

Haiku graphene nanoribbons with tunable topology

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On-surface synthesis

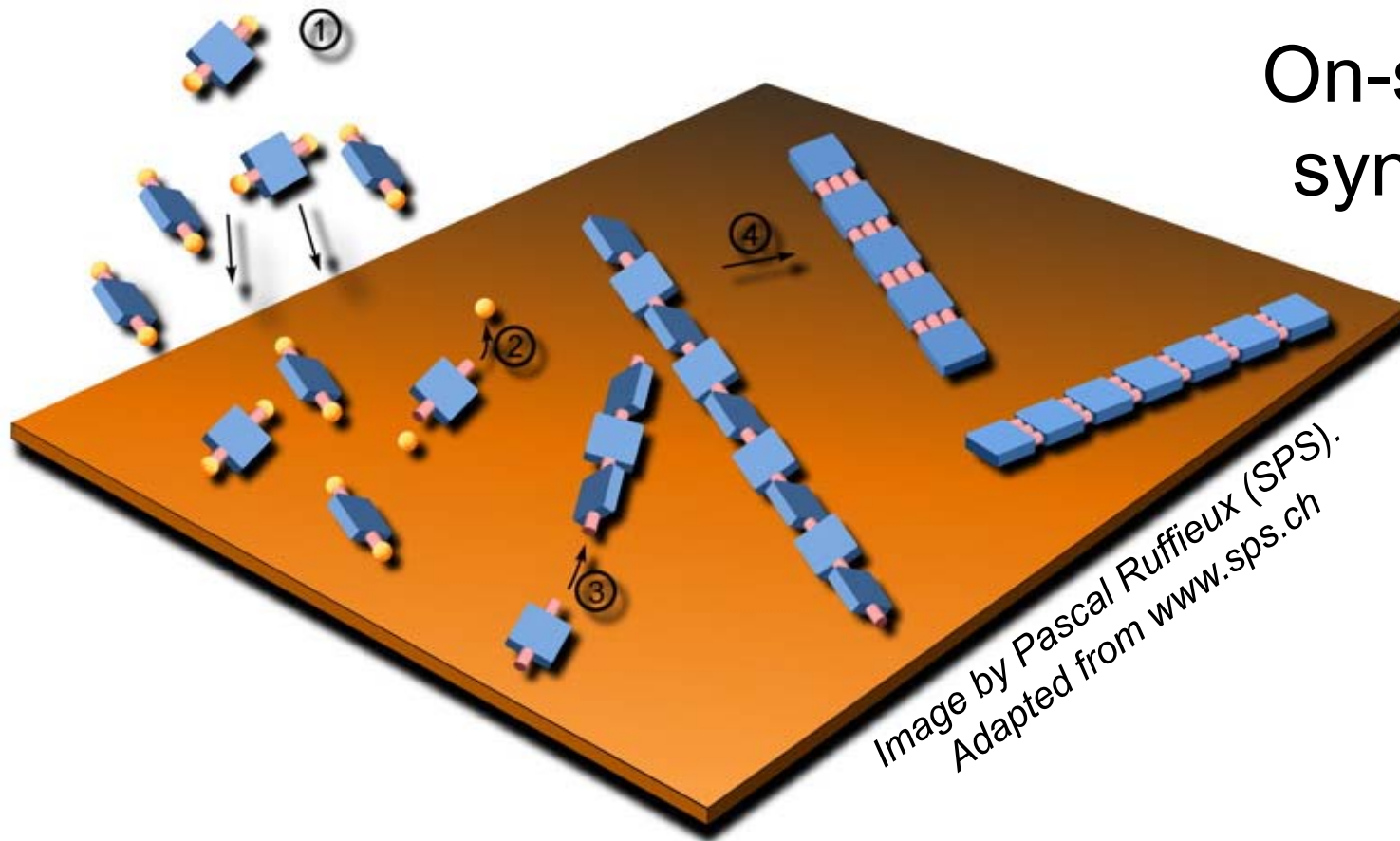
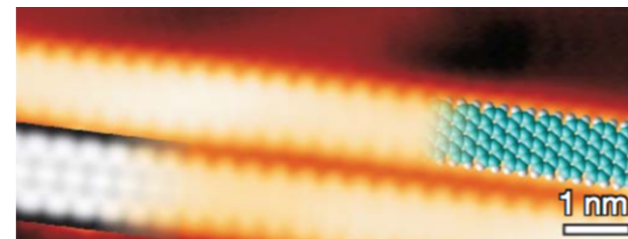
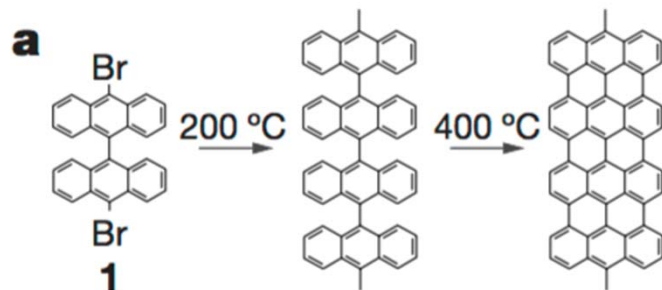


Image by Pascal Ruffieux (SPS).
Adapted from www.sps.ch

Armchair graphene nanoribbons (AGNR)



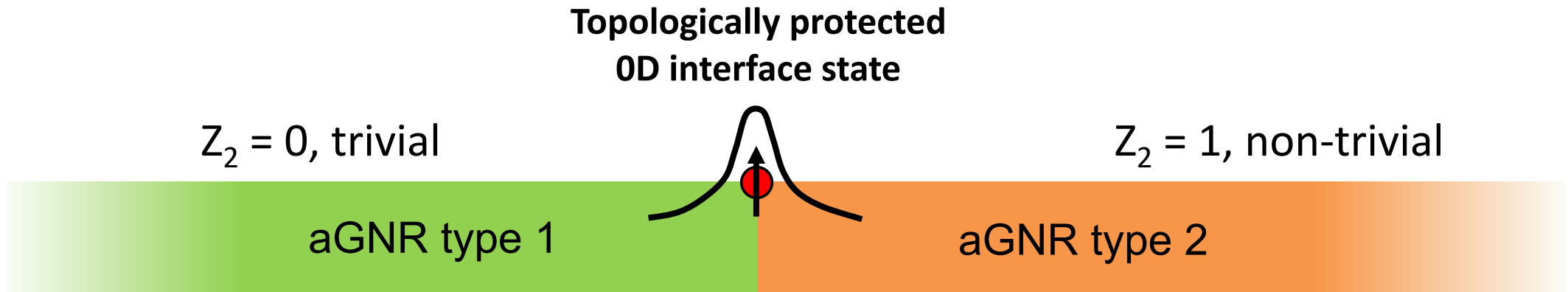
Cai et al., Nature 466, 470 (2010)

Bottom-up fabrication of graphene nanostructures

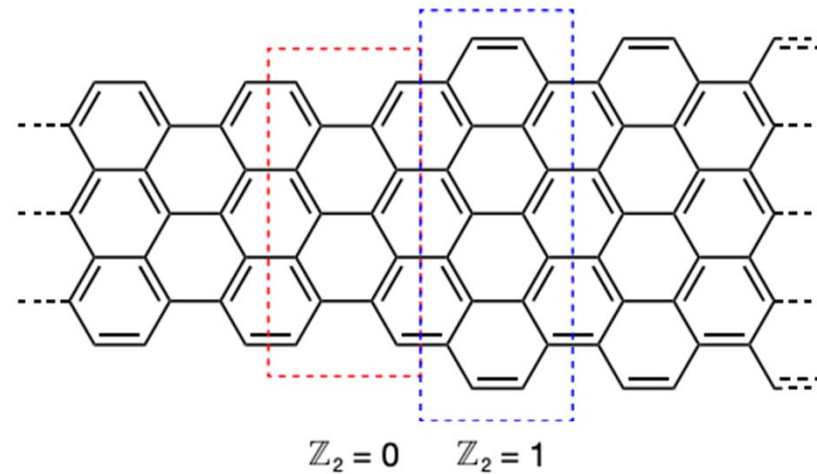


Bottom-up fabrication of graphene nanostructures

Topological Phases in Graphene Nanoribbons



7/9-AGNR heterojunctions



Cao et al., PRL 119, 076401 (2017)

Topological Phases in Graphene Nanoribbons

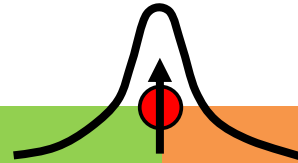
Topologically protected
0D interface state

$Z_2 = 0$, trivial

$Z_2 = 1$, non-trivial

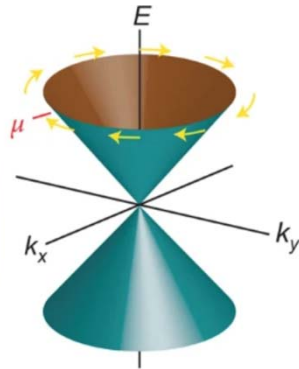
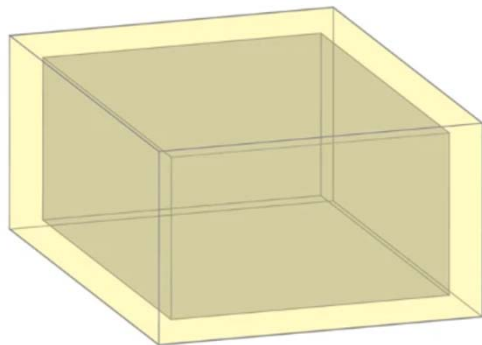
aGNR type 1

aGNR type 2



3D topological insulators

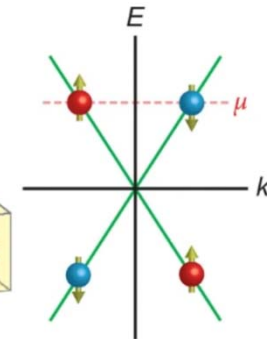
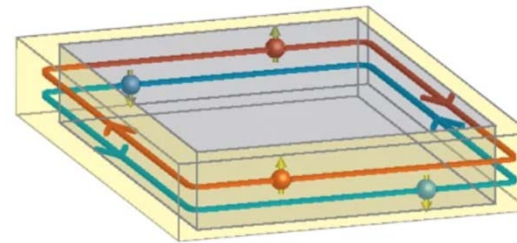
b



Surface state (2D)

2D topological insulators

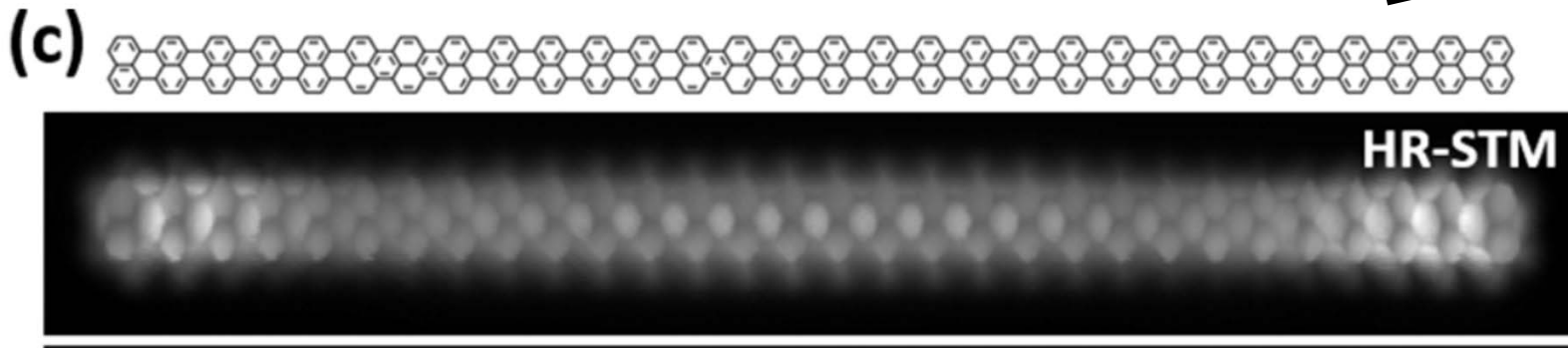
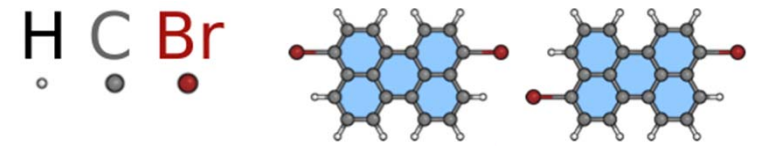
a



Edge state (1D)

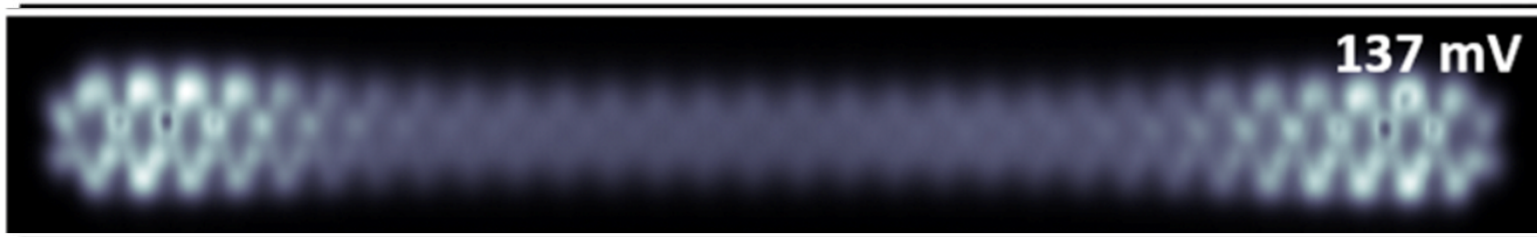
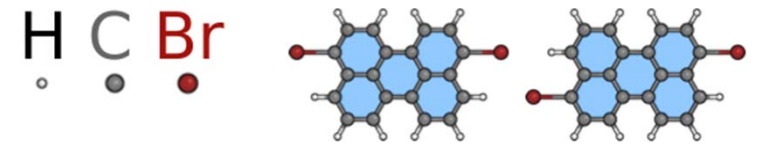
5-Armchair GNRs: topological end states

Lawrence et al., ACS Nano 14, 4499 (2020)

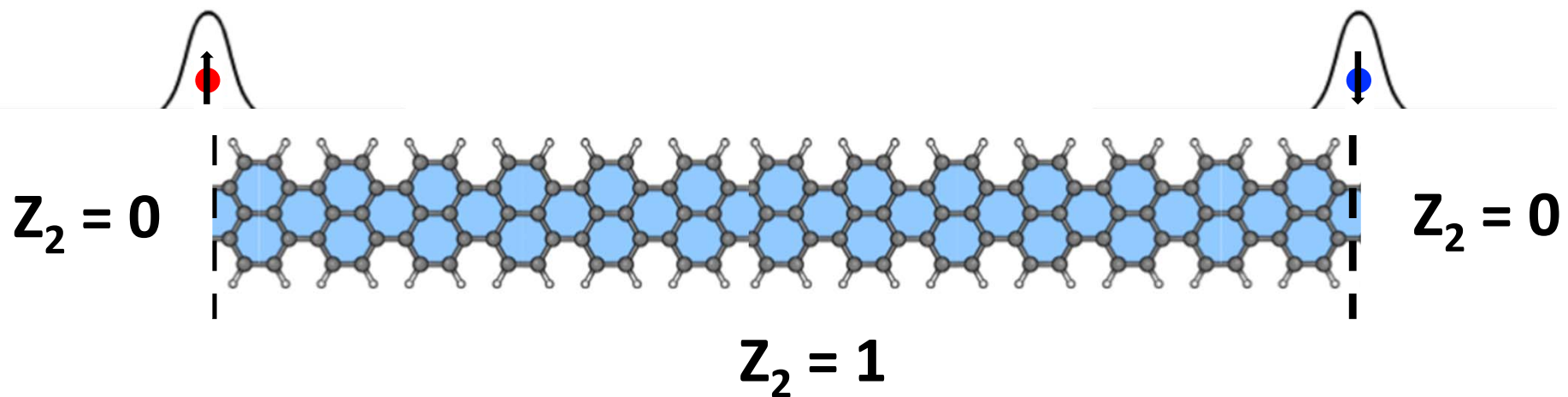


5-Armchair Graphene Nanoribbons

Lawrence et al., ACS Nano 14, 4499 (2020)

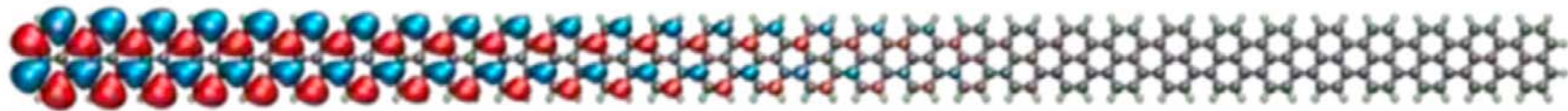
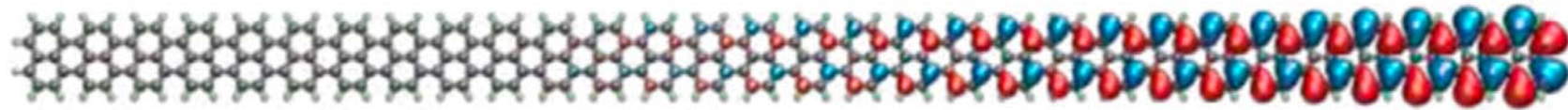
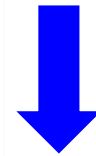
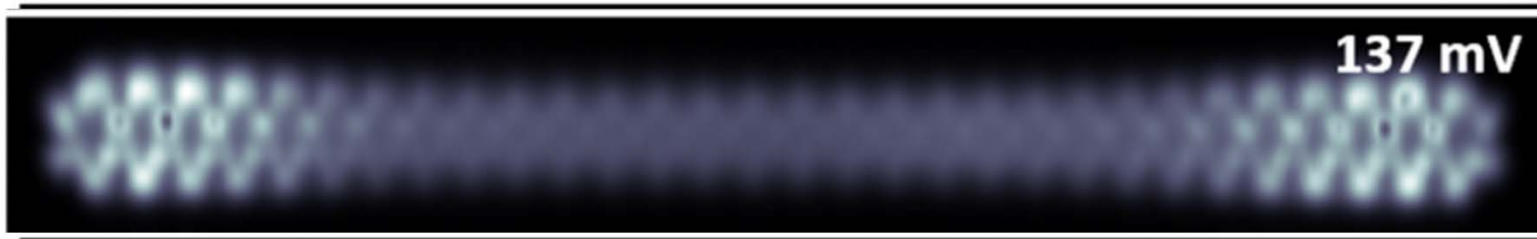
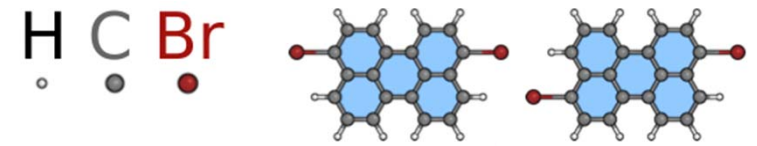


Magnetic topological end states

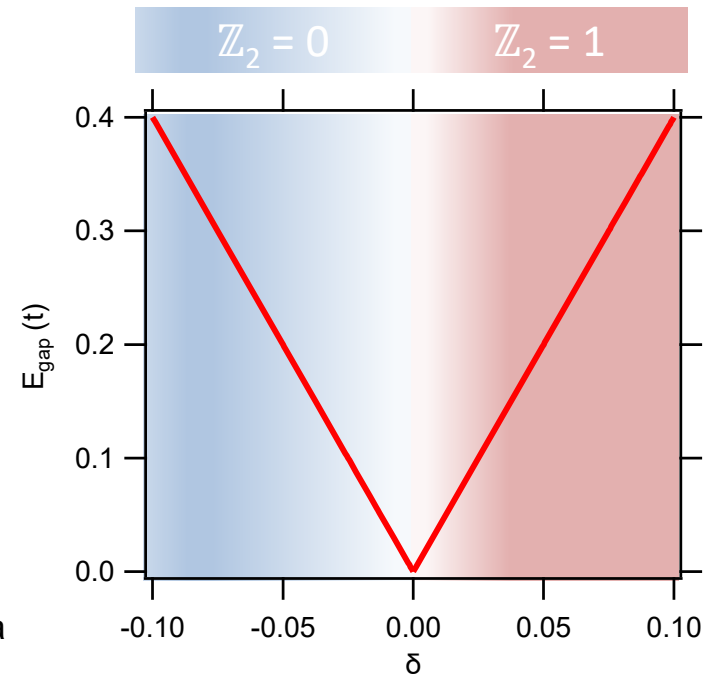
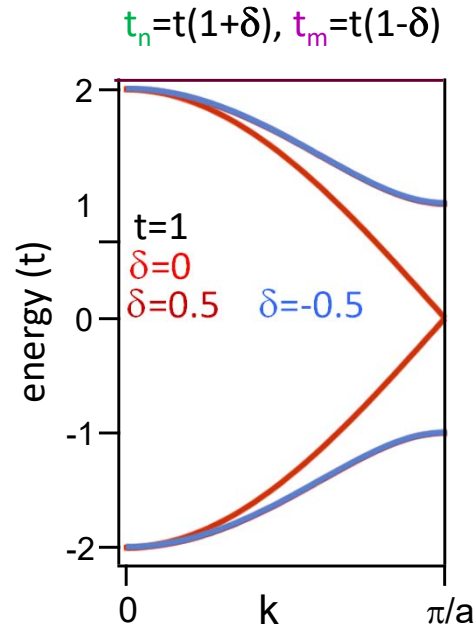
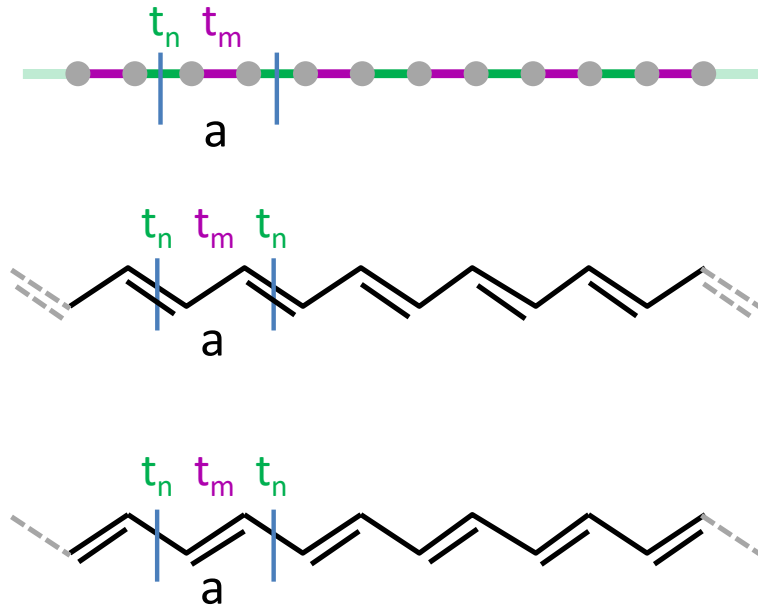


5-Armchair Graphene Nanoribbons

Lawrence et al., ACS Nano 14, 4499 (2020)



Su-Schrieffer-Heeger (SSH) model and topology



$$E(k) = \pm \sqrt{t_n^2 + t_m^2 + 2t_n t_m \cos(ka)}$$

Wave function

$$\psi_k(x) = e^{ikx} u_k(x)$$

Zak Phase

$$\gamma = i \int_{-\pi/a}^{\pi/a} dk u_k \frac{\partial}{\partial k} u_k$$

Symmetry: $\gamma = 0$ or π

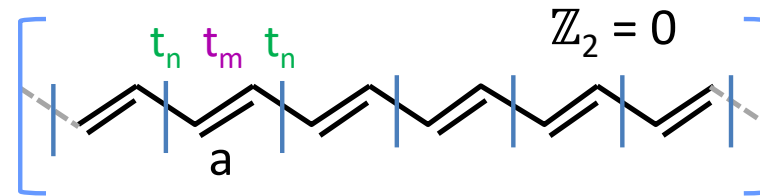
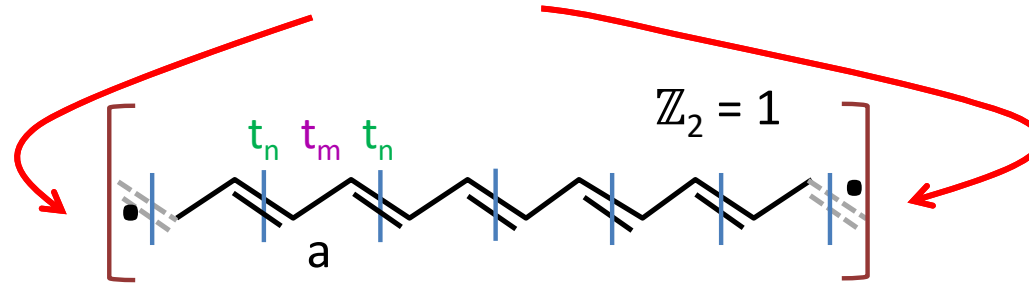
$$\mathbb{Z}_2 \text{ Invariant: } e^{i\gamma} = (-1)^{\mathbb{Z}_2}$$

$$\mathbb{Z}_2 = 0 \text{ ("trivial")}$$

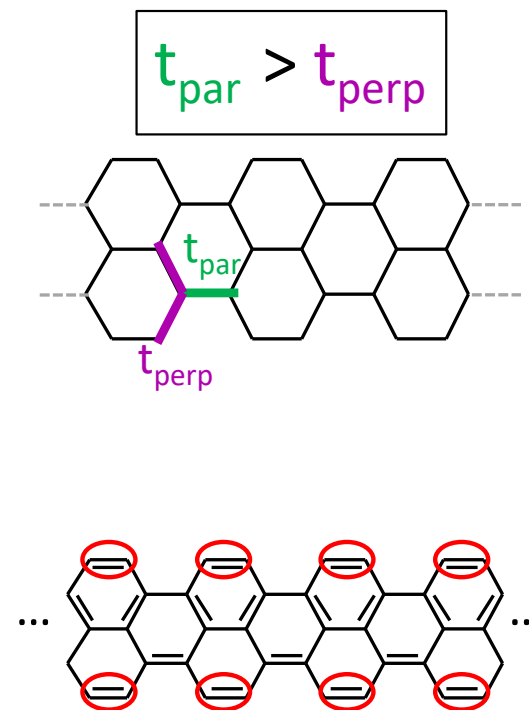
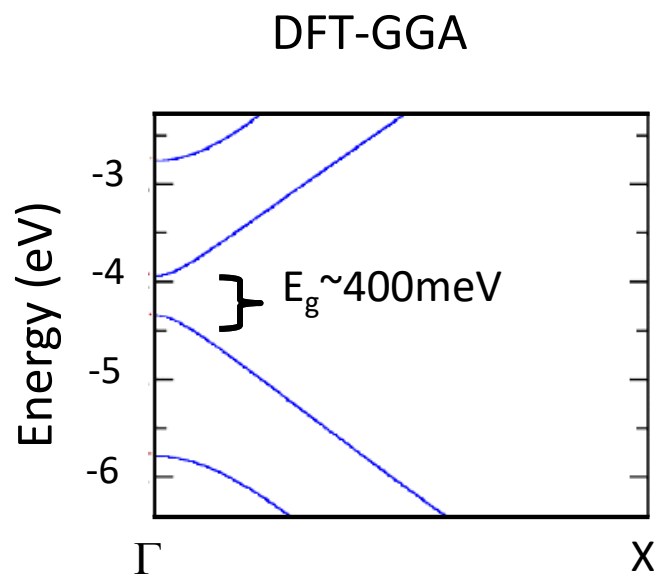
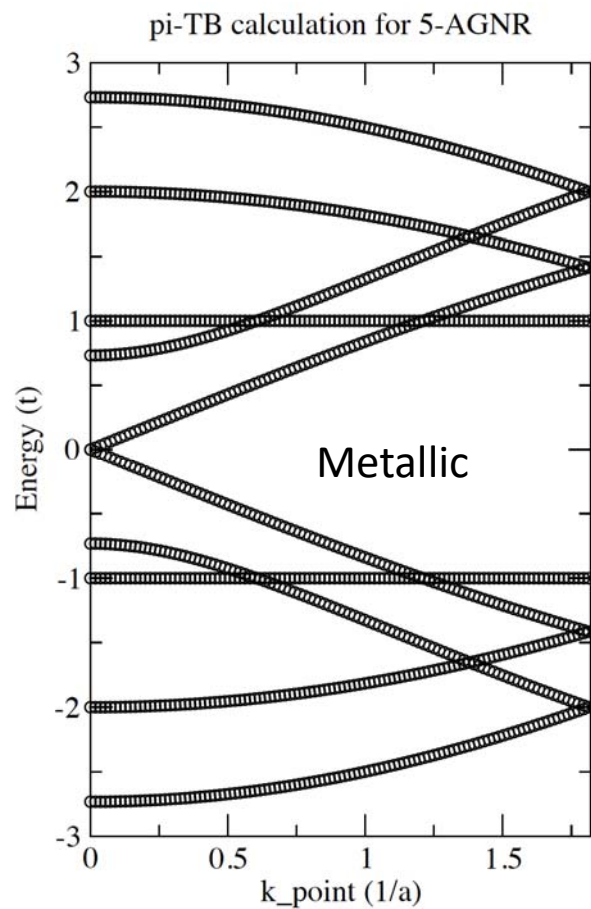
$$\mathbb{Z}_2 = 1 \text{ ("topological")}$$

Su-Schrieffer-Heeger (SSH) model and topology

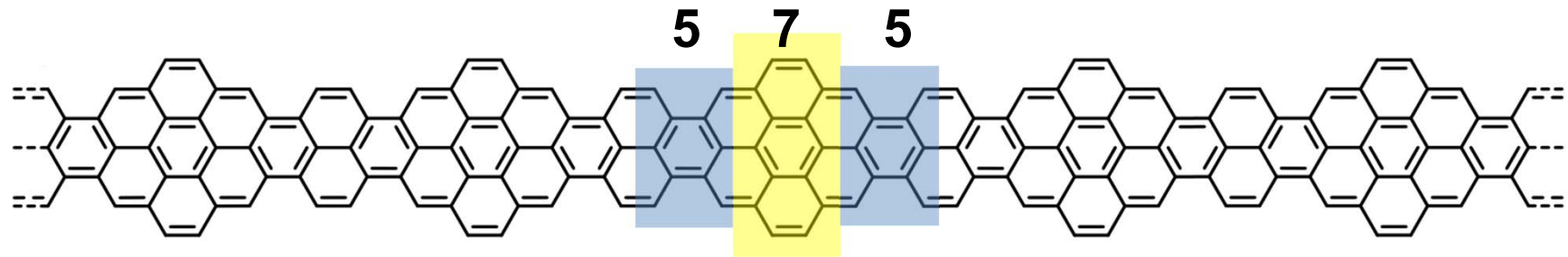
End states



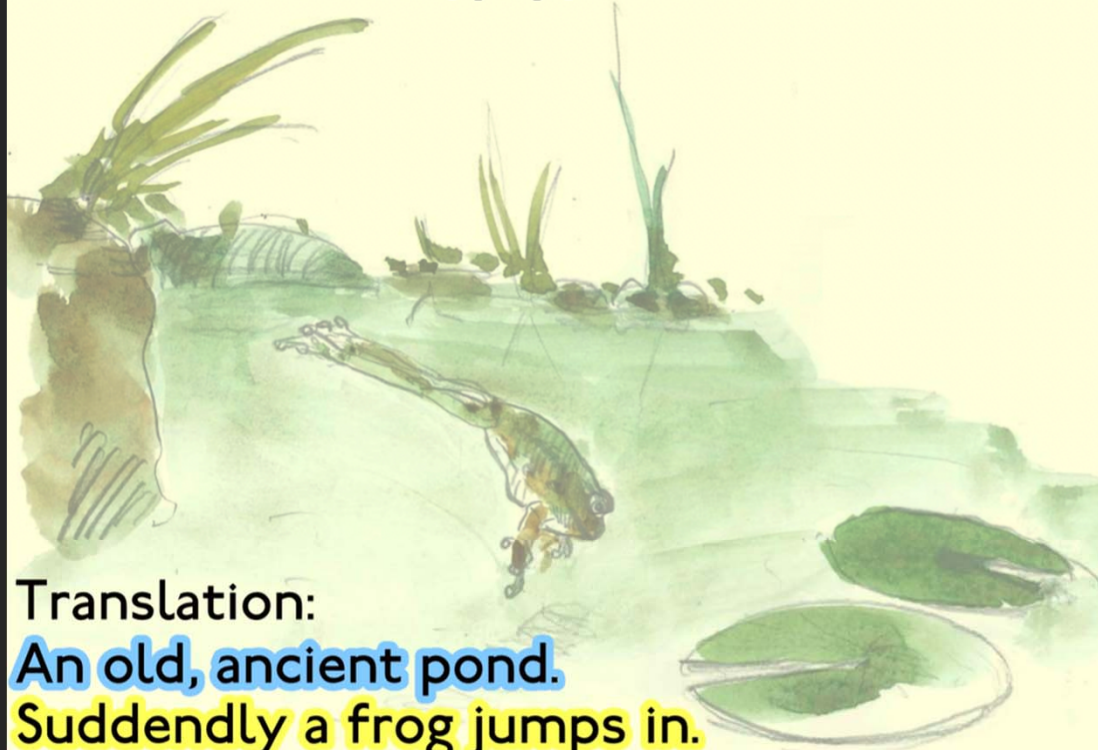
Electronic gap in 5-aGNRs ?



Haiku graphene nanoribbons



5/7/5 Example of a haiku:

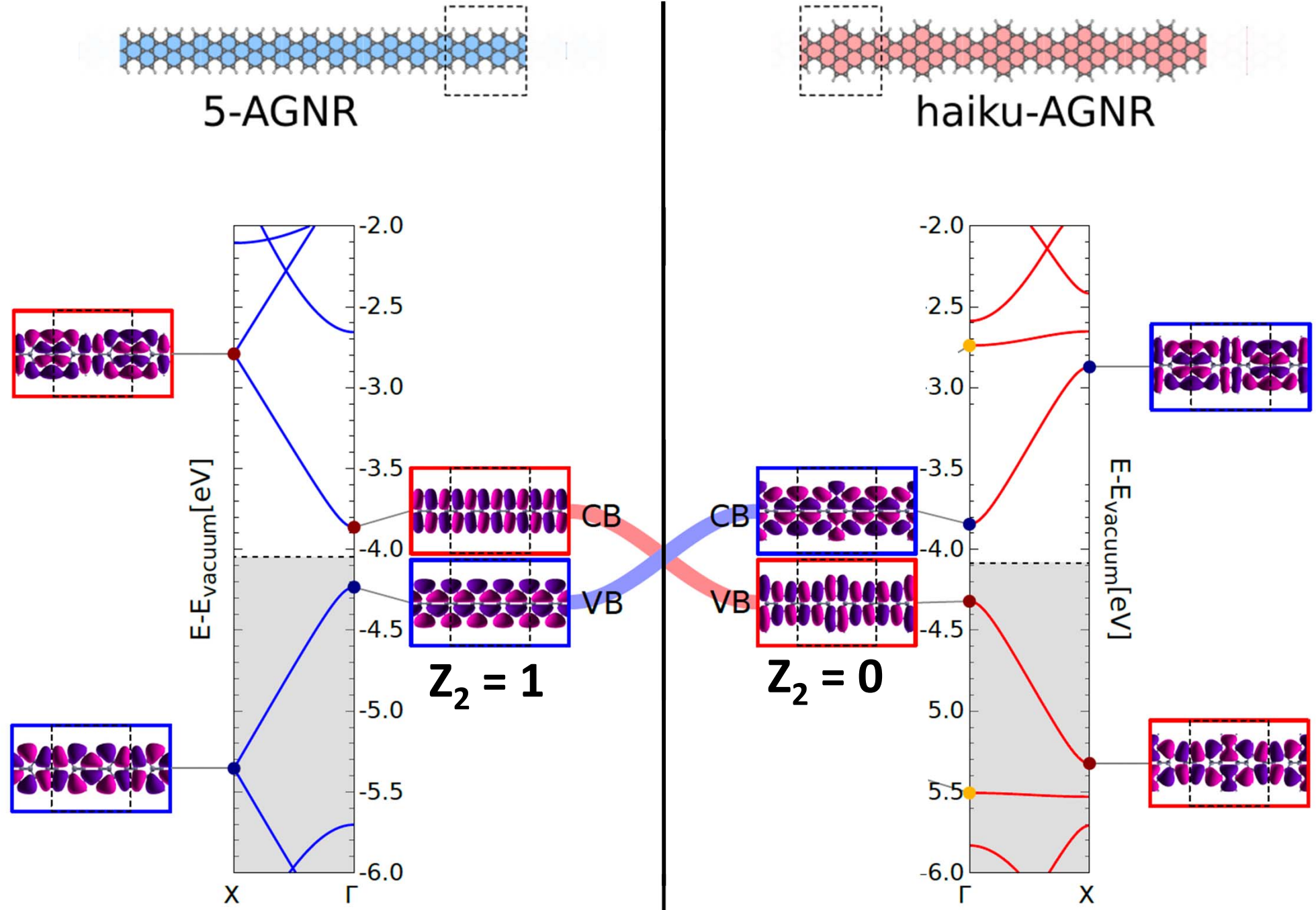


Translation:

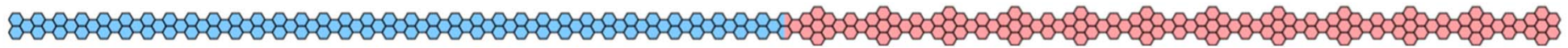
An old, ancient pond.
Suddendly a frog jumps in.
Sound of watersplash.

み_{mi} か_{ka} ふ_{fu}
ず_{zu} わ_{wa} る_{ru}
の_{no} ず_{zu} い_i
お_o と_{to} け_{ke}
と_{to} び_{bi} や_{ya}
こ_{ko}
む_{mu}

Changes in topology : bands & wavefunctions

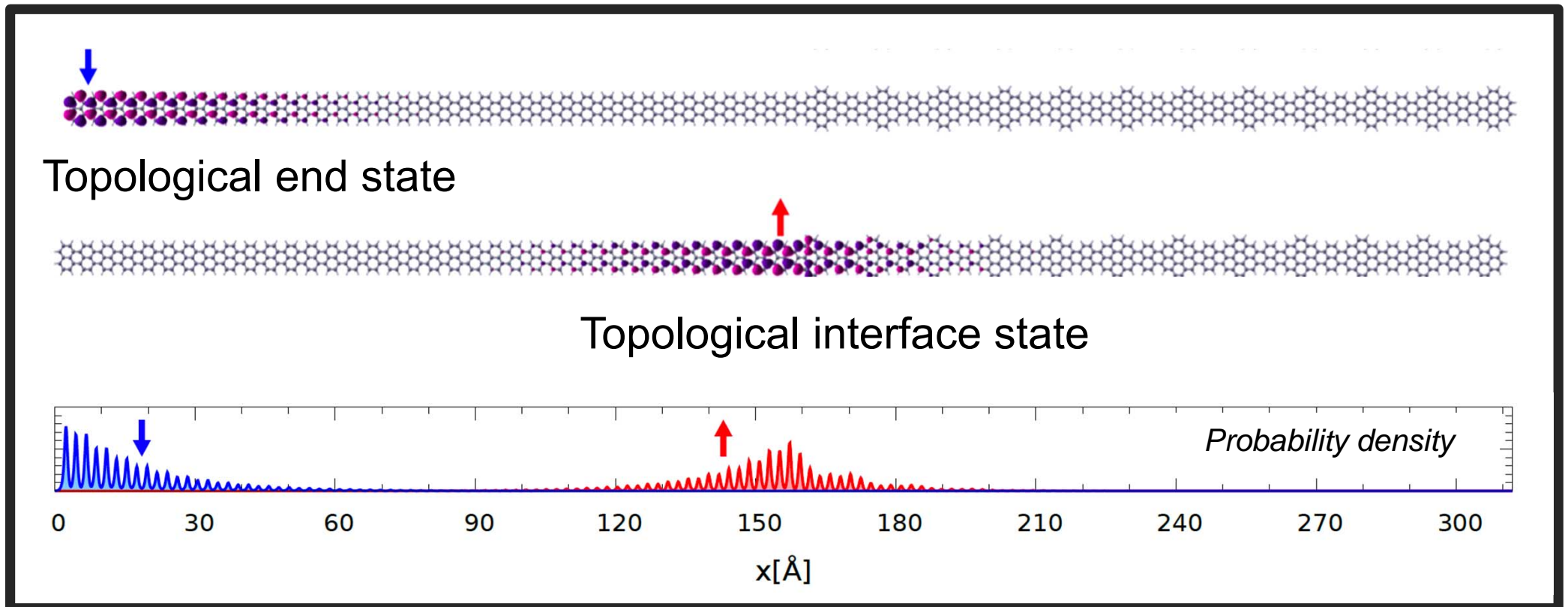


Heterojunction: 5AGNR and Haiku-AGNR



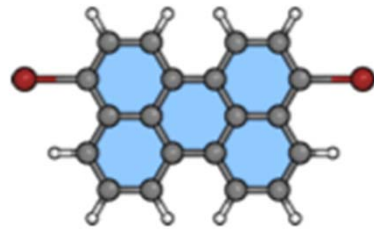
$$Z_2 = 1$$

$$Z_2 = 0$$

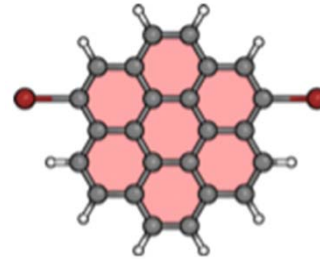


Can we tune the topological end/interface states?

Hybrid GNRs: theoretical experiment



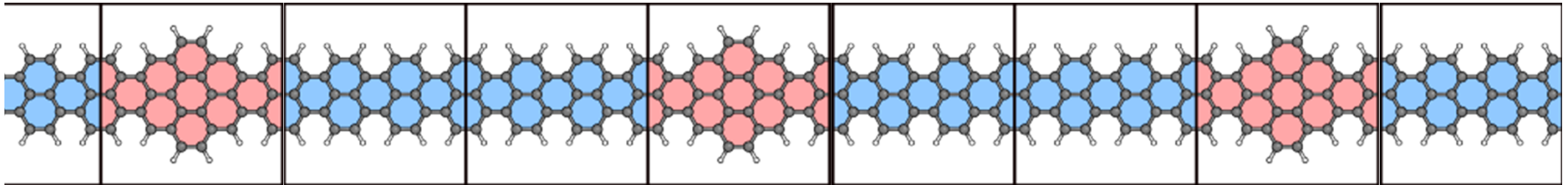
*Precursor for
5-AGNR*



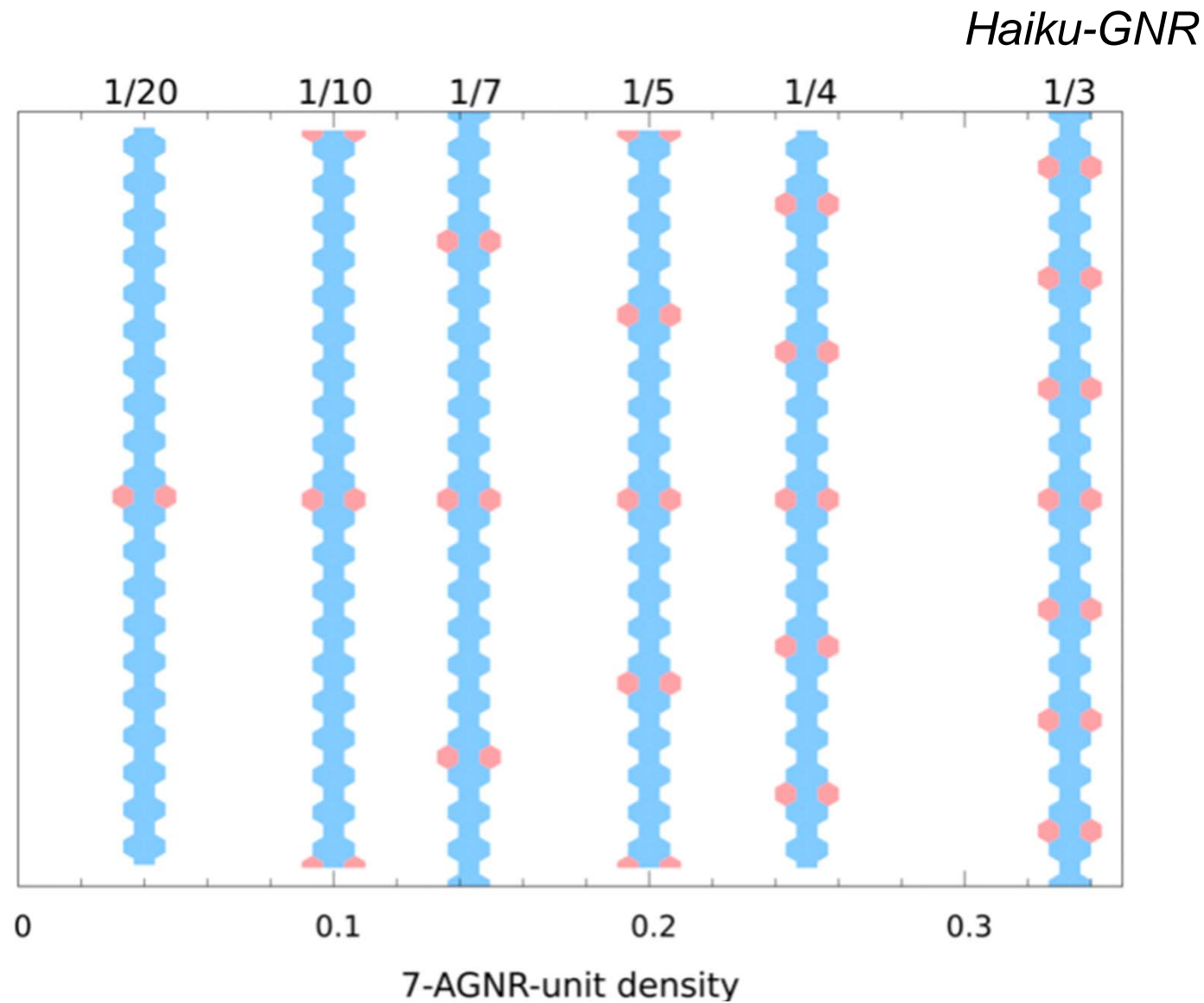
*Precursor for
Haiku-AGNR*



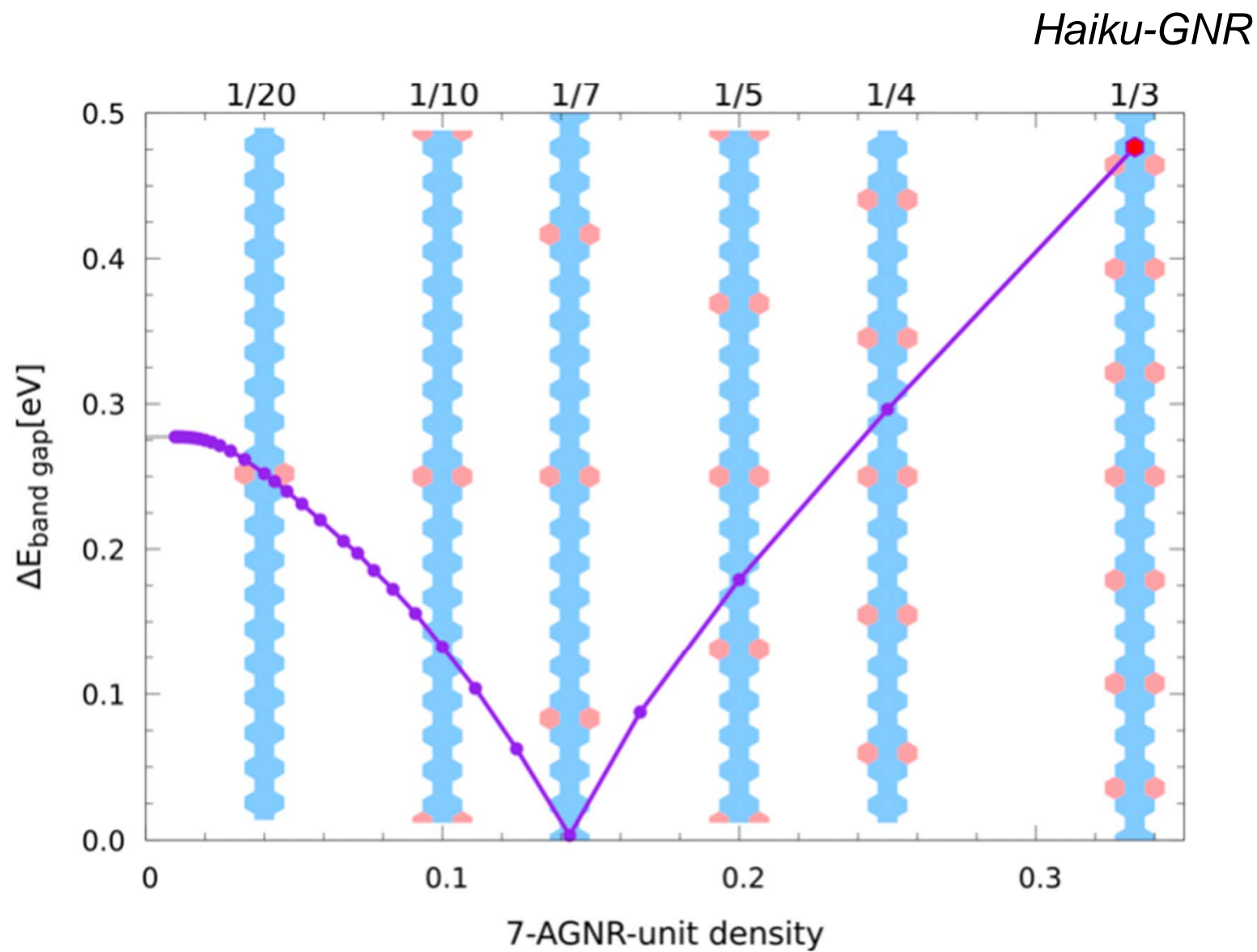
Hybrid GNRs



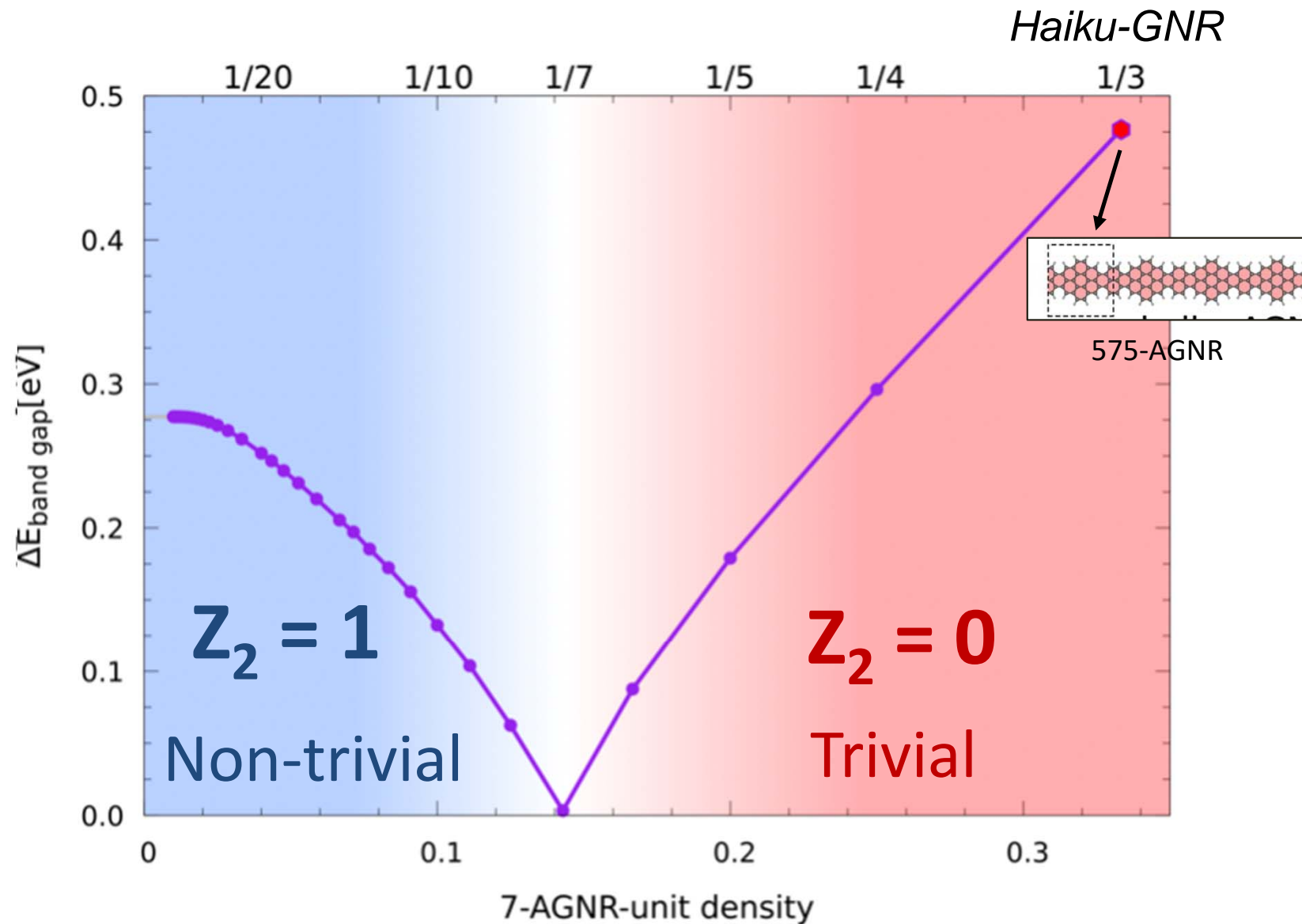
Tunable topology in hybrid-GNRs



Tunable topology in hybrid-GNRs

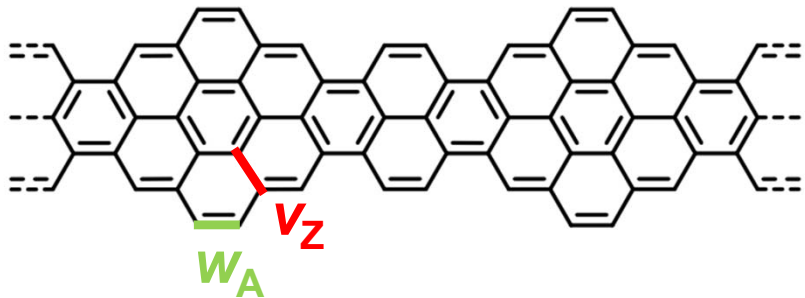


Tunable topology in hybrid-GNRs



Tight-binding for Haiku GNRs

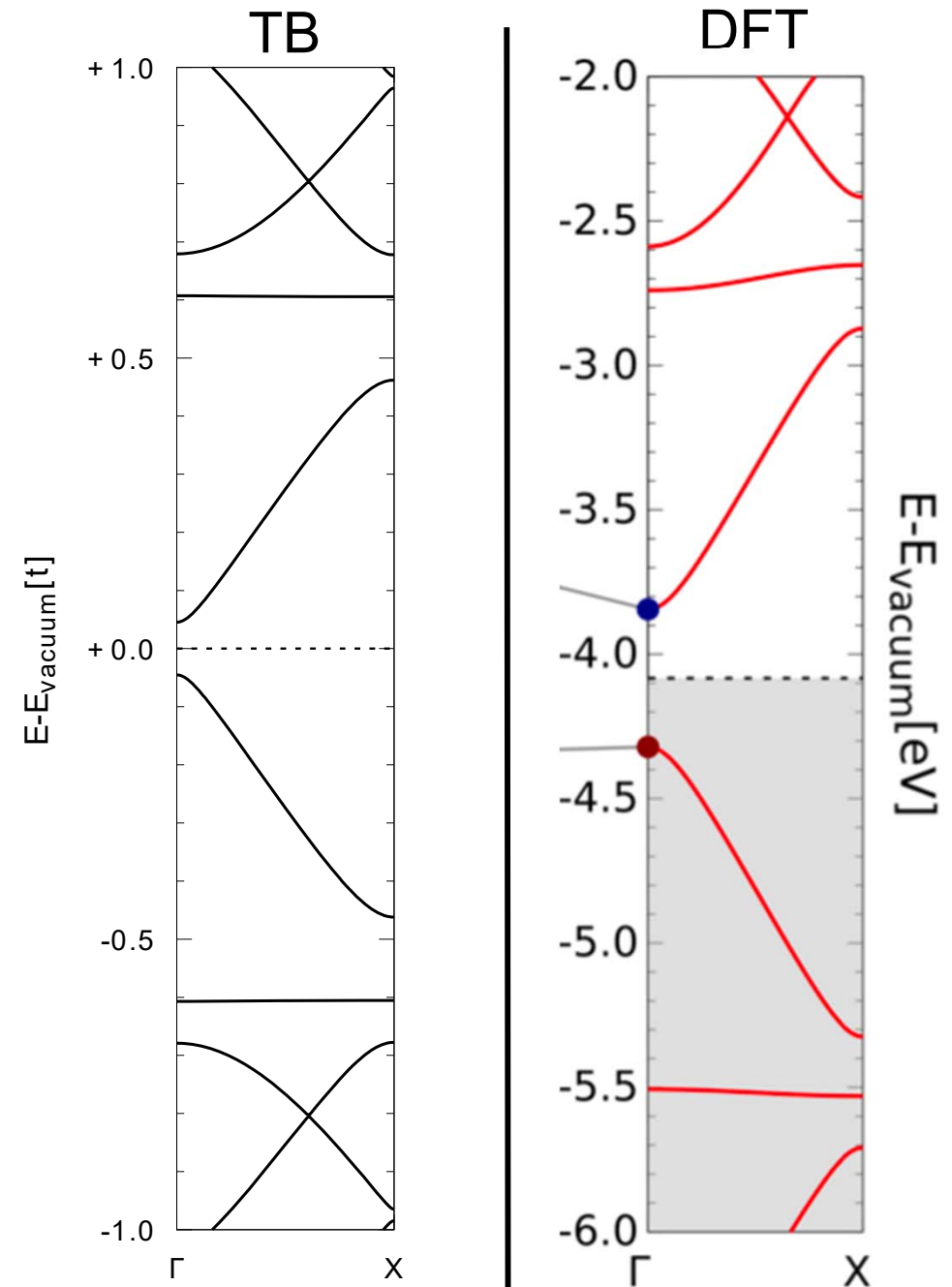
Anisotropic TB model



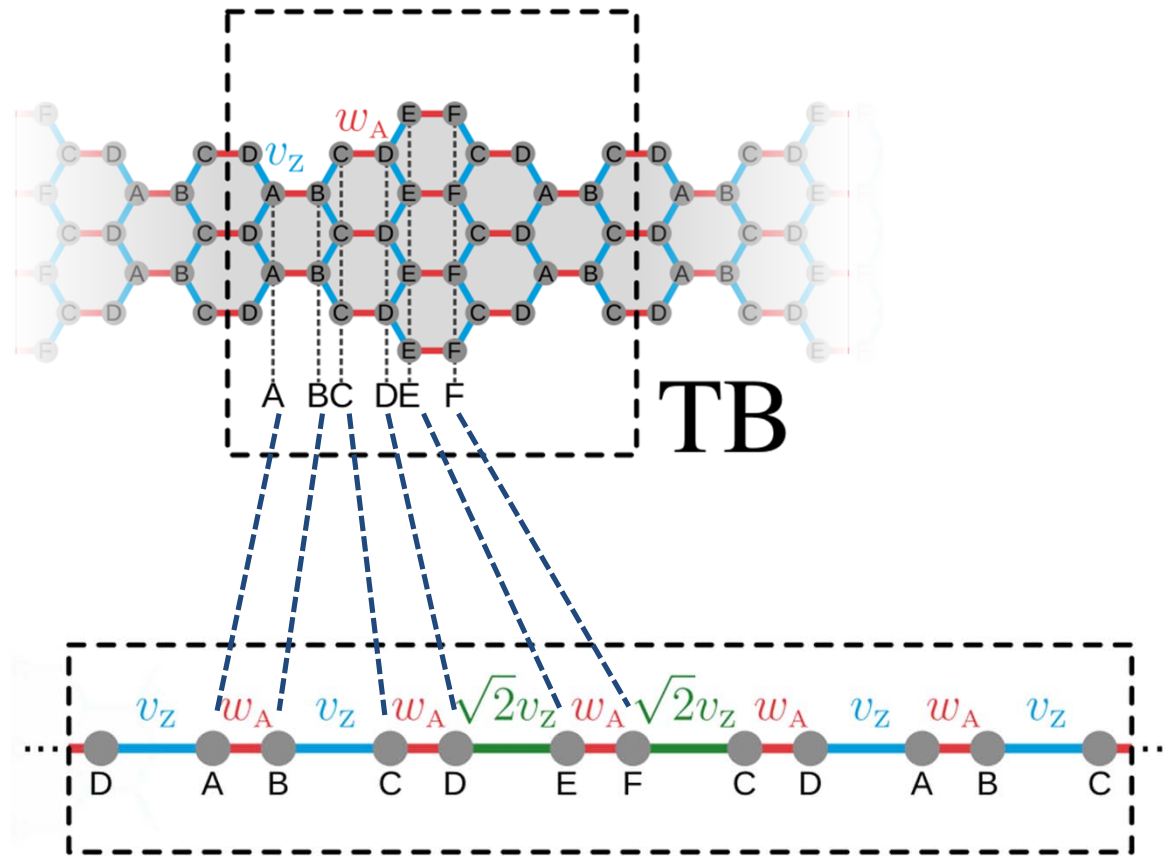
Lawrence et al., ACS Nano 14, 4499 (2020)

$$W_A = 1.075 v_Z$$

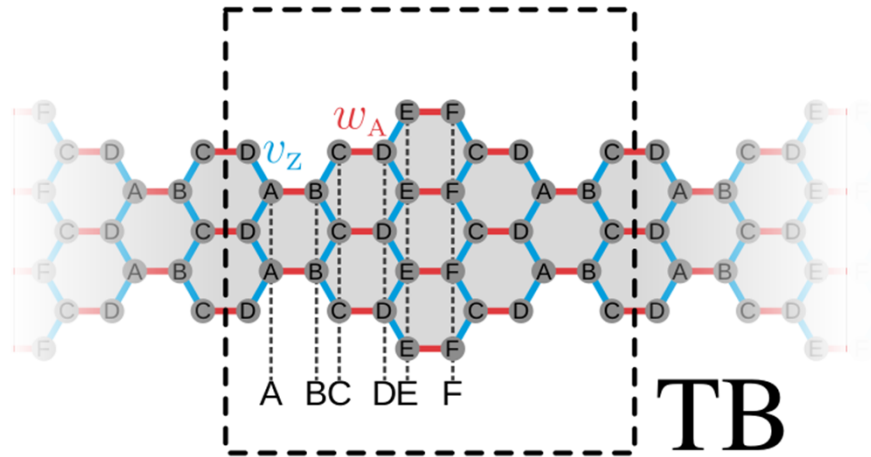
$$v_Z = t = 2.7 \text{ eV}$$



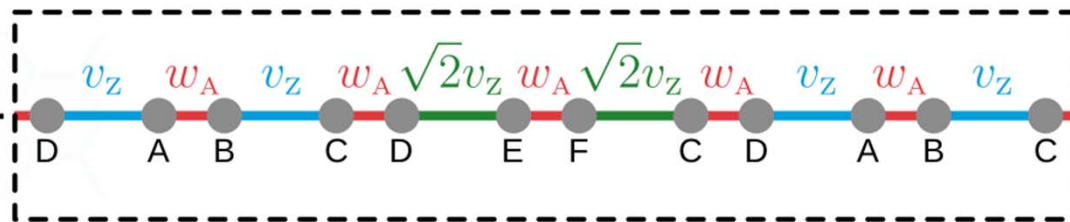
Generalized SSH model for Haiku GNRs



Generalized SSH model for Haiku GNRs

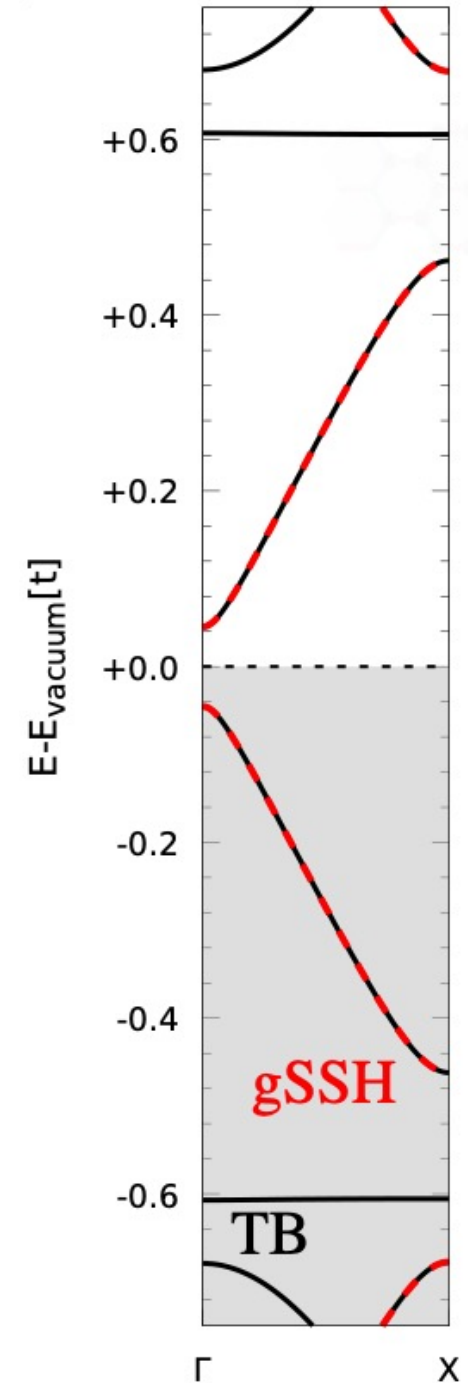


Frontier bands

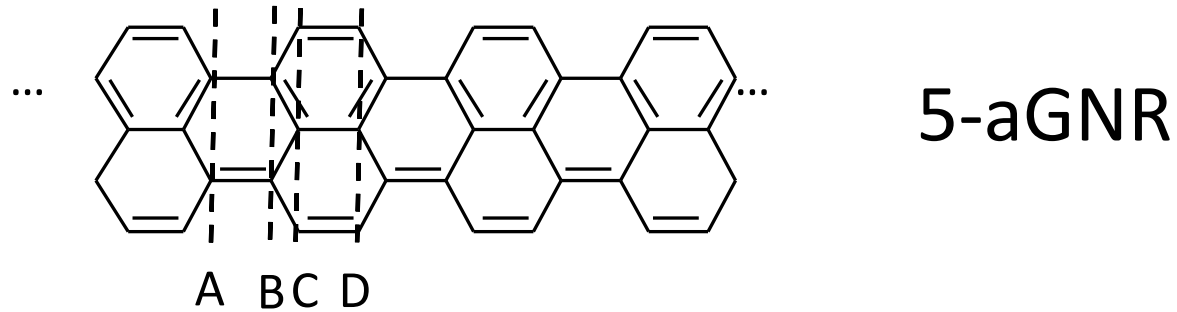


gSSH

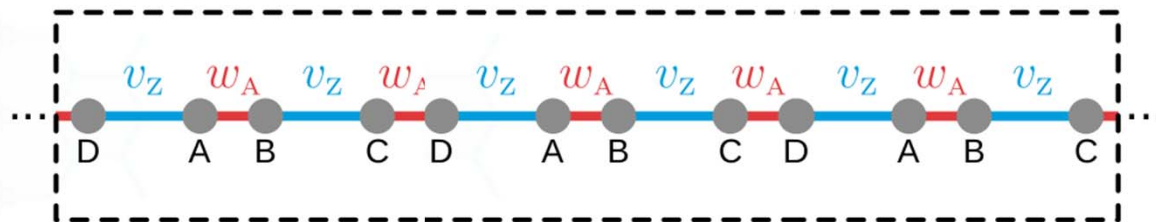
generalized Su-Schrieffer-Heeger model



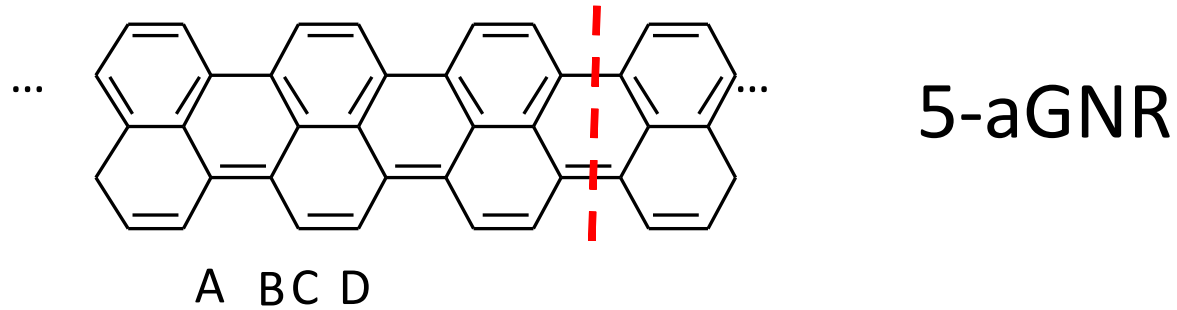
Normal SSH model for 5-aGNR valence band



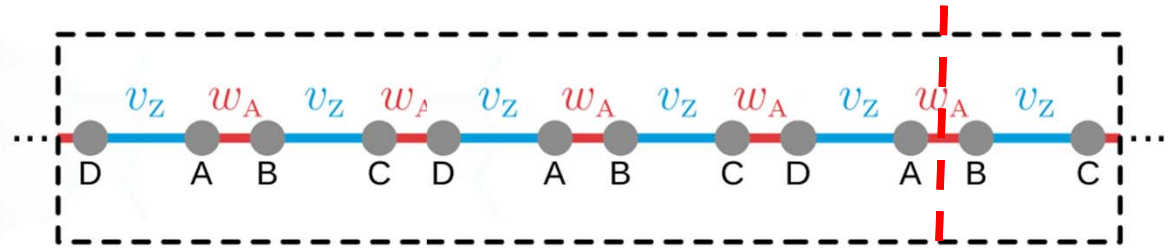
$$W_A > V_Z$$



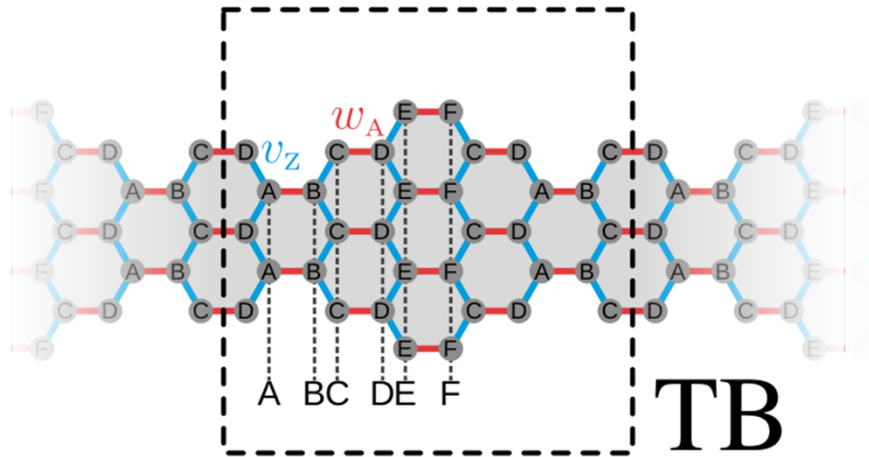
Normal SSH model for 5-aGNR valence band



$$W_A > V_Z$$

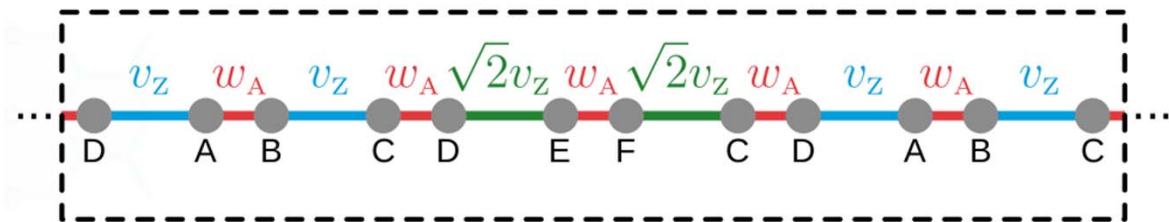


Generalized SSH model for Haiku GNRs



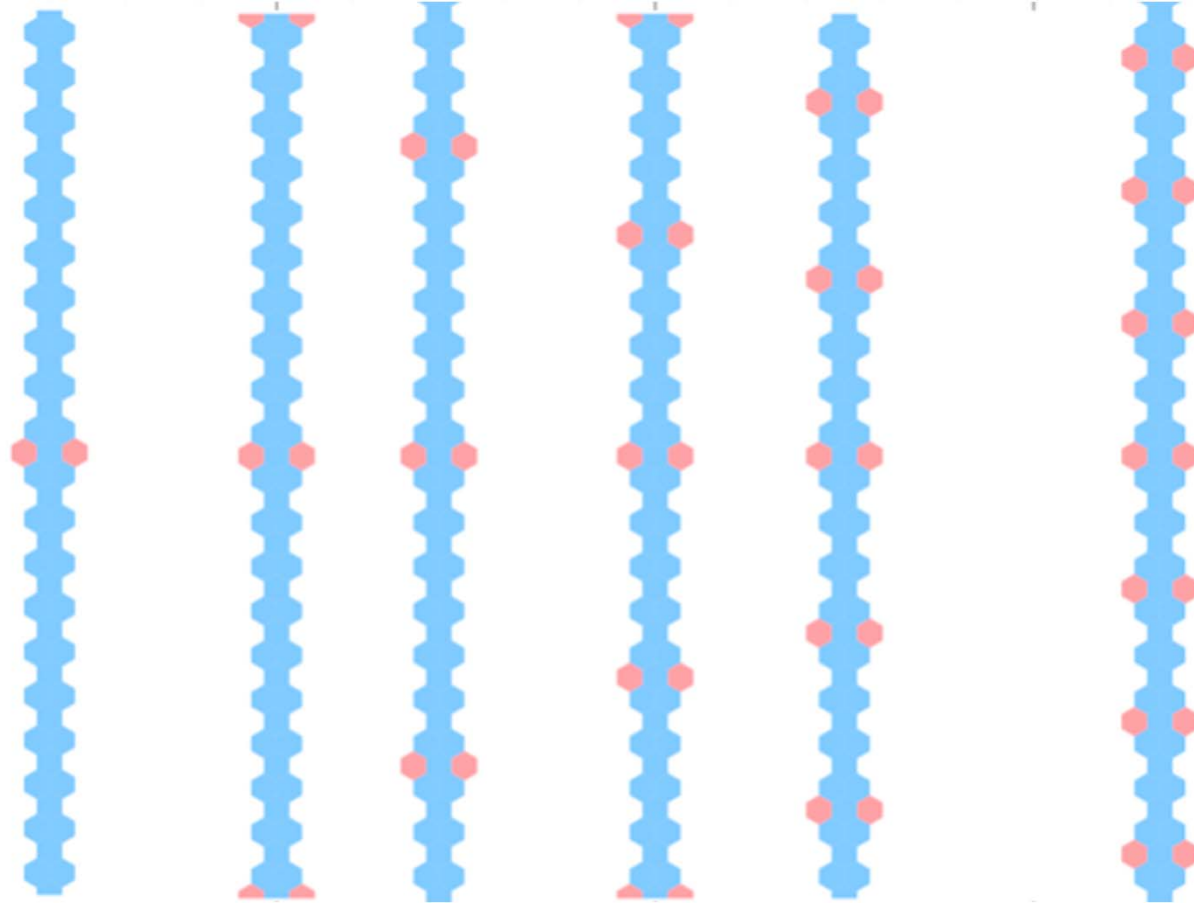
$$\sqrt{2} V_Z > W_A > V_Z$$

Tends to change topology

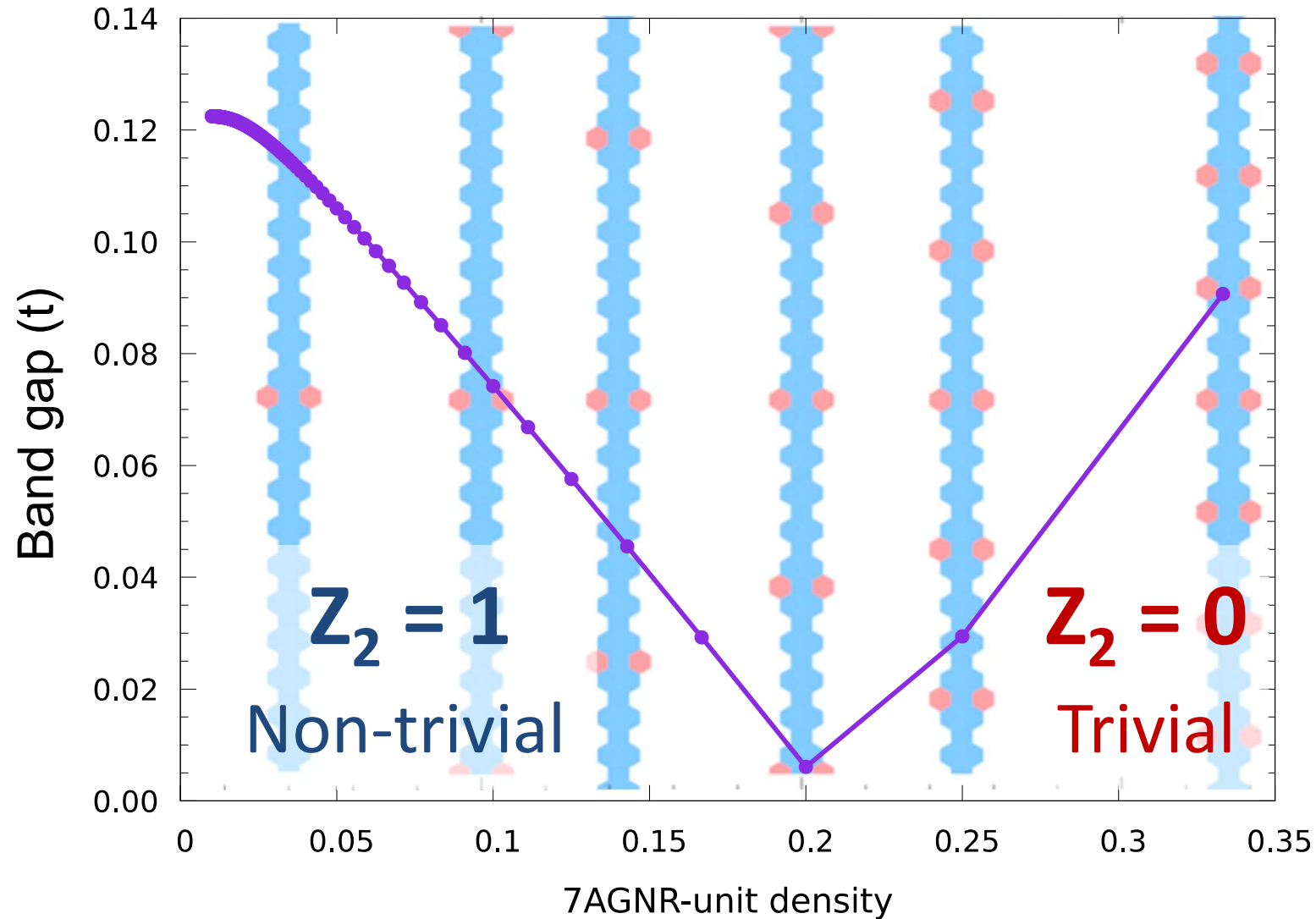


gSSH

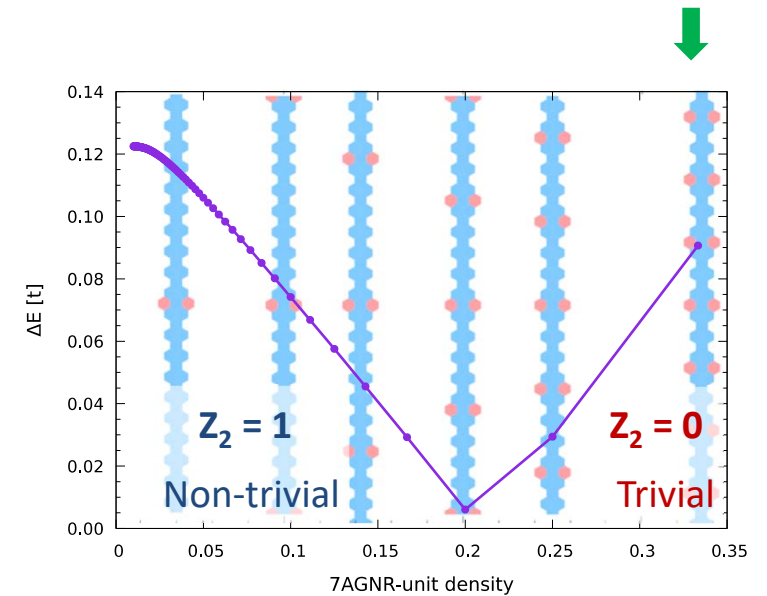
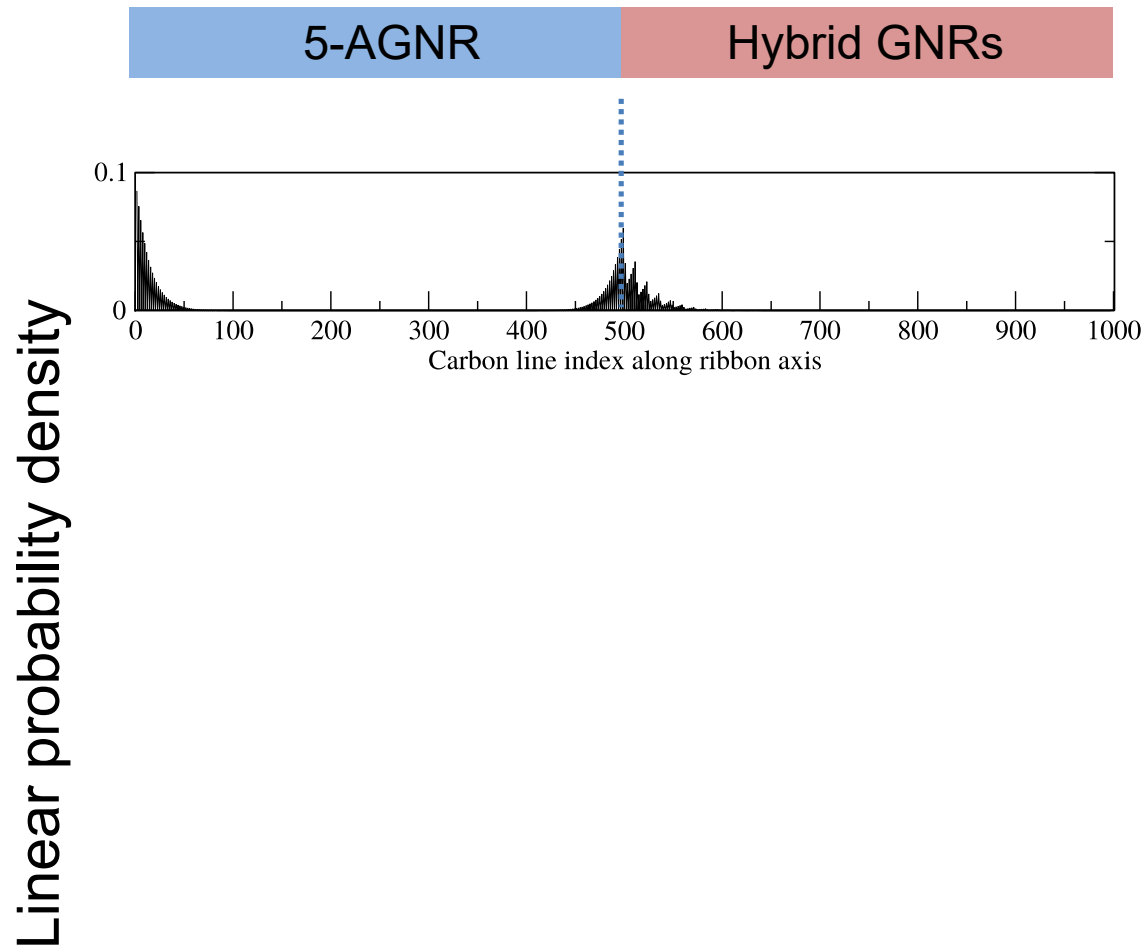
Topological phase transition with g-SSH model



Topological phase transition with g-SSH model

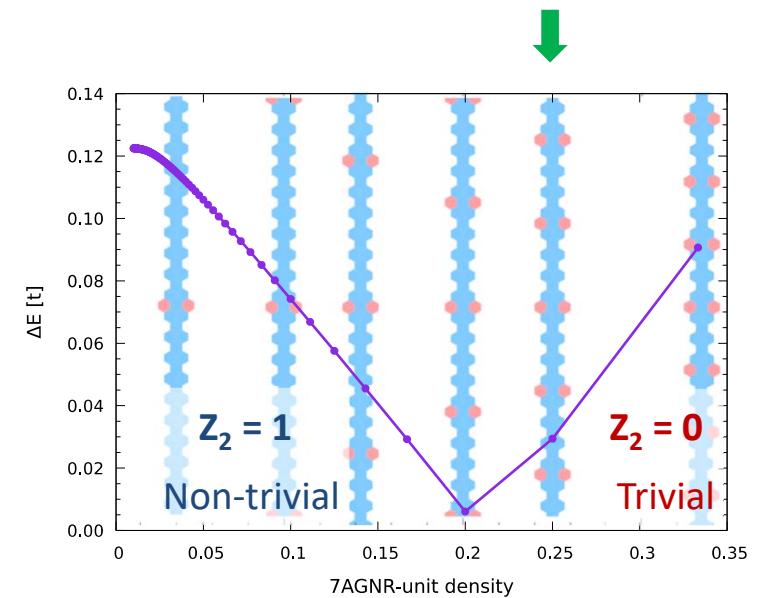
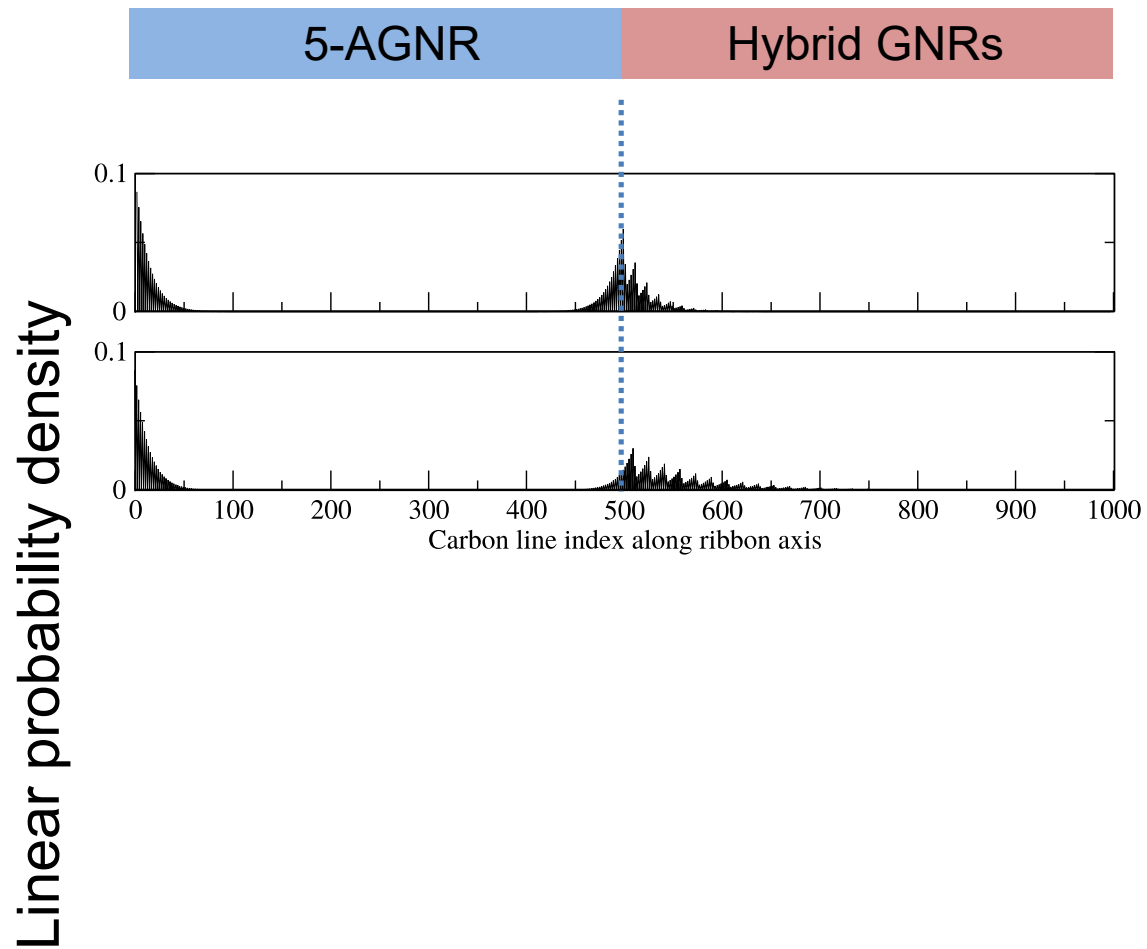


Tuning topological states in hybrid Haiku GNRs



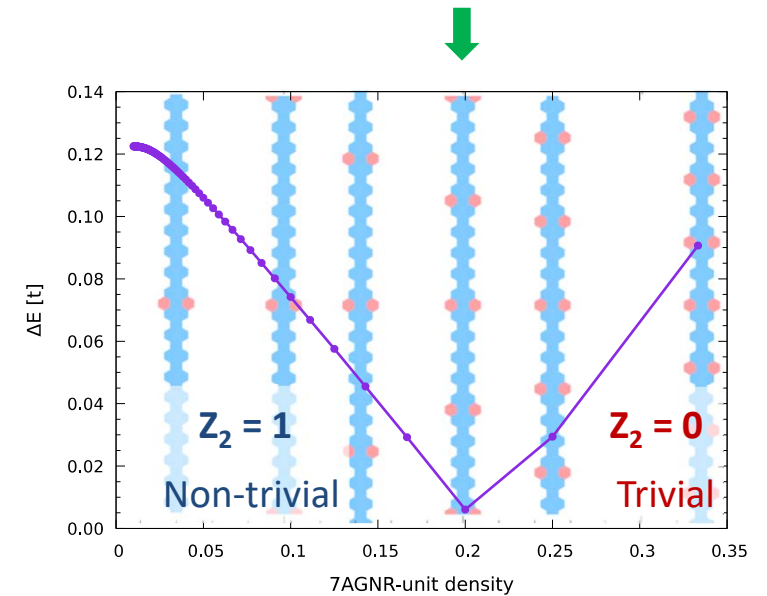
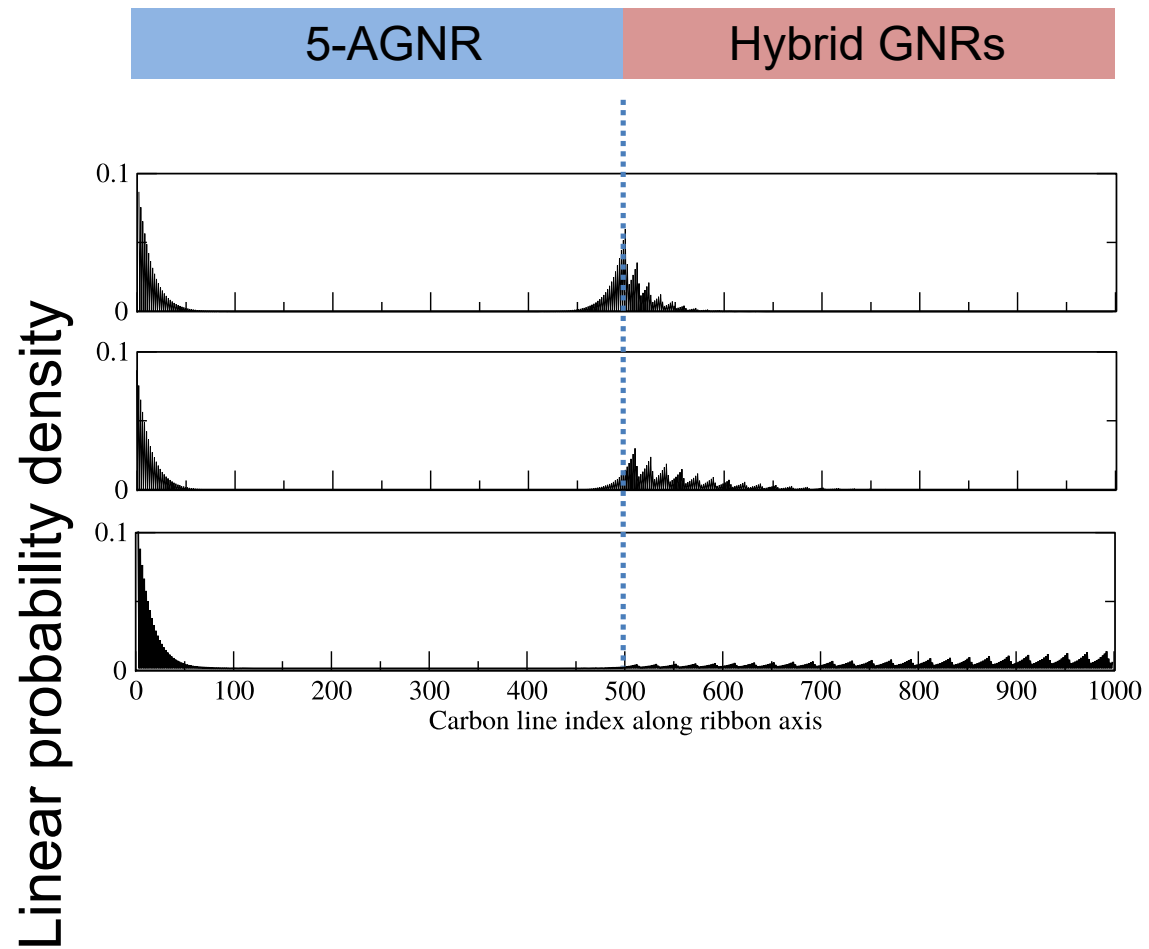
R. Menchón et al. (in preparation)

Tuning topological states in hybrid Haiku GNRs



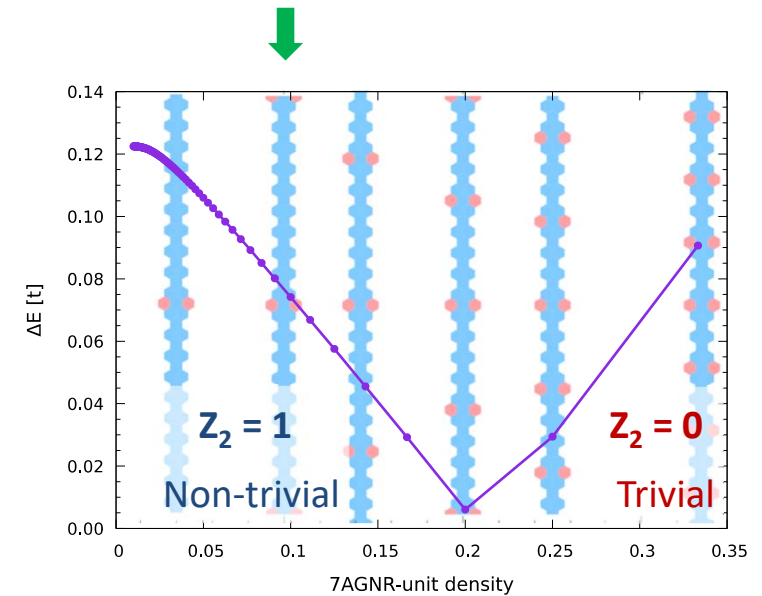
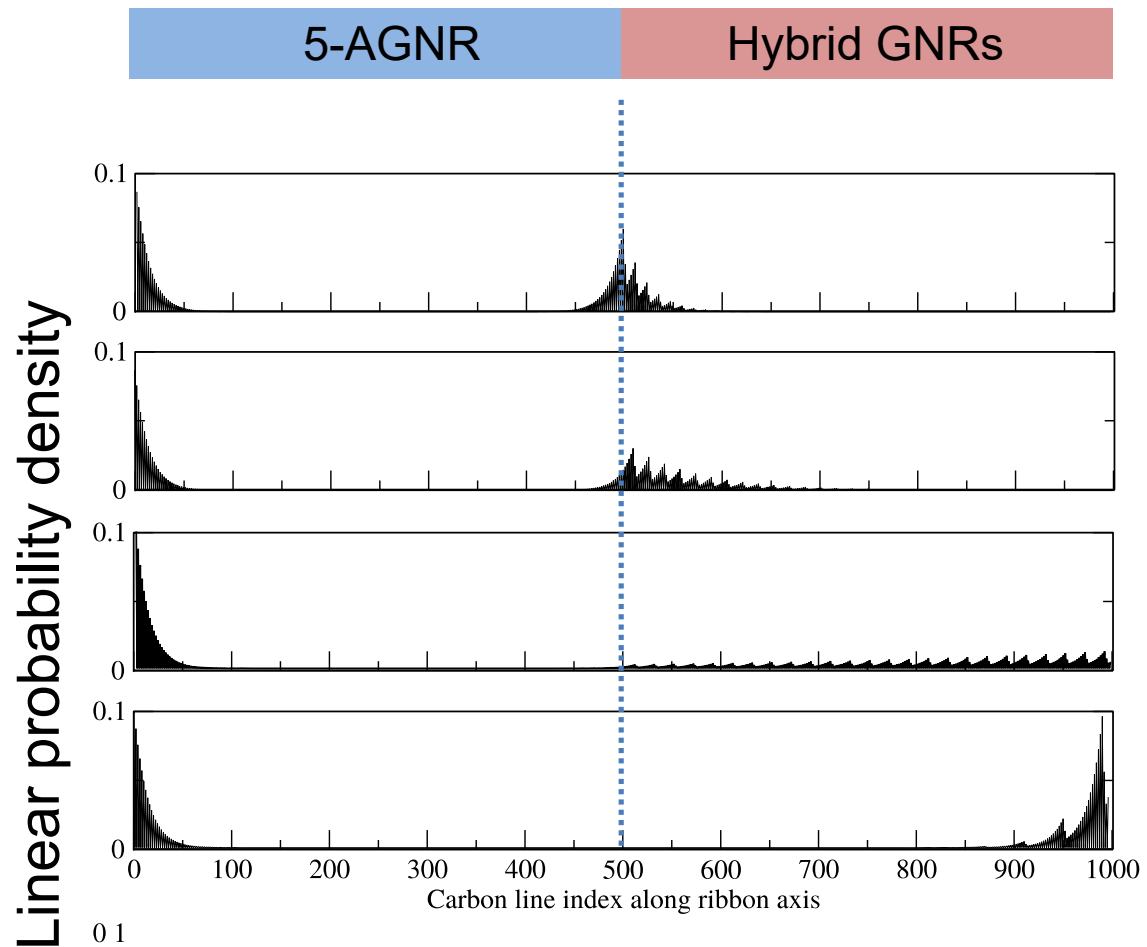
R. Menchón et al. (in preparation)

Tuning topological states in hybrid Haiku GNRs



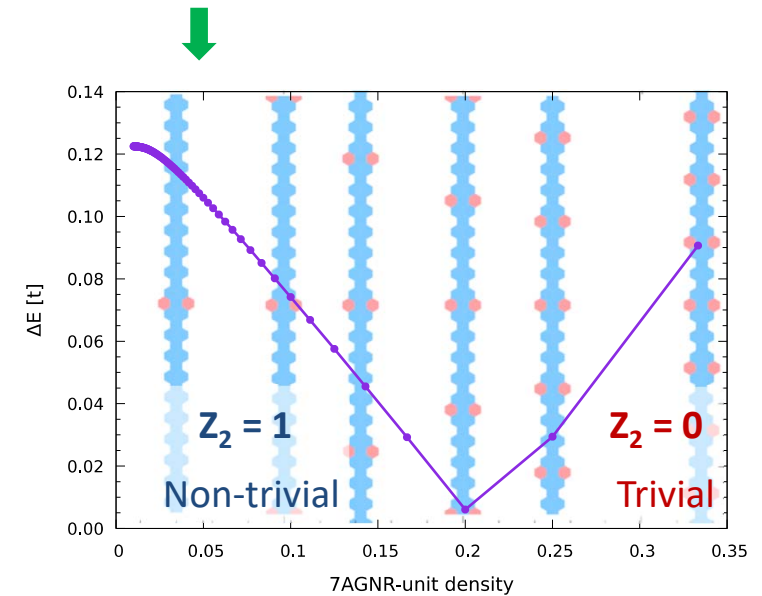
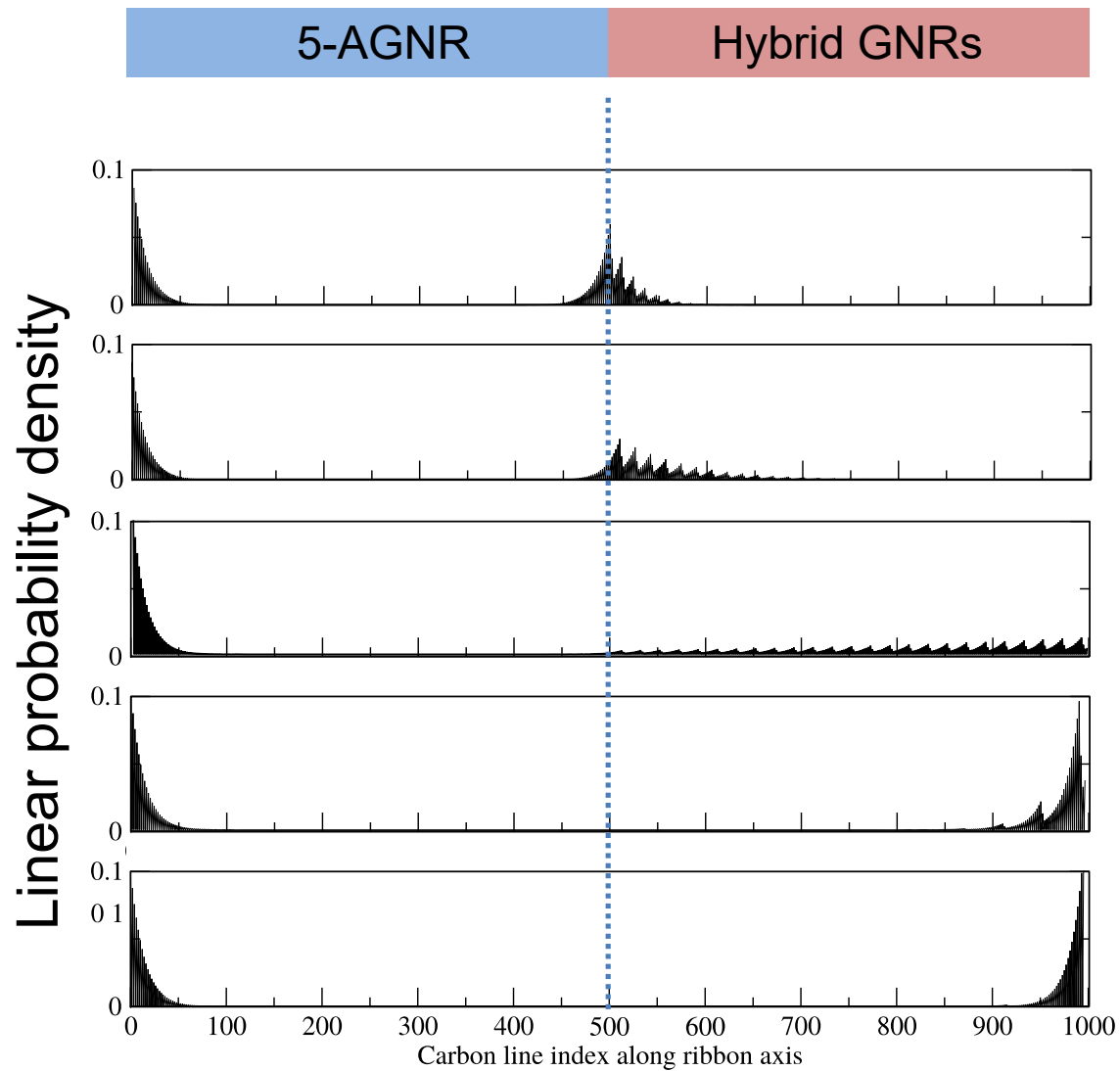
R. Menchón et al. (in preparation)

Tuning topological states in hybrid Haiku GNRs



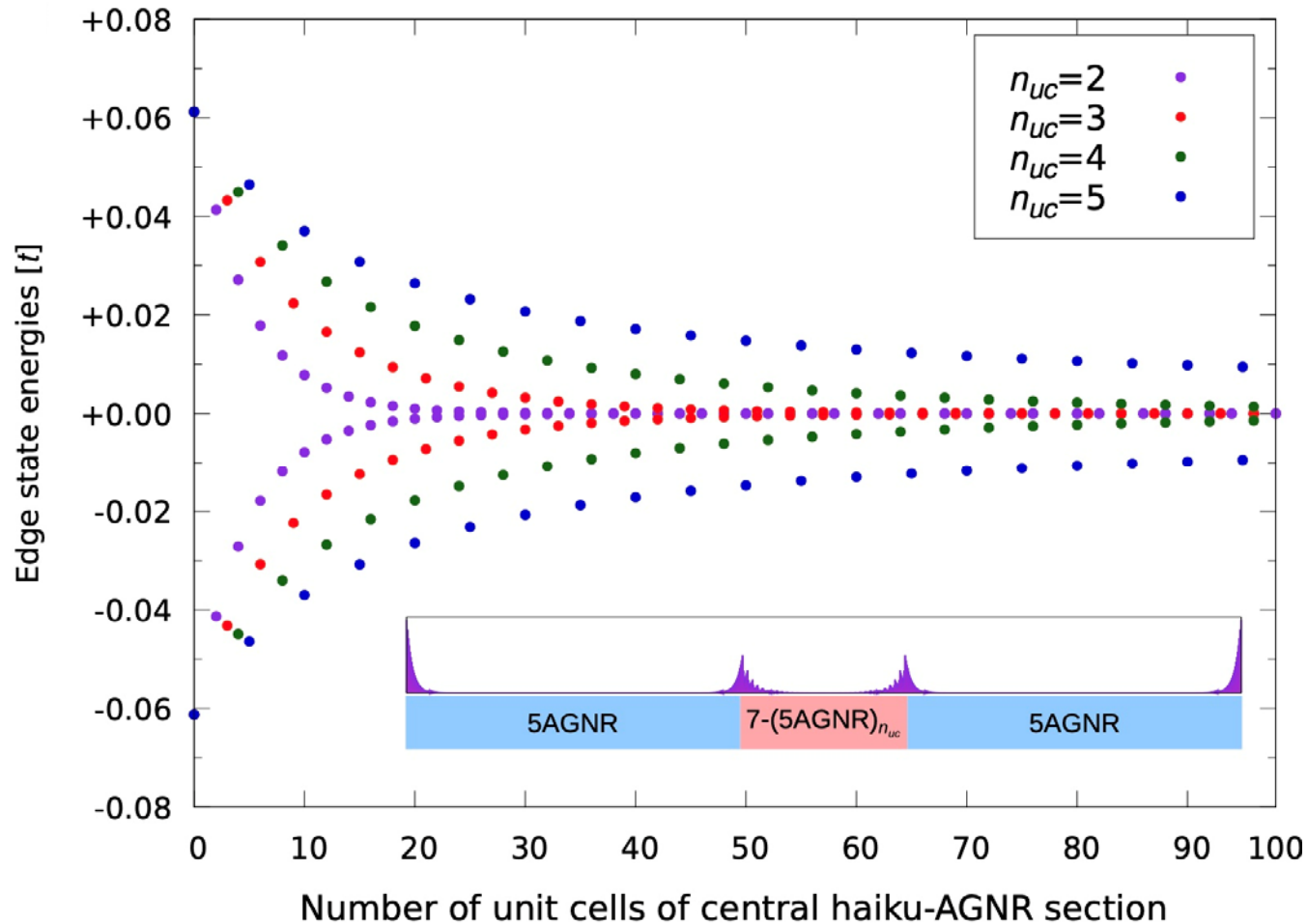
R. Menchón et al. (in preparation)

Tuning topological states in hybrid Haiku GNRs

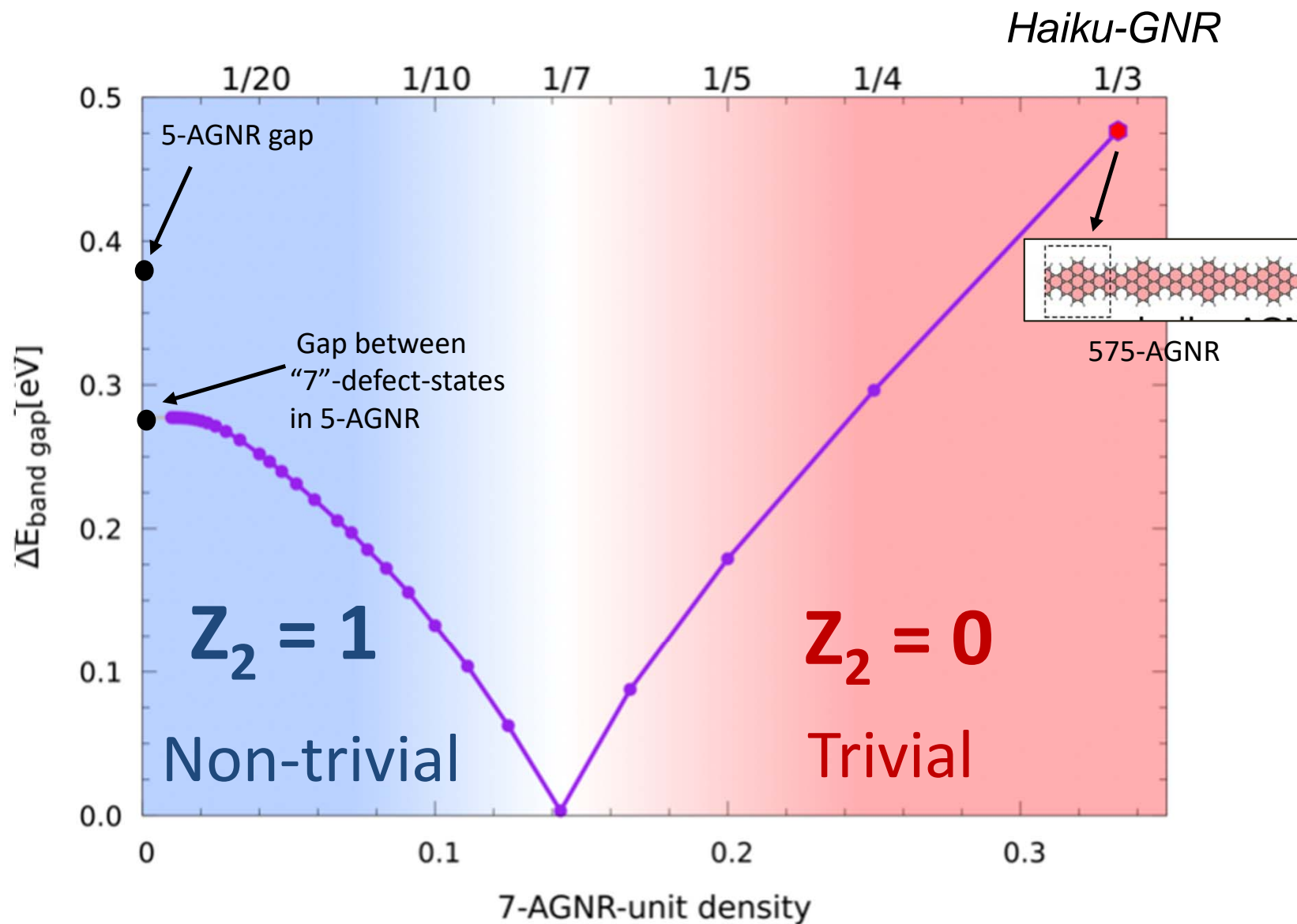


R. Menchón et al. (in preparation)

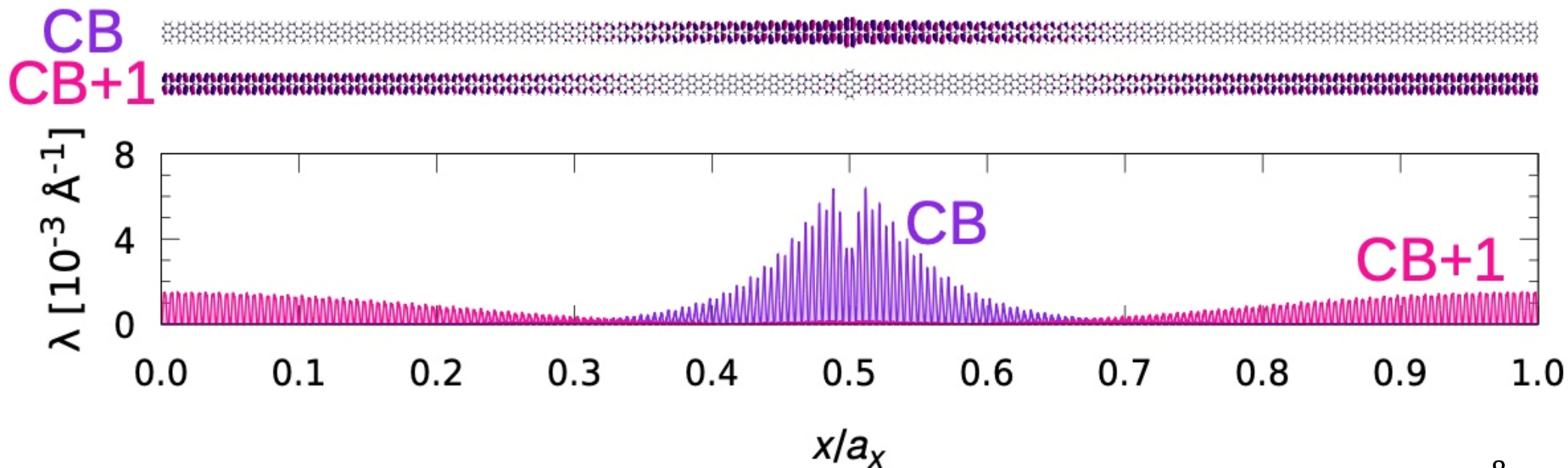
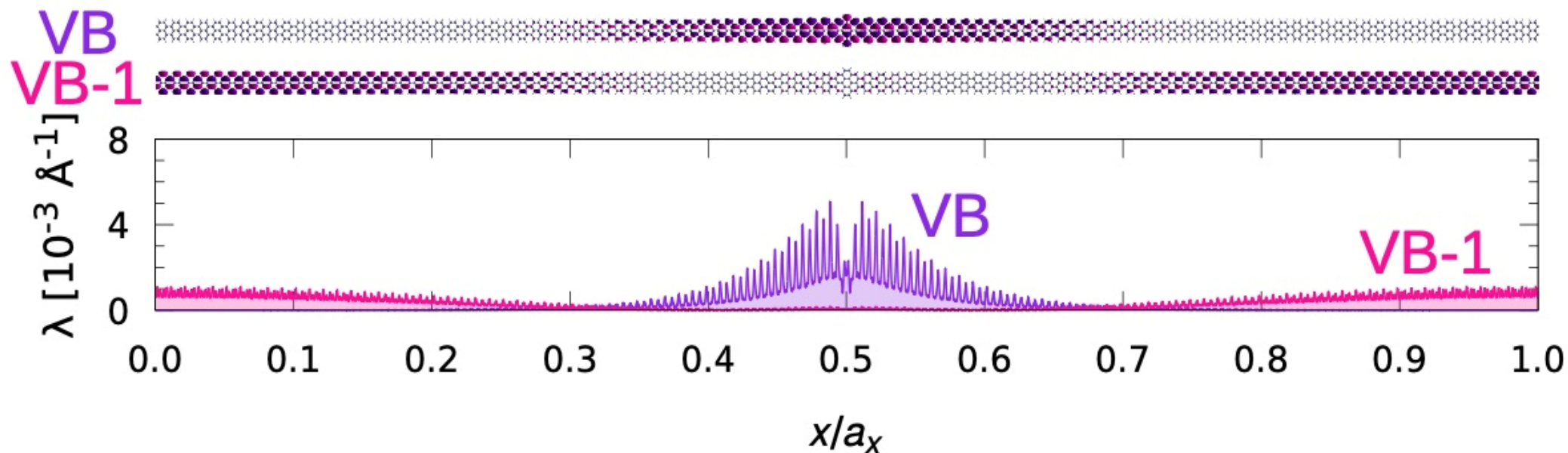
Larger systems with the g-SSH model: topological transition and the appearance of in gap interfacial states



Tunable topology in hybrid-GNRs

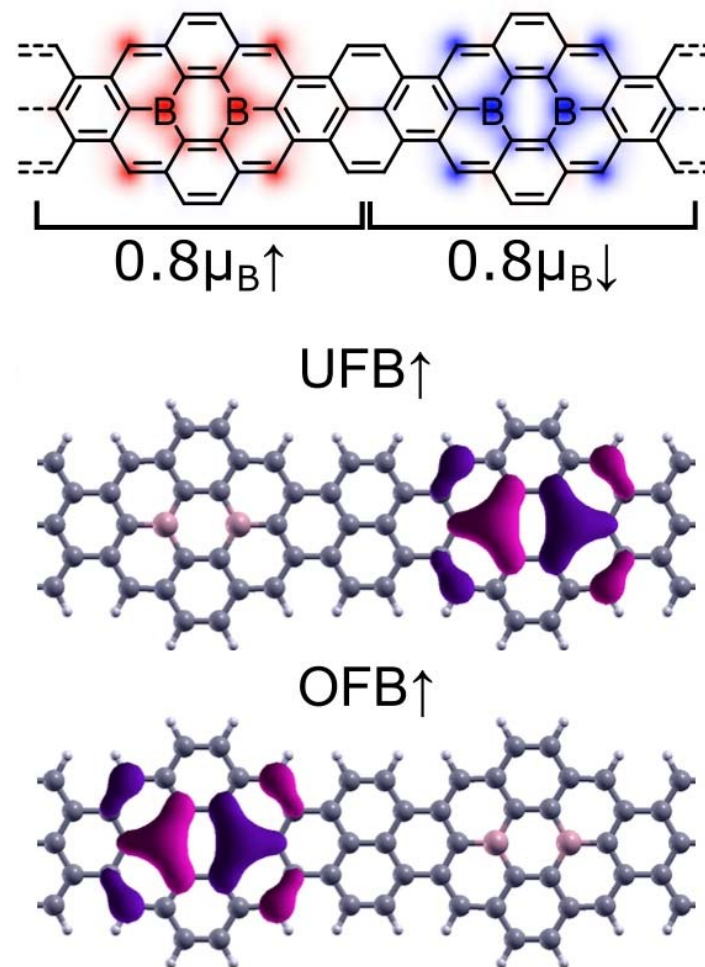
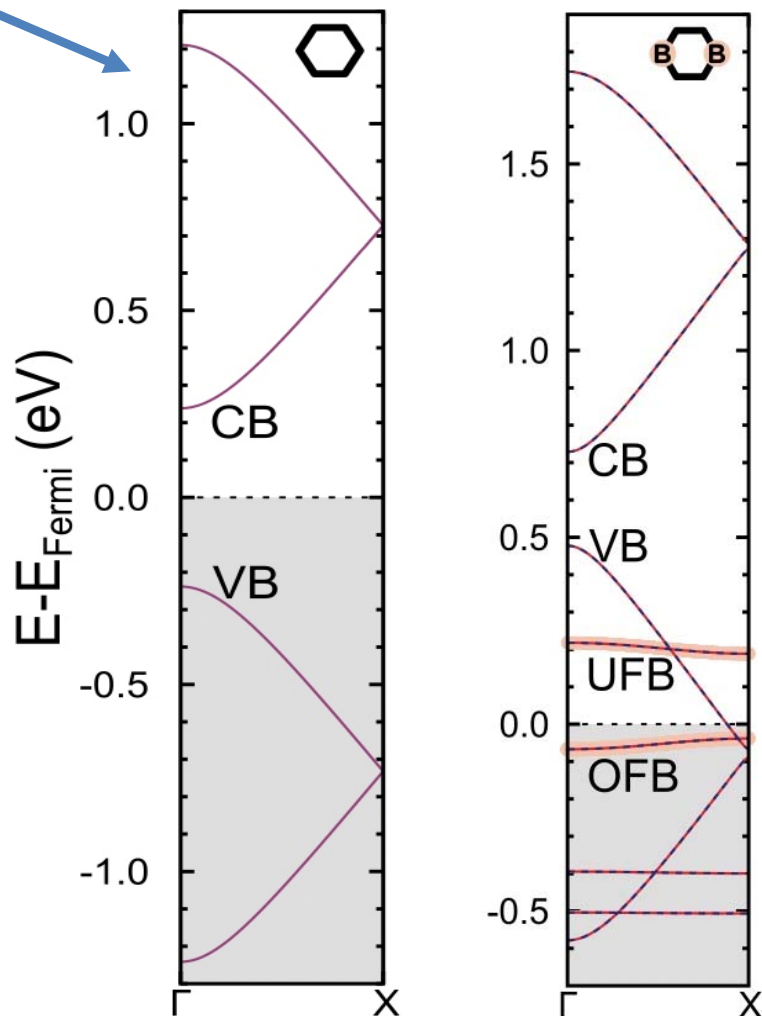
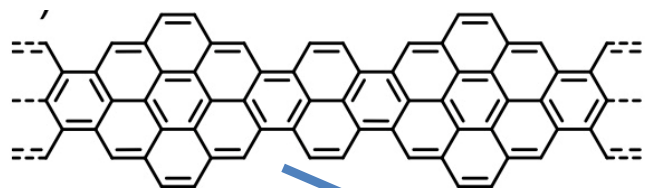


"7"-defect-states in the very dilute limit



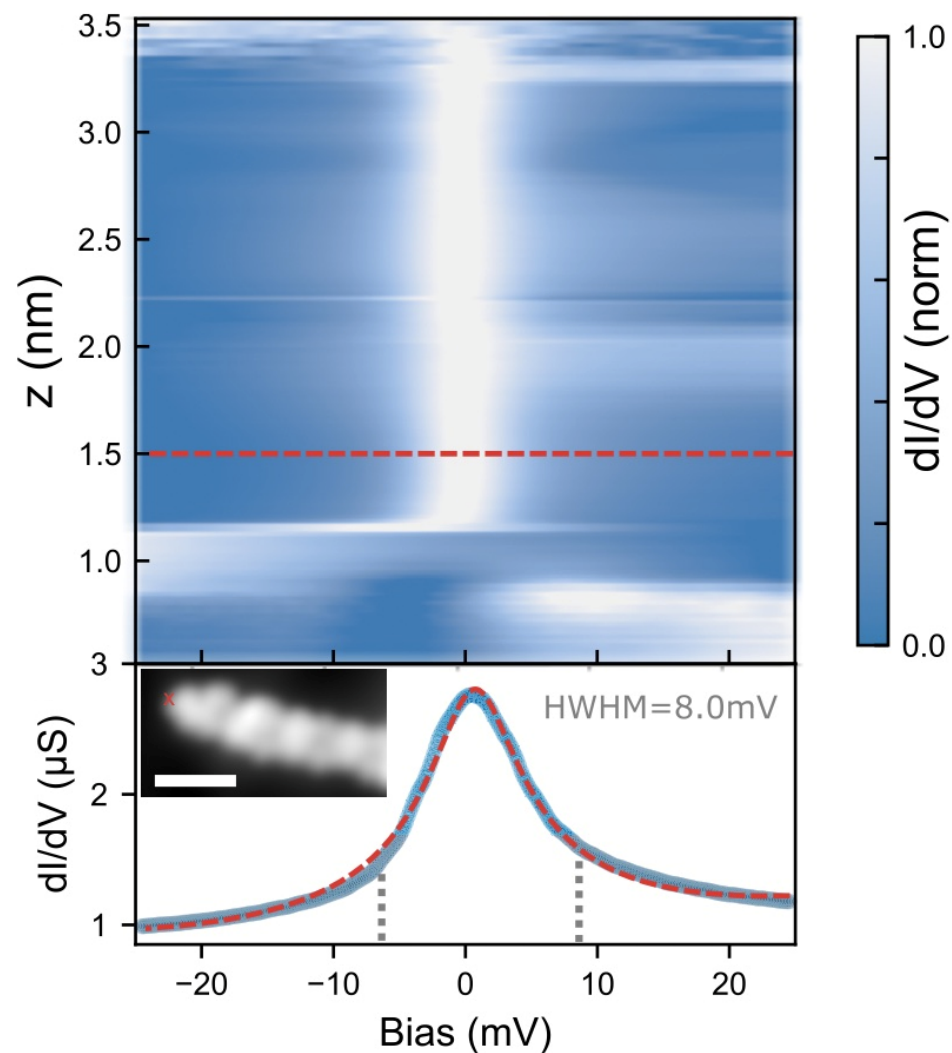
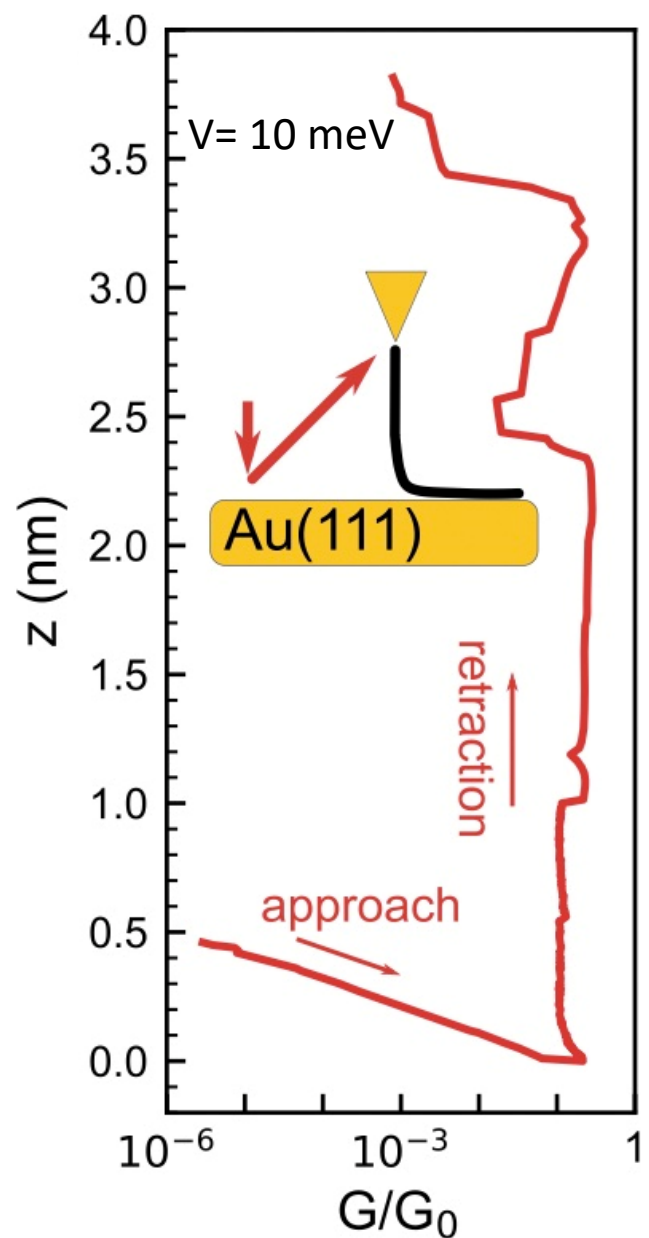
$a_x \sim 100$ unit cells $\sim 426 \text{ \AA}$

2B-575-AGNR



N. Friedrich, R. E. Menchón, I. Pozo, J. Hieulle, A. Vegliante, J. Li, D. Sánchez-Portal, D. Peña, A. Garcia-Lekue, and J. I. Pascual, *ACS Nano* 2022, 16, 14819–14826

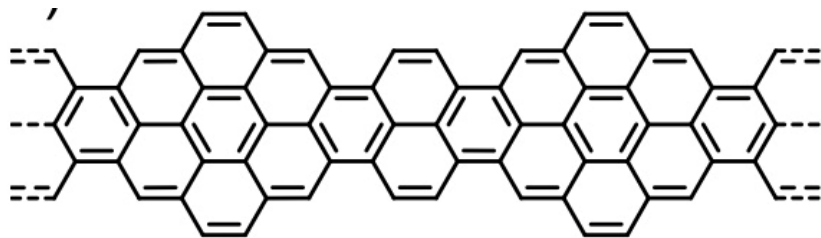
2B-575-AGNR



N. Friedrich, R. E. Menchón, I. Pozo, J. Hieulle, A. Vegliante, J. Li, D. Sánchez-Portal, D. Peña, A. Garcia-Lekue, and J. I. Pascual, *ACS Nano* 2022, 16, 14819–14826

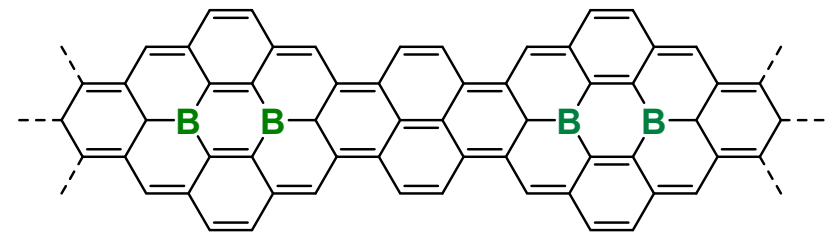
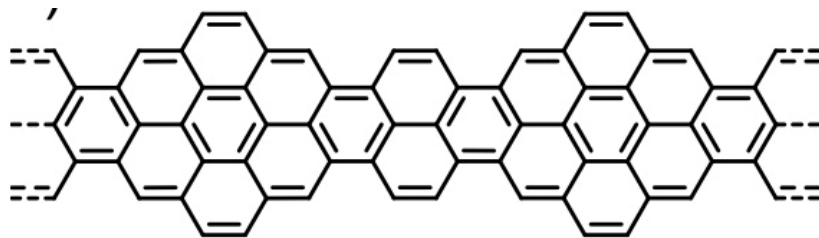
Summary & perspectives

- Haiku-GNRs $7-(5\text{-AGNR})_n$ suffer a topological transition as the concentration of “7” widenings is varied as demonstrated by DFT and simple TB calculations
- The results can be understood with a simple model (g-SSH) that allows computing much larger systems and, eventually, explore different possible devices and disordered systems



Summary & perspectives

- Haiku-GNRs $7-(5\text{-AGNR})_n$ suffer a topological transition as the concentration of “7” widenings is varied as demonstrated by DFT and simple TB calculations
- The results can be understood with a simple model (g-SSH) that allows computing much larger systems and, eventually, explore different possible devices and disordered systems
- While the interfacial states that appears in Haiku/5-aGNR combinations develop spin polarization, chemical substitution with B drives the system metallic and creates localized magnetic moments as shown in both exp. and calculations.



ACKNOWLEDGEMENTS

Theory and calculations (CFM-CSIC and DIPC, San Sebastián, Spain)

- **Dr. Rodrigo E. Menchón**
- **Dr. Pedro Bradimarte Mendonça**
- **Dr. Aran García-Lekue**

Experiments (nanoGUNE and CFM, San Sebastián, Spain)

- **Dr. Niklas Friedrich**
- **Prof. Jose I. Pascual & his team**

- **Dr. J. Lawrence**
- **Prof. Dimas G. de Oteyza & his team** (now at CINN-CSIC, Asturias, Spain) +
Dr. Ch. C. Leon & Dr. A. Grewal (Max Planck Solid State Research, Germany)

Synthesis

- **Dr. I. Pozo & Prof. D. Peña** (USC, Santiago Compostela, Spain)



MAT2016-78293-C6
PID2019-107338RB



FET-Open project
SPRING Grant. No. 863098



Acknowledgements



THANK YOU FOR YOUR ATTENTION!!



**Gipuzkoako Foru Aldundia
Diputación Foral de Gipuzkoa**

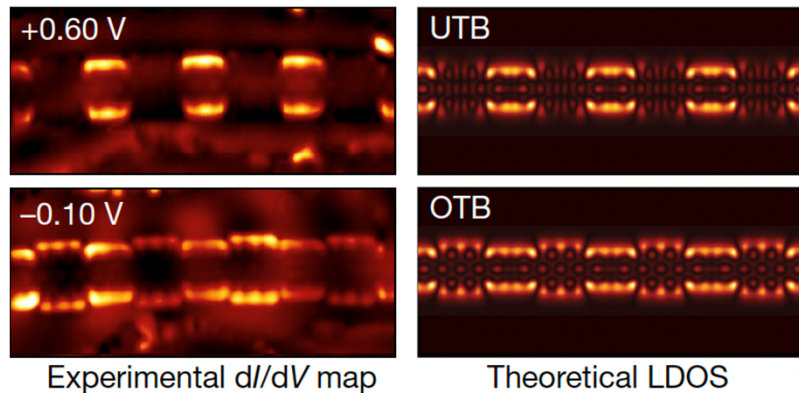
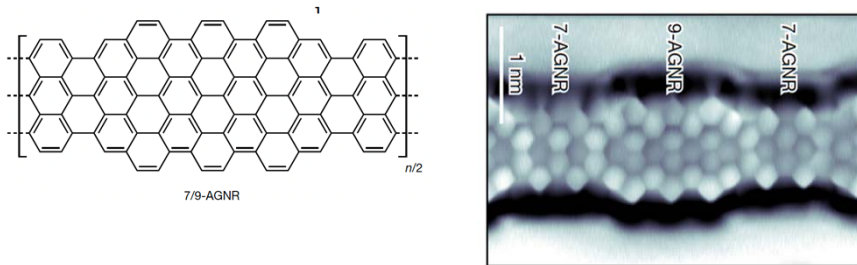


Topological Phases in Graphene

Topological band engineering of graphene nanoribbons

[Daniel J. Rizzo](#), [Gregory Veber](#), [Ting Cao](#), [Christopher Bronner](#), [Ting Chen](#), [Fangzhou Zhao](#), [Henry Rodriguez](#), [Steven G. Louie](#) ✉, [Michael F. Crommie](#) ✉ & [Felix R. Fischer](#) ✉

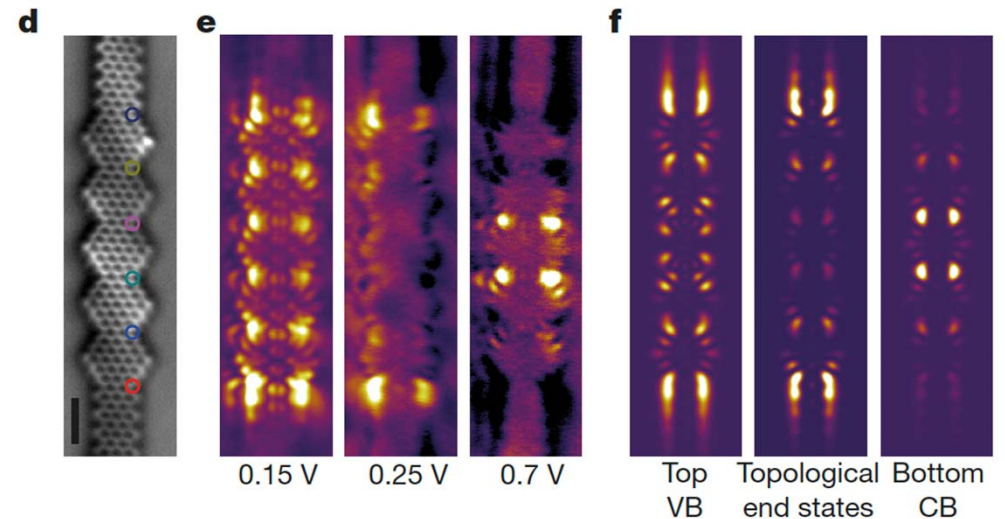
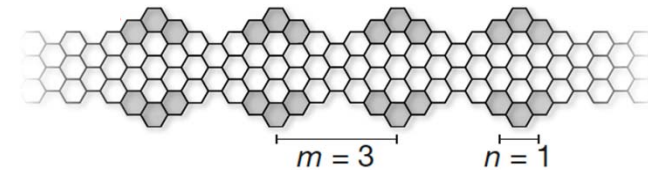
Nature **560**, 204–208 (2018) | [Cite this article](#)



Engineering of robust topological quantum phases in graphene nanoribbons

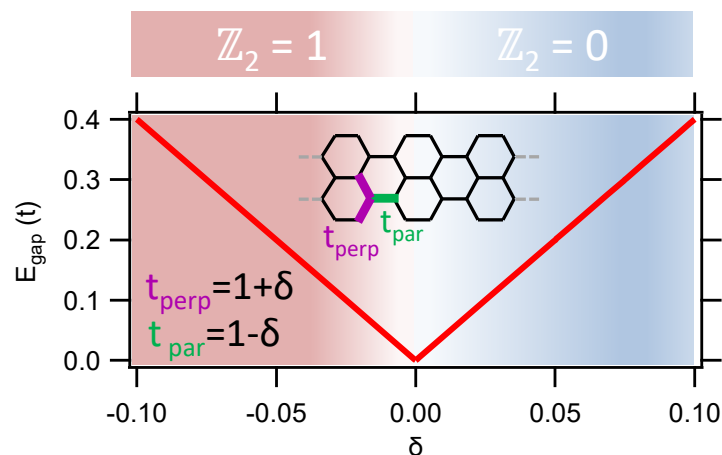
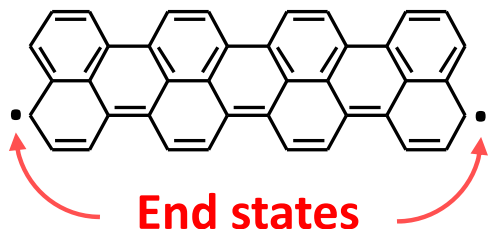
[Oliver Gröning](#) ✉, [Shiyong Wang](#), [Xuelin Yao](#), [Carlo A. Pignedoli](#), [Gabriela Borin Barin](#), [Colin Daniels](#), [Andrew Cupo](#), [Vincent Meunier](#), [Xinliang Feng](#), [Akimitsu Narita](#), [Klaus Müllen](#), [Pascal Ruffieux](#) & [Roman Fasel](#)

Nature **560**, 209–213 (2018) | [Cite this article](#)

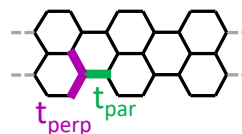
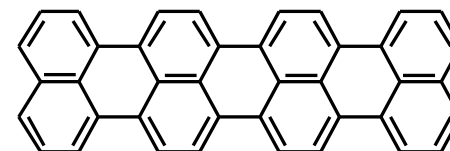


“Topological” phase diagram of 5-aGNRs

$$\delta < 0 \Rightarrow t_{\text{par}} > t_{\text{perp}}$$

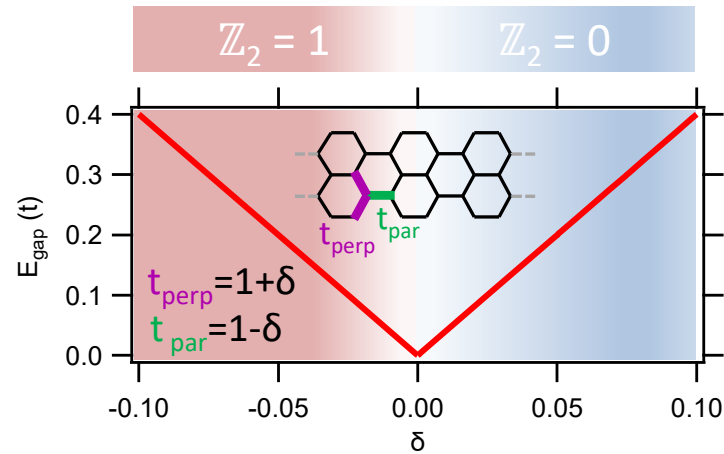
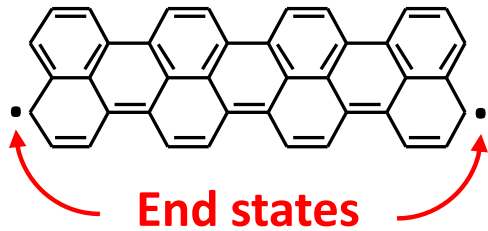


$$\delta > 0 \Rightarrow t_{\text{perp}} > t_{\text{par}}$$

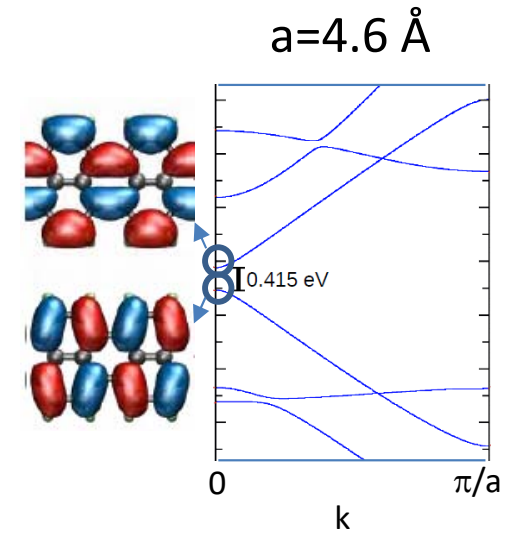
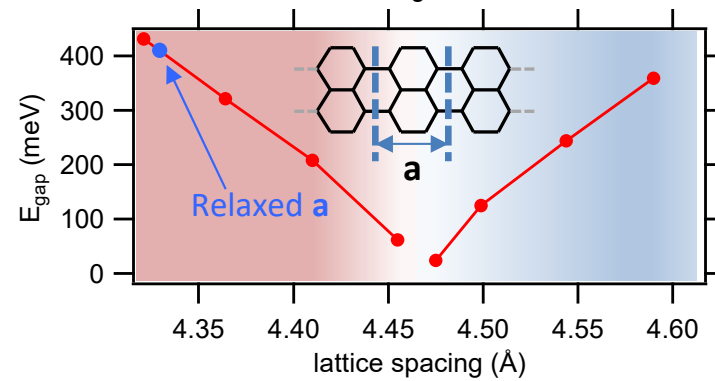
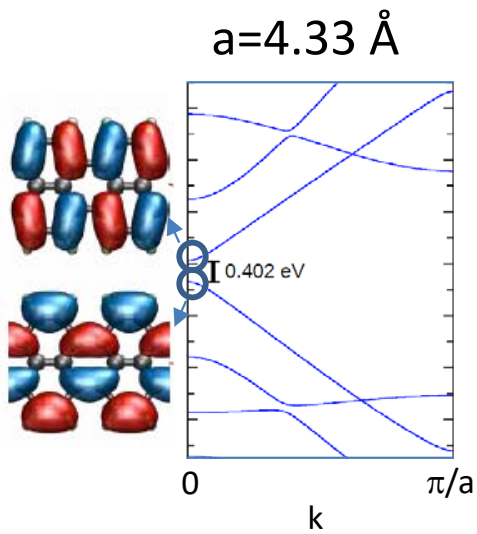
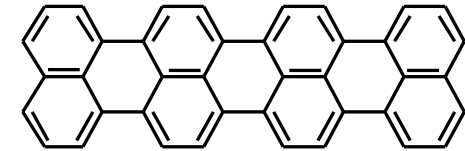


“Topological” phase diagram of 5-aGNRs

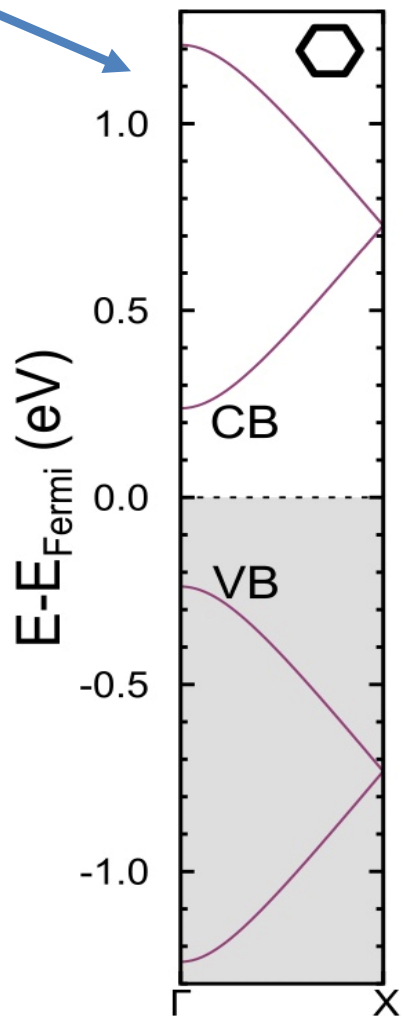
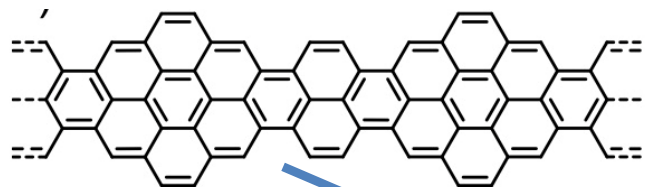
$\delta < 0 \Rightarrow t_{\text{par}} > t_{\text{perp}}$



$\delta > 0 \Rightarrow t_{\text{perp}} > t_{\text{par}}$

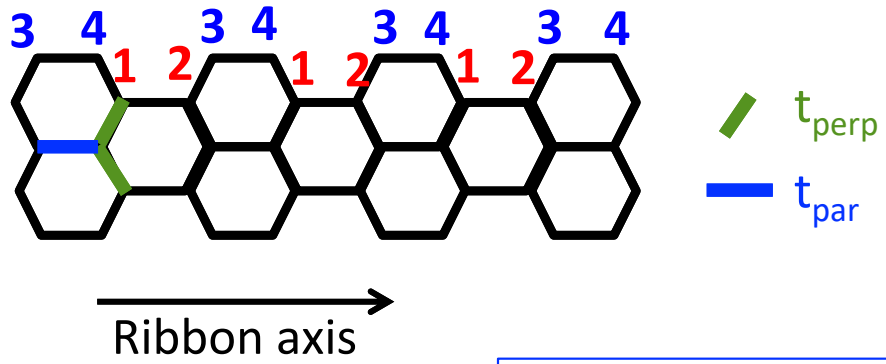


2B-575-AGNR



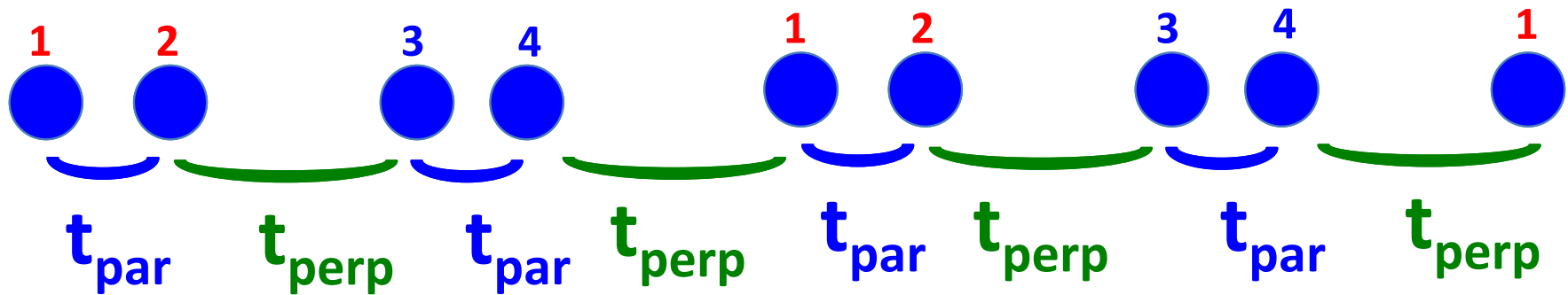
N. Friedrich, R. E. Menchón, I. Pozo, J. Hieulle, A. Vegliante, J. Li, D. Sánchez-Portal, D. Peña, A. Garcia-Lekue, and J. I. Pascual, *ACS Nano* 2022, 16, 14819–14826

A simple SSH model is enough to understand ...

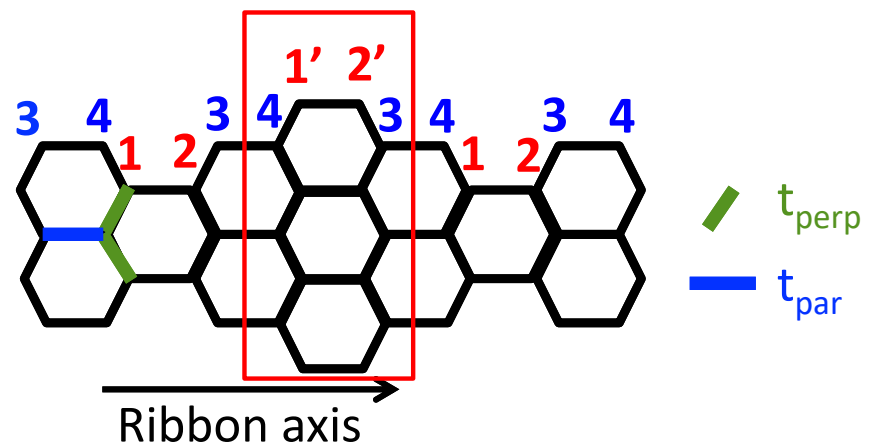


.... 5-aGNR valence band

$$t_{\text{par}} > t_{\text{perp}} \quad \longrightarrow \quad t_{\text{par}} \sim 1.075 t_{\text{perp}}$$

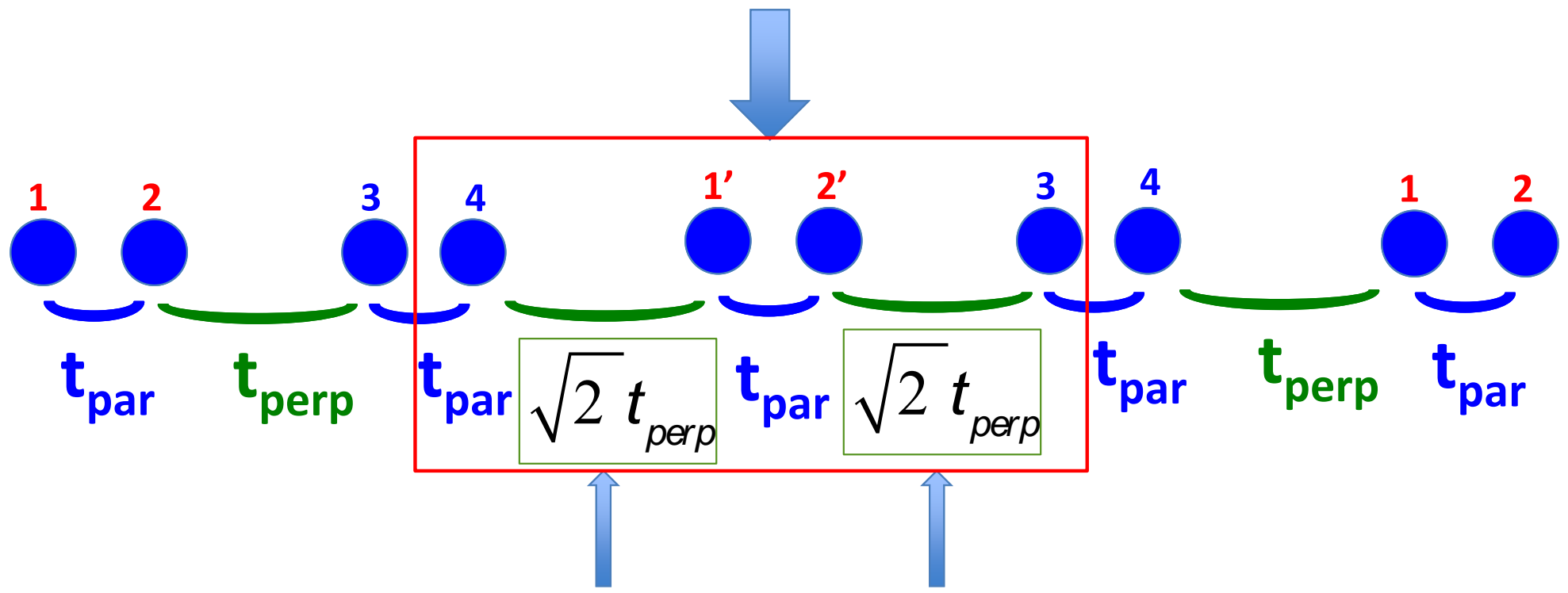


A *modified* SSH model is enough to understand ...



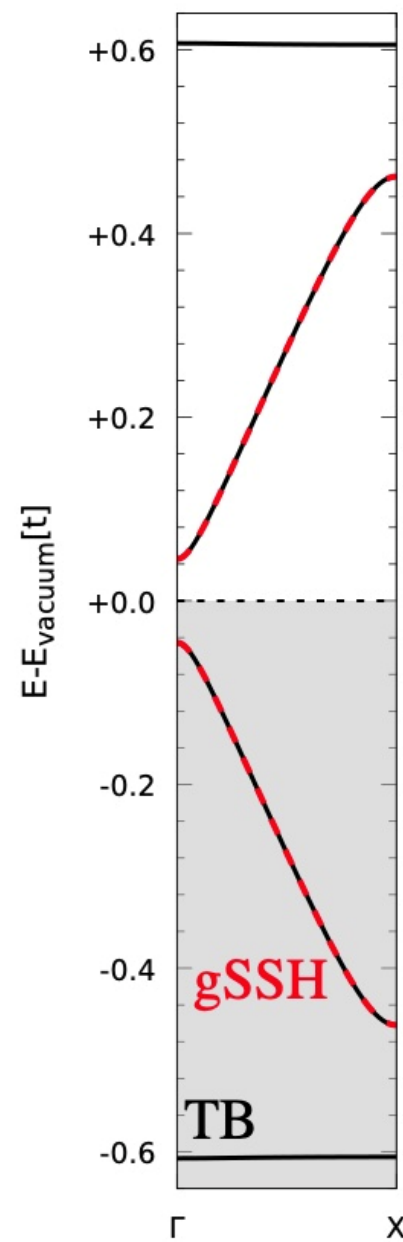
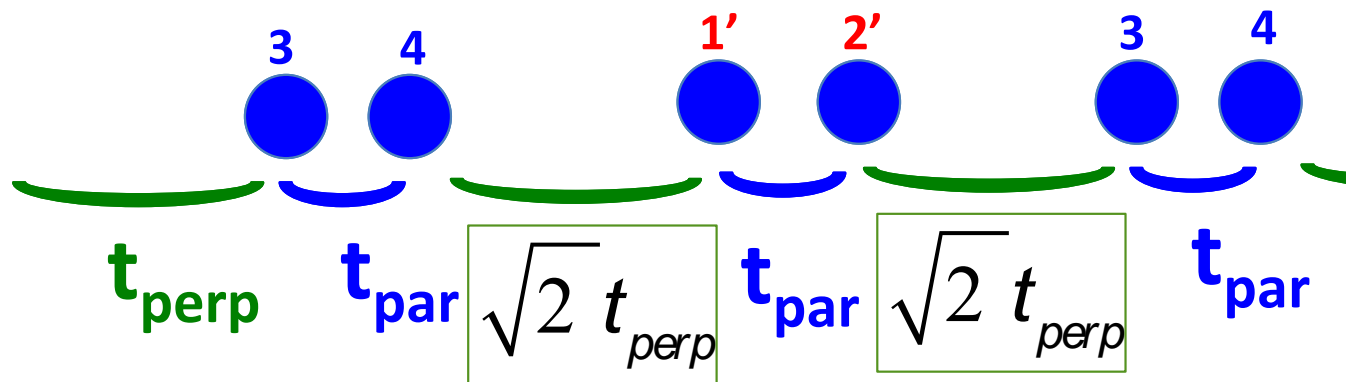
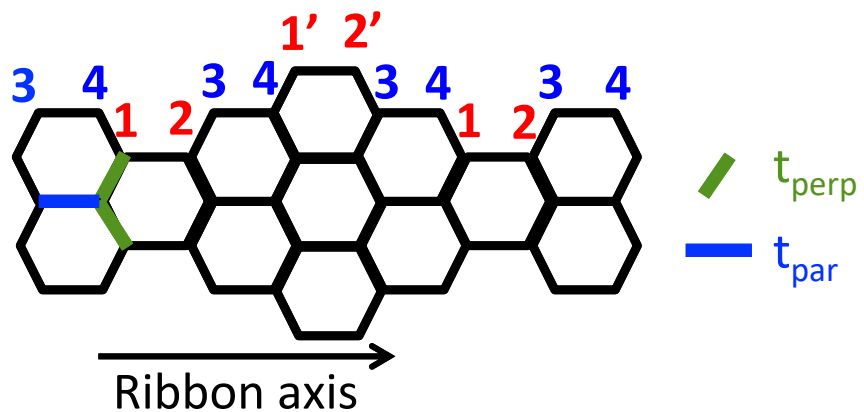
... a575-aGNR val. band

Position of the n=7 widening

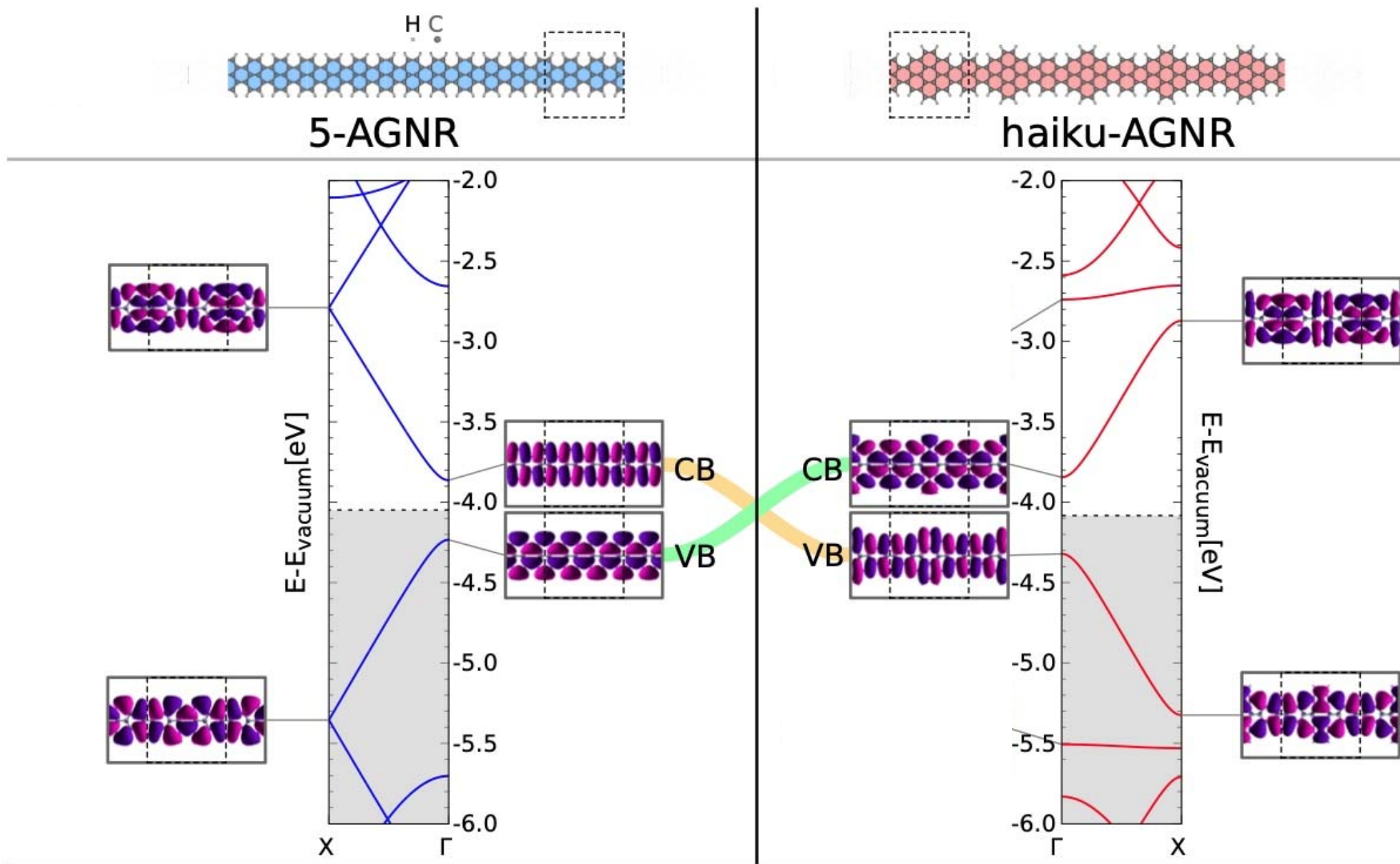


Enhanced t_{perp} hoppings

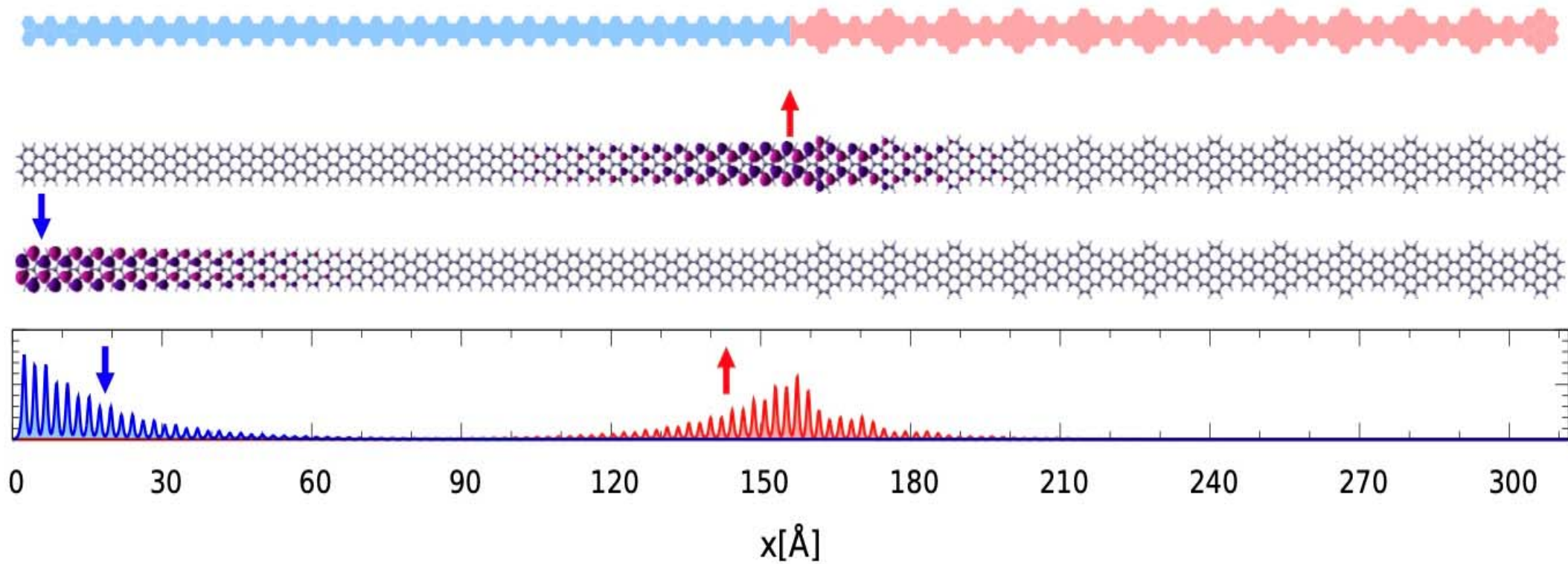
Generalized-SSH model for 575-aGNR valence band



Band structure 5-aGNR vs. 575-aGNR: reversed topology

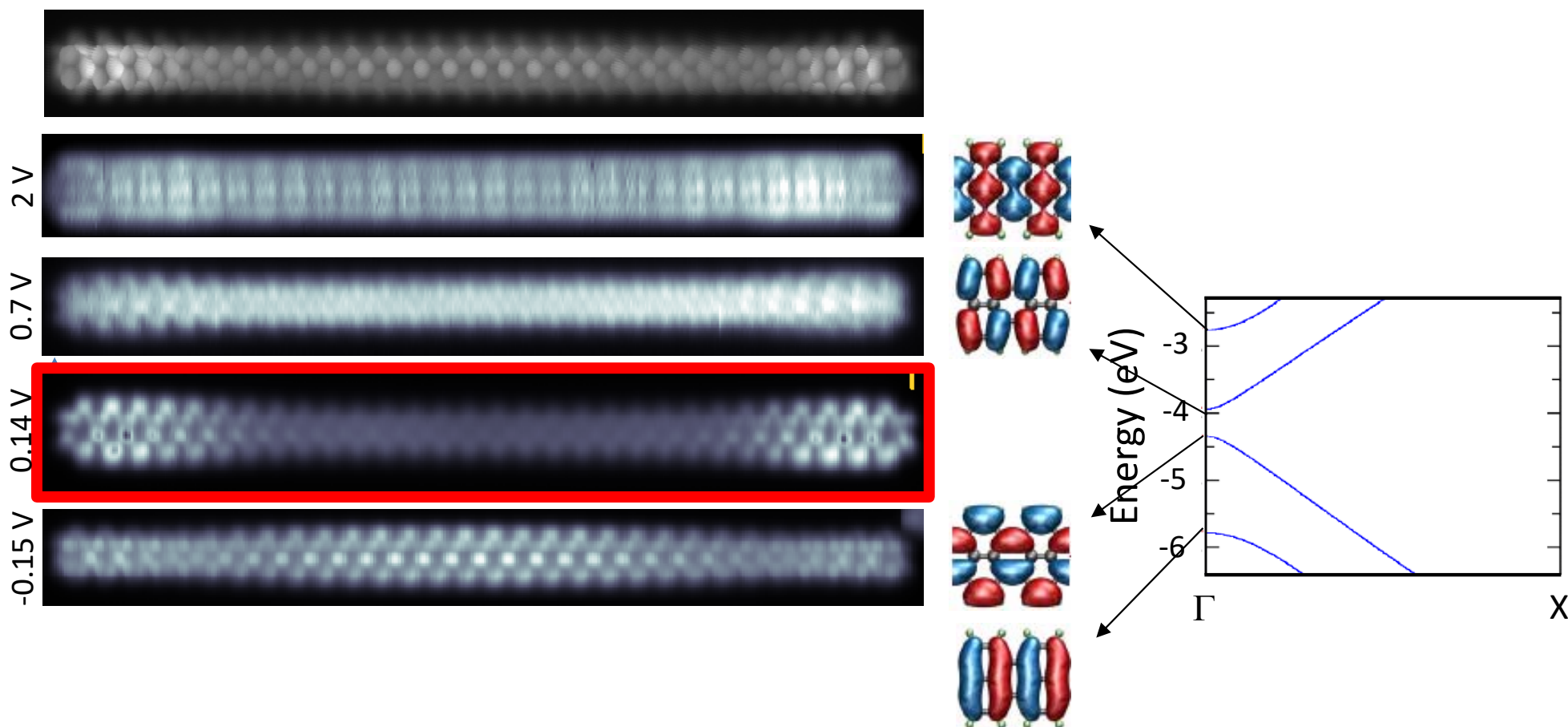


Interface states at the 5-aGNR/575-aGNR boundary



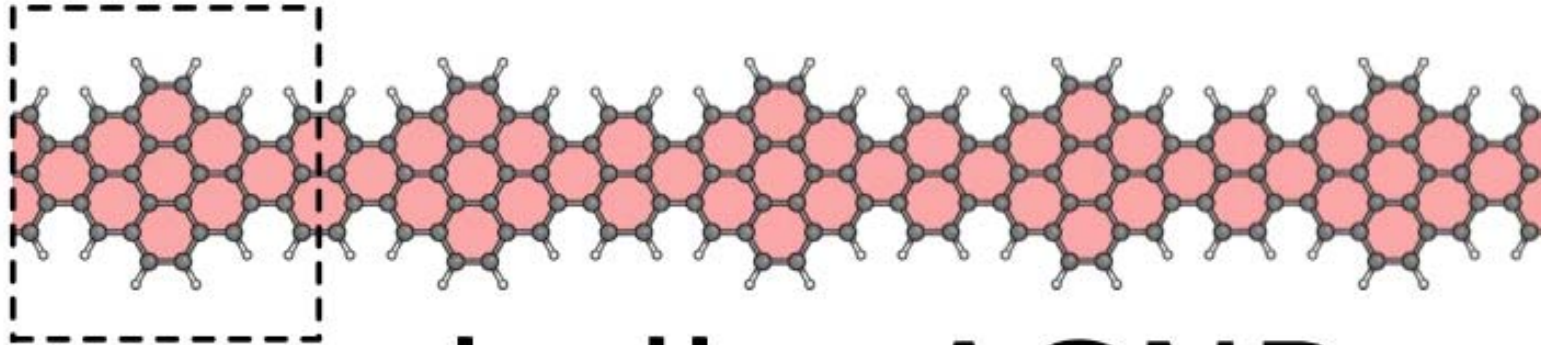
Topological End-states in 5-AGNRs

30 unit cells (UC) / 15 precursor units (PU) on Au(111)



J. Lawrence, P. Brandimarte, A. Berdonces-Layunta, M. S. G. Mohammed, A. Grewal, Ch. C. Leon, D. Sánchez-Portal and D. G. de Oteyza, *ACS Nano* 2020, 14, 4499–4508

575-AGNR

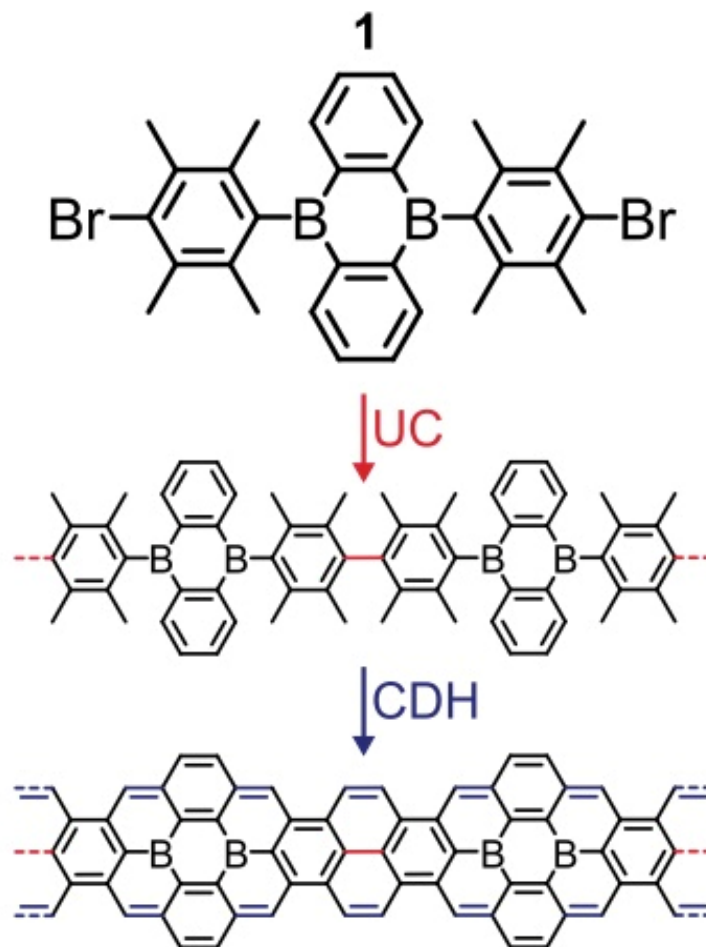


haiku-AGNR

7-(5-AGNR)_n

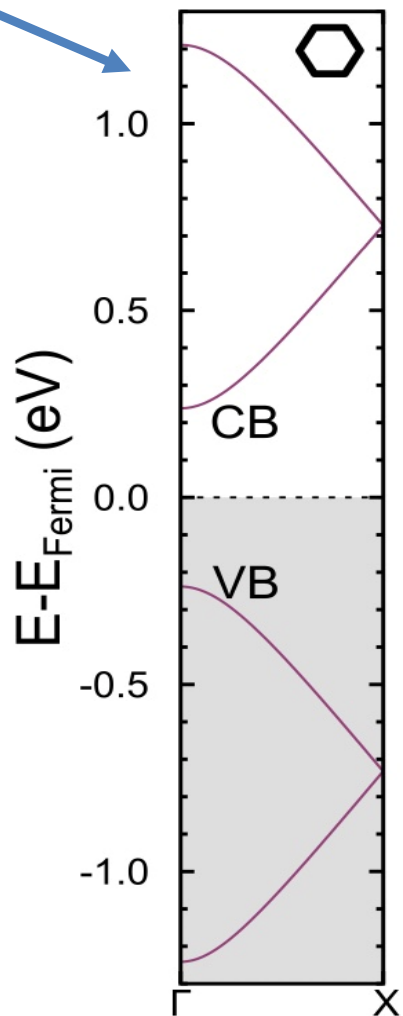
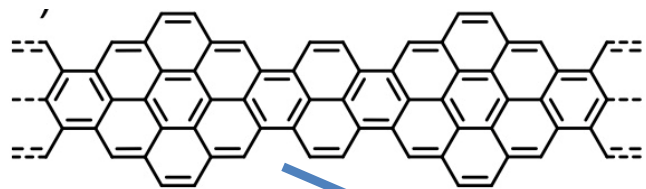
Experimental Motivation I: 2B-575-AGNRs

2B-575-AGNR



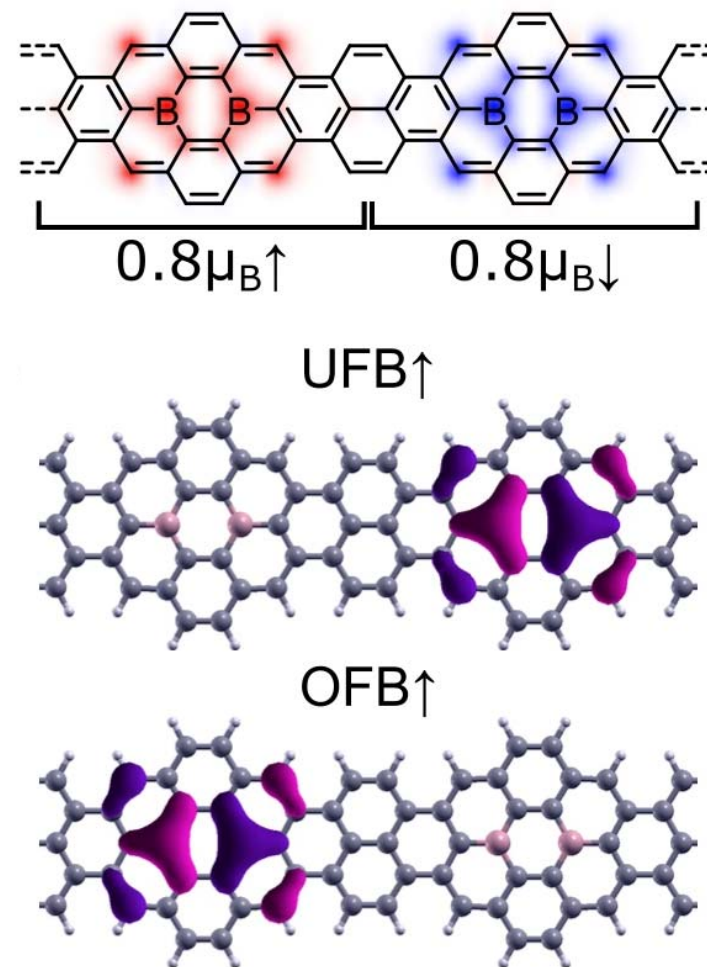
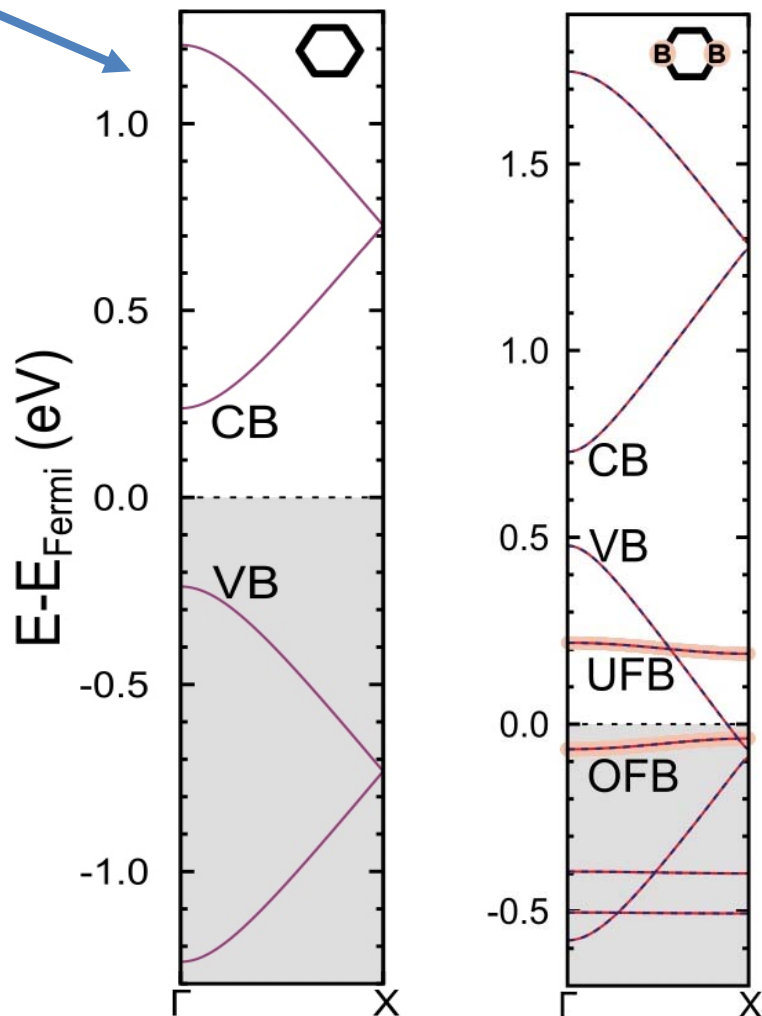
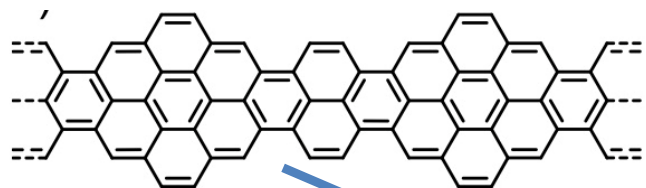
N. Friedrich, R. E. Menchón, I. Pozo, J. Hieulle, A. Vegliante, J. Li, D. Sánchez-Portal, D. Peña, A. Garcia-Lekue, and J. I. Pascual, *ACS Nano* 2022, 16, 14819–14826

2B-575-AGNR



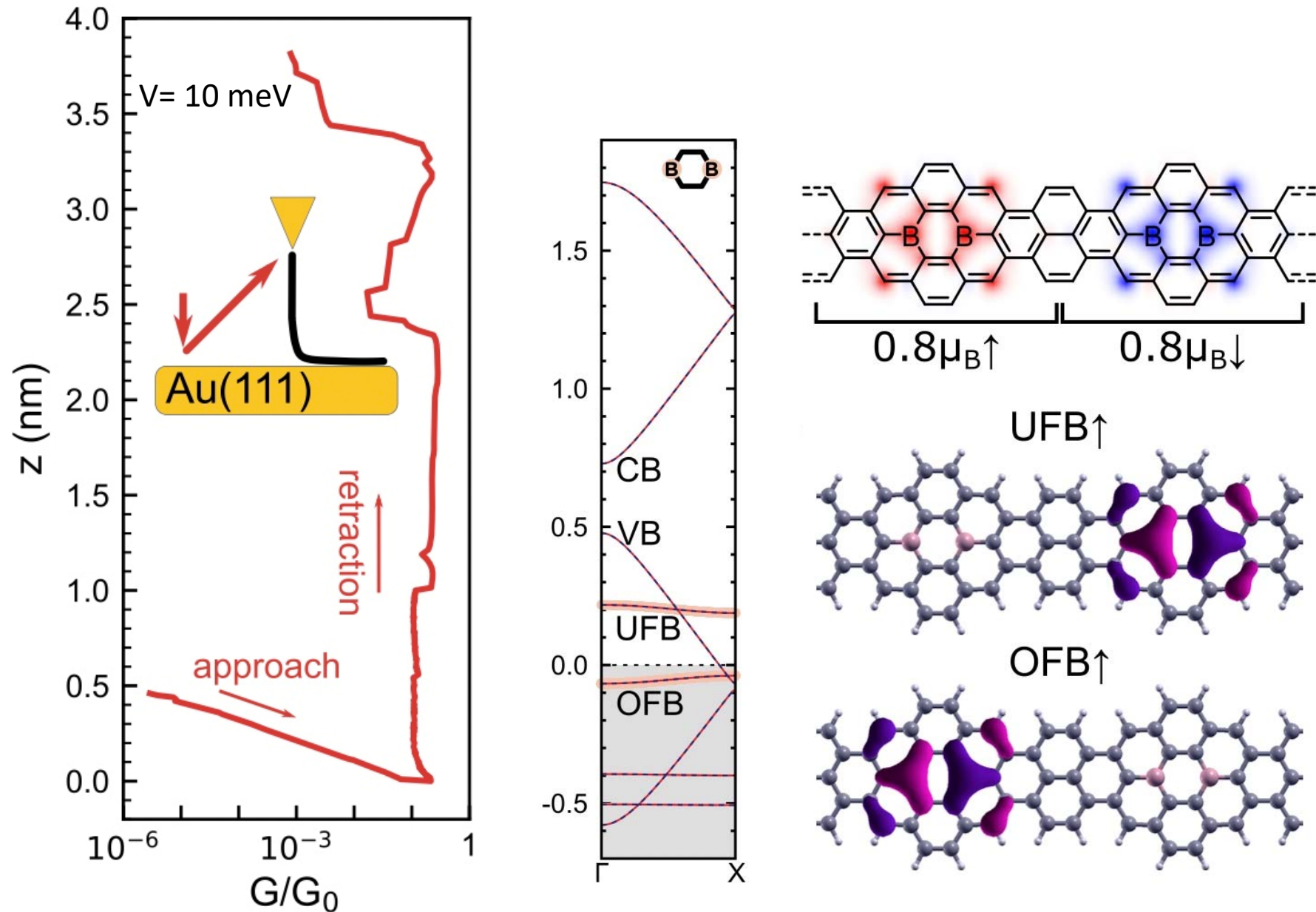
N. Friedrich, R. E. Menchón, I. Pozo, J. Hieulle, A. Vegliante, J. Li, D. Sánchez-Portal, D. Peña, A. Garcia-Lekue, and J. I. Pascual, *ACS Nano* 2022, 16, 14819–14826

2B-575-AGNR



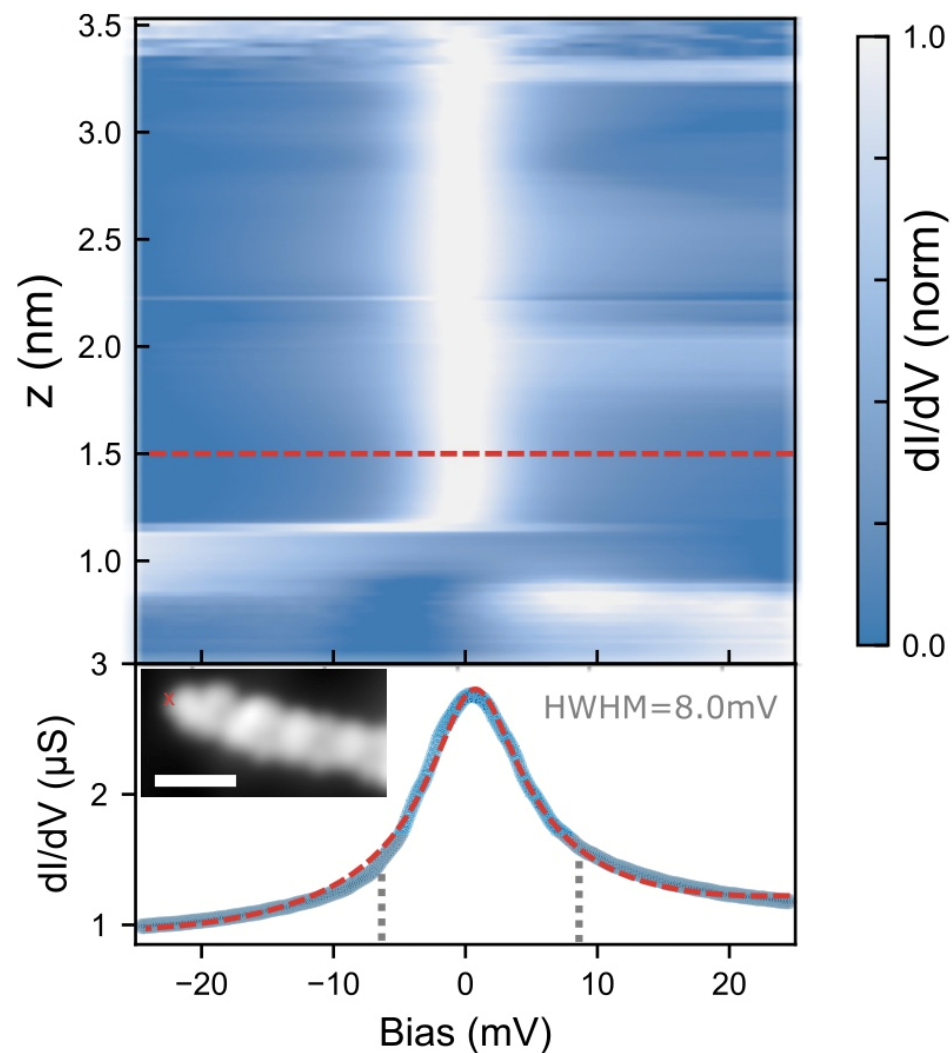
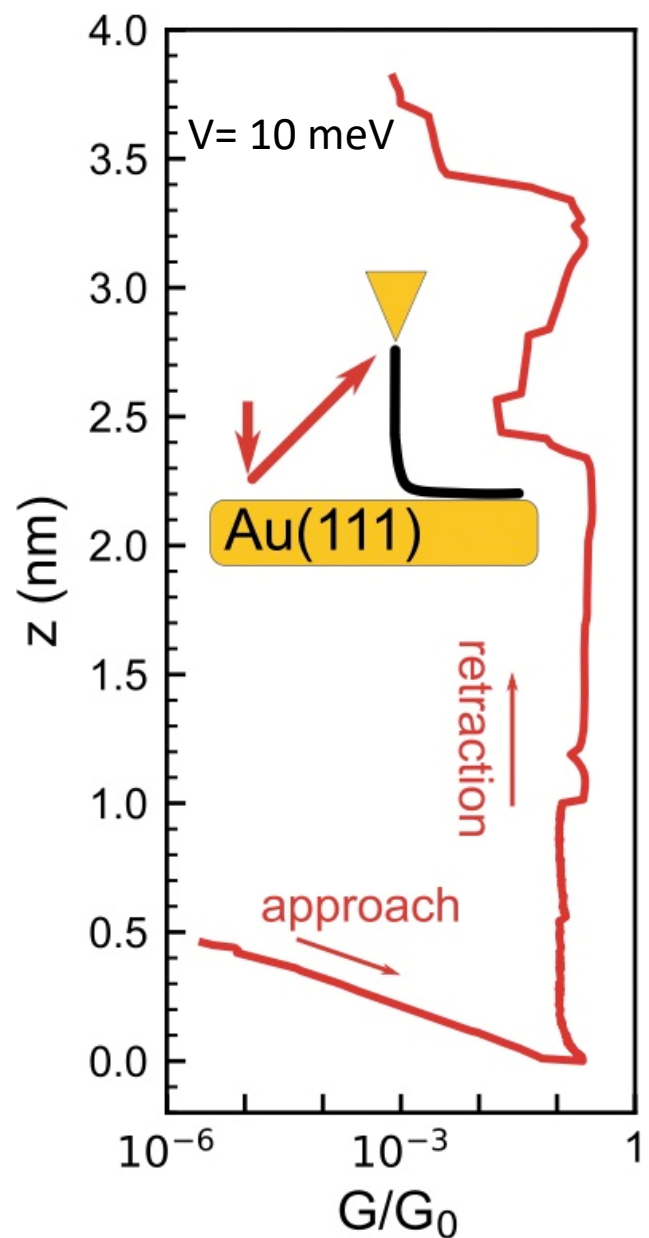
N. Friedrich, R. E. Menchón, I. Pozo, J. Hieulle, A. Vegliante, J. Li, D. Sánchez-Portal, D. Peña, A. Garcia-Lekue, and J. I. Pascual, *ACS Nano* 2022, 16, 14819–14826

2B-575-AGNR



N. Friedrich, R. E. Menchón, I. Pozo, J. Hieulle, A. Vegliante, J. Li, D. Sánchez-Portal, D. Peña, A. Garcia-Lekue, and J. I. Pascual, *ACS Nano* 2022, 16, 14819–14826

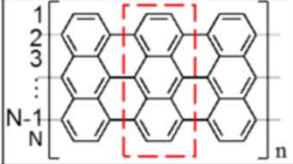
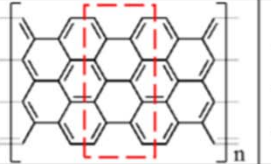
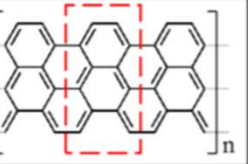
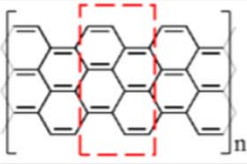
2B-575-AGNR



N. Friedrich, R. E. Menchón, I. Pozo, J. Hieulle, A. Vegliante, J. Li, D. Sánchez-Portal, D. Peña, A. Garcia-Lekue, and J. I. Pascual, *ACS Nano* 2022, 16, 14819–14826

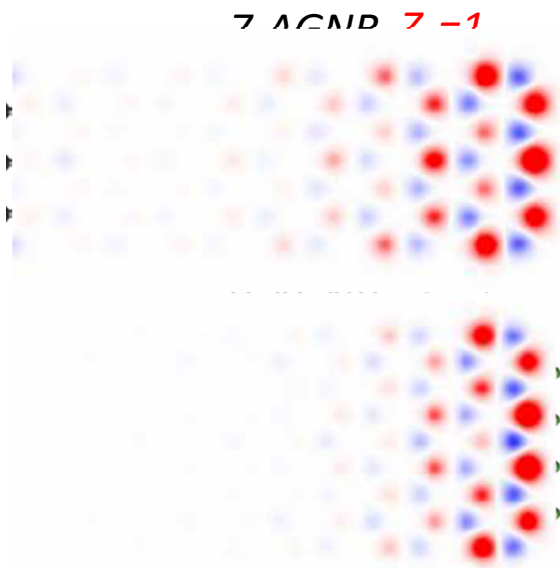
Experimental Motivation II: 5-AGNRs

Topology of GNRs band structure

Termination type	Zigzag ($N = \text{Odd}$)	Zigzag' ($N = \text{Odd}$)	Zigzag ($N = \text{Even}$)	Bearded ($N = \text{Even}$)
Unit cell shape				
Bulk Symmetry	Inversion/mirror	Inversion/mirror	Mirror	Inversion
Z_2	$\frac{1 + (-1)^{\lfloor \frac{N}{3} \rfloor + \lfloor \frac{N+1}{2} \rfloor}}{2}$	$\frac{1 - (-1)^{\lfloor \frac{N}{3} \rfloor + \lfloor \frac{N+1}{2} \rfloor}}{2}$		$\frac{1 - (-1)^{\lfloor \frac{N}{3} \rfloor}}{2}$

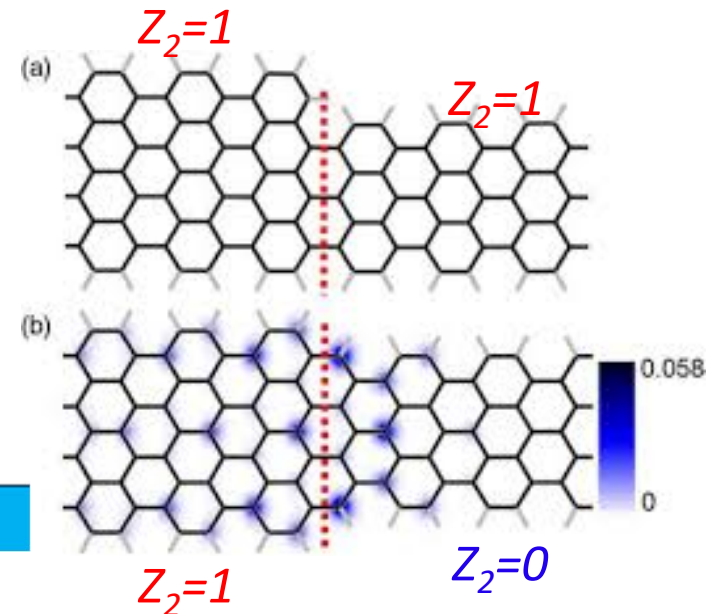
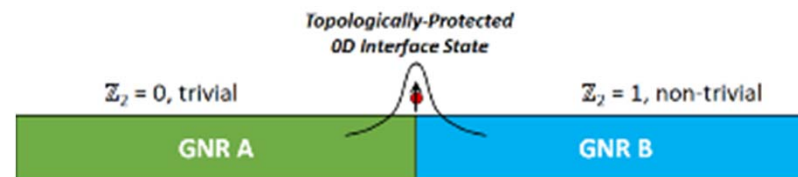
T. Cao, F. Zhao, S.G. Louie, *PRL* **119**, 076401 (2017)

- Global invariants of GNR bands from integrating Zak phases
- Unit Cell determined by boundary/termination

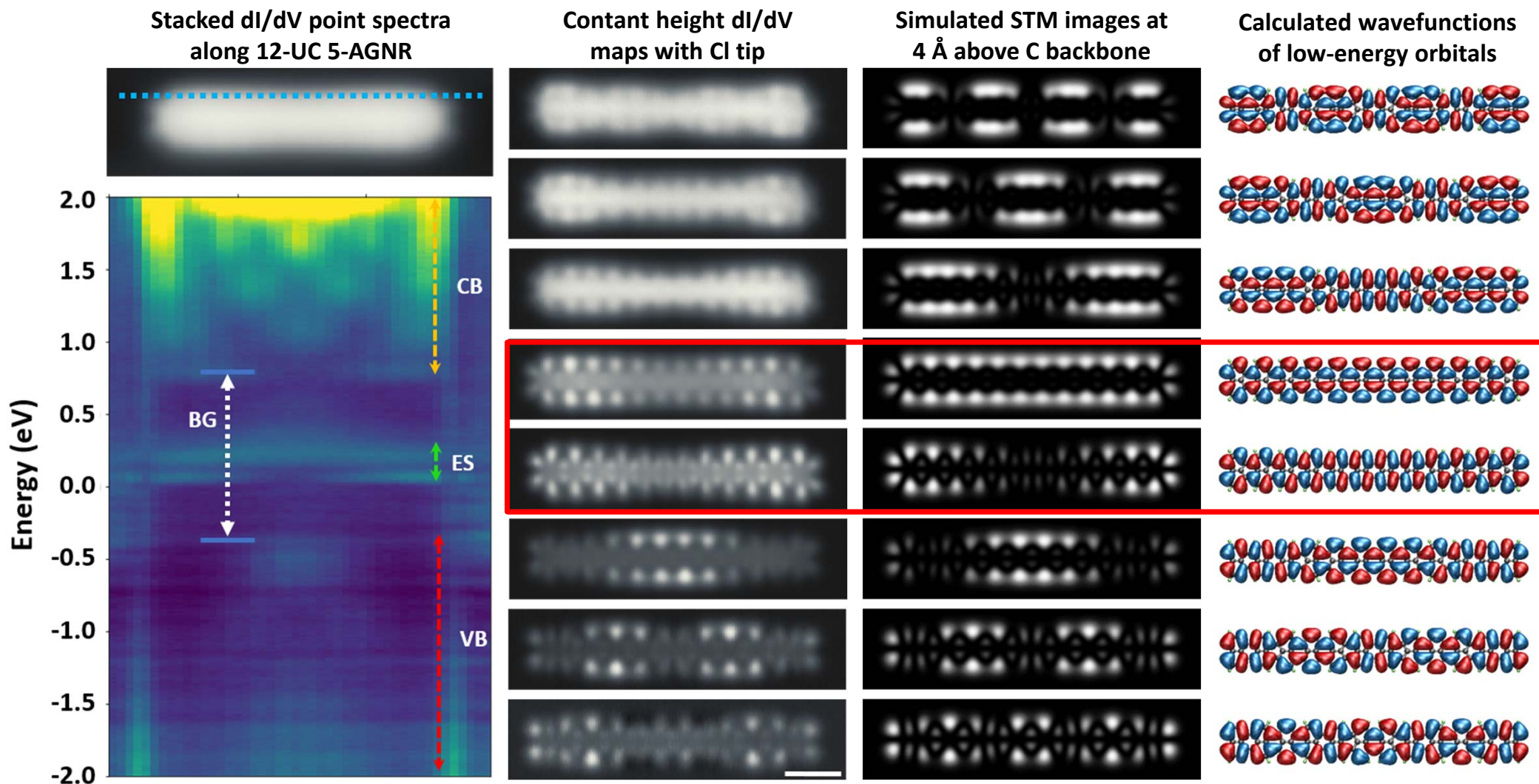


Topological
end states

Topological
boundary states



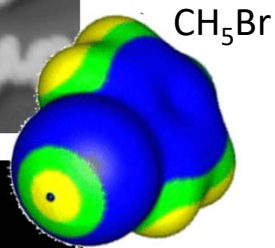
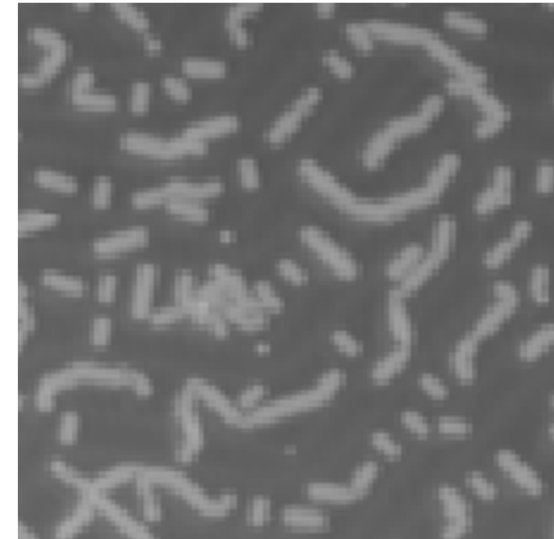
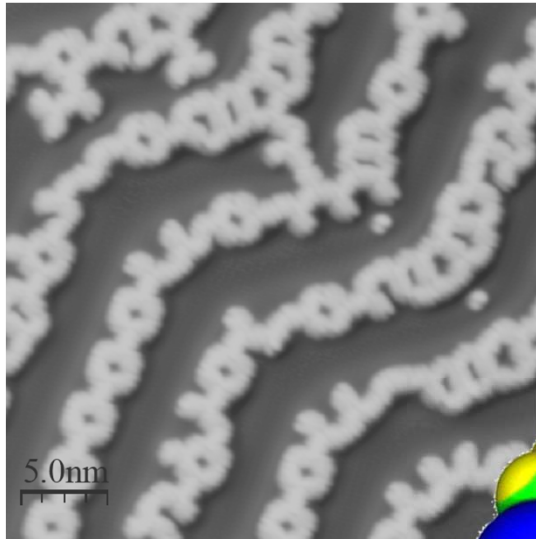
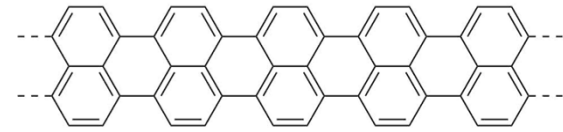
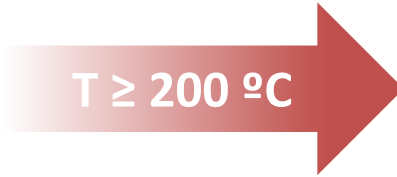
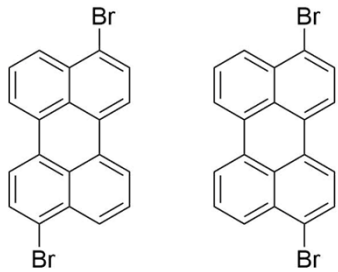
Finite size effects



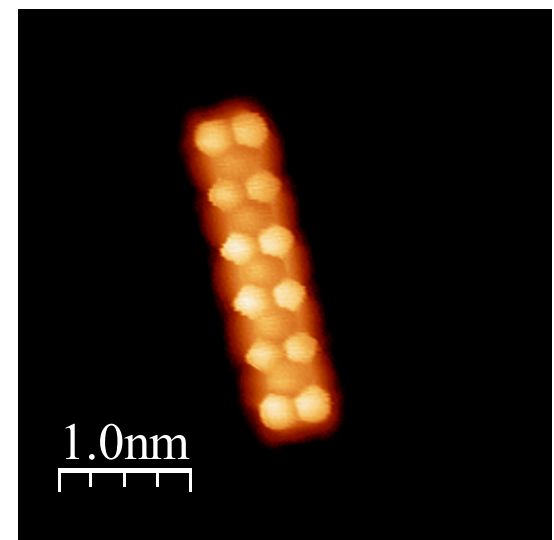
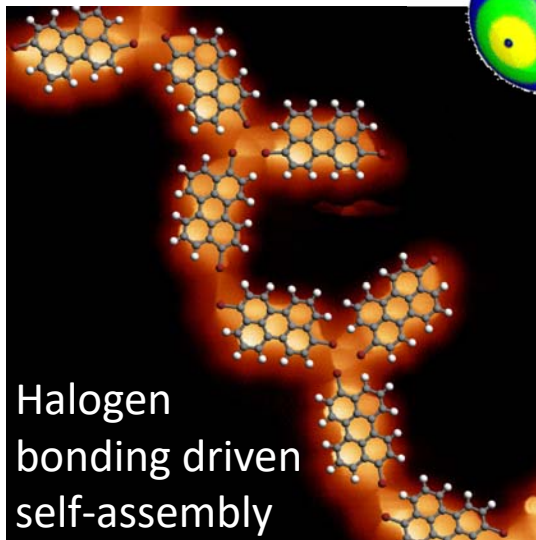
Excellent agreement between experiment and theory simulations

Hardly perturbed orbitals on Au(111)

Synthesis of 5-aGNRs



Riley et al., *J. Mol. Model.* **2011**, 17, 3309



Band structure 5-aGNR vs. 575-aGNR: reversed topology

