Deciphering the electronic structure of 5-armchair graphene nanoribbons and its topological end-states

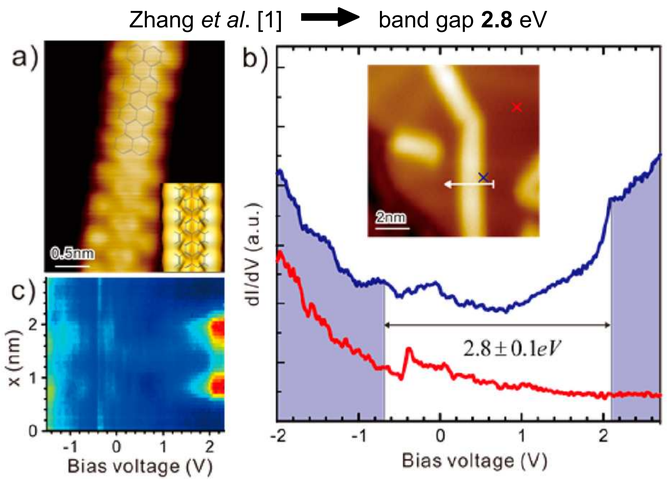
Pedro Brandimarte,*[1] James Lawrence,*[1,2] Alejandro Berdonces-Layunta,[1,2]
brandimarte@pm.me
Mohammed S. G. Mohammed,[1,2] Dimas G. de Oteyza,[1,2,3] and Daniel Sánchez-Portal[1,2]

[1] *Donostia International Physics Center (DIPC), Spain*
[2] *Centro de Física de Materiales (CFM), Spain*
[3] *IKERBASQUE, Basque Foundation for Science, Spain*

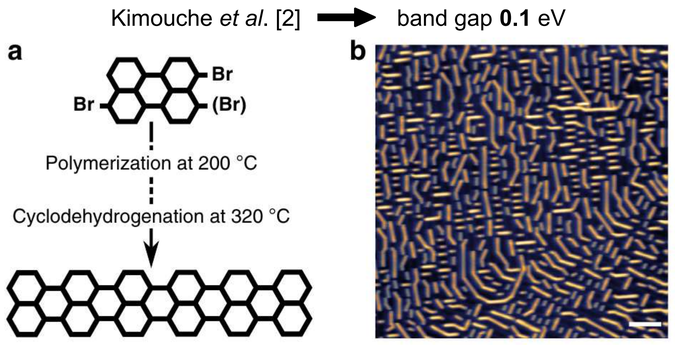
PREVIOUS SYNTHESIS AND CHARACTERIZATION

Previous 5-AGNRs metal-catalysed on-surface synthesis:

Zhang *et al*. [1] → band gap **2.8** eV

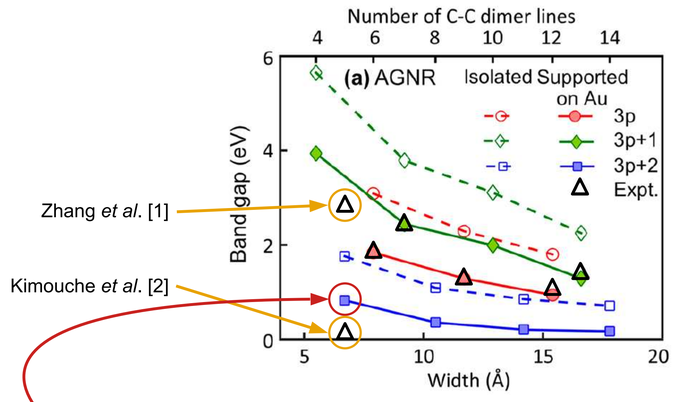


Kimouche *et al*. [2] → band gap **0.1** eV



PREDICTION FROM THEORY

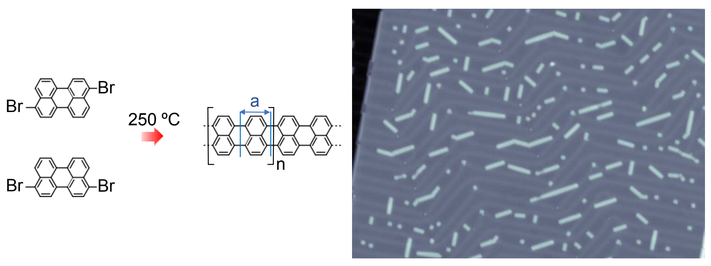
GW formalism with semi-empirical substrate screening [3] provides a good agreement with with experimental band gap values for larger widths:



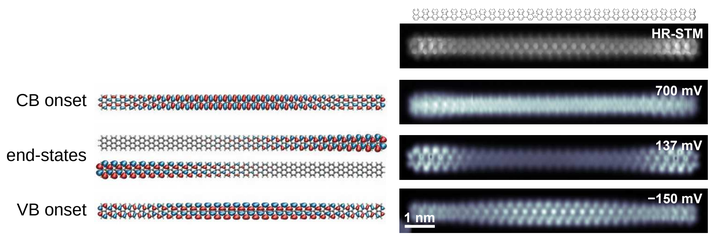
Theory (GW+screening) [3]: band gap ≈**0.85** eV on Au(111)

OUR RESULTS [4]

5-AGNR synthesis on Au(111):



30 unit-cell (UC) long 5-AGNR: DFT *versus* constant height dI/dV



band gap **0.85** eV (**!!!**) + **in-gap states**

TOPOLOGICAL ORIGIN OF THE END-STATES

Topology of 1D system is characterized by the Zak phase [5]:

$$\varphi = i \sum_{n}^{filled} \int_{BZ} dk \, \langle u_{n,k} | \, \partial_k \, | u_{n,k} \rangle \xrightarrow[\text{1D systems (mod 2π)}]{\text{inversion-symmetric}} \begin{matrix} \varphi = 0 \ \text{(trivial)} \\ \text{or} \\ \varphi = \pi \ \text{(non-trivial)} \end{matrix}$$

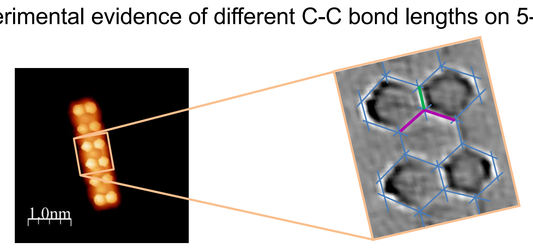
where $\Psi_{n,k} = \frac{e^{ikx}}{\sqrt{N}} u_{n,k}$ is the Bloch function.

In terms of the $\mathbb{Z}_2$ invariant:

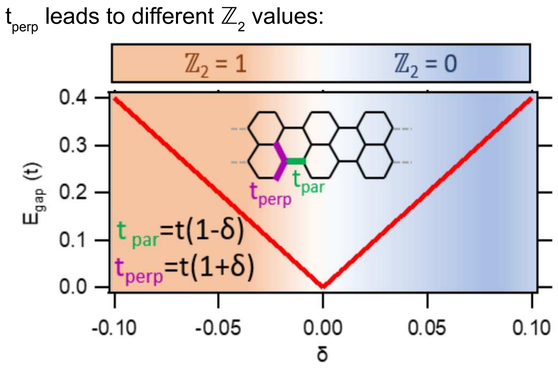
$$(-1)^{\mathbb{Z}_2} = -ie^{i}\varphi \longrightarrow \begin{matrix} \mathbb{Z}_2 = 0 \ \text{(trivial)} \\ \text{or} \\ \mathbb{Z}_2 = 1 \ \text{(non-trivial)} \end{matrix}$$

In the interface between a topological non-trivial and a trivial insulator (e.g. vacuum) an **odd** number of localized states should emerge **in the band gap**.

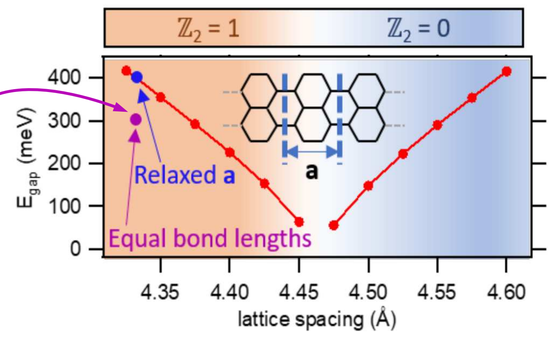
Experimental evidence of different C-C bond lengths on 5-AGNR:



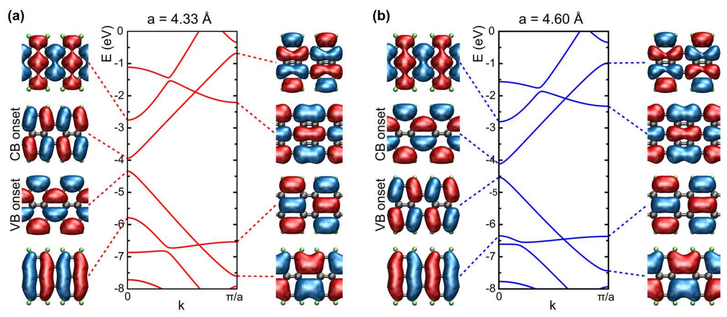
Simple π tight-binding model with varying hopping constants t_{par} and t_{perp} leads to different $\mathbb{Z}_2$ values:



DFT calculations varying the unit cell lattice:

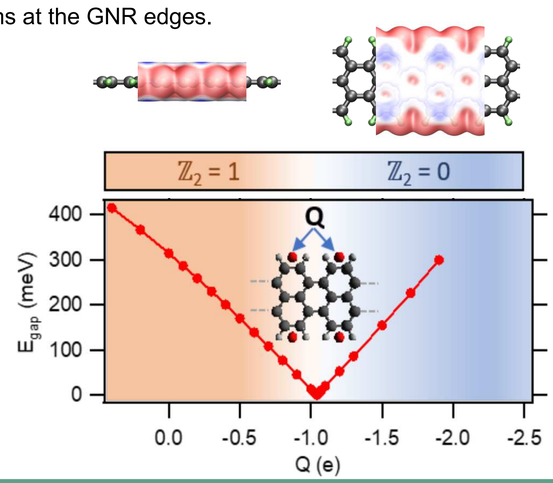


Wavefunctions for **a** = 4.33 Å and 4.60 Å appear exchanged at Γ for either topological class:



Bond length relaxations does not explain why the 5-AGNRs open a band gap that relaxes towards the non-trivial regime.

Our proposal: band gap opening driven by the anisotropic electrostatic profile caused by the positive partial charge on the H atoms at the GNR edges.

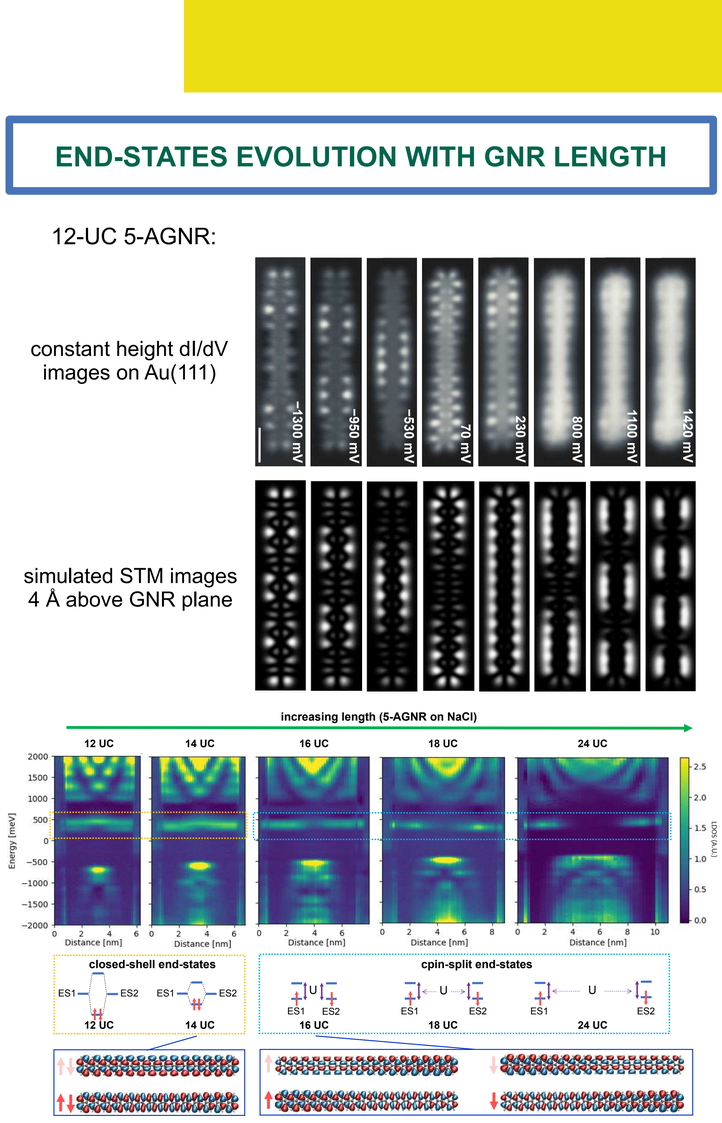


END-STATES EVOLUTION WITH GNR LENGTH

12-UC 5-AGNR:

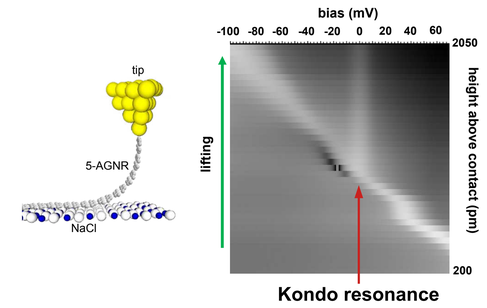
constant height dI/dV images on Au(111)

simulated STM images 4 Å above GNR plane



MAGNETIC NATURE OF THE END-STATES

Transport across the 5-AGNR in a two-terminal setup:



2D conductance map of dI/dV spectra lifting a 22-UC 5-AGNR

CONCLUSIONS

- 5-AGNRs on Au(111) display a semiconducting gap of 0.85 eV
- Anisotropic electrostatic potential from partial charges of the H atoms along the edges favors the opening of the gap towards the topological non-trivial band structure
- 5-AGNRs present topological in-gap states
- In-gap states undergo a transition from a closed-shell form to singly occupied spin-split states after reaching the length of 16-UC
- Upon lifting the GNRs the end-states become filled as the electrostatic influence of the high work function substrate fades
- As the states become occupied a Kondo resonance appears, providing direct proof of their magnetic nature

REFERENCES

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MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD