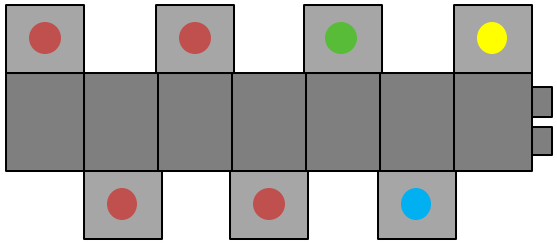


Chemical doping

Topological properties



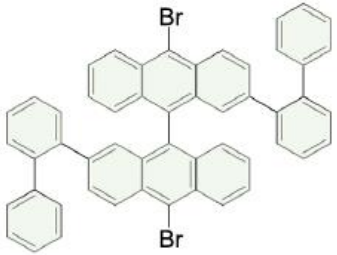
Hybrid nanoarchitectures



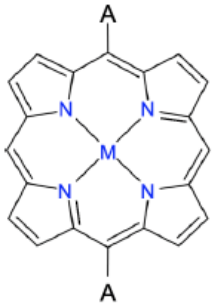
Atomically precise graphene nanoarchitectures

Computational design of hybrid GNRs

GNR base unit

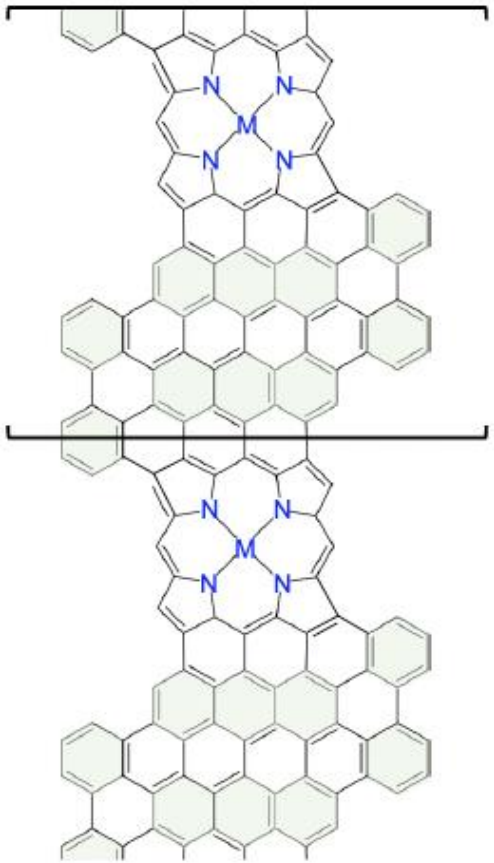


Porphyrin units



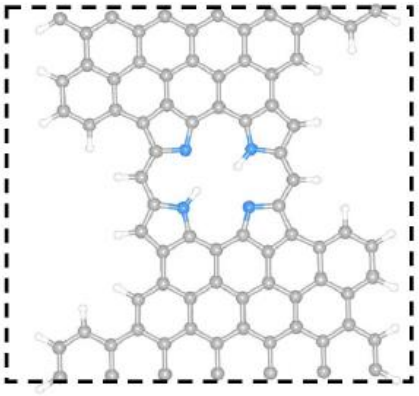
$M = H_2$, Fe

Porphyrin-GNR hybrids

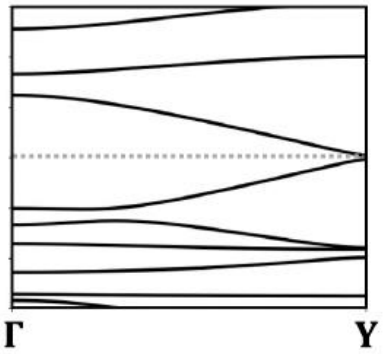


Electronic properties of hybrid GNRs

Non-metalized por-GNR



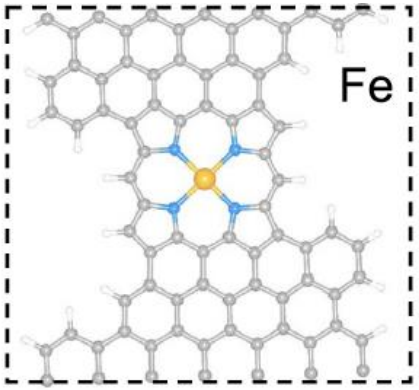
DFT



Very small energy gap

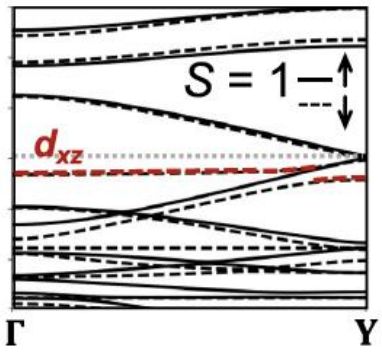
Suitable as electrode

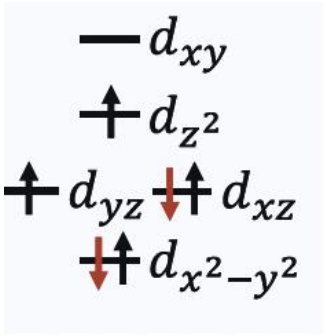
Fe-por-GNR



SIESTA simulations

DFT+U

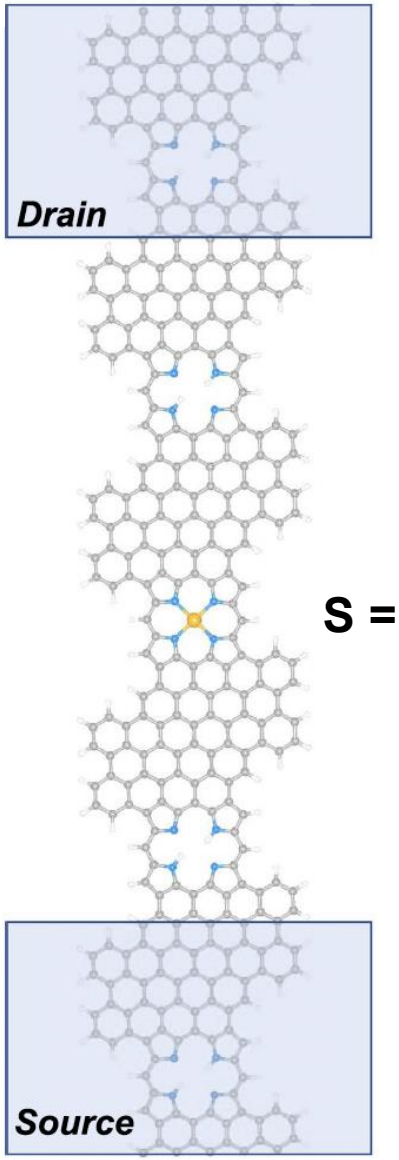




d-orbitals close to Fermi

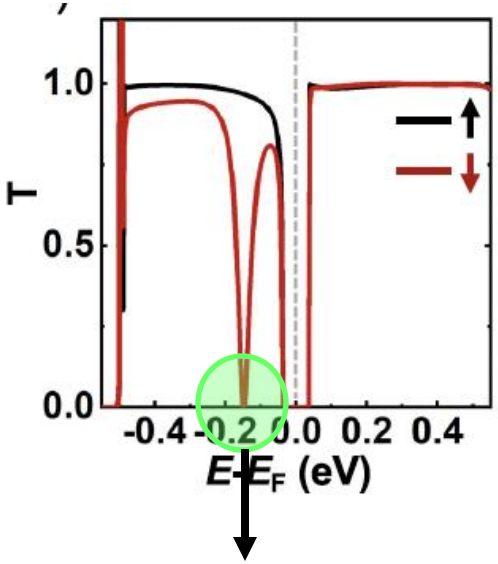
Tunable magnetism expected

Spin transport in hybrid GNRs



S = 1

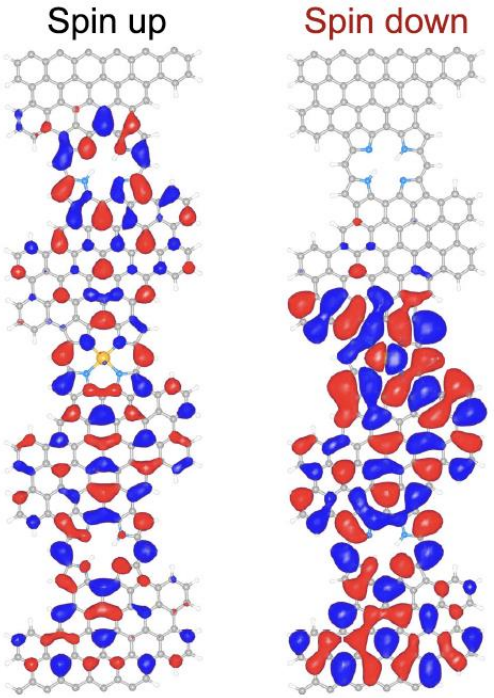
Spin-polarized electronic transmission



Quenching of spin-down transport

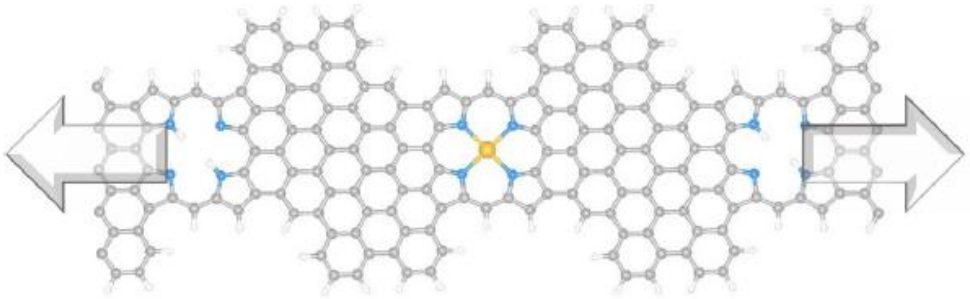
TranSIESTA simulations

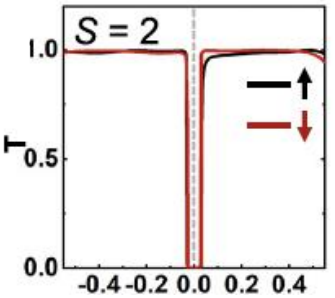
Eigenchannels

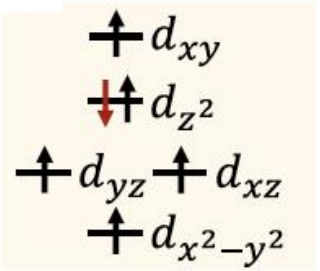


Spin cross-over in por-GNR hybrids

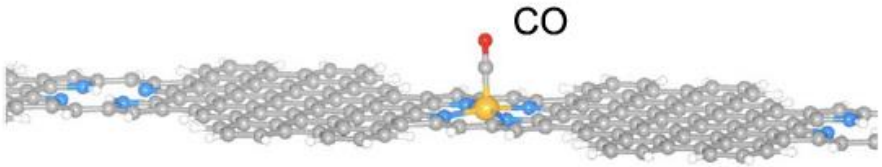
Effect of strain (S=1 → S=2)

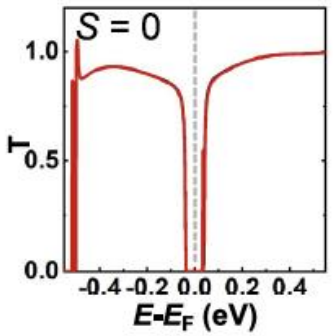


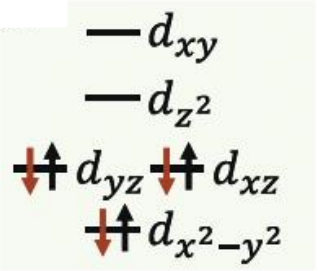




Attachment of molecules (S =1 → S=0)

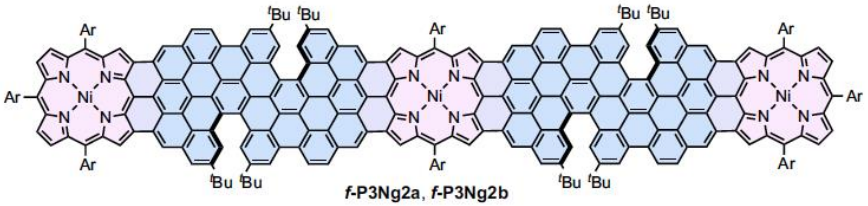


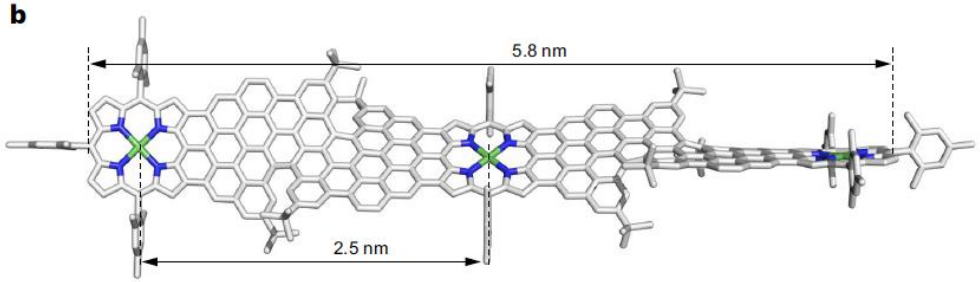


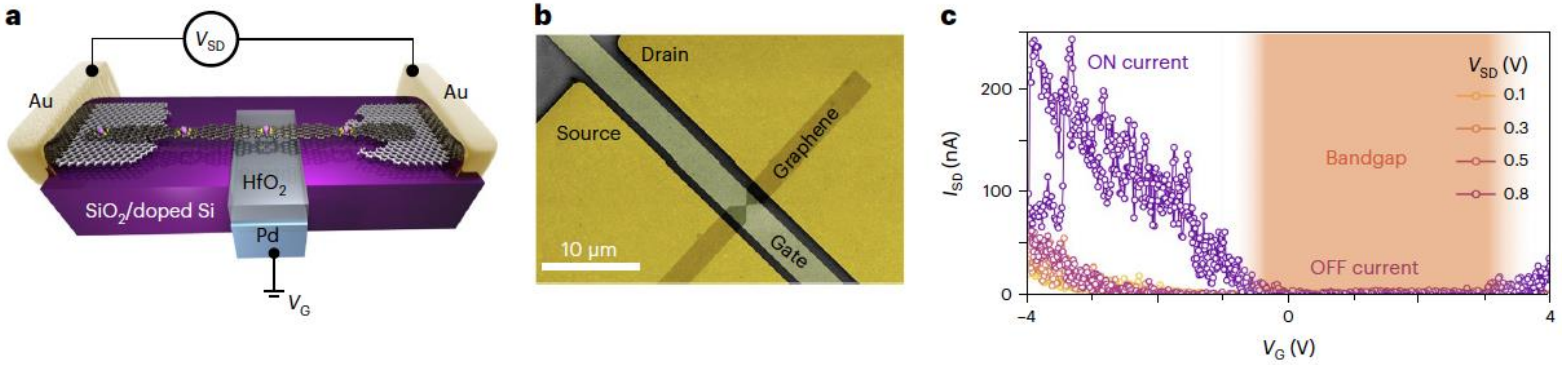


F. Gao, AGL et al., Comm. Phys. 6, 115 (2023)

Solution-synthesis of porphyrin-fused GNRs

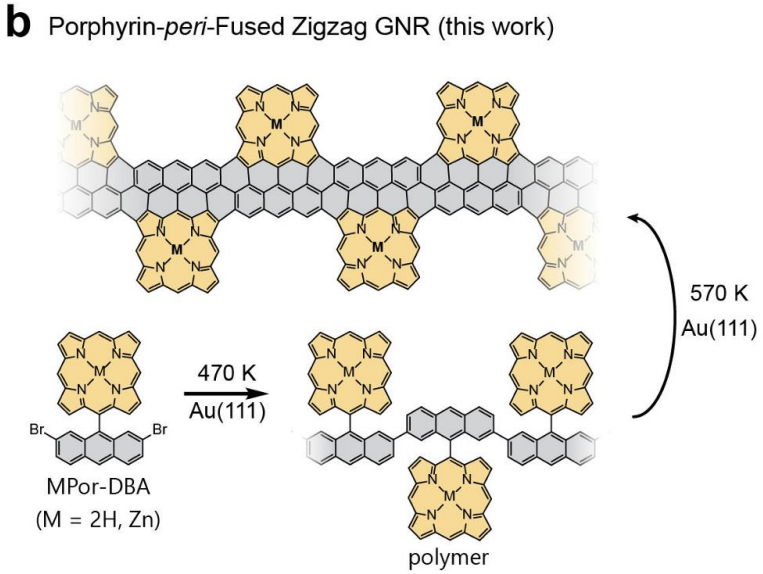


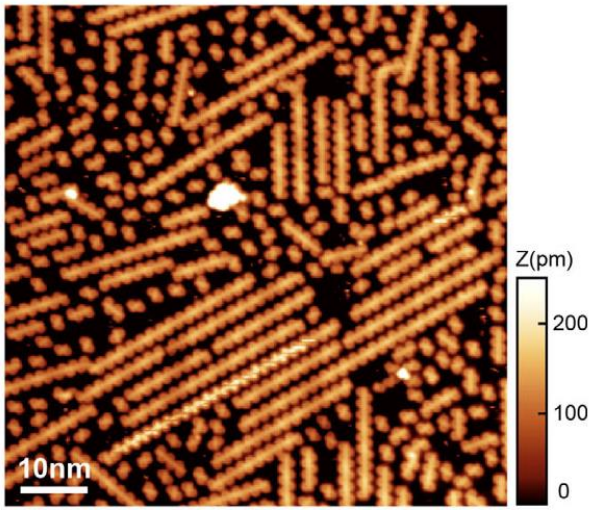


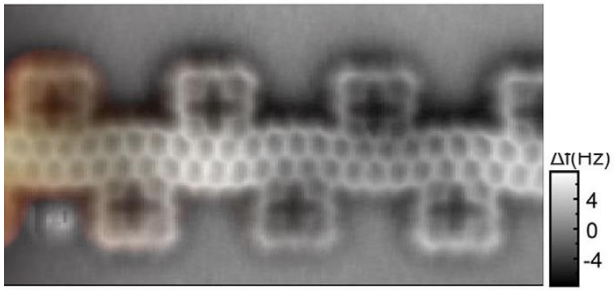


Q. Chen et al., Nat. Chemistry (2024).
https://doi.org/10.1038/s41557-024-01477-1

On-surface synthesis of hybrid GNRs



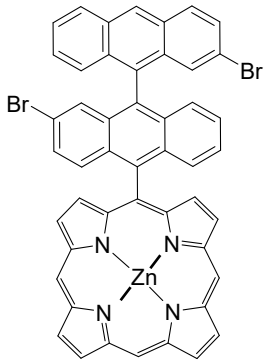




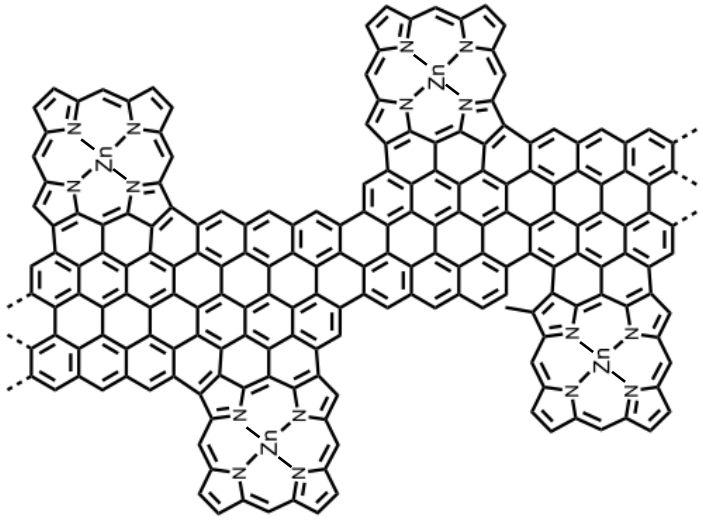
Xiang et al. ChemRxiv. 2024; doi:10.26434/chemrxiv-2024-z9rgh

On-surface synthesis of hybrid GNRs

Molecular precursor: D. Peña (CIQUS)



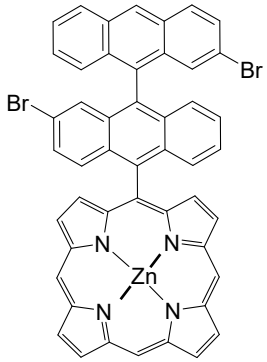
OSS



Zn-Por chiral GNRs

On-surface synthesis of hybrid GNRs

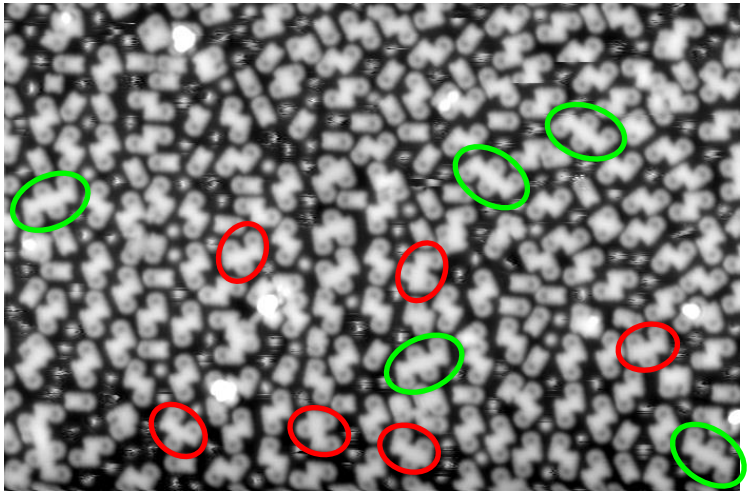
Molecular precursor: D. Peña (CIQUS)



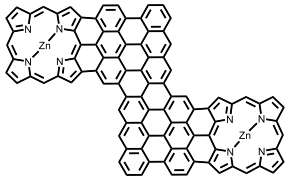
OSS

OSS + STM experiments:

D.G. de Oteyza (CINN), M. Corso (CFM)

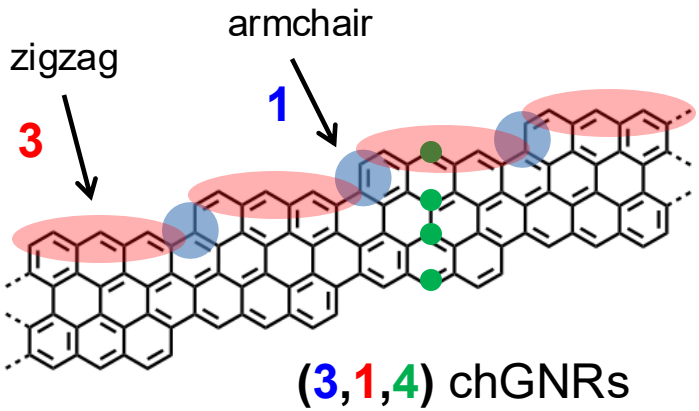


- Preferential formation of dimers

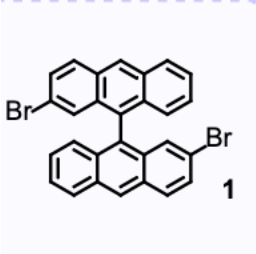


- Long annealing@350ºC leads to lateral fusion: formation of 3ZnPor-and 4ZnPor-chGNRs

Chiral GNRs

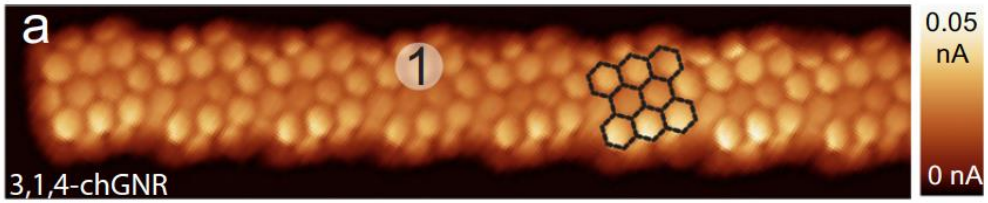


Molecular precursor: D. Peña (CIQUS)



OSS

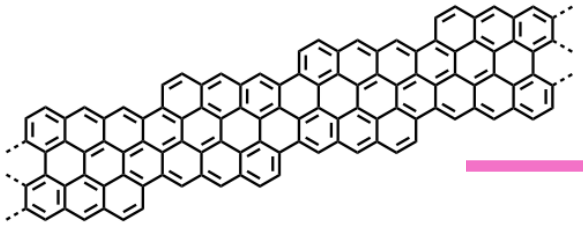
OSS + STM experiments: J.I. Pascual (Nanogune)



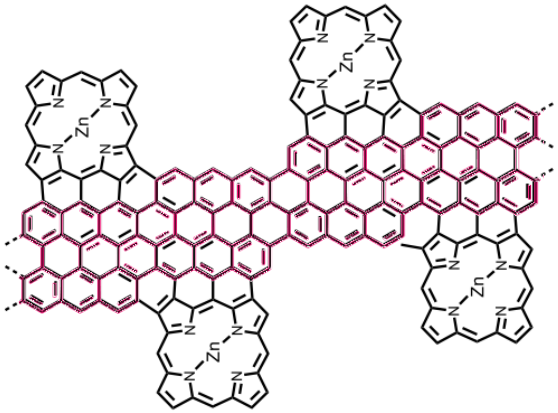
J. Li, AGL et al., Nat. Commun. 12, 5538 (2021)

ZnPor-chiralGNRs

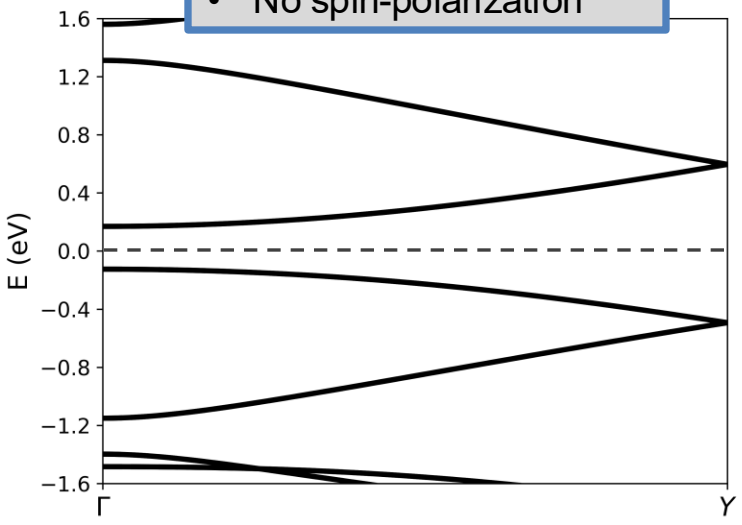
(3,1,4) chGNRs



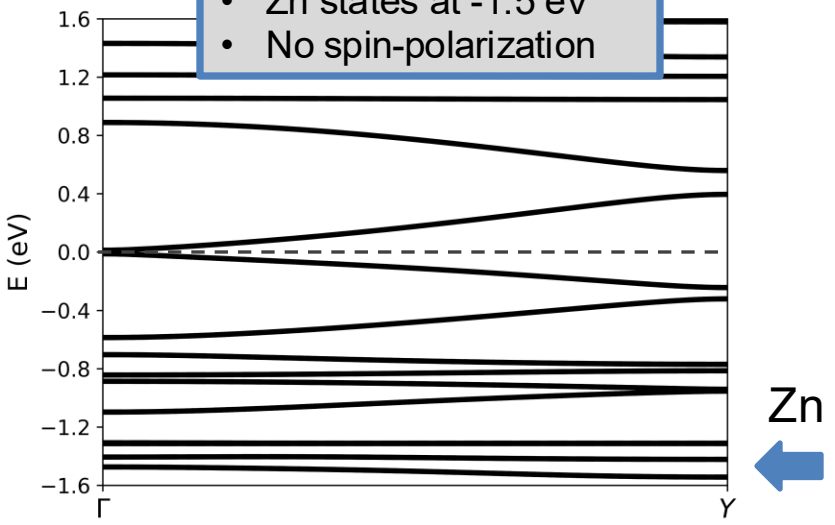
Zn-Por chiral GNRs



- Semiconducting system
- No spin-polarization



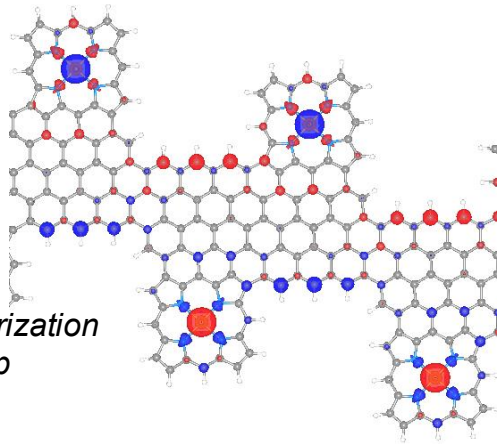
- Metallic system
- Zn states at -1.5 eV
- No spin-polarization



F. Gao, AGL et al. (in preparation)

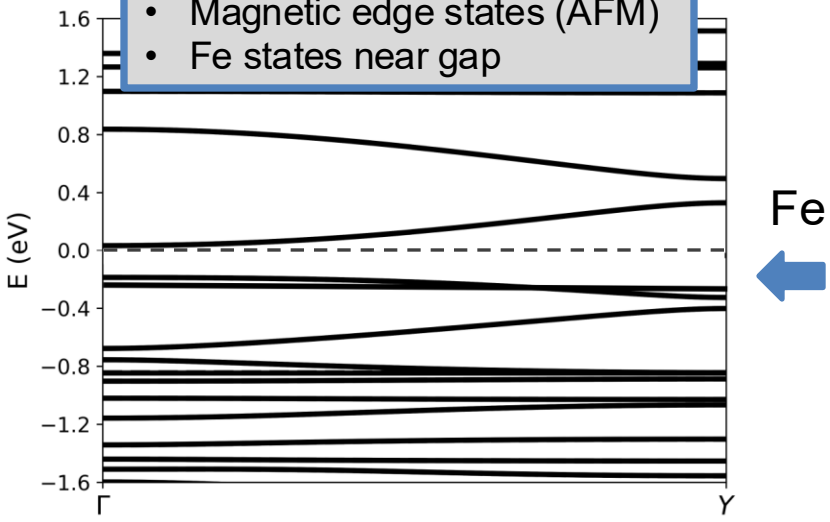
Changing the metallic center…

Fe-Por chiral GNRs



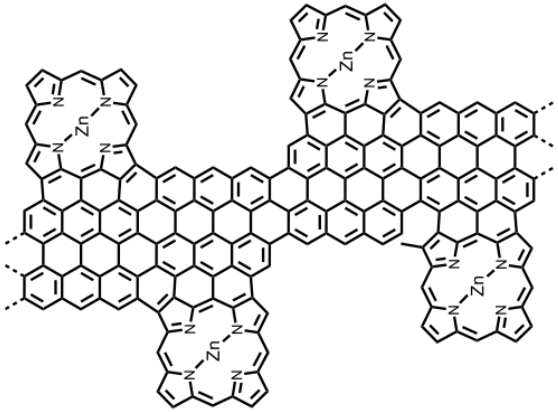
Spin-polarization map

- Semiconductor
- Magnetic edge states (AFM)
- Fe states near gap

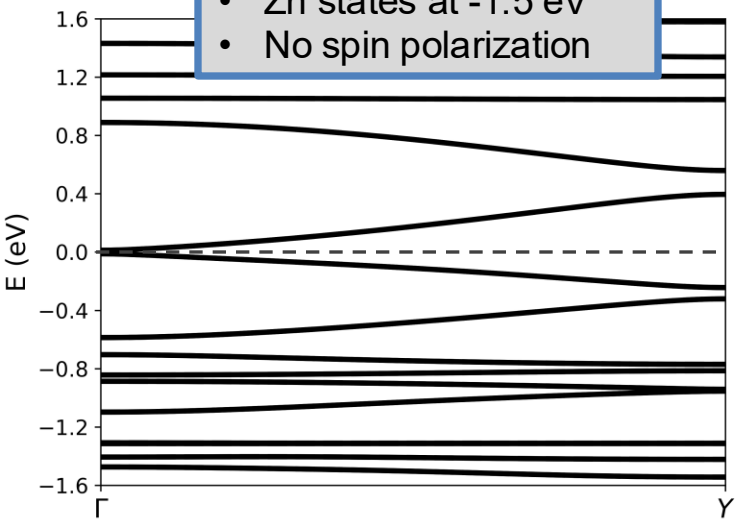


Fe

Zn-Por chiral GNRs



- Metallic system
- Zn states at -1.5 eV
- No spin polarization

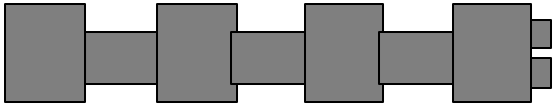


Zn

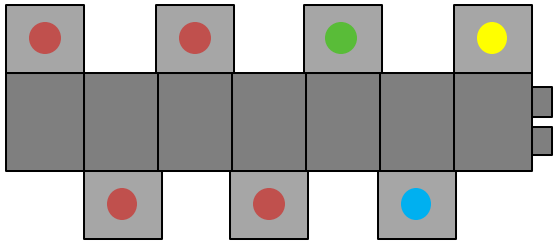
F. Gao, AGL et al. (in preparation)

Chemical doping

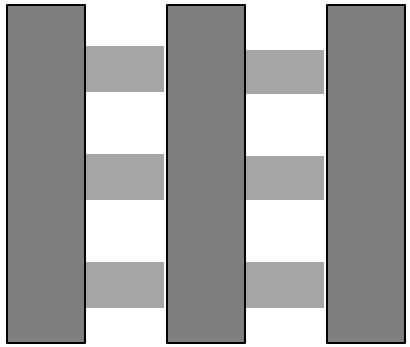
Topological properties



Hybrid nanoarchitectures



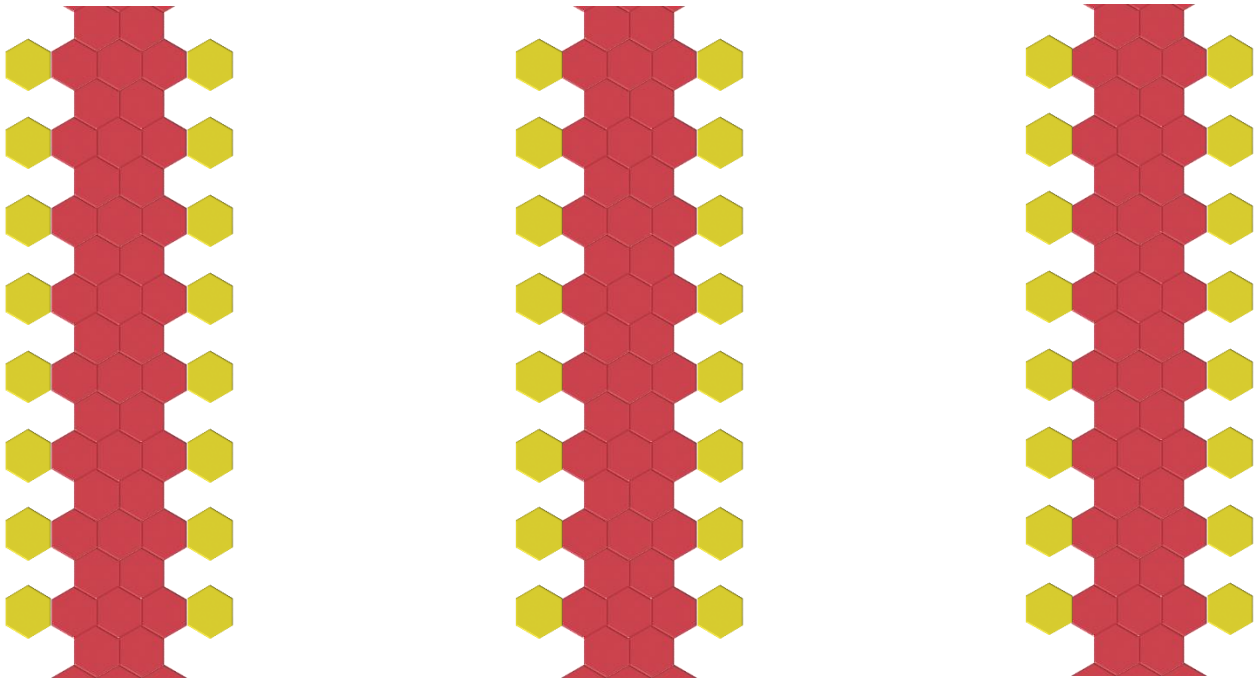
From 1D to 2D



Electronic properties explored by SIESTA simulations

From 1D to 2D

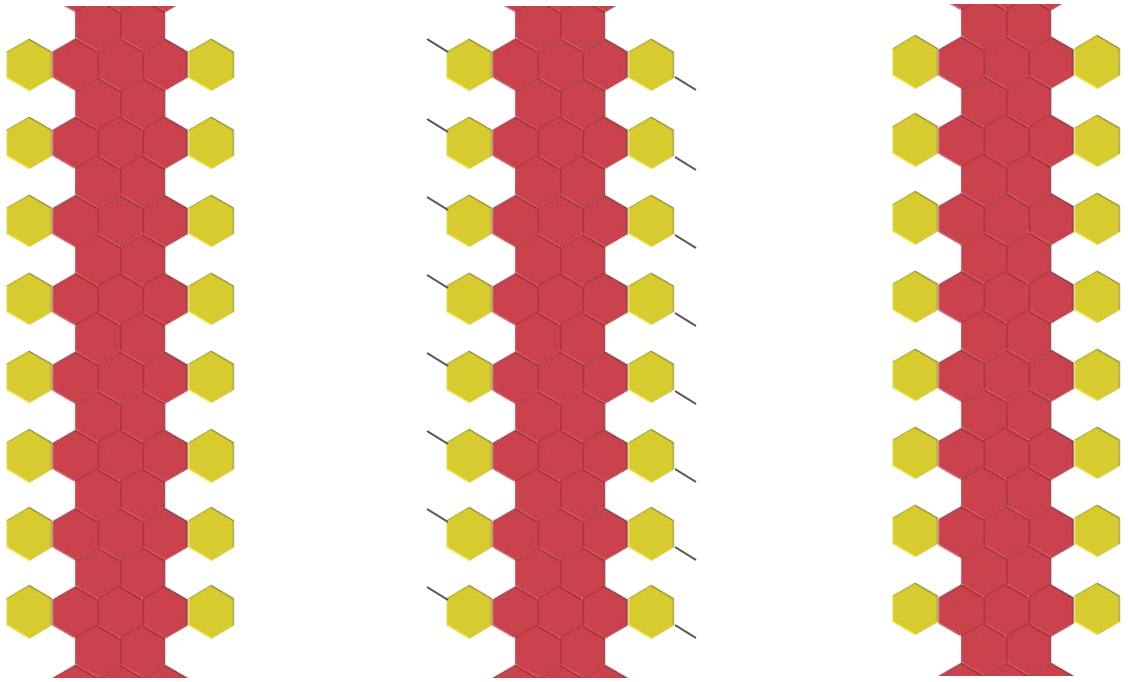
1D nanostructures with specific coupling bridges



7aGNRs with additional phenyls

From 1D to 2D

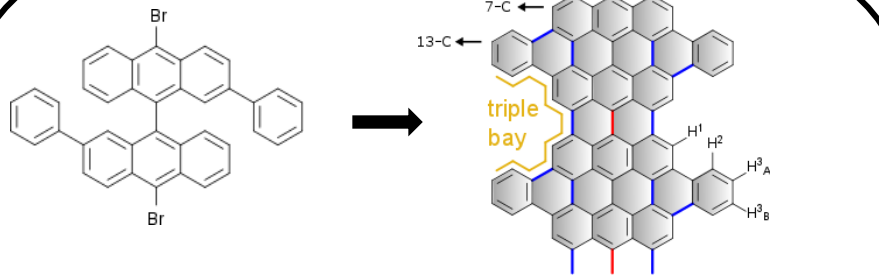
1D nanostructures with specific coupling bridges



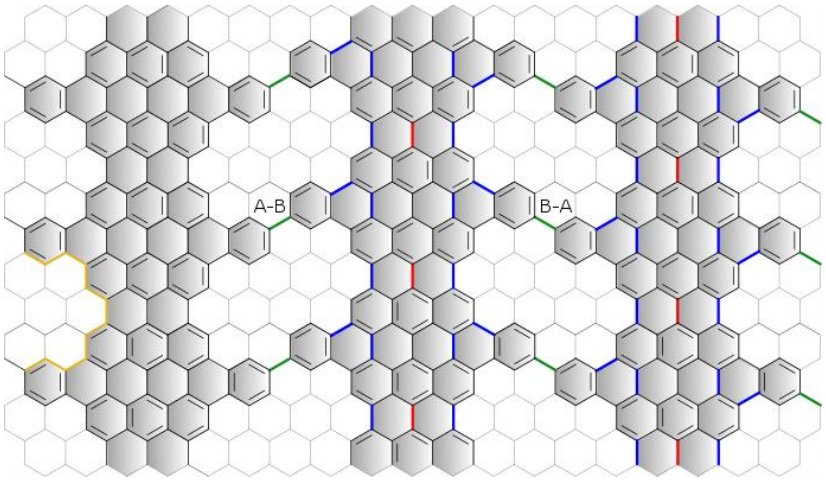
7AGNRs with additional phenyls

From 1D to 2D nanoarchitectures

Nanoporous Graphene: on-surface synthesis

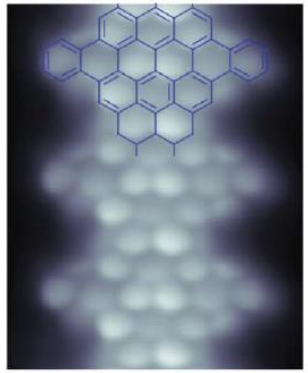


Monomer **Graphene Nanoribbon**

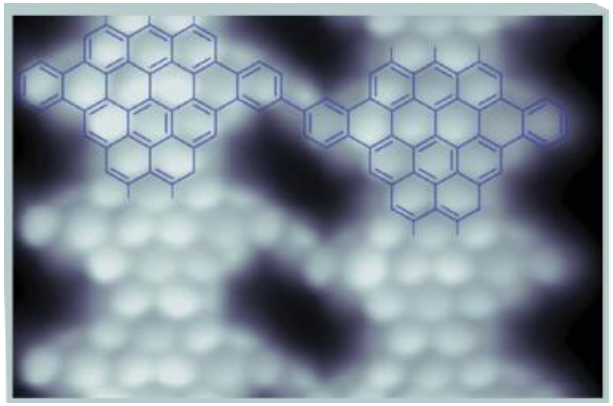


Nanoporous Graphene (NPG)

STM images with CO tip



GNR (1D)



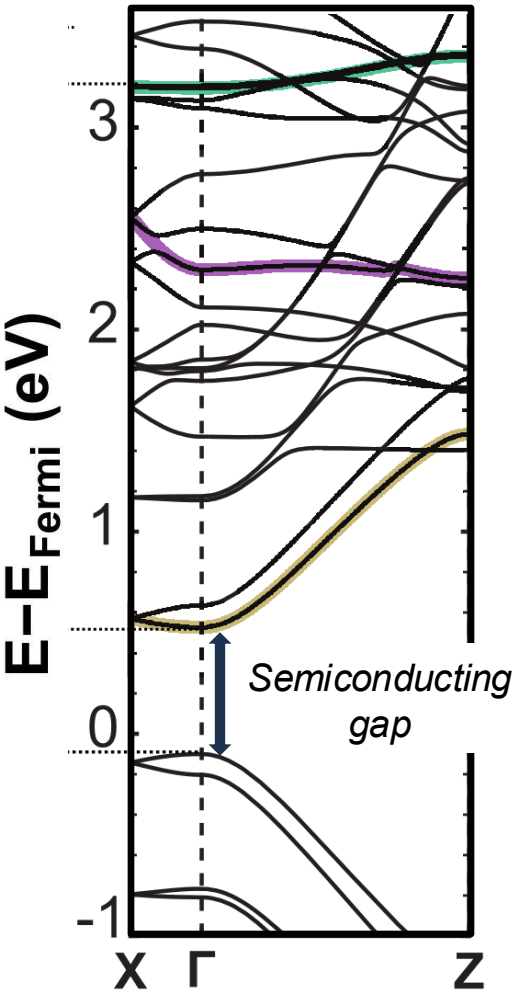
NPG (2D)

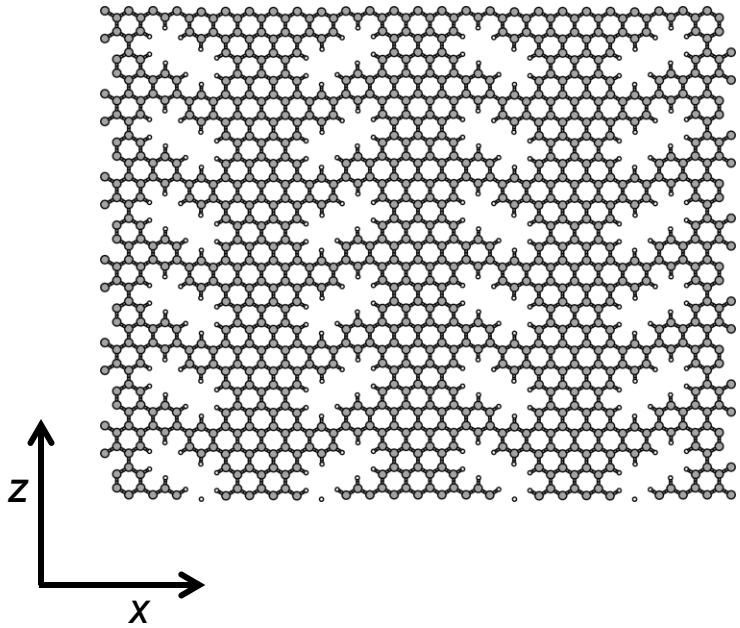
C. Moreno, AGL et al., Science 360, 199 (2018)

Precursors: D. Peña (CIQUS) / OSS and STM experiments: A. Mugarza, ICN2

NPG: anisotropic electronic properties

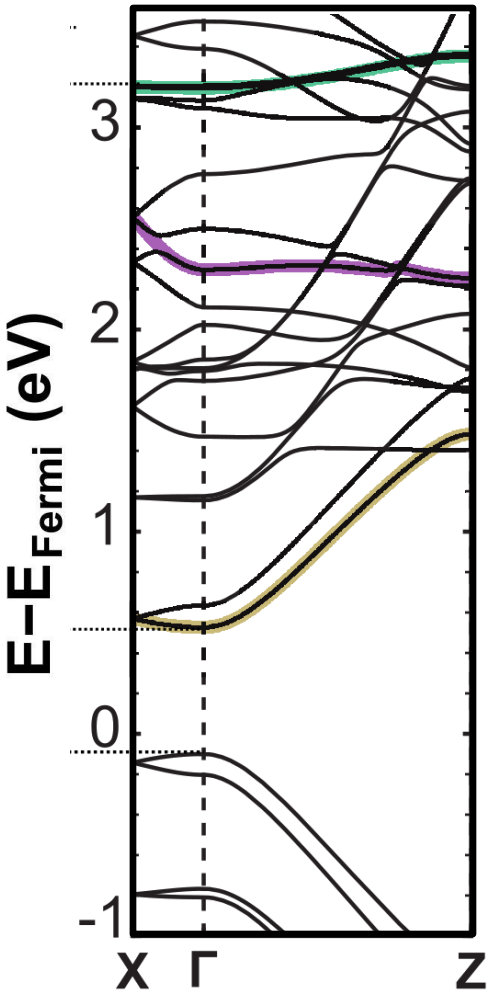
Electronic Band Structure
(DFT / SIESTA)



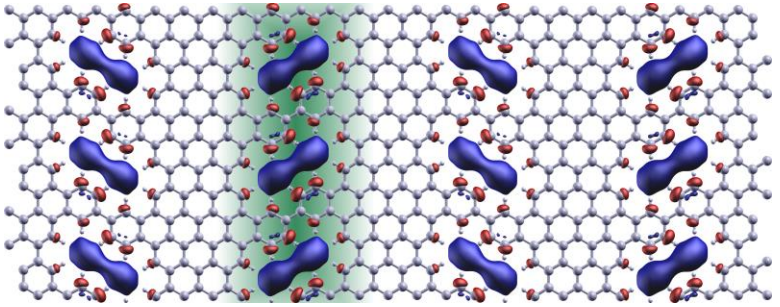


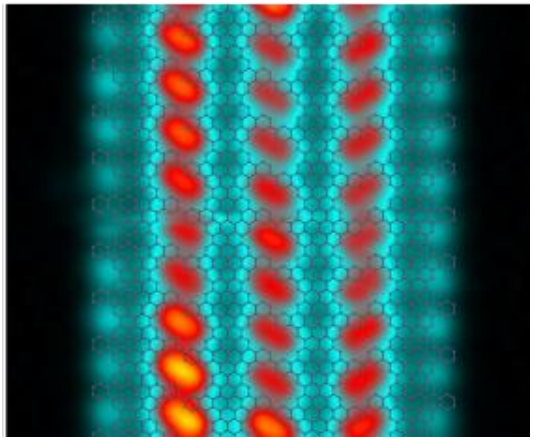
NPG: anisotropic electronic properties

Electronic Band Structure
(DFT / SIESTA)



Pore states

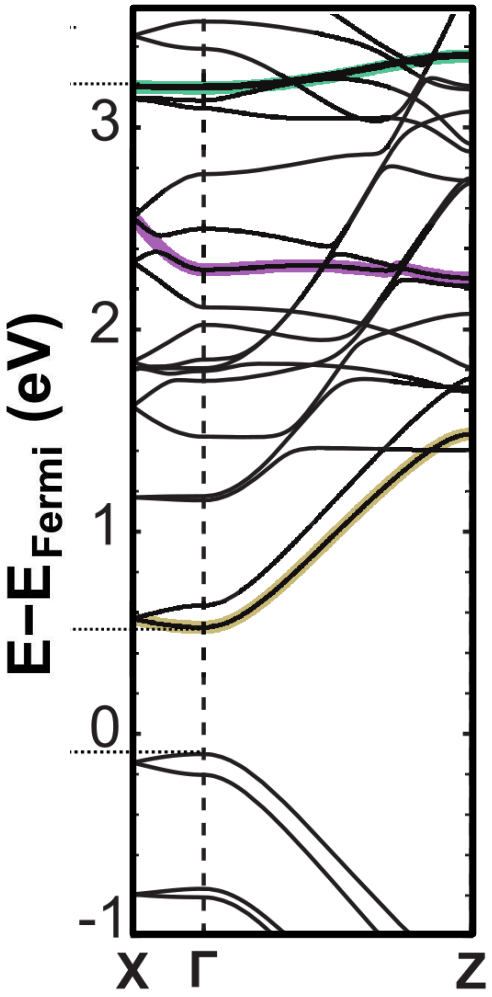




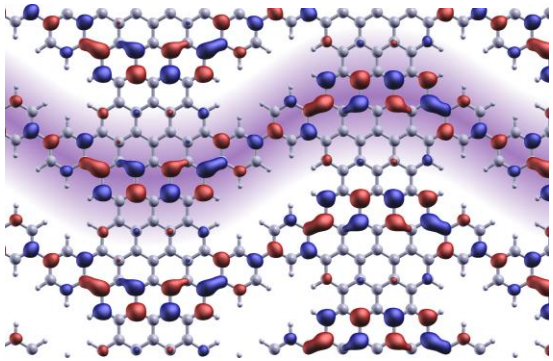
STM (dI/dV map at 2.3V)

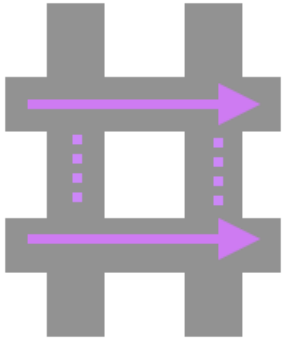
NPG: anisotropic electronic properties

Electronic Band Structure
(DFT / SIESTA)

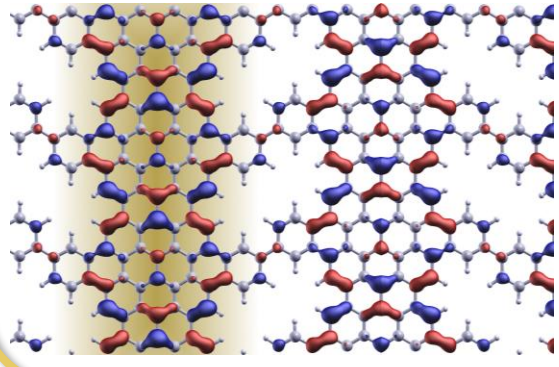


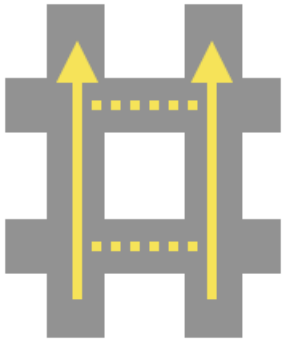
Transversal band



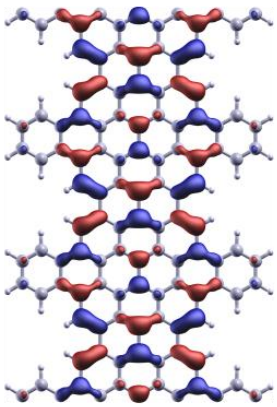


Longitudinal band

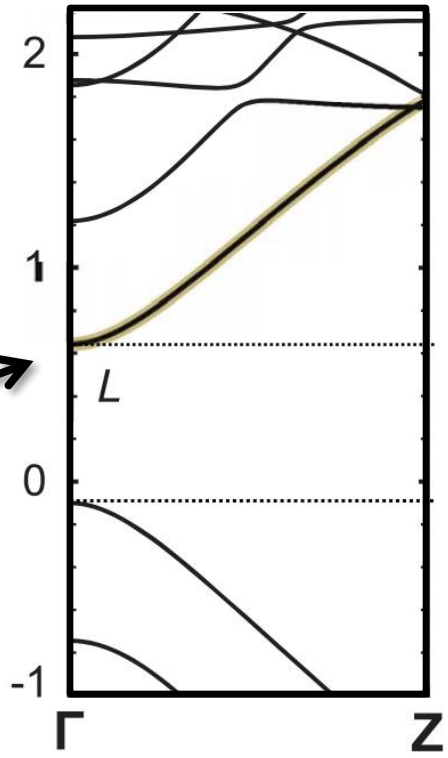




NPG: longitudinal bands

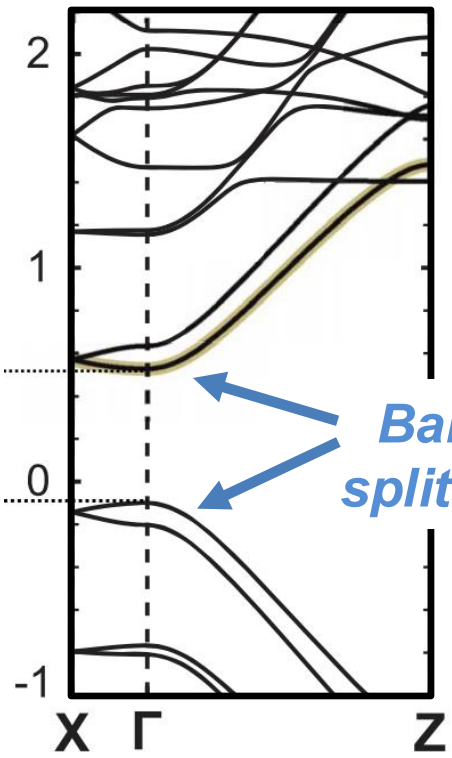


Graphene nanoribbon

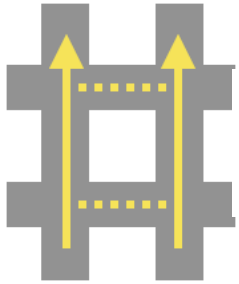


Lateral fusion

NPG

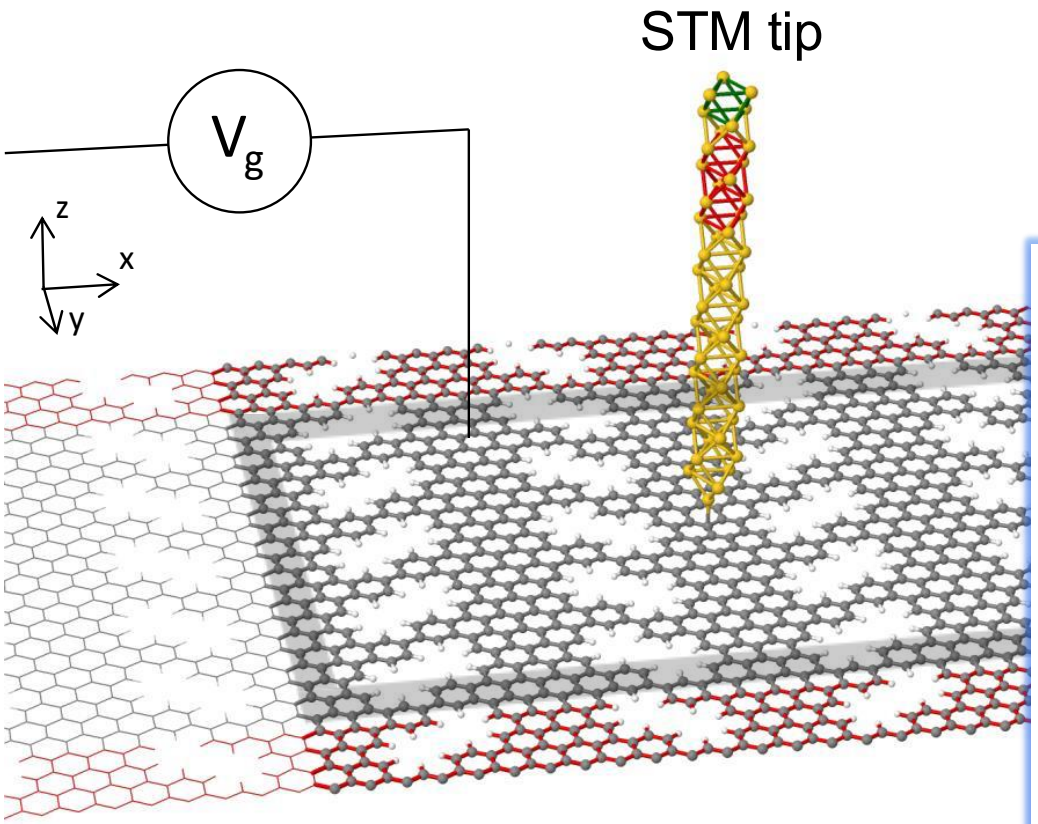


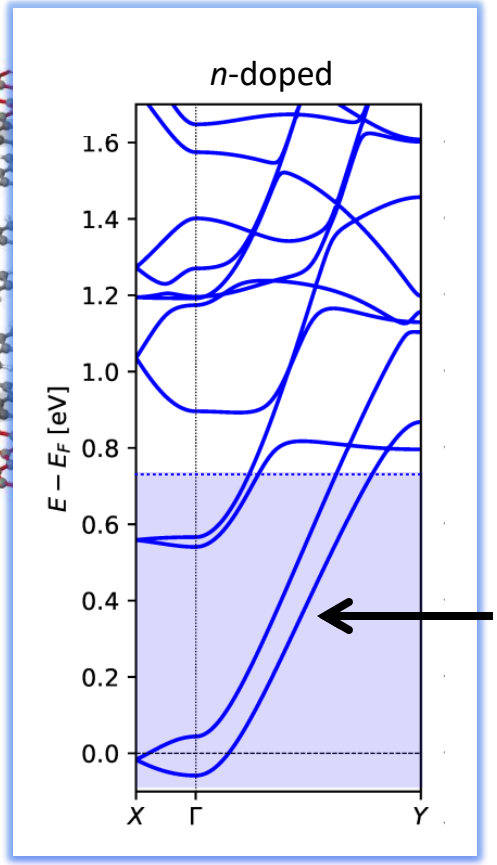
Band splitting



Interribon coupling

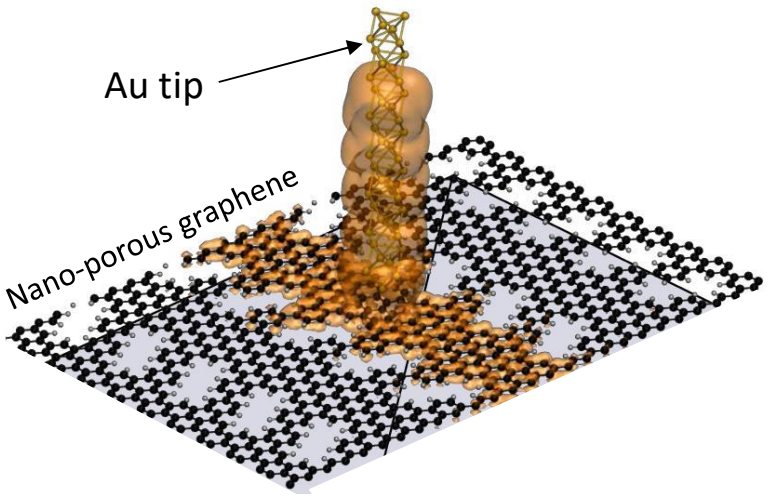
Simulating electron propagation in NPG





Longitudinal band

Multiscale method based on DFT+TB+NEGF



Full DFT simulation for NPG in contact with a metallic tip

DFT + NEGF ~ 1500 atoms

Details of the method: Calogero et al., Nanoscale 11, 6153 (2019)

Multiscale method based on DFT+TB+NEGF

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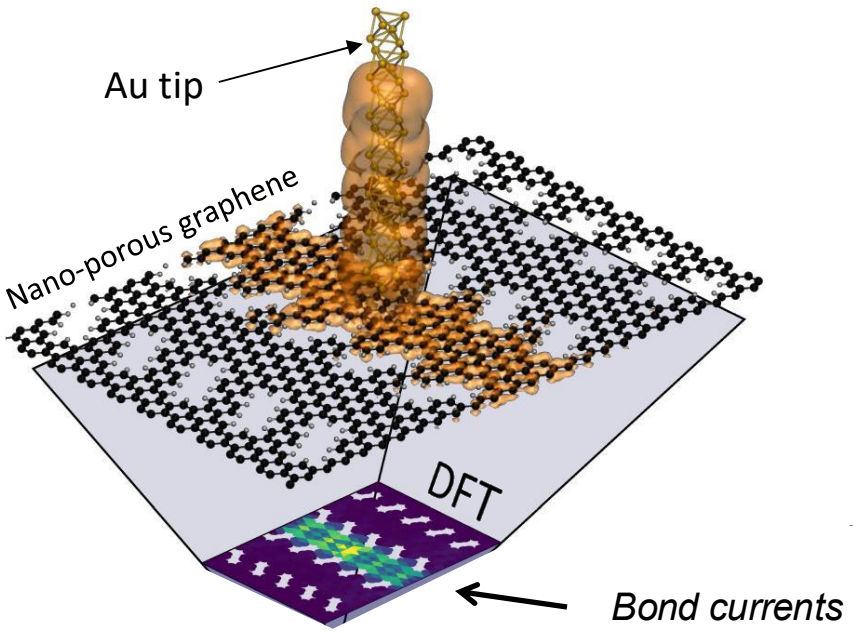


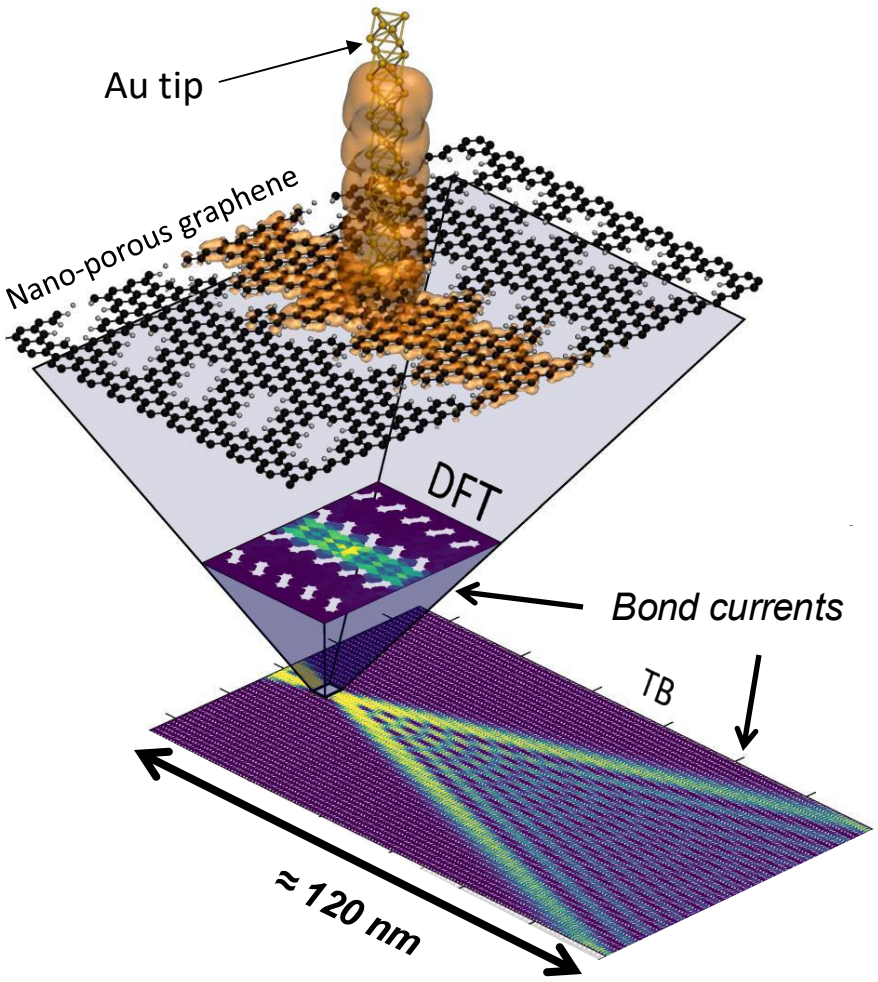
Full DFT simulation for NPG in contact with a metallic tip

DFT + NEGF ~ 1500 atoms

Link the perturbed contact region described by DFT…

Details of the method: Calogero et al., Nanoscale 11, 6153 (2019)

Multiscale method based on DFT+TB+NEGF



Full DFT simulation for NPG in contact with a metallic tip

DFT + NEGF ~ 1500 atoms

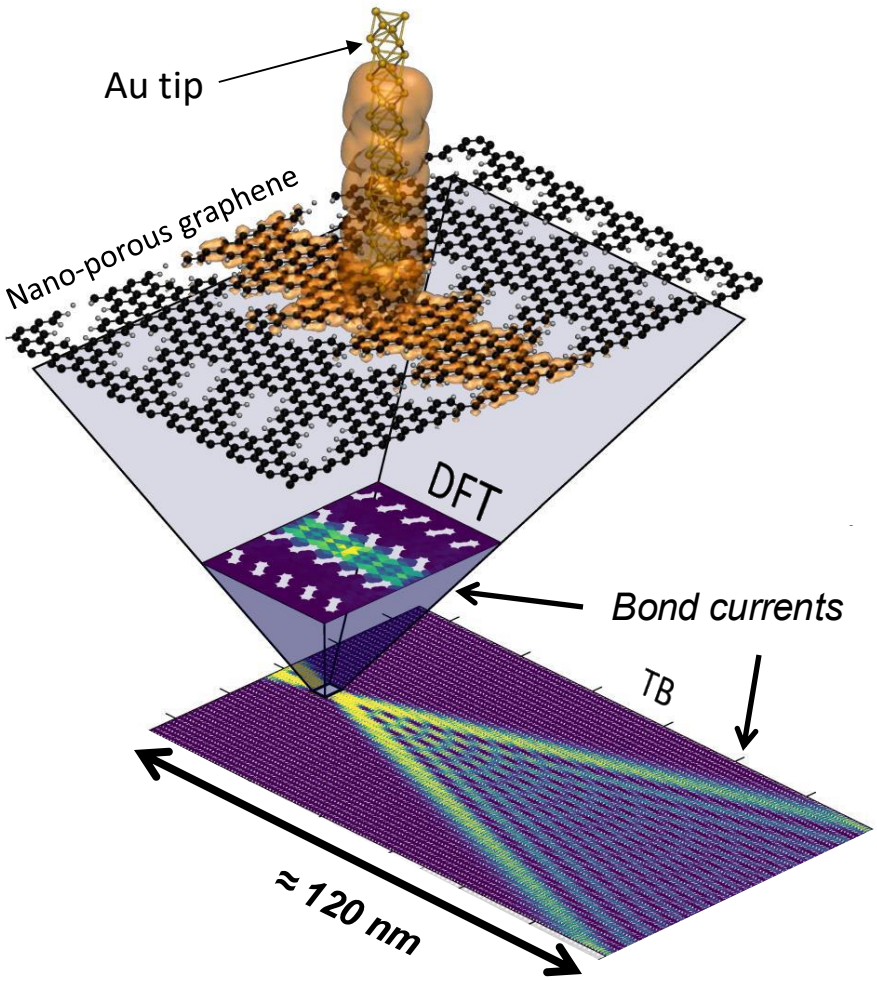
Link the perturbed contact region described by DFT…

…with an unperturbed large-scale region described by tight-binding

TB + NEGF ~ 360000 atoms

Details of the method: Calogero et al., Nanoscale 11, 6153 (2019)

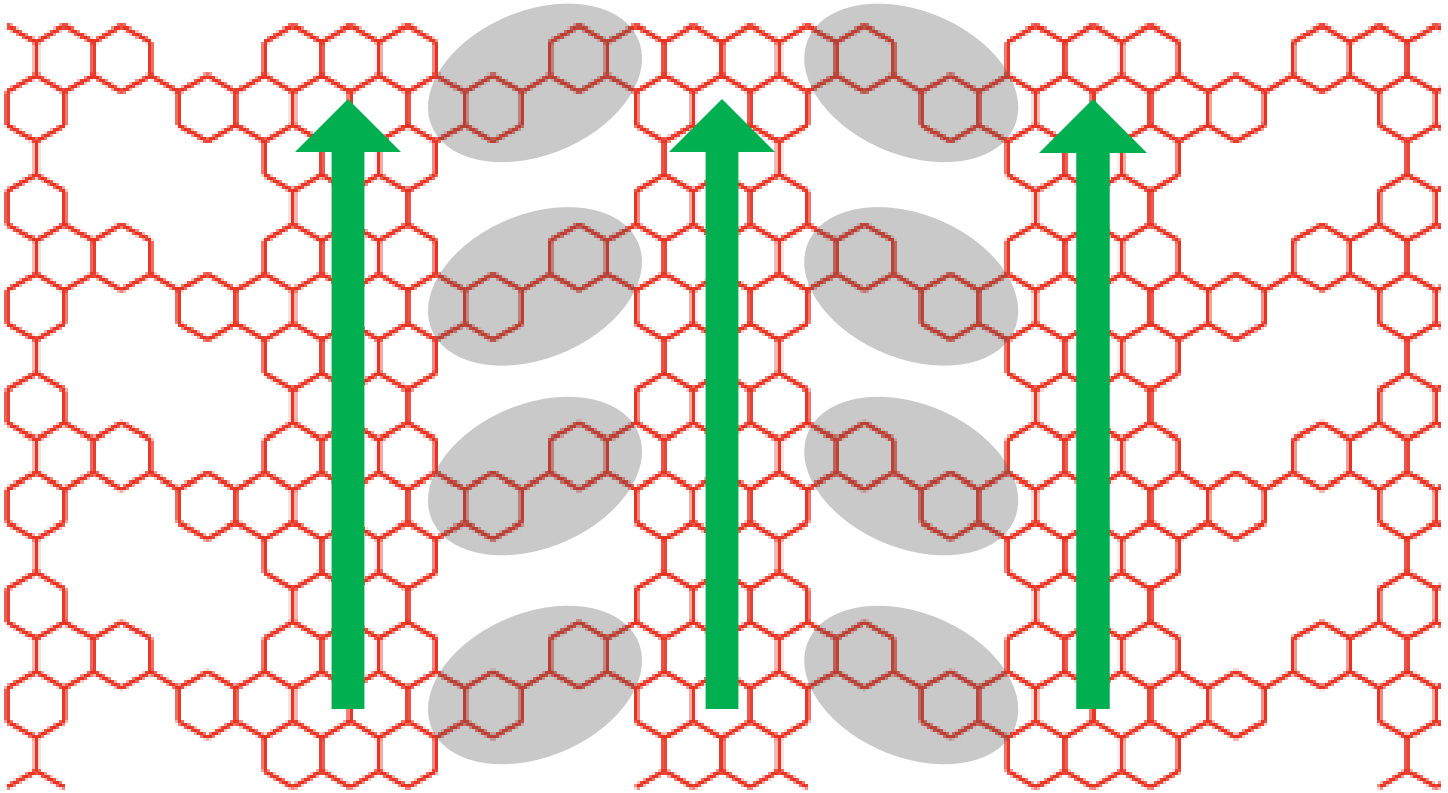
Multiscale method based on DFT+TB+NEGF



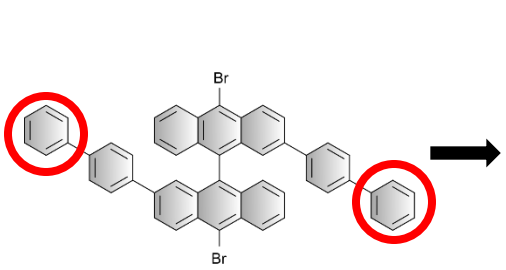
Electronic Talbot effect

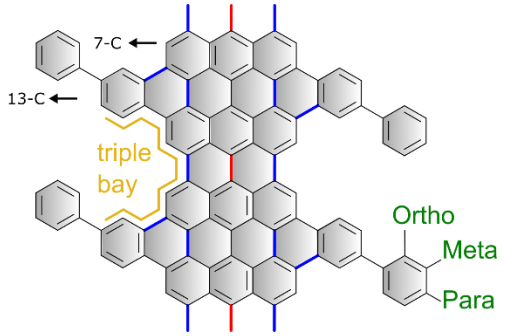
G. Calogero, AGL et al., Nano Lett. 19, 576 (2019)

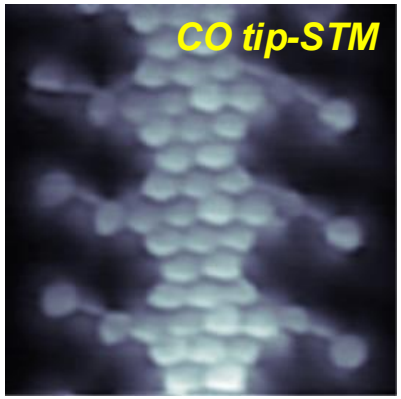
Bridge engineering in NPG



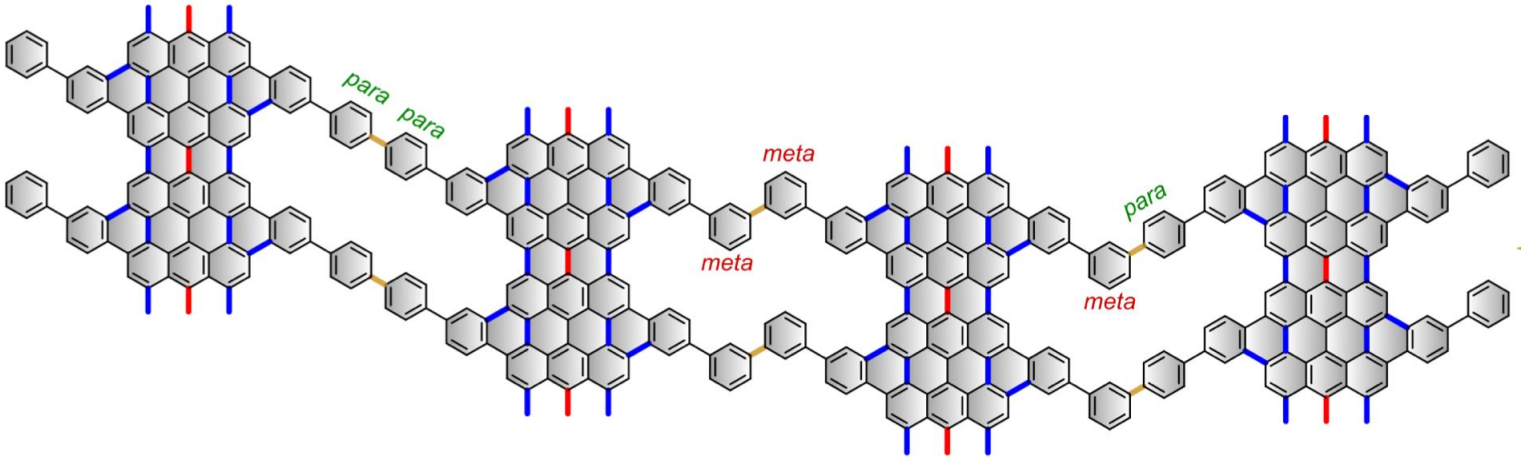
OSS of phenylated-NPG



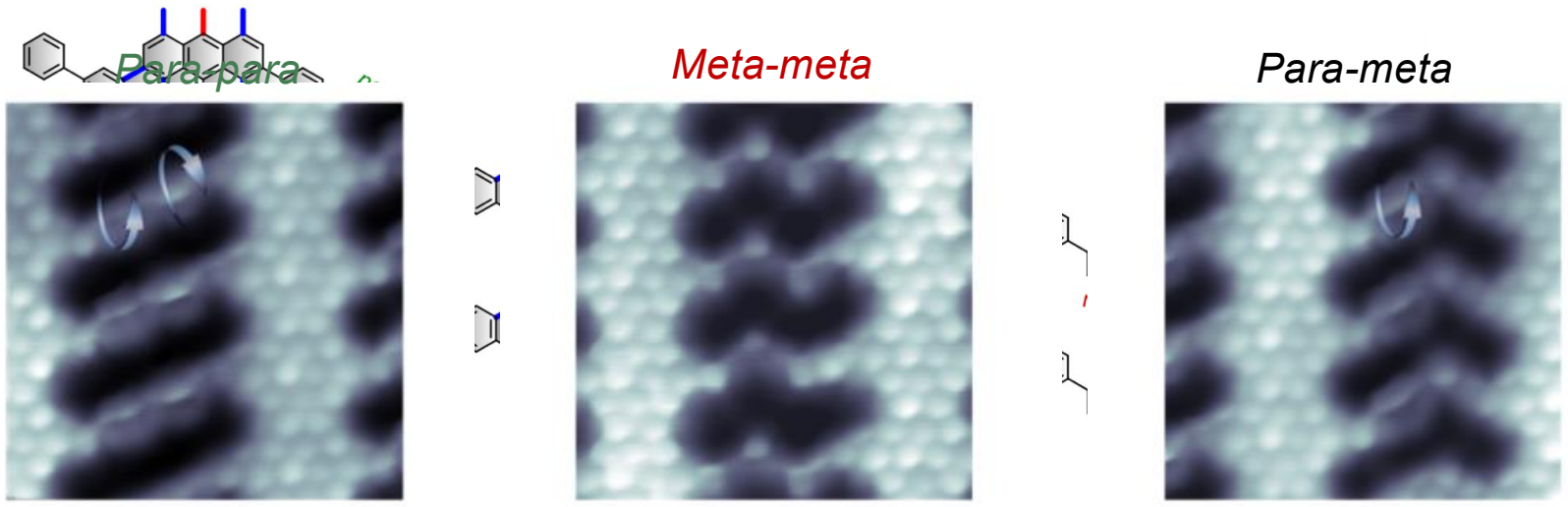




Monomers by D.Peña (CIQUS), STM by A. Mugarza (ICN2)

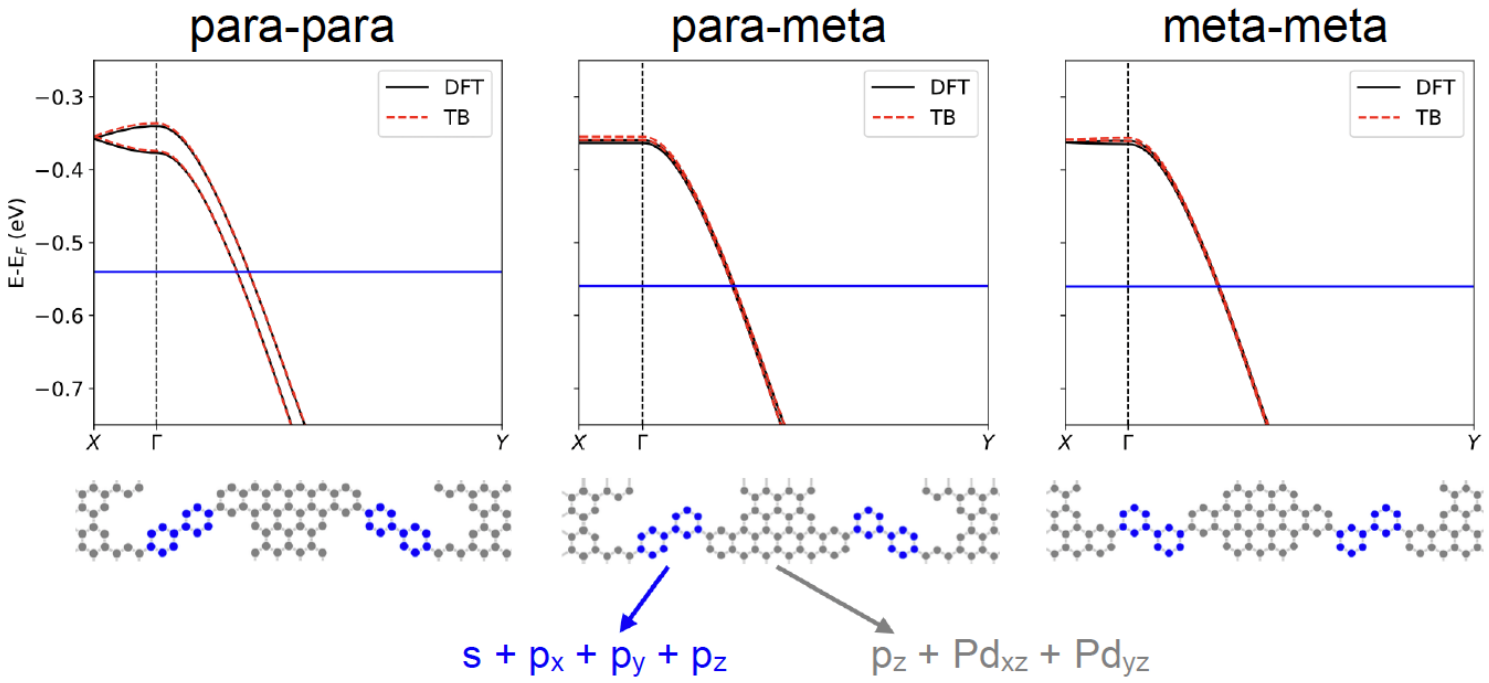


OSS of phenylated-NPG



Electron transport simulations in ph-NPG

Tight-binding Hamiltonians ("Pruned DFT"):
obtained by projecting unit-cell DFT Hamiltonians on a reduced subset of atomic orbitals using SISL [sisl.Hamiltonian.sub()]

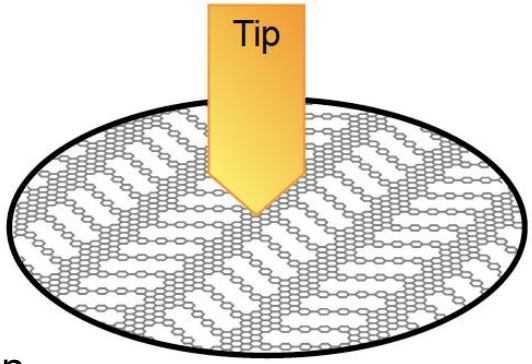


Excellent agreement with full DFT for longitudinal bands within |E −EF | < 1 eV

Electron transport simulations in ph-NPG

TranSIESTA simulations: pruned DFT + NEGF

Ph-NPG flakes: 43 nm x 65 nm
(~ 70.200 atoms).

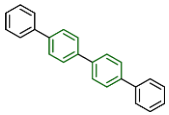


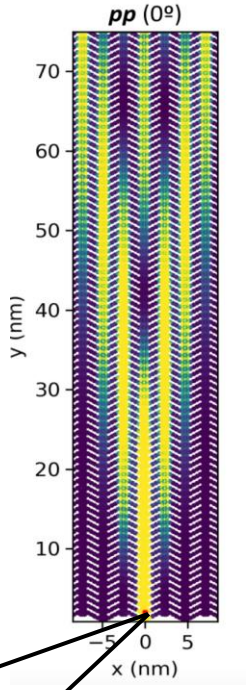
Approximate metallic tip via an on-site imaginary self-energy $i\Gamma$ in the contact atom, where Γ represents the decay rate into the tip.

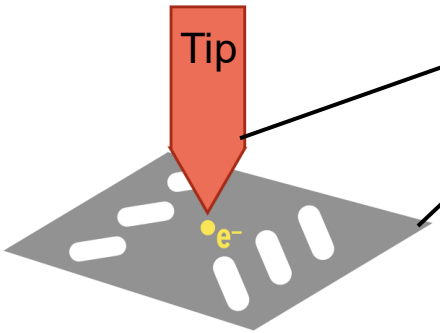
Complex adsorbing potential (CAP) to avoid backscattering off the device edges

Tuning electronic anisotropy in ph-NPG

para-para

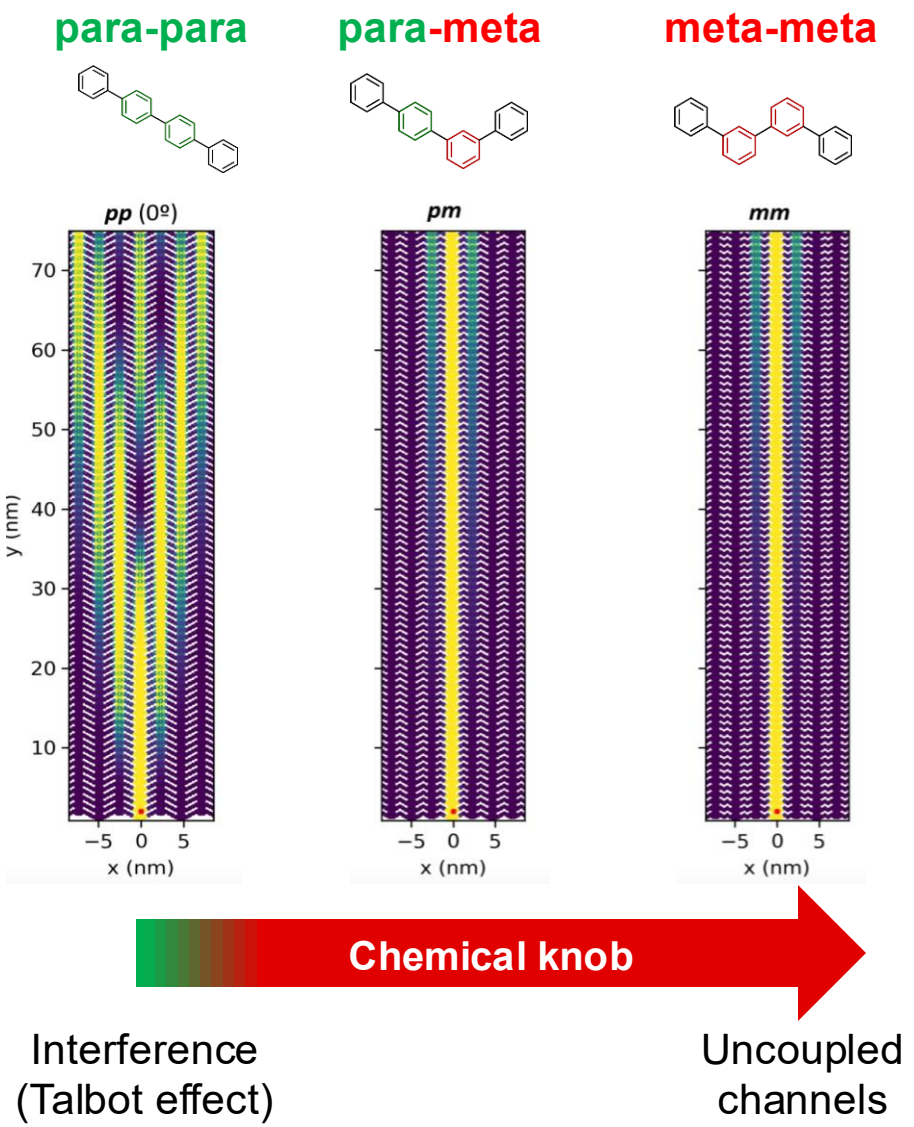




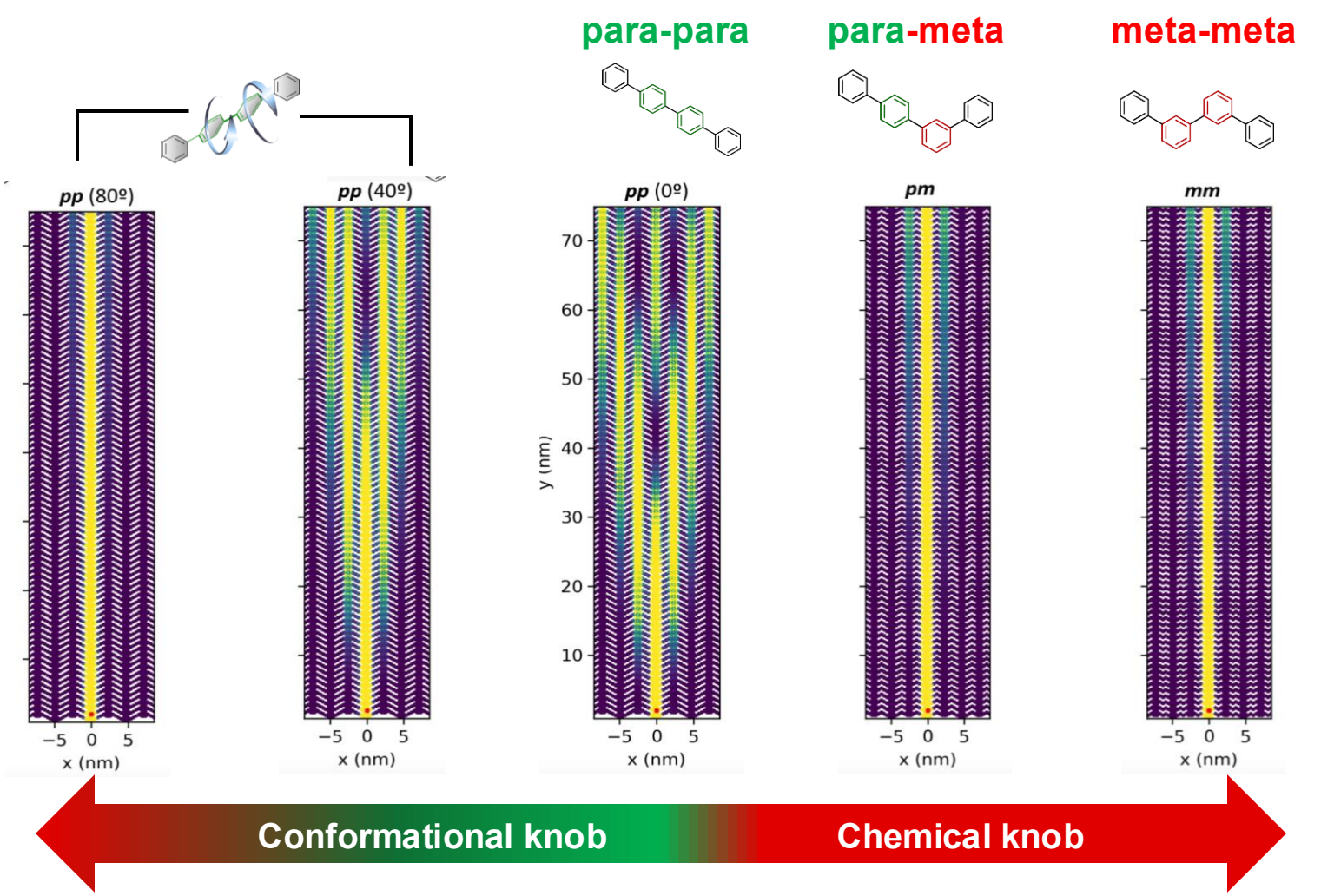


Interference
(Talbot effect)

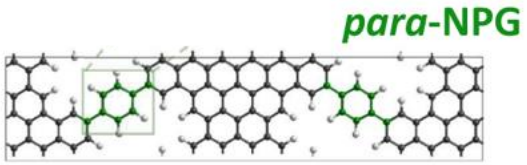
Tuning electronic anisotropy in ph-NPG

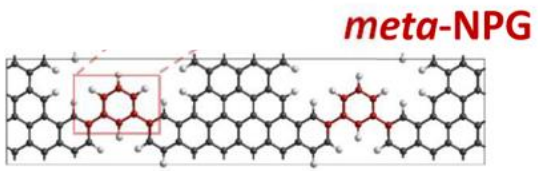


Tuning electronic anisotropy in ph-NPG



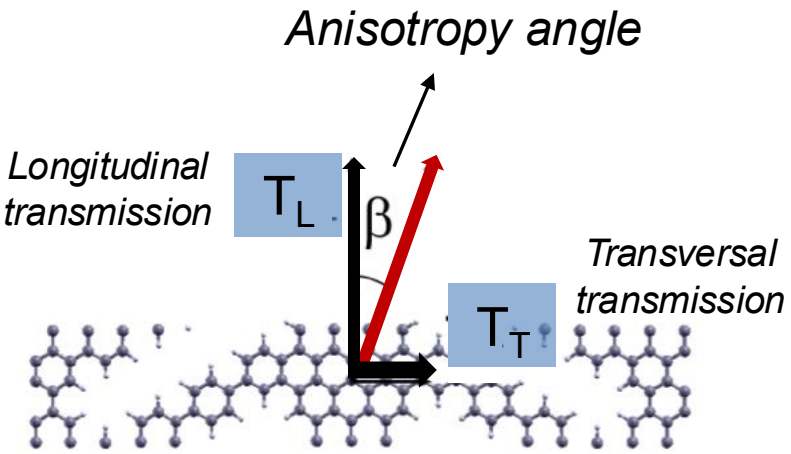
Bridge-engineering in NPG: anisotropy





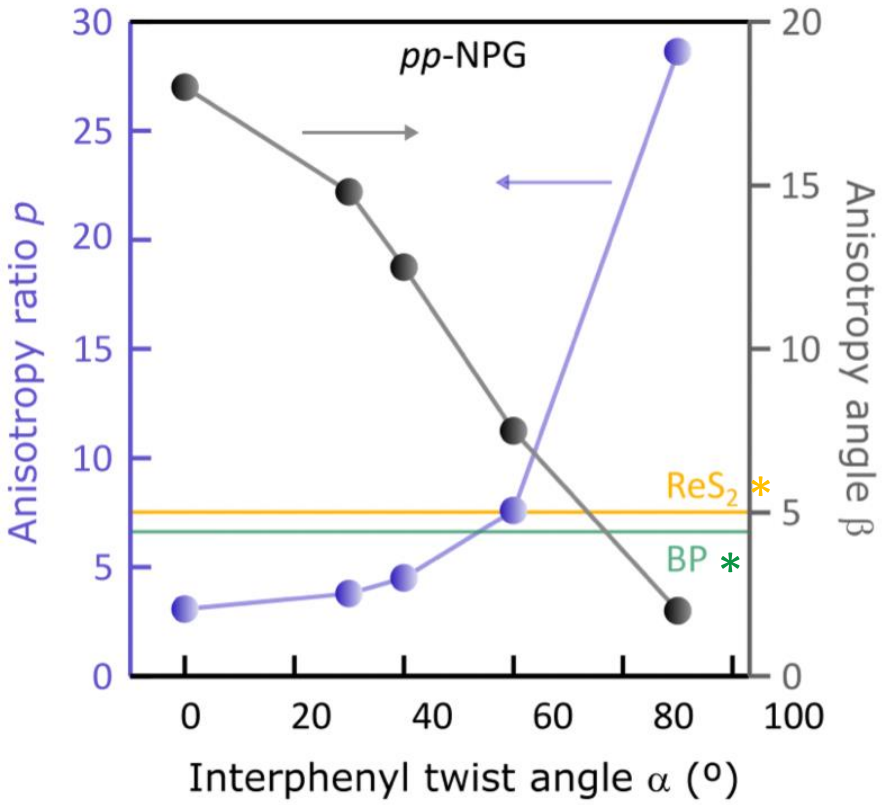
Calogero et al., JACS 141, 13081 (2019) – M. Brandbyge's group (DTU)

Anisotropy evolution in pp-NPG



$$p = \tan \beta = T_L/T_T$$

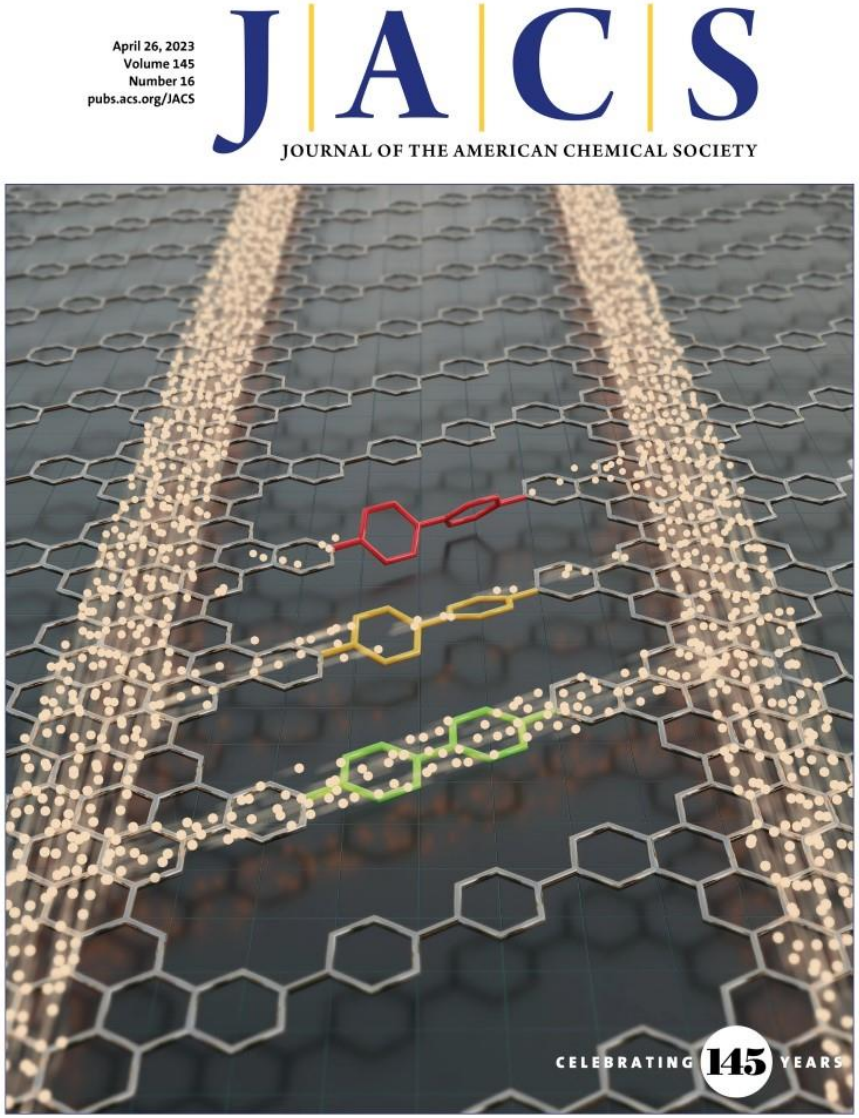
Anisotropy ratio



* Liu et al., Phys. Rev. B 93, 1 (2016)

* Liu et al., Nat. Commun. 6, 6991 (2015)

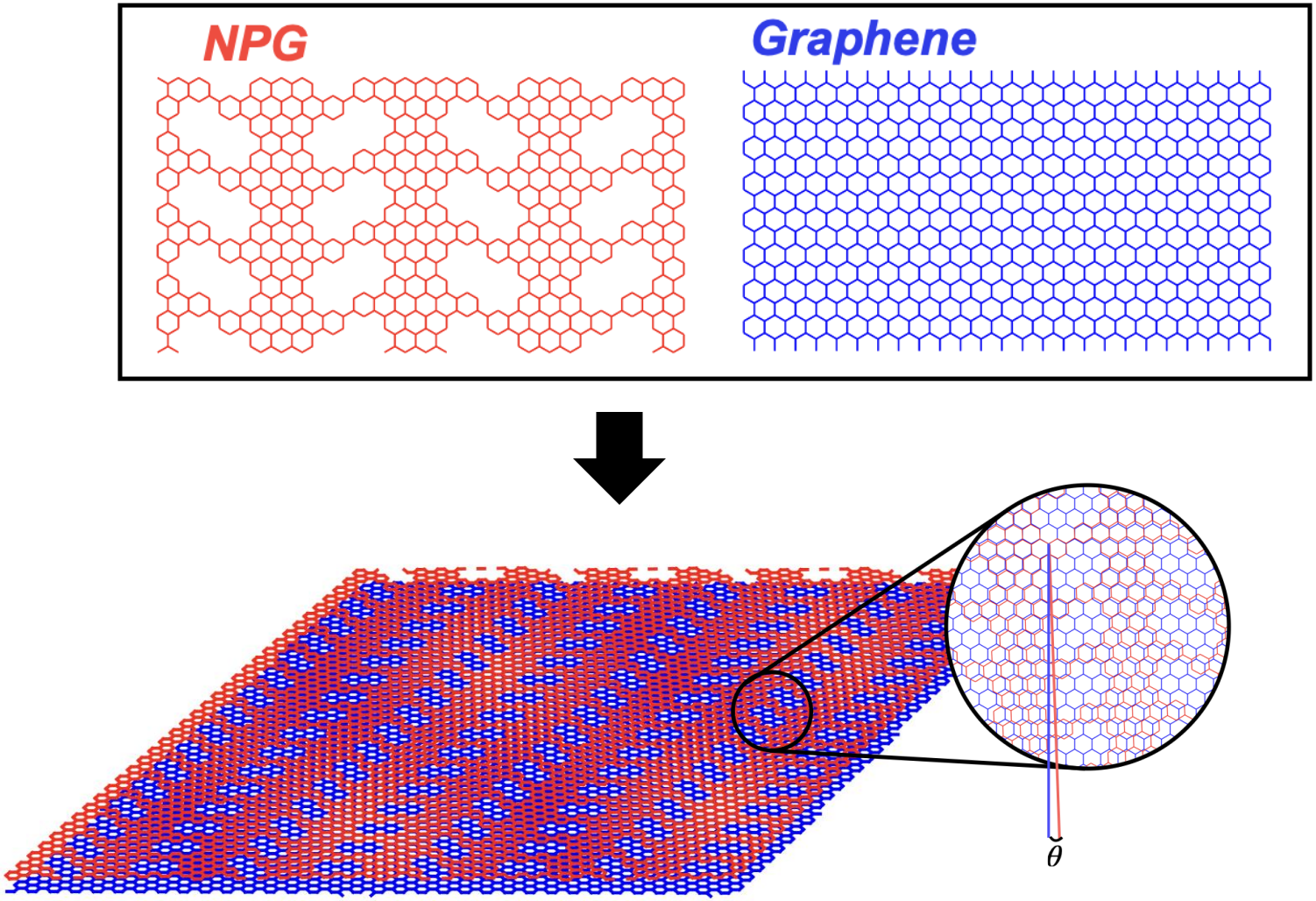
Bridge engineering of current injection



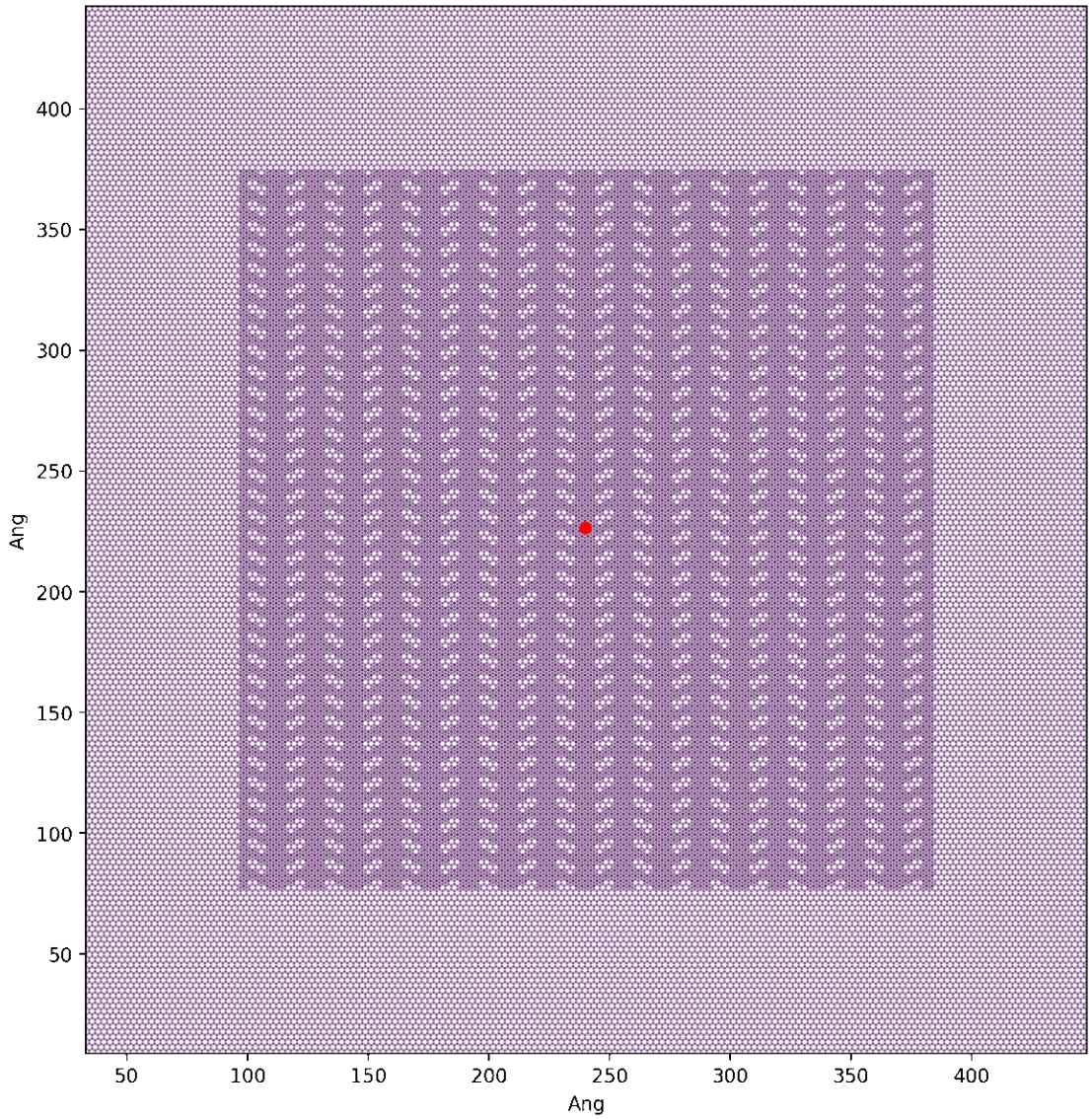
C. Moreno, AGL *et al.*
JACS 145, 8988 (2023)

C. Moreno, AGL *et al.*
Comm. Chem. 7, 219 (2024)

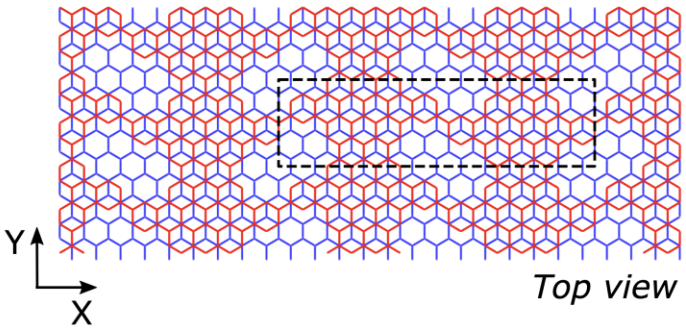
Nanoporous graphene / graphene bilayers



Nanoporous graphene / graphene bilayers



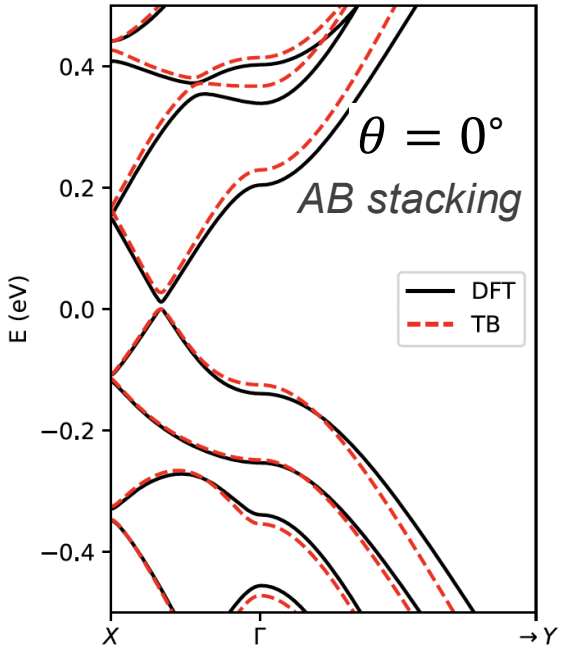
Tight-binding model for NPG/Gr



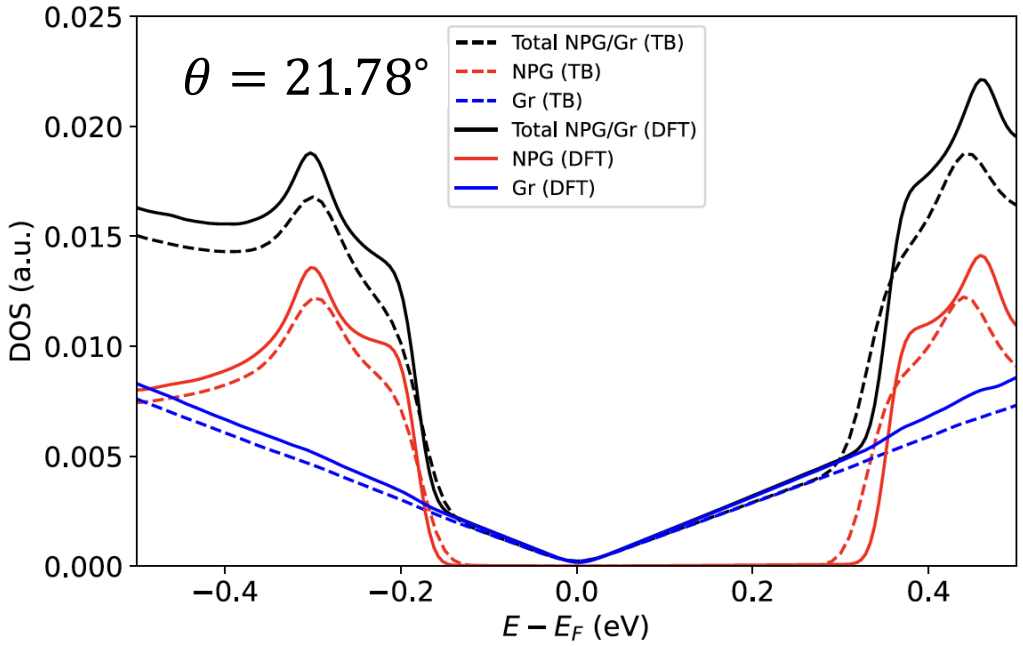
Tight-binding model:

- In-plane: 1st nearest neighbours
- Out-of-plane: Slater-Koster type integrals

Fit to DFT / SIESTA

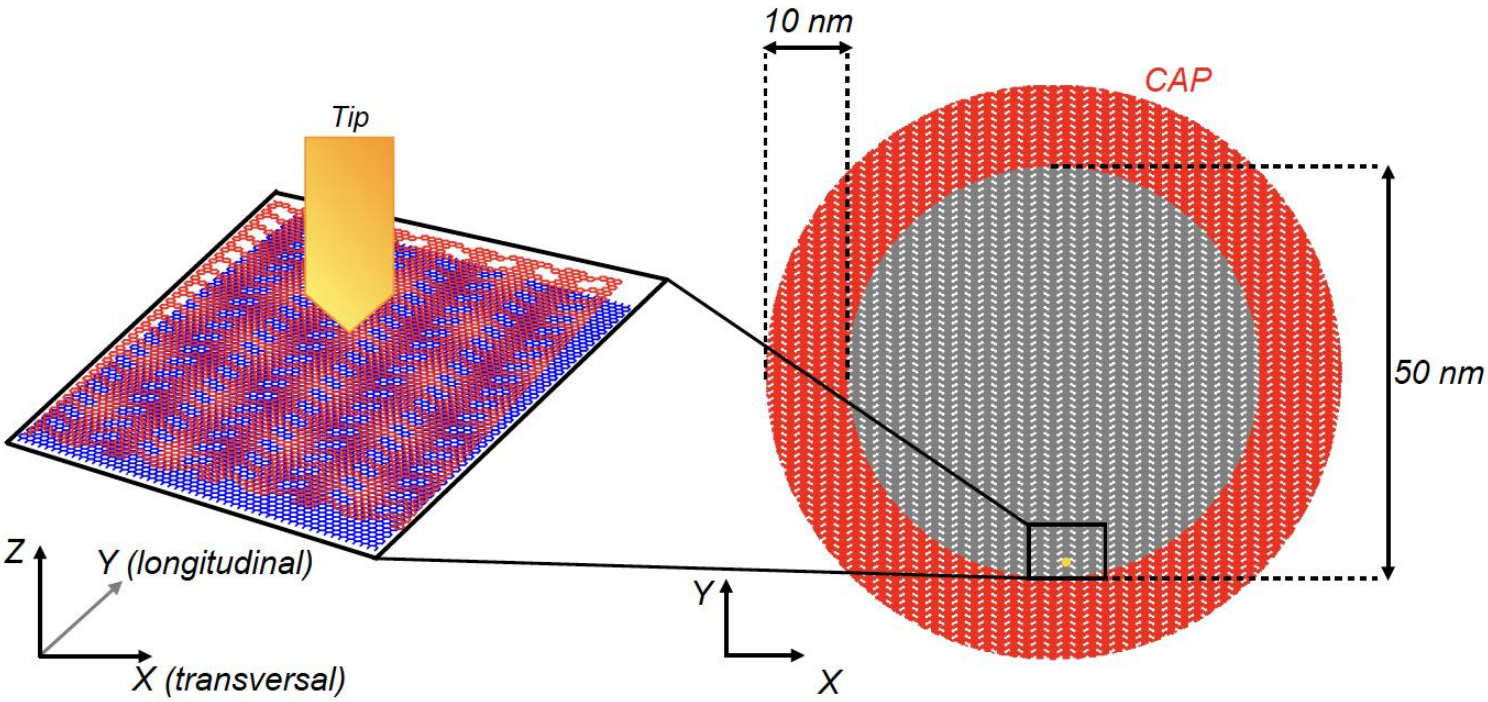


Validity of TB model for twisted NPG/Gr



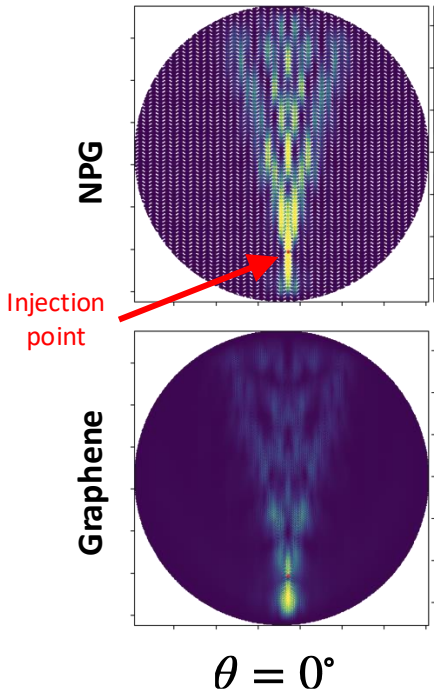
NPG/Gr: transport set-up

TranSIESTA simulations: Tight-binding + NEGF

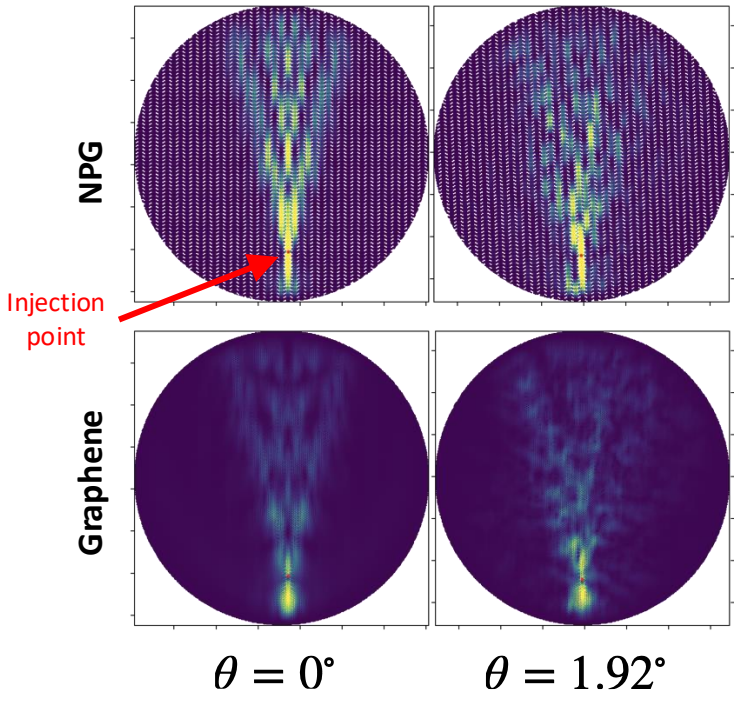


- Single-electrode set-up: circular bilayer disk in contact with a metallic tip
- Finite samples (70 nm, ~ 200.000 atoms)
- Circular complex adsorbing potentials

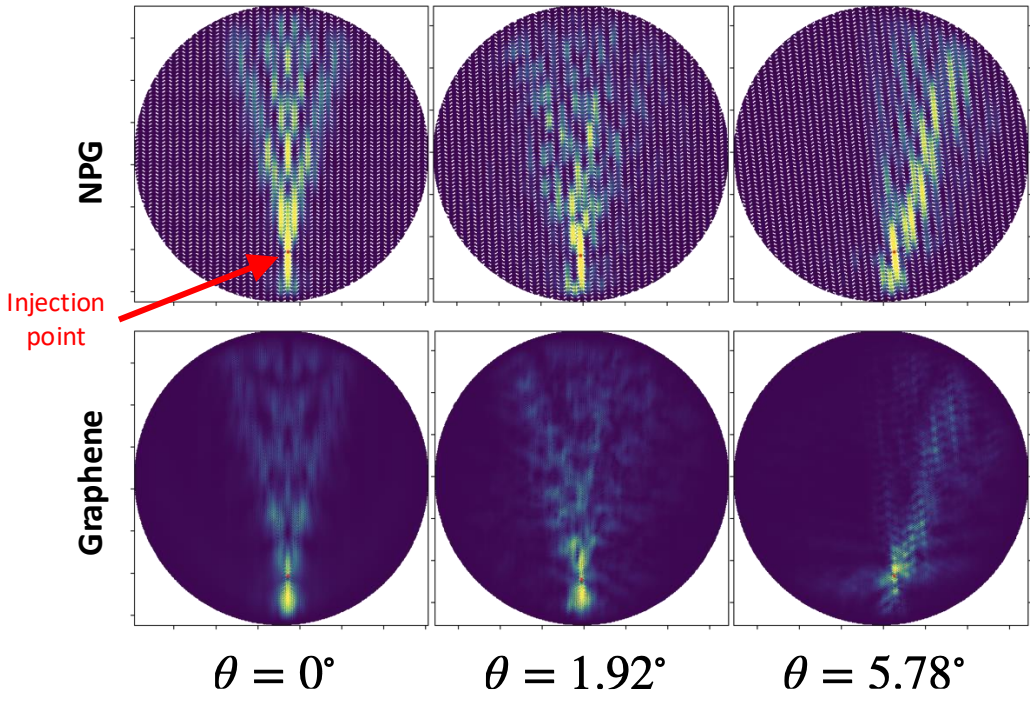
NPG/Gr: current propagation vs twist-angle



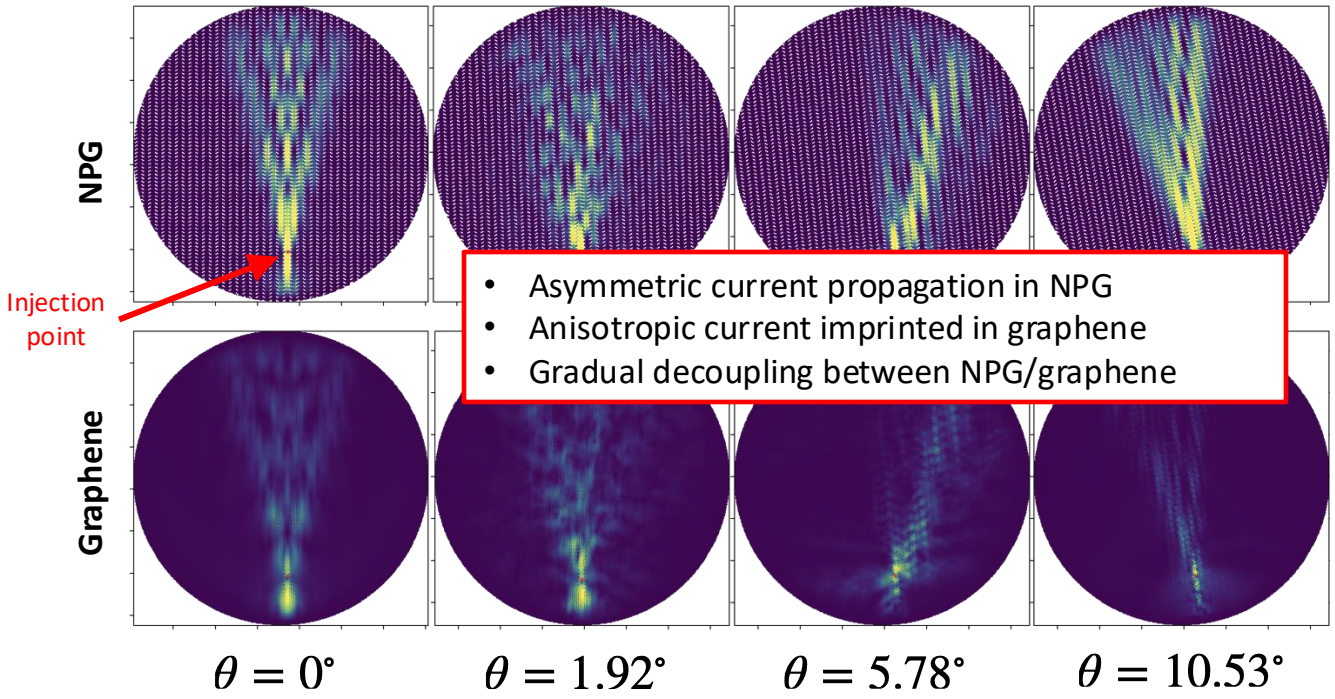
NPG/Gr: current propagation vs twist-angle



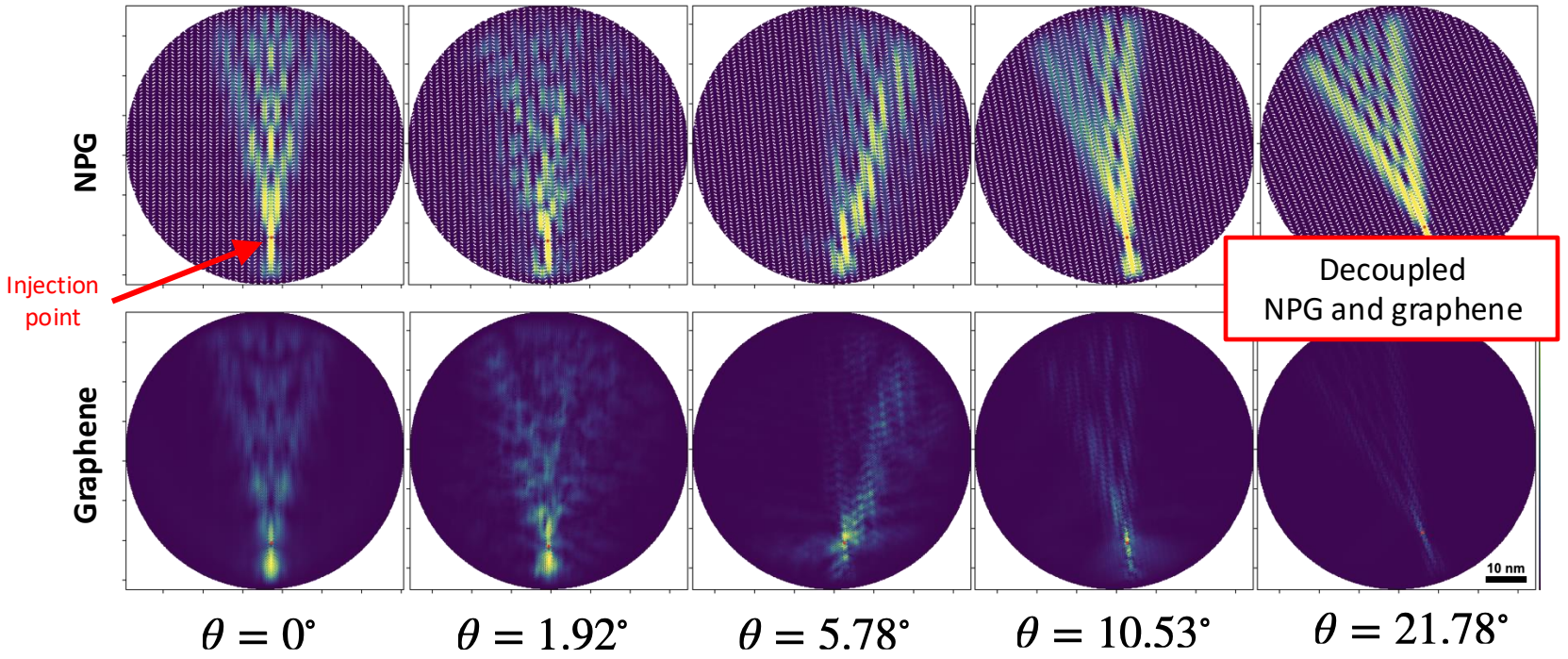
NPG/Gr: current propagation vs twist-angle



NPG/Gr: current propagation vs twist-angle

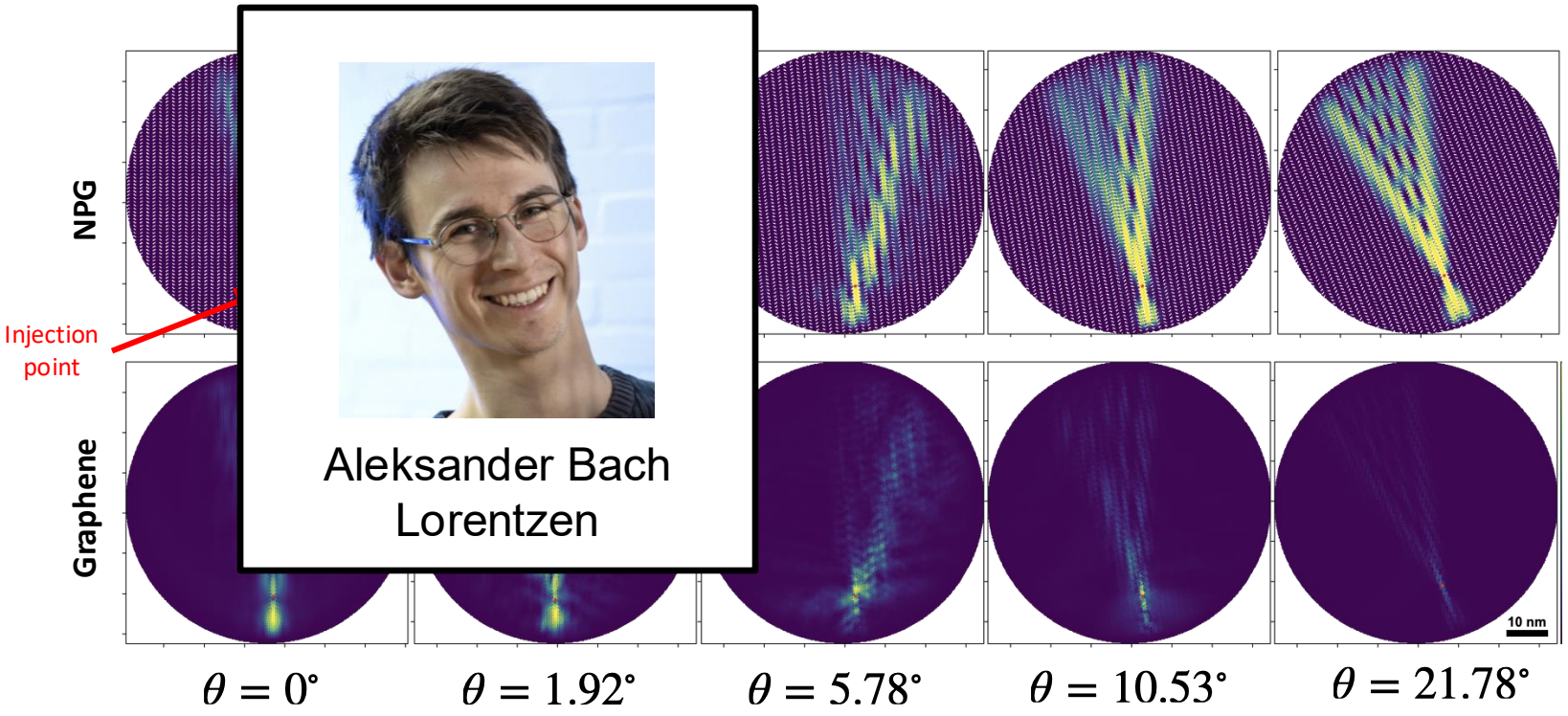


NPG/Gr: current propagation vs twist-angle



NPG/Gr: current propagation vs twist-angle

X. Diaz de Cerio, AGL *et al.,* Nano Lett. 25, 1281 (2025)



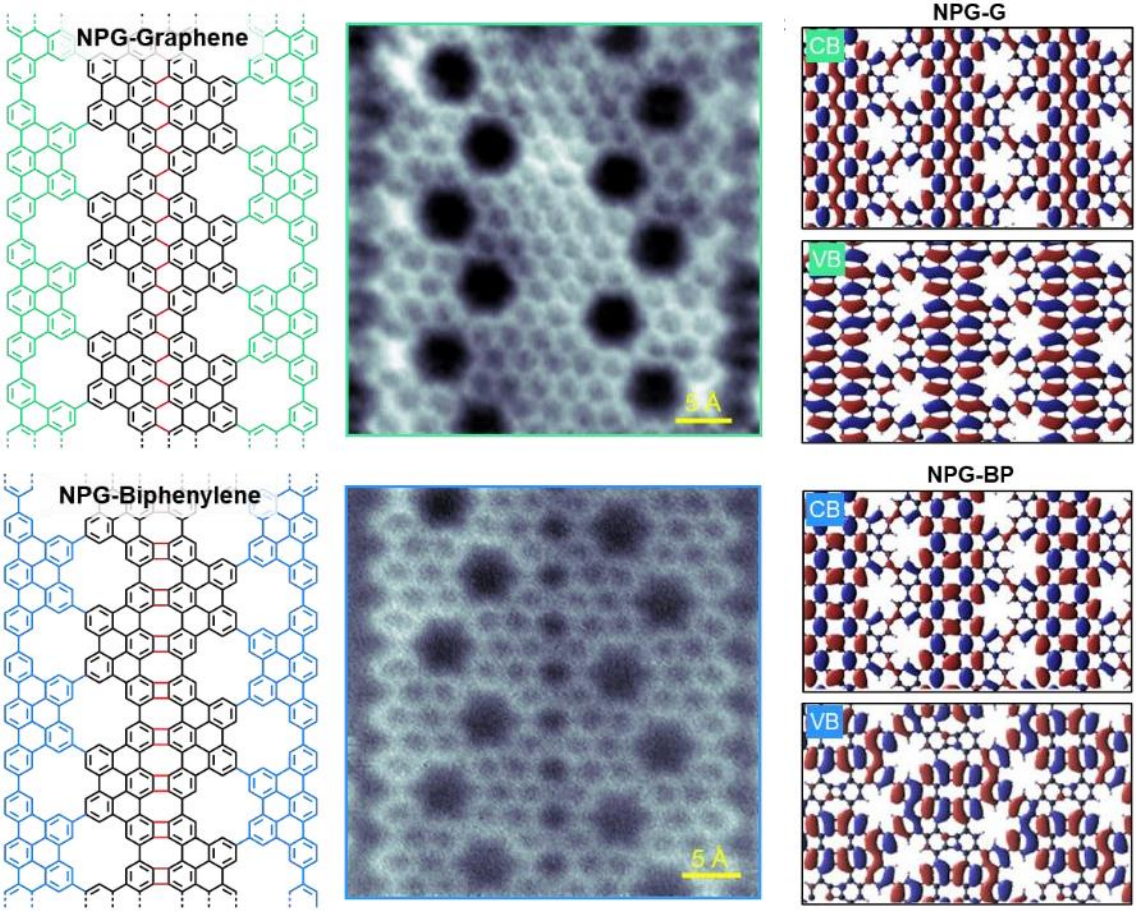
Aleksander Bach Lorentzen

Coupled ⟵ ⟶ Uncoupled

Interlayer twist-angle = coupling knob

NPG: a new whole family

Graphene allotrope with biphenylene units



POSTER:

Martin Irizar

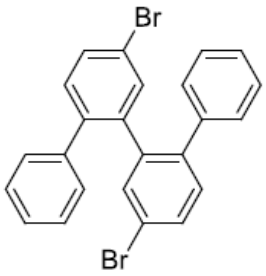
OSS + STM experiments:

D.G. de Oteyza (CINN), M. Corso (CFM)

NPG: a new whole family

Gulf-type GNR (g-GNR)

g-NPG



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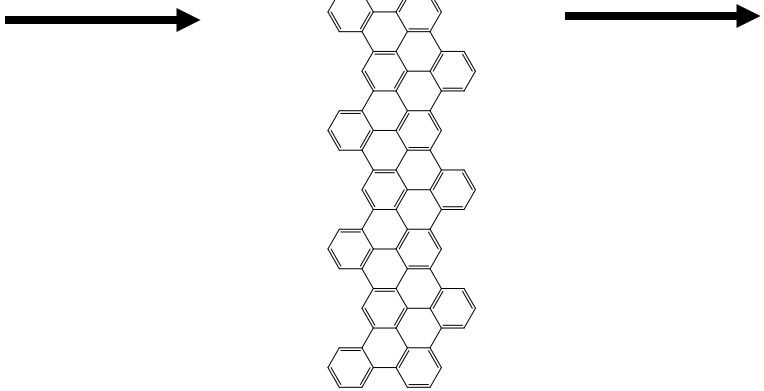
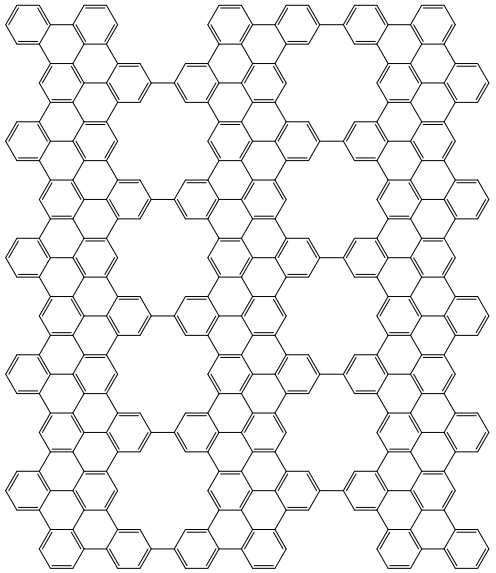


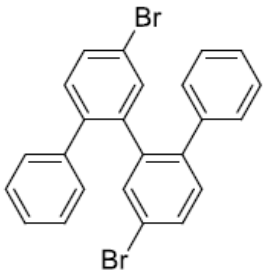


Experiments performed at J. Barth's group, TUM

NPG: a new whole family

Gulf-type GNR (g-GNR)

g-NPG



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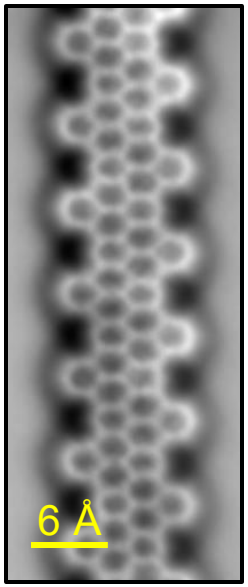
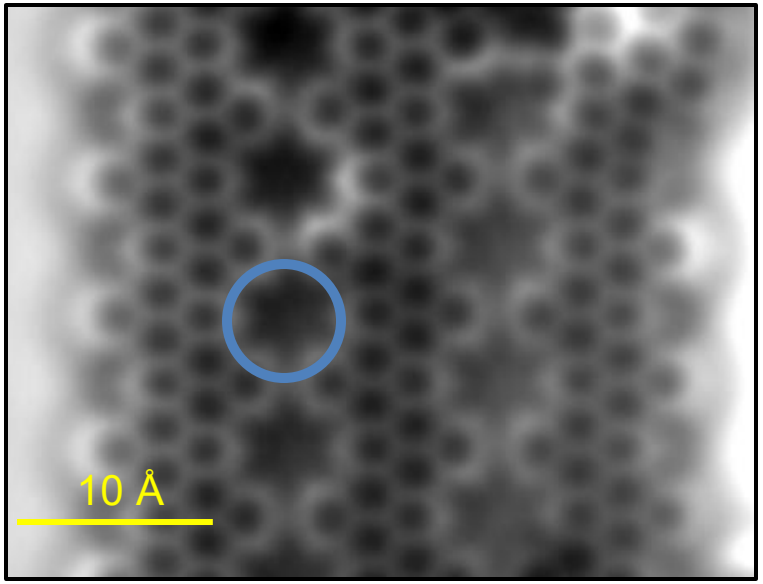
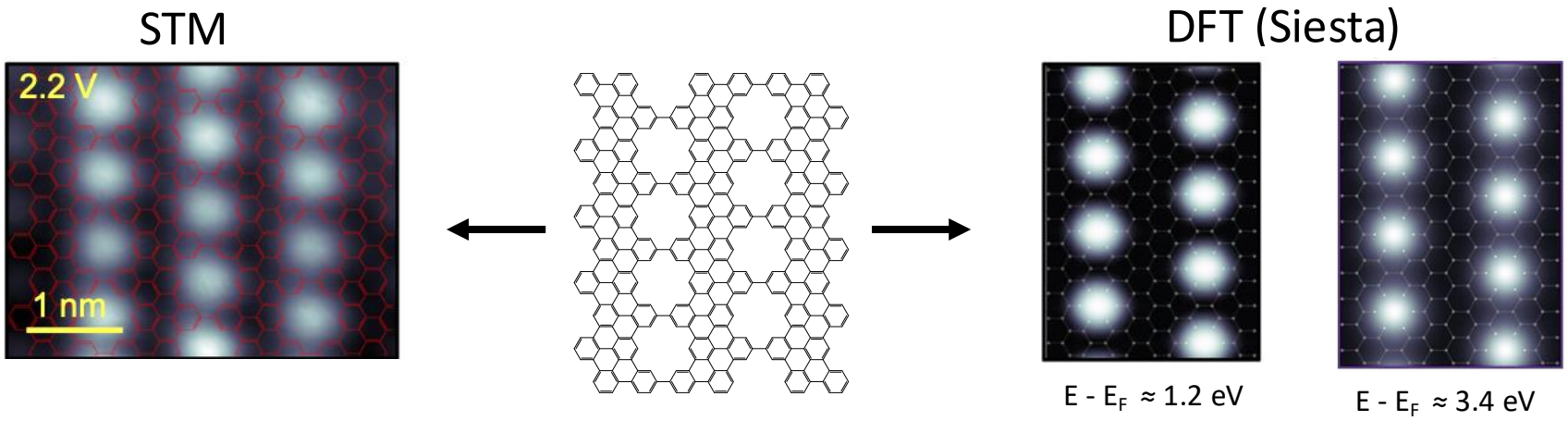




Minimum pore size

Experiments performed at J. Barth's group, TUM

Electronic confinement at the pores electronic



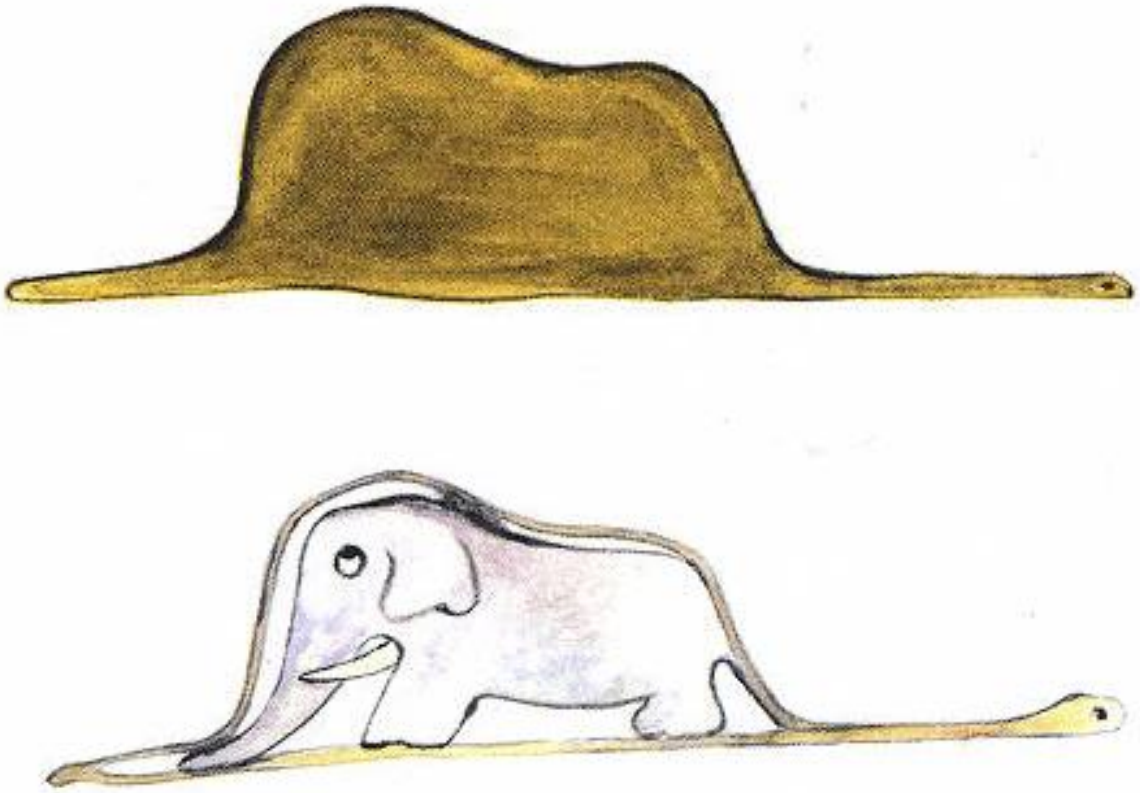
Electronic states "localized" at the pores

…but NO pore states!!

Article https://doi.org/10.1038/s41467-024-45138-w

Deceptive orbital confinement at edges and pores of carbon-based 1D and 2D nanoarchitectures

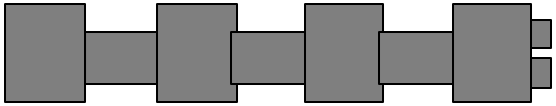
I. Piquero-Zulaica, AGL, *et al.* Nat. Commun. 15, 1062 (2024)



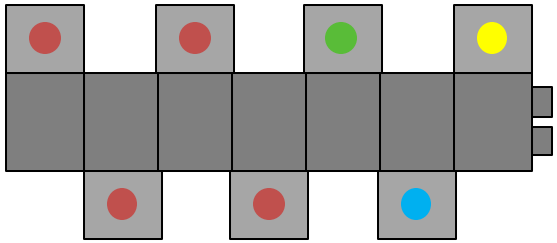
Le petit prince (Antoine de Saint-Exupéry, 1943)

Chemical doping

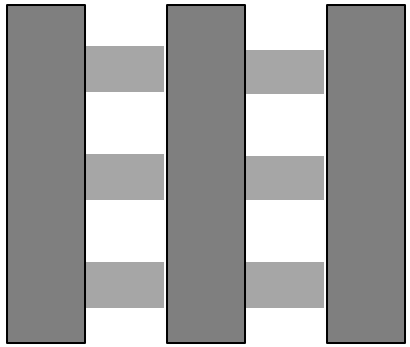
Topological properties



Hybrid nanoarchitectures



From 1D to 2D



Electronic properties explored by SIESTA simulations

- **Theory & simulations**

X. Diaz de Cerio (LIST, former DIPC)

F. Gao (DIPC)

A. Bach Lorentzen (DIPC)

R. Menchón (former DIPC)

P. Brandimarte (former DIPC)

A. Sarasola (DIPC, UPV/EHU)

D. Sánchez-Portal (CFM)

G. Calogero (CNR-IMM)

N. Papior (DTU)

M. Brandbyge (DTU)

- **OSS + STM experiments**

N. Friedrich (Nanogune)

J.I. Pascual (Nanogune)

C. Moreno (Univ. Cantabria)

A. Mugarza (ICN2)

I. Piquero-Zulaica (CFM, former UTM)

E. Corral-Carrascón (UTM)

J. Barth (UTM)

- **Synthesis of precursors**

M. Vilas-Varela (CIQUS)

I. Pozo (CIQUS)

D. Peña (CIQUS)

H. Sakaguchi (U. Kyoto)

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ikur estrategia

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Gipuzkoako Foru Aldundia
Diputación Foral de Gipuzkoa

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MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD