Progress in graphene nanoribbon project: **Topological band engineering & metallic GNRs**

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Center for Energy Efficient Electronics Science

Some important issues on GNRs for nanoelectronics

- GNRs with appropriate band gaps for transistors and other applications
- GNRs as metallic wires
- Very narrow-band metallic GNRs to beat the 60 meV/decade switching limit

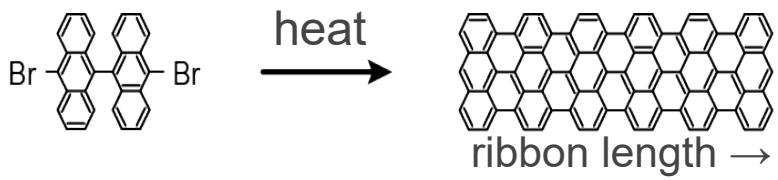
Outline of Talk

- Topological quantum band engineering
  - Topological invariants and junction states in GNRs
  - Engineering band gap with topology
- Design and synthesis of metallic GNRs
  - Dopants and structural changes
  - Electron topology

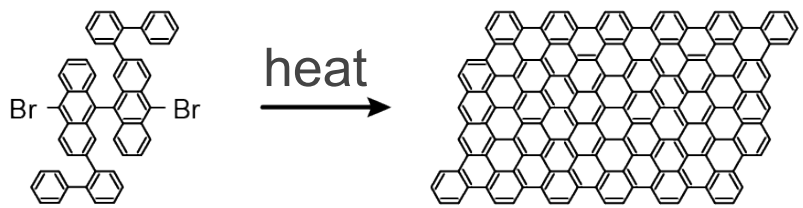
Bottom-up synthesis of GNRs with precursor molecules

- Perfect *arm-chair* or *zigzag* GNRs of widths (~1-3 nm) and lengths (~50-100 nm) synthesized on surfaces or in solutions

Synthesis procedure [J. Cai, R. Fasel, et al, Nature (2010)]:

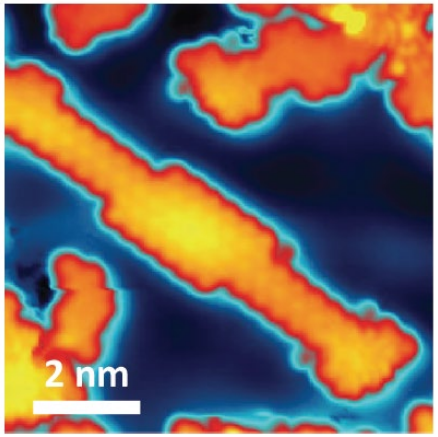


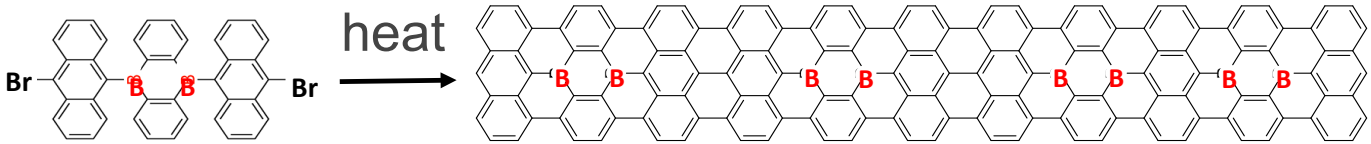
7-AGNR



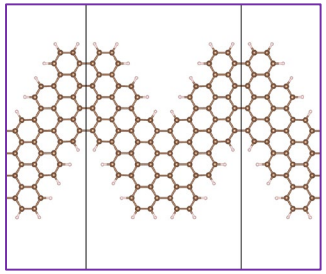
13-AGNR

7-13-AGNR junctions





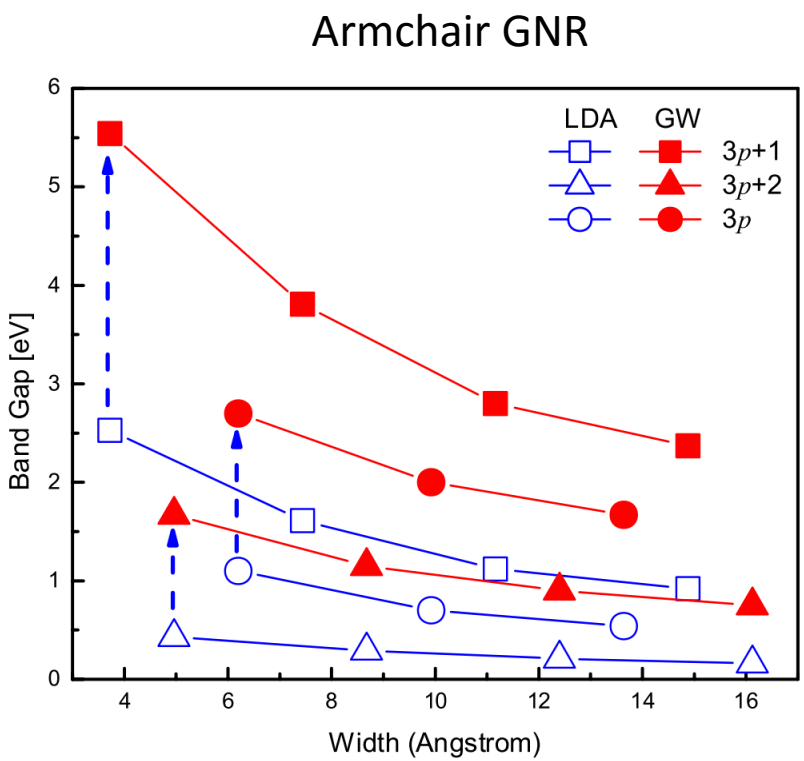
B2-7AGNR



Chevron GNR

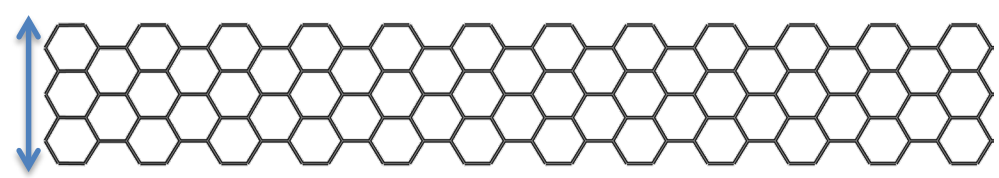
Chen, Louie, Crommie, et al
Nature Nanotechn. (2015)

Background: Graphene Nanoribbons (GNRs) - Bandgap vs. Width



L. Yang, S. G. Louie, et al, PRL (2007).

- Large band gap for most GNRs due to quantum confinement & large self-energy effect from strong many-electron interactions
- Band gaps decrease with width, but bottom-up synthesized GNRs have very narrow width
- Engineer small bandgap ribbons from large bandgap ribbons by using a novel topological concept



Armchair GNR

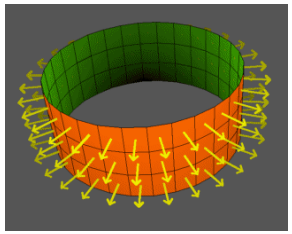
Topological phases in graphene nanoribbons

- Electron states confined in BZ, a compact geometric manyfold. Distinct topology!
- Non-trivial topology of Bloch bands ⇒ protected boundary states, integer quantum Hall effect, new phases of matter, … **(Nobel prize 2016 –** *Thoules, Haldane, Kosterlitz***)**
- Symmetry protected topological (SPT) phases in 1D ⟺ quantized Berry phase (intercell) γ across the BZ of *all* the occupied bands, which may be specified by an invariant: **Z_2 = 0 or 1**

$$(-1)^{Z_2} = e^{i\sum_n \gamma_n}$$

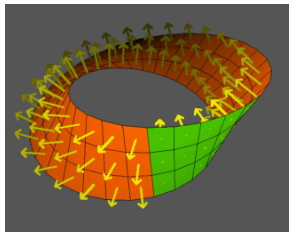
$$\gamma_n = i\left(\frac{2\pi}{d}\right)\int_{-\pi/d}^{\pi/d} dk \left\langle u_{nk} \middle| \frac{\partial u_{nk}}{\partial k} \right\rangle$$

$Z_2 = 0$ (trivial)



(Regular strip)

$Z_2 = 1$ (non trivial)



(Mobius strip)

Cao, Zhao and Louie, ***PRL*** 119, 076401 (2017)

Topological phases in graphene nanoribbons

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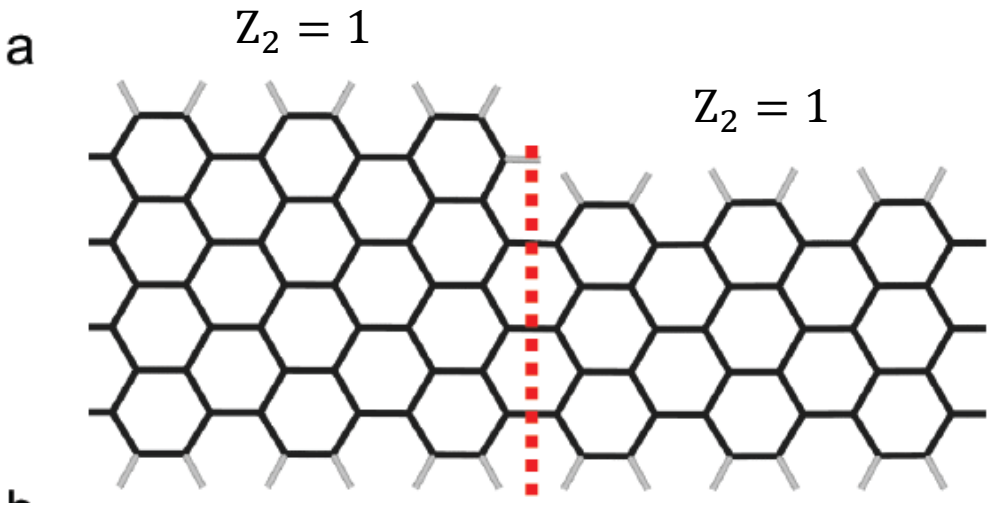
- ***Discovered all GNRs (with spatial symmetry) are large gap insulators that host SPT phases***
- Bulk-boundary correspondence ⇒ **boundary states** between topological distinct segments
- Z_2 can change with different terminating unit cell (it changes the Berry's phases)

Cao, Zhao and Louie, ***PRL*** 119, 076401 (2017)

GNR Heterostructure: Topological vs. non-topological

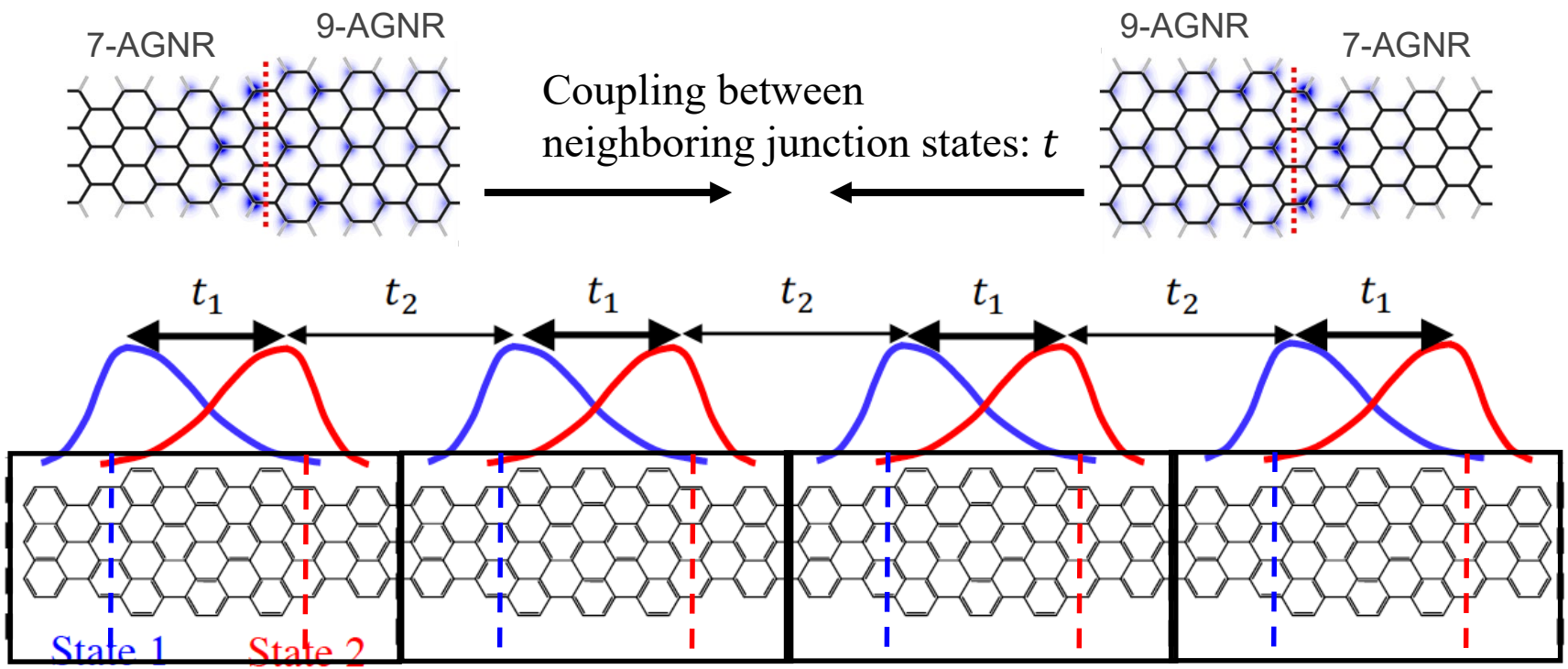
9-AGNR/**7**-AGNR heterostructure



Topologically *equivalent*
No interface state!

Cao, Zhao and Louie, ***PRL*** 119, 076401 (2017)

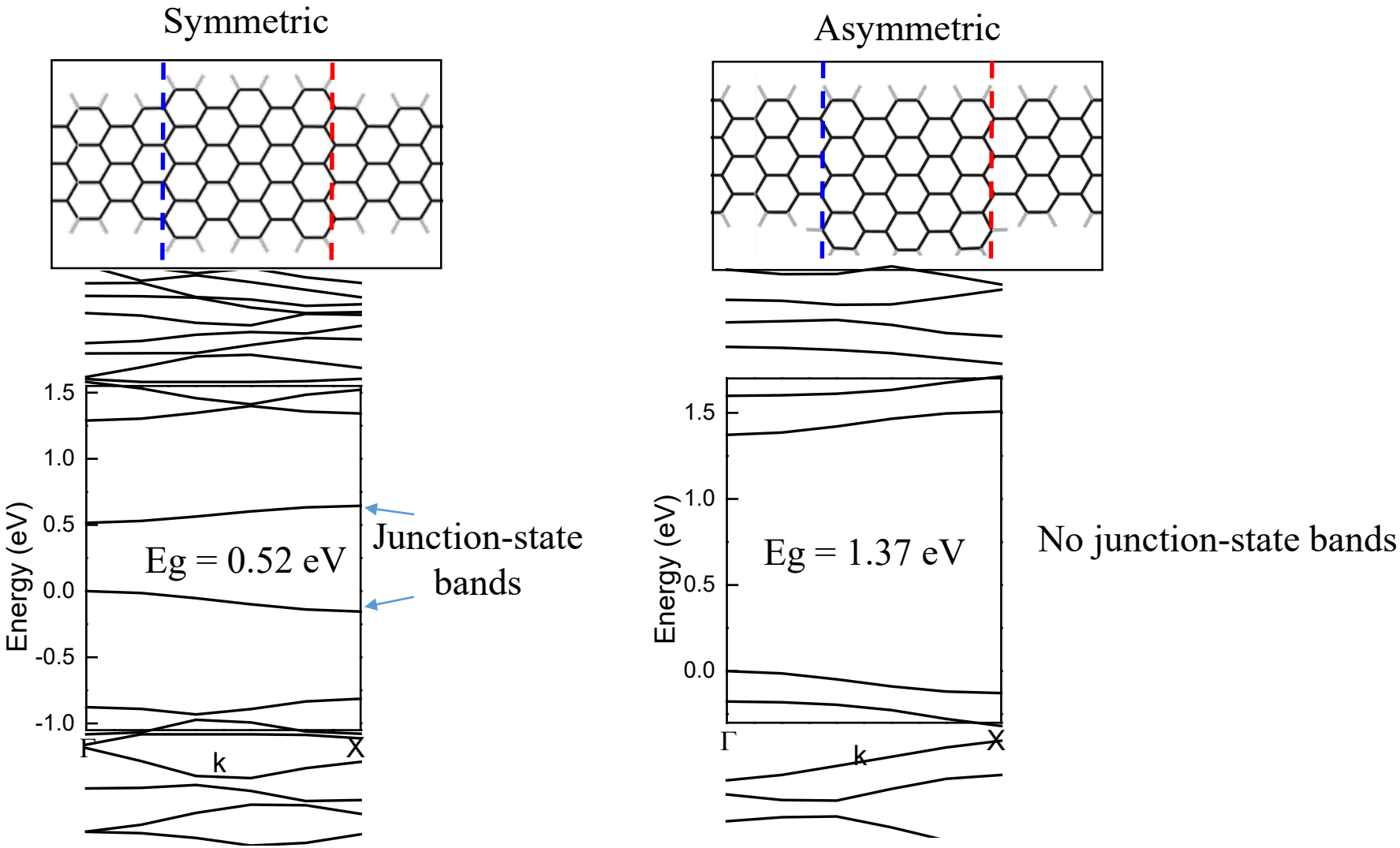
Topological Quantum Engineering: Creating topological bands in 7-9 AGNR superlattices



- Eg (7-AGNR) > Eg (9-AGNR) → Longer decay length in 9AGNR
- Bigger coupling through N=9 than N=7: $|t_1| > |t_2|$
- *Topological junction states* form 2 bands within the bulk band gap whose properties may be tuned with the length of the segments.

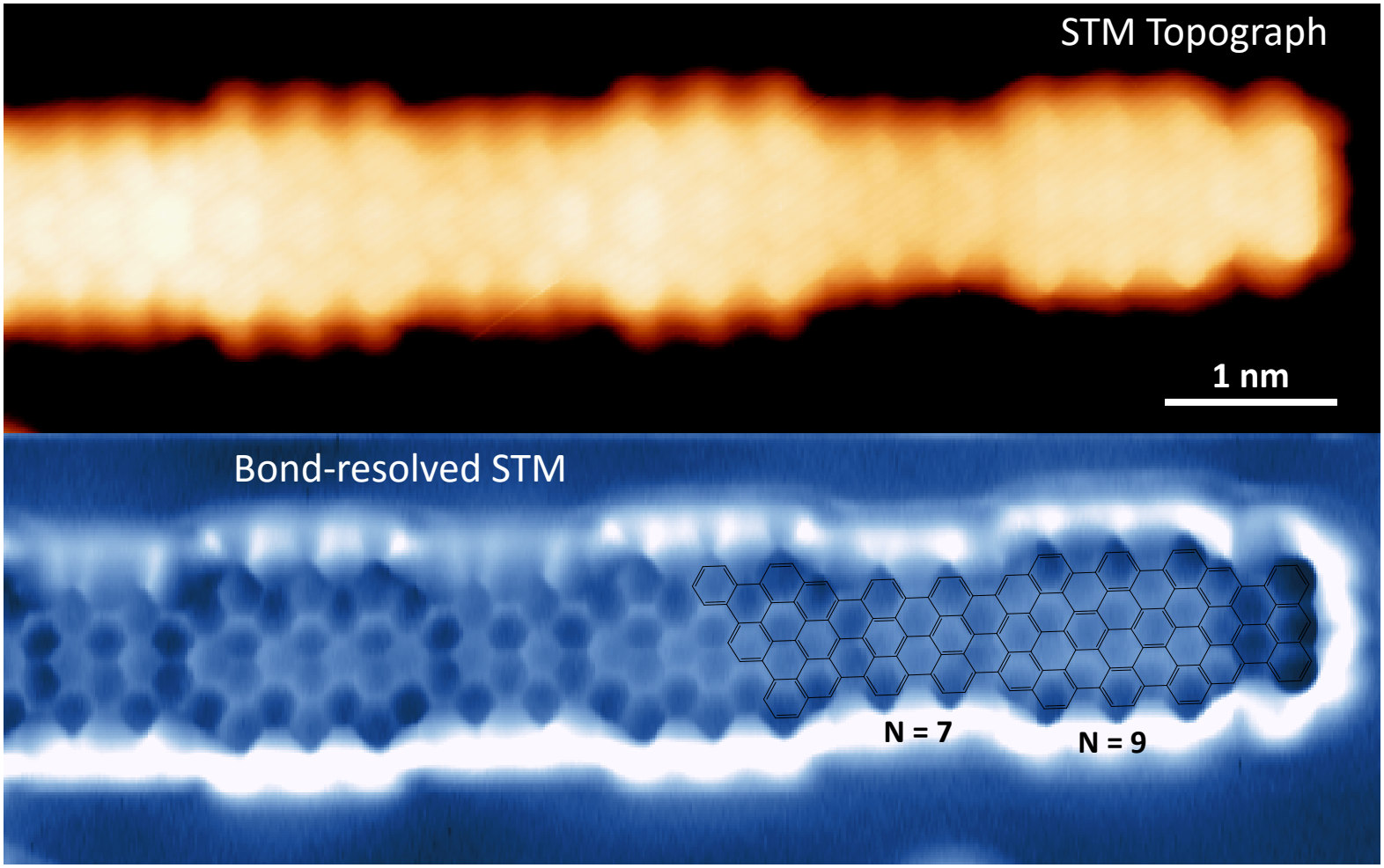
Cao, Zhao and Louie, *PRL* **119**, 076401 (2017)

Symmetric vs. Asymmetric Superlattices



- Band gap difference between the two configurations arise from topological effects.
- Gap values correspond to system on metal substrate.

Bond-resolved STM Image of 7-9 GNR Superlattice



BRSTM imaging parameters:
- dI/dV image
- V_{DC} = 20 mV, V_{AC} = 12 mV, I = 80 pA
- (feedback on)

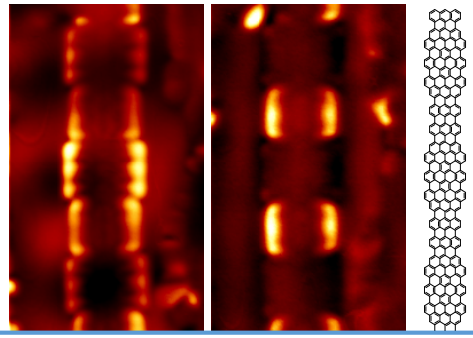
Crommie, Fischer, Louie, et al, ***Nature*** 560, 204 (2018)

Spectroscopy vs. Theory for Topological 7-9 GNR Superlattices

New topological bands

TB1 *TB2*

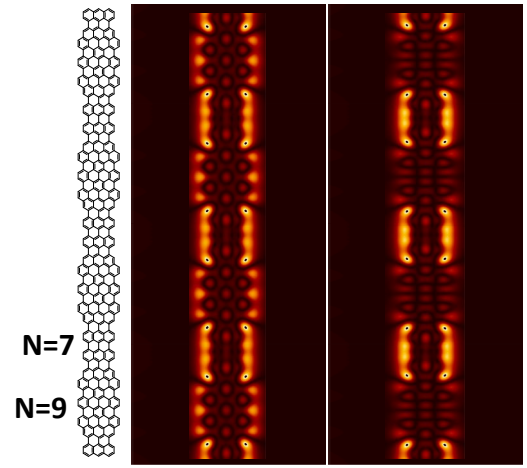
dI/dV mapping



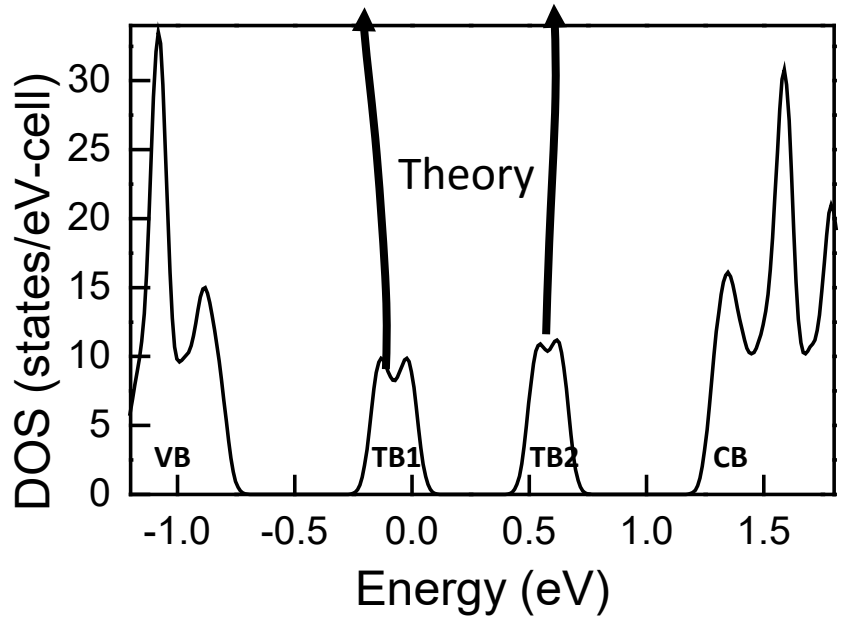
New topological bands

TB1 *TB2*

LDOS



- Can *change* the bandgap and bandwidth by changing the segment lengths!
- Expect a magnetic ground state if the on-site Coulomb $U > Eg \sim 2t_1$.
- Stable spin centers (magnetism) develop with bigger U or smaller t_1.



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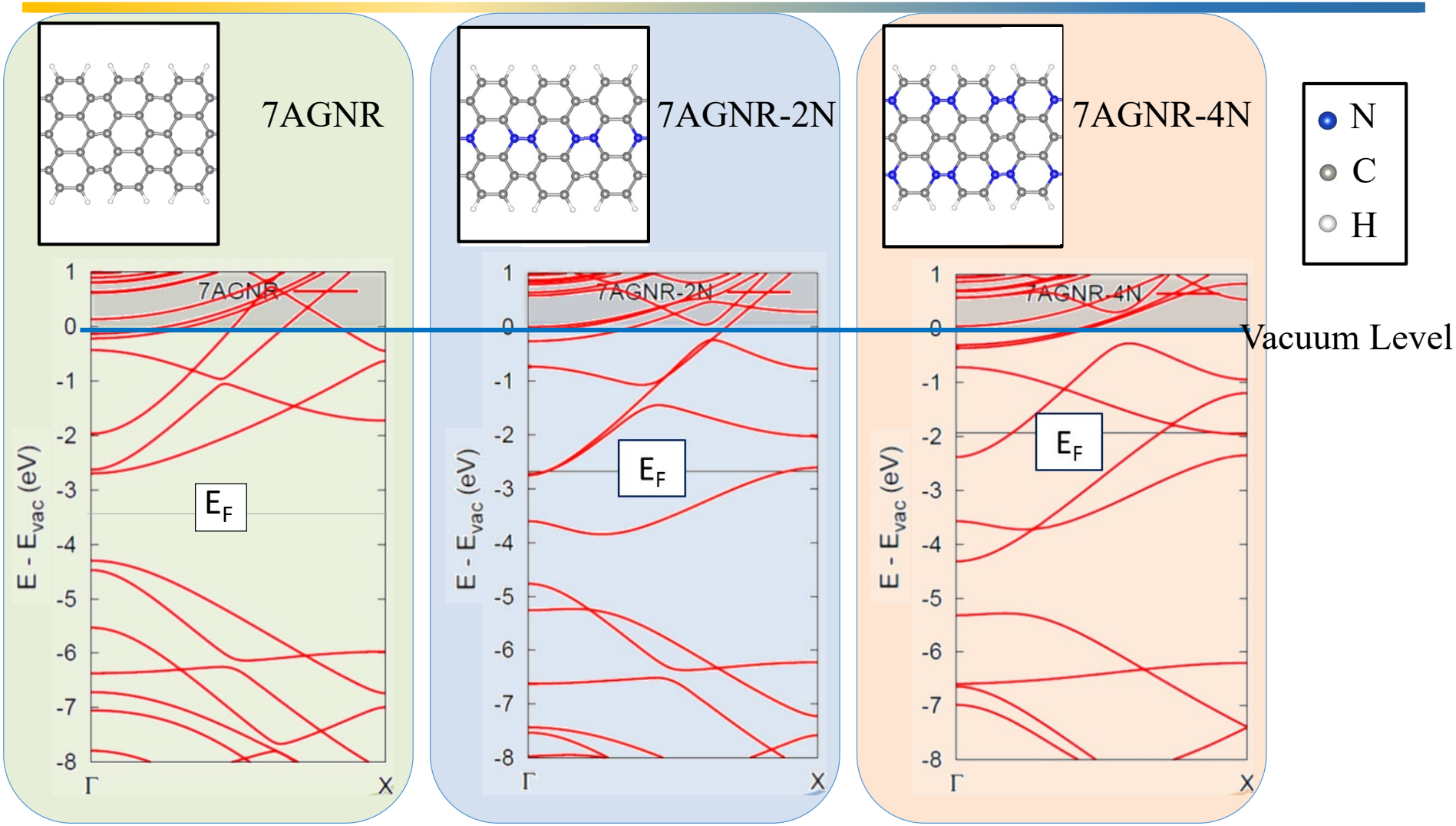
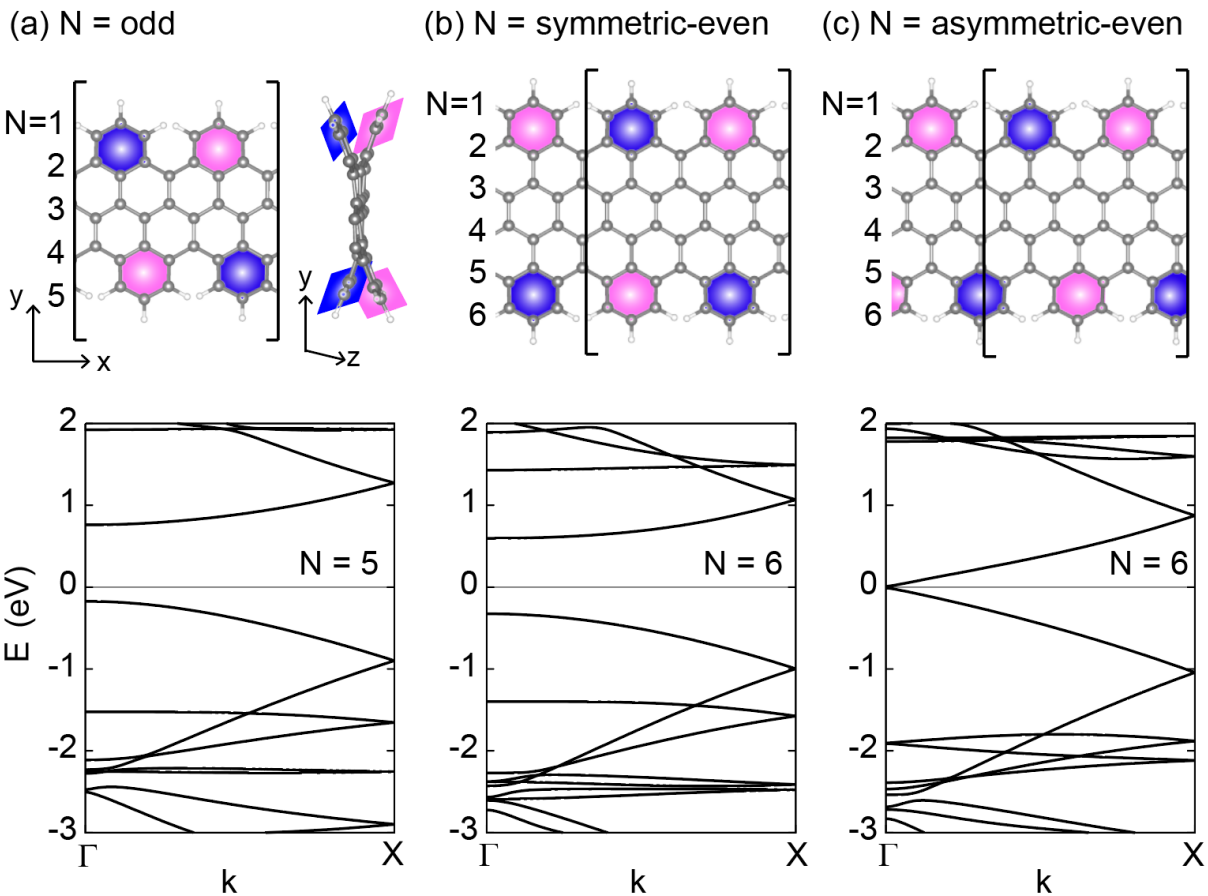
Nitrogen doped 7AGNRs as metallic leads

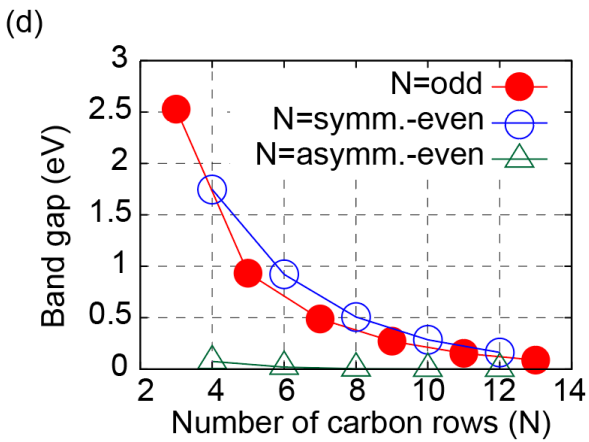


- Nitrogen doped GNRs can be good metals.
- 7AGNR/7AGNR-4N junction *likely* has an ohmic contact.

Lee, Cao, Zhao and Louie (2018)

Cove-edged GNRs as metallic leads

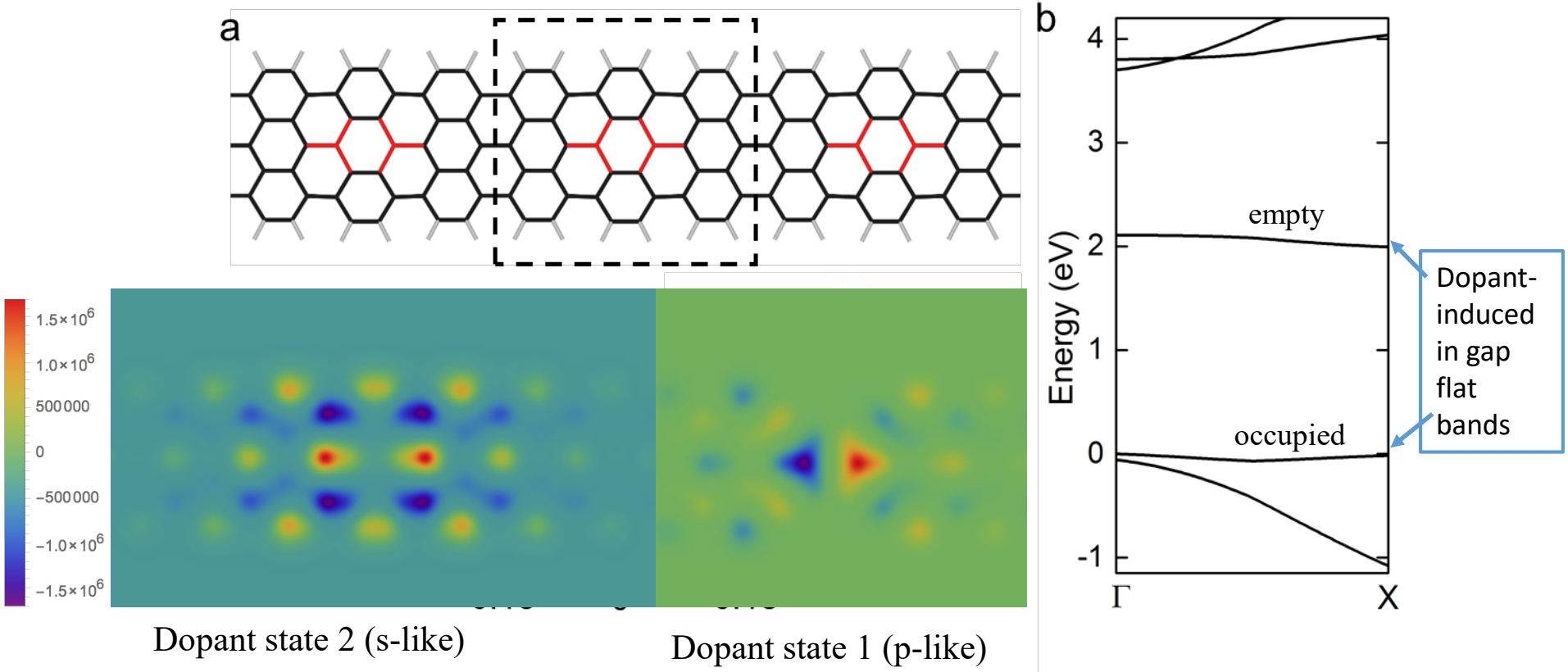




- Gapless for width N = even, asymmetric staggering case
- Should be a good metal

Lee, Zhao, Cao and Louie, accepted by *Nano letters*

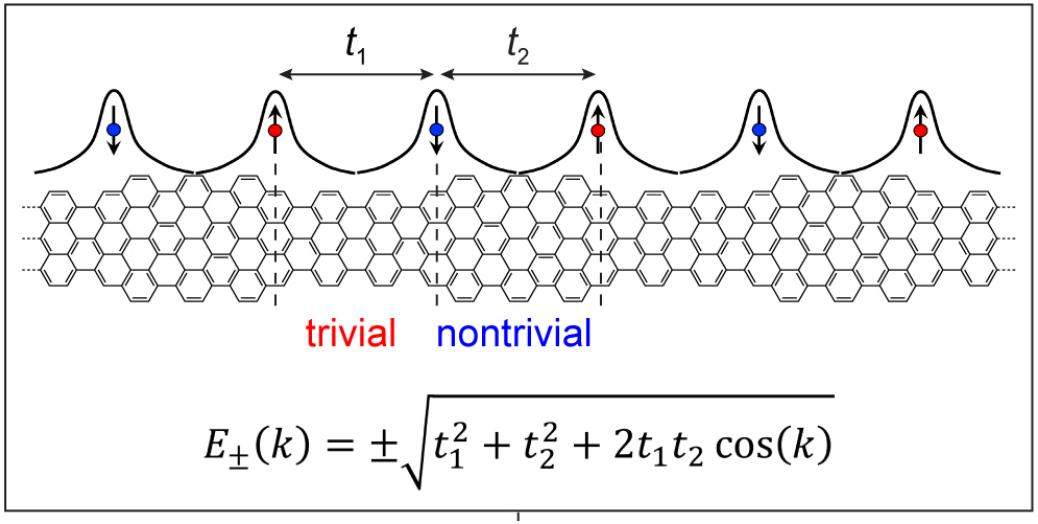
Boron-dimer periodic-doped GNRs as narrow band metallic leads



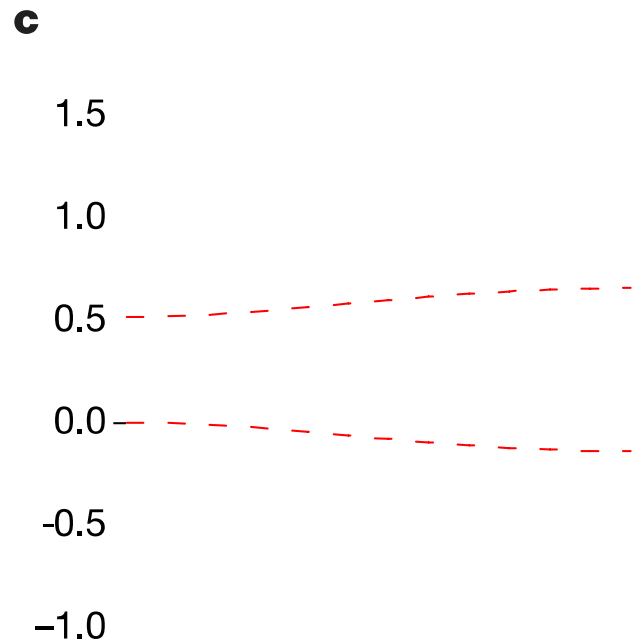
- Nearly dispersionless boron-dimer-induced bands because of symmetries
- When doped ➡ very narrow metallic bands (both small t and U)

Cao, Zhao and Louie, *PRL* **119**, 076401 (2017); ibid, to be published.

Engineering Metallic GNRs from Topological Superlattices



$$E_{\pm}(k) = \pm\sqrt{t_1^2 + t_2^2 + 2t_1t_2\cos(k)}$$



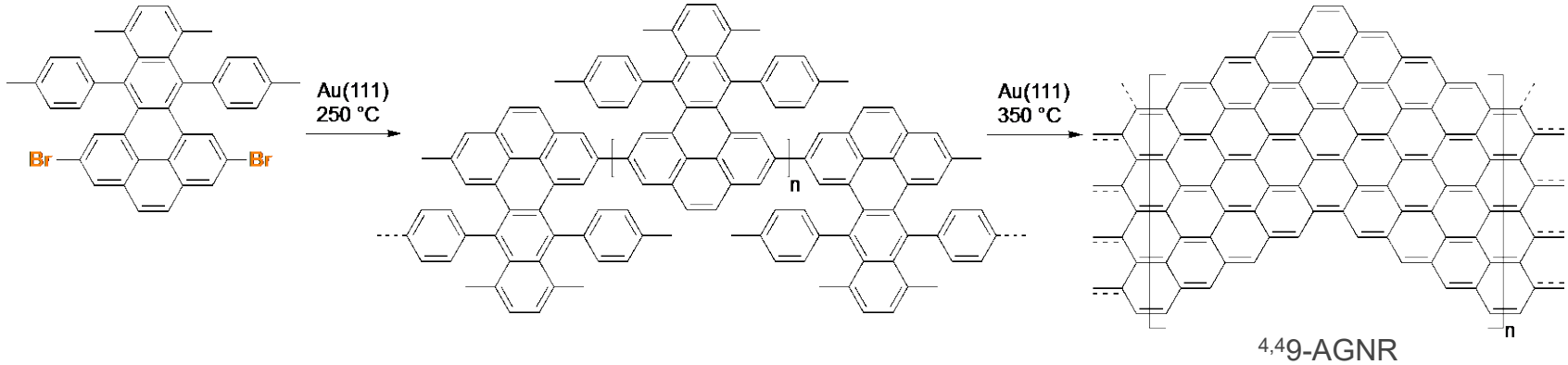
$E_g = 2\,|t_1 - t_2|$

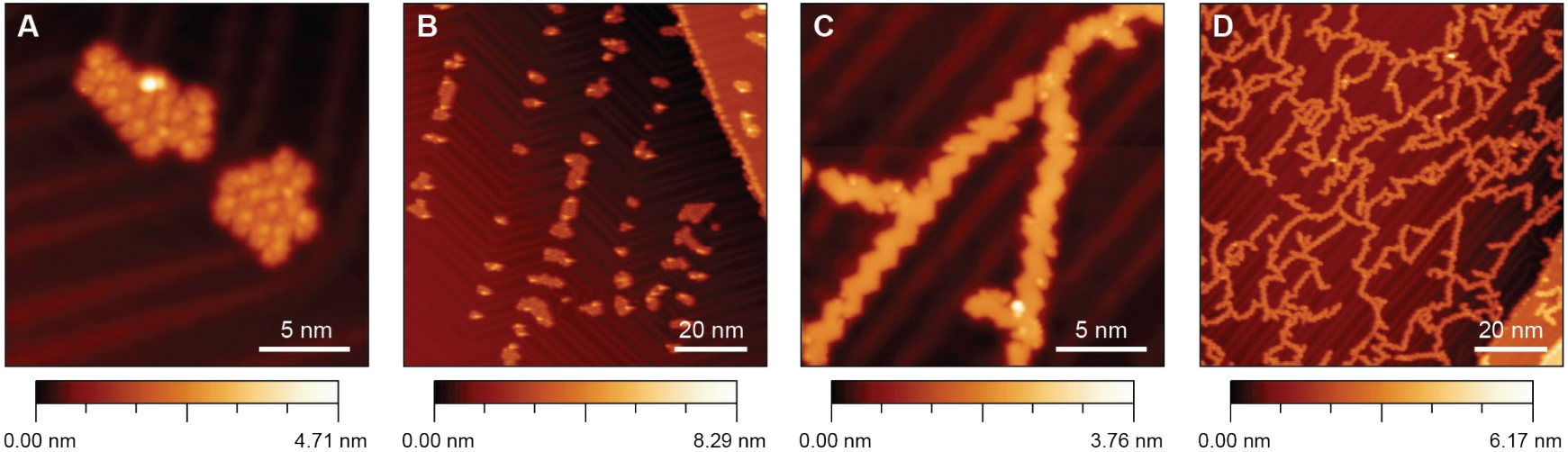
Semiconductor Band Structure for: $t_1 \neq t_2$; $E_g > 0$

Metallic Band Structure for: $t_1 = t_2$; $E_g = 0$

(Fischer, Crommie and Louie groups)

Possible Ultra-Small Bandgap Graphene Nanoribbons: 4,4-9-AGNRs





F. Fischer group

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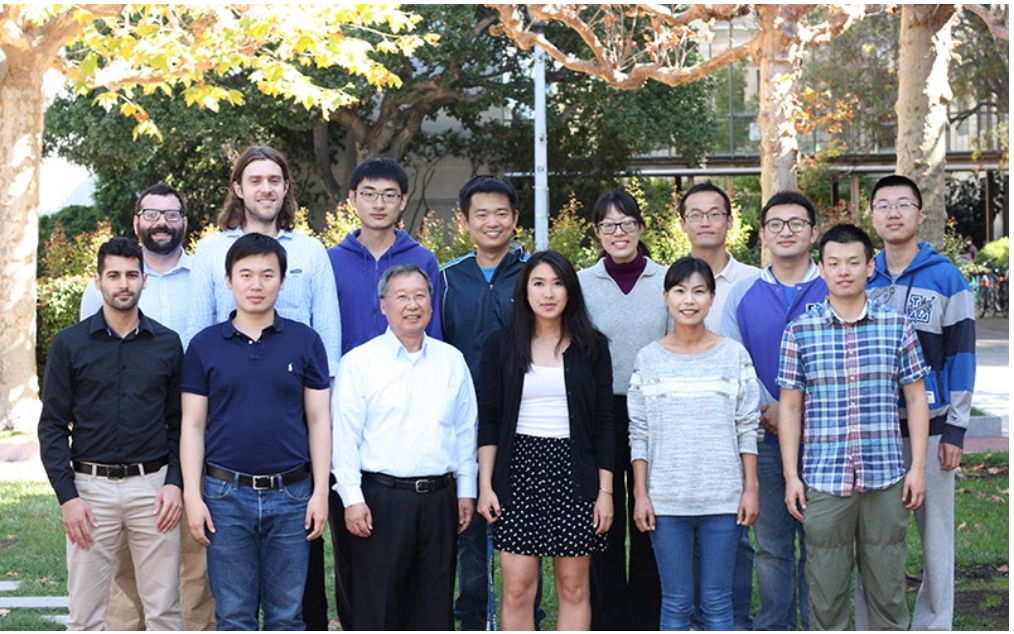
Prof. Michael Crommie
Prof. Felix Fischer

The Louie Group (2018)



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