Light Emission from Ultranarrow Graphene Nanoribbons

Edge and Termini Effects

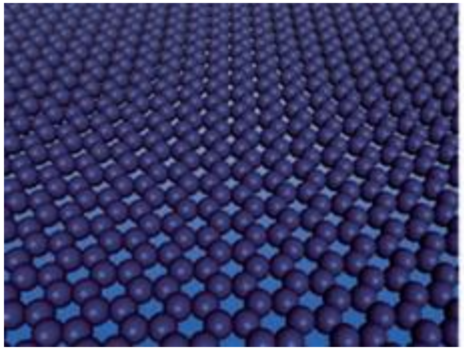
Deborah Prezzi

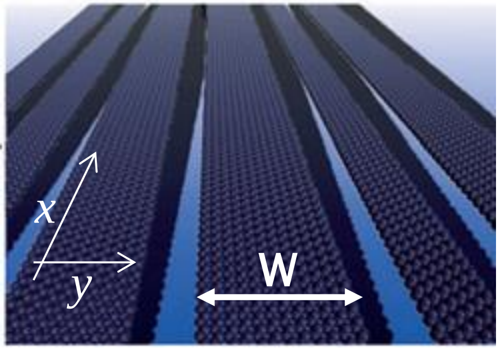
CNR Nanoscience Institute,
Modena, Italy

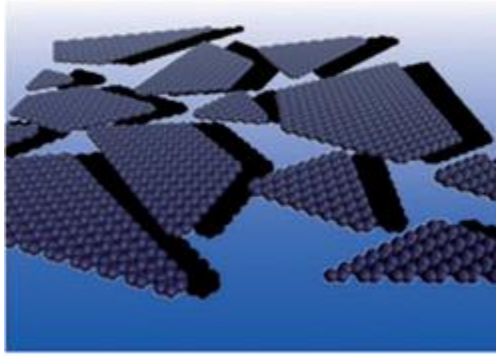
DRIVING THE EXASCALE TRANSITION

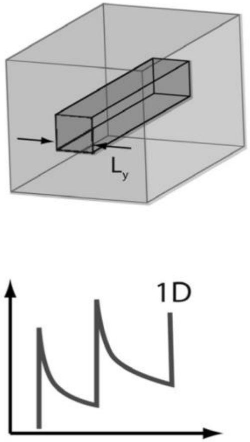
Graphene Nanostructures
Quantum Confinement

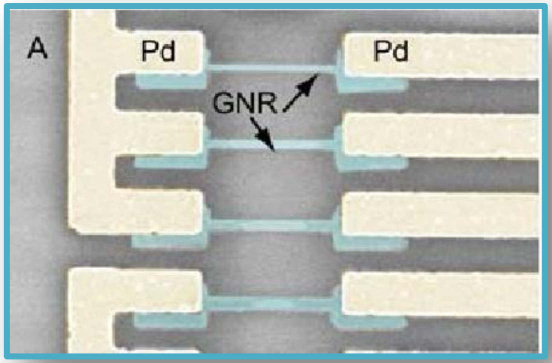
Open a band gap by confining electrons into 1D stripes (W << L) & 0D QDs

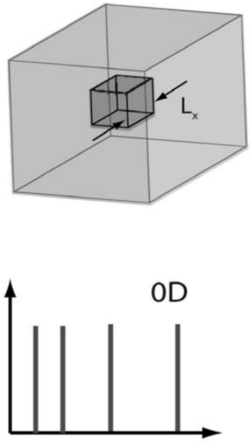


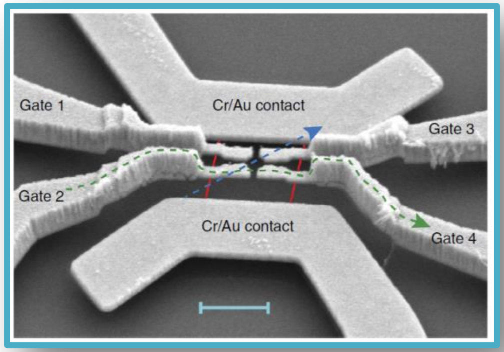






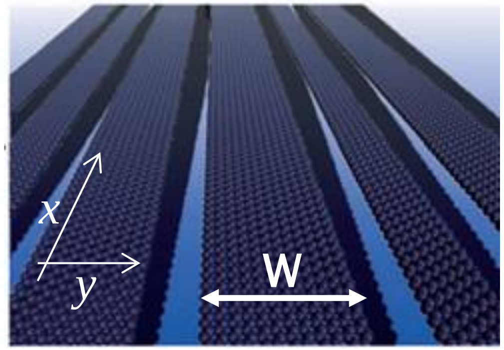


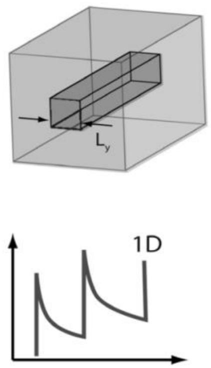




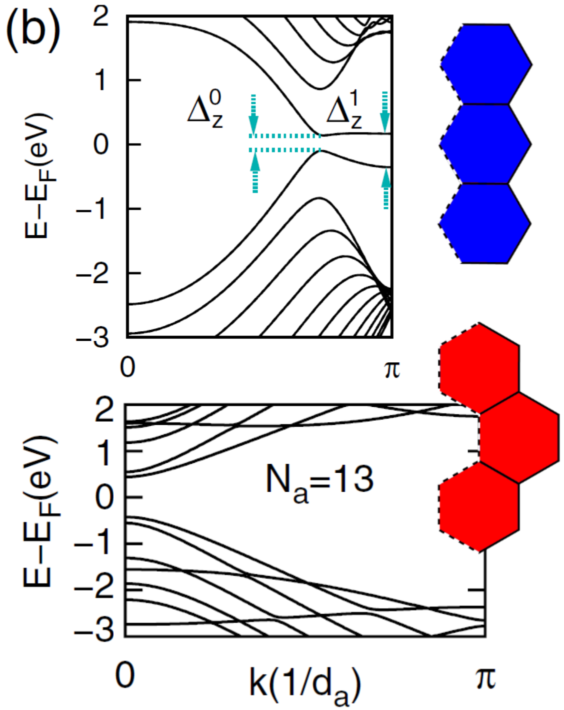
Graphene Nanoribbons
Gap Tunability

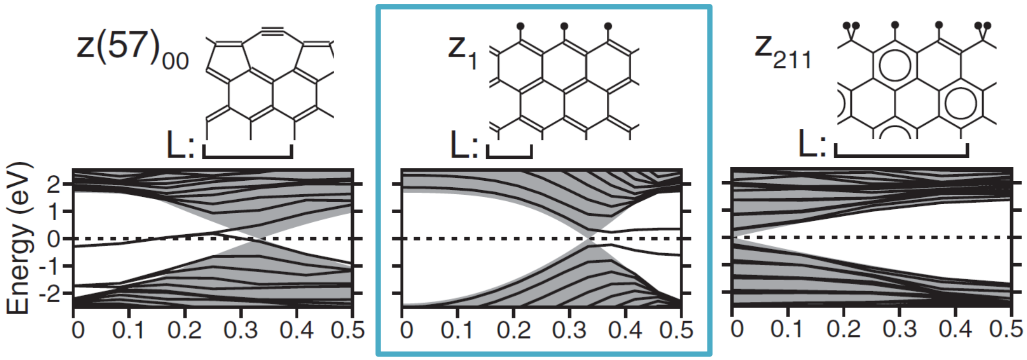
Quantum Confinement: open a band gap by confining electrons into 1D stripes (W << L)





Chirality/Edge Effects: besides the **size** *W*, also the *cutting direction matters, as well as* the *local edge conformation & functionalization*

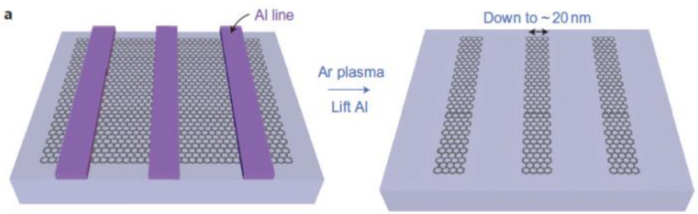




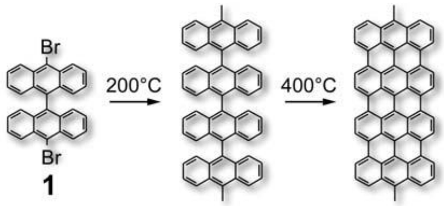
See e.g. Son etal., PRL (2006); Wassmann et al, PRL (2008); Osella et al, ACS Nano (2012)

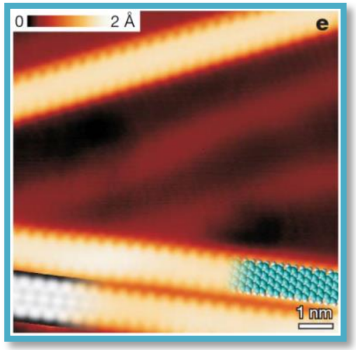
Ultranarrow Graphene Nanoribbons
Production Techniques

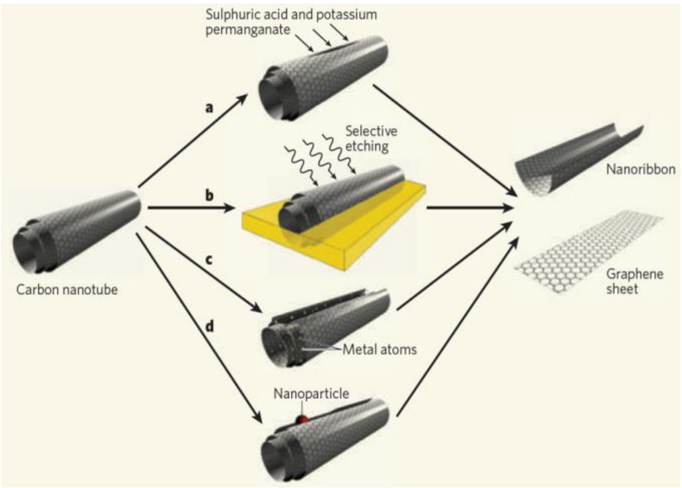
Intense work to achieve nm-scale sizes & full edge control



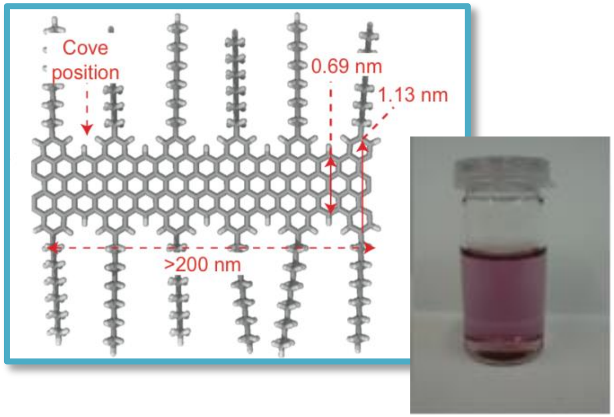
Wang & Dai Nature Chem. **2**, 661 (2010)

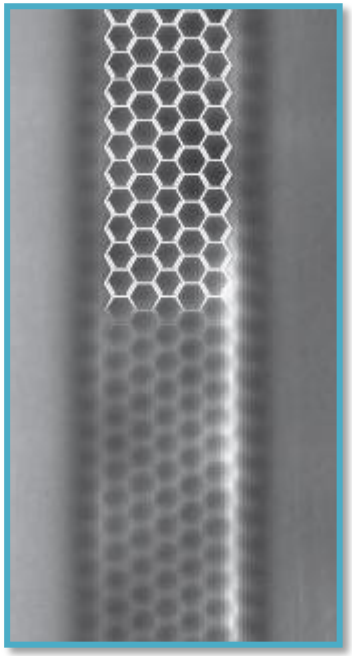






*Nature **458**, 872 (2009); Nature **458**, 877 (2009); Elias et al., Nano Lett. (2009).*





J. Cai *et al.*, Nature (2010); A. Narita et al, Nature Chem. (2014); ACS Nano (2014); P. Ruffieux et al., Nature (**2016**)

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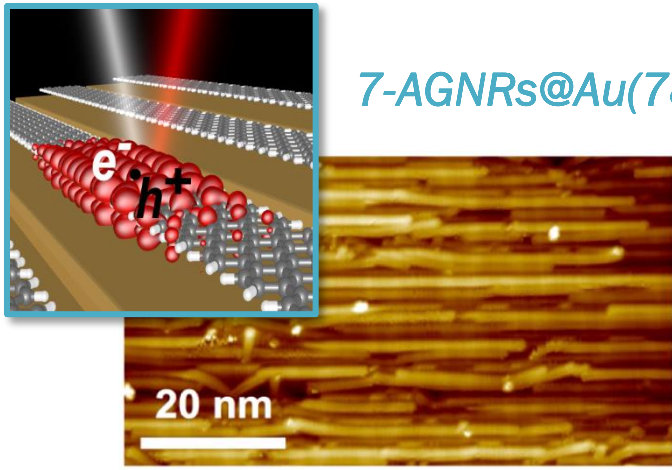
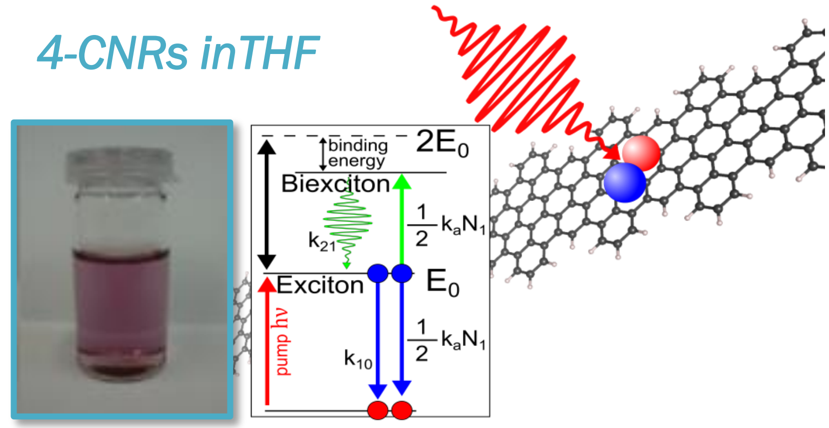
Ultranarrow Graphene Nanoribbons
Optical properties

Denk et al., Nature Commun. 5, 4253 (2014)





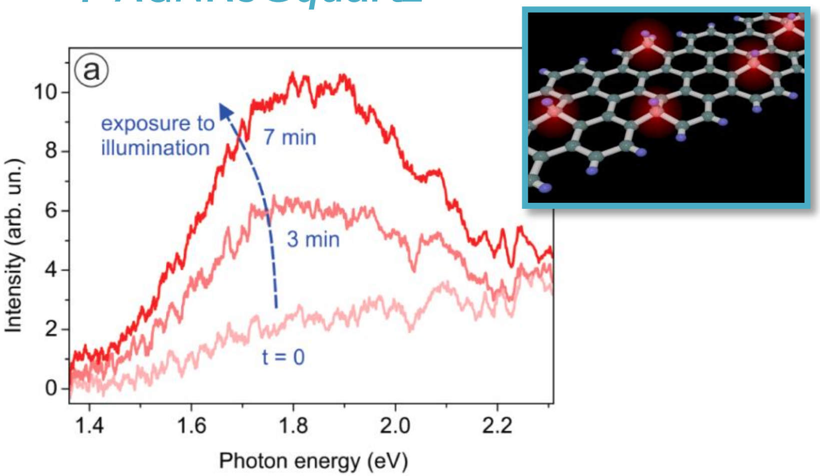
Soavi et al., Nature Commun. 7, 11010 (2016)

- ✓ Optical properties have been probed both on substrate and in solutions
- ✓ Role of quasiparticles & multiparticle excitations (bandgap renormalization, excitons, biexcitons, …) have been assessed from both theoretical modelling & experiments
- ✓ Functionalization for fine-tuning of the optical properties

→ GNRs hold promise for next generation optoelectronic devices

Ultranarrow Graphene Nanoribbons
Light Emission

7-AGNRs@quartz



Senkovskyi et al., NL 17, 4029 (2017)

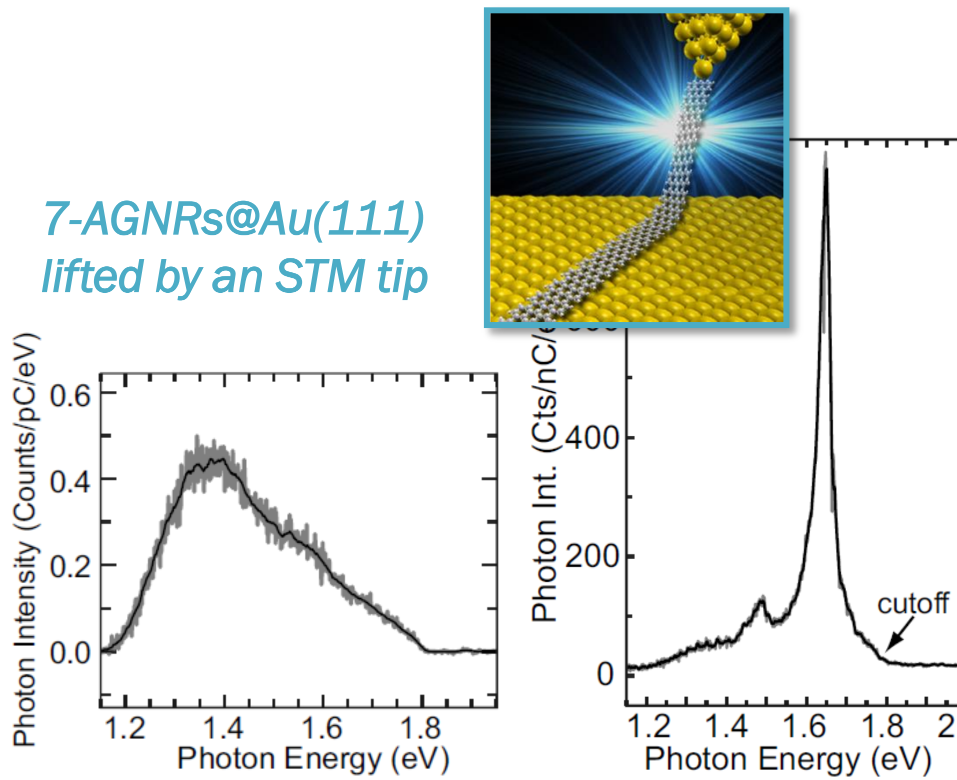
✓ <u>Erratic emission features</u>:

- Weak and feaureless PLE from pristine 7-AGNRs

- Featureless spectra for as grown GNRs, bright emission after abrupt change in the current

Chong et al., private commun.

7-AGNRs@Au(111) lifted by an STM tip



Understanding the origin of STM-induced light emission

Collaboration with CNRS – Strasbourg

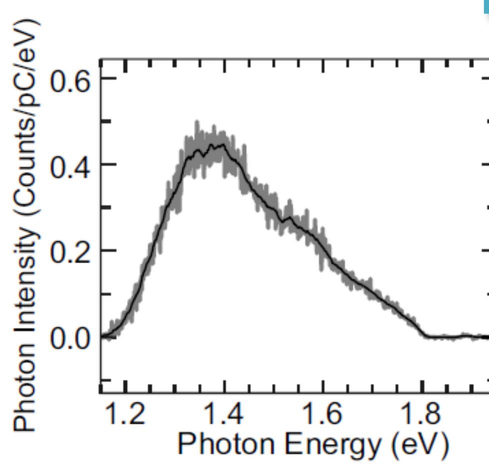
Michael Chong

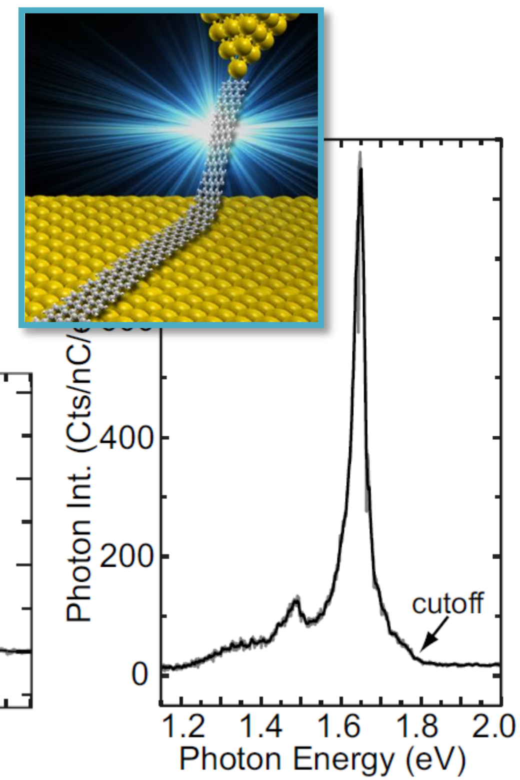
Guillaume Schull

- Measurements on a single GNR
- STM manipulation of the structures & imaging

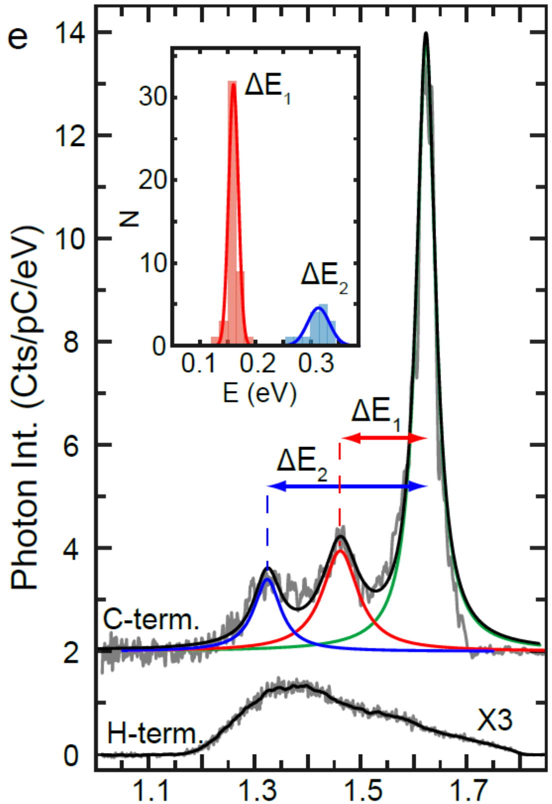
Chong et al., private commun.

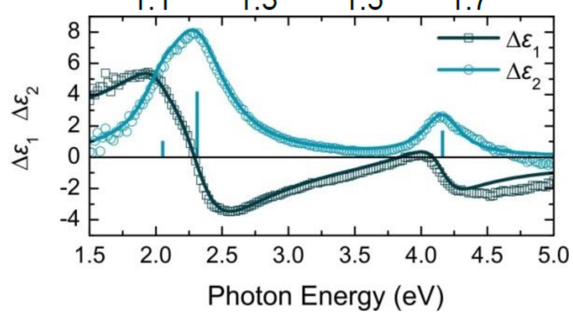
7-AGNRs@Au(111) lifted by an STM tip

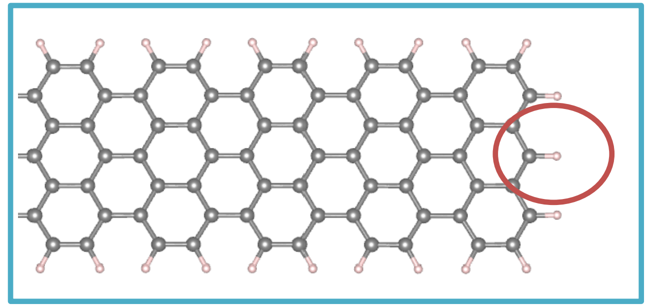


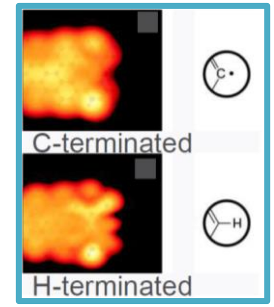


STM-induced Light Emission



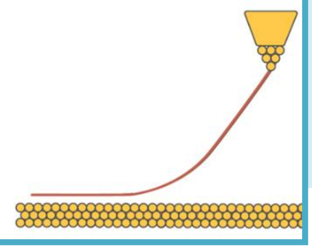




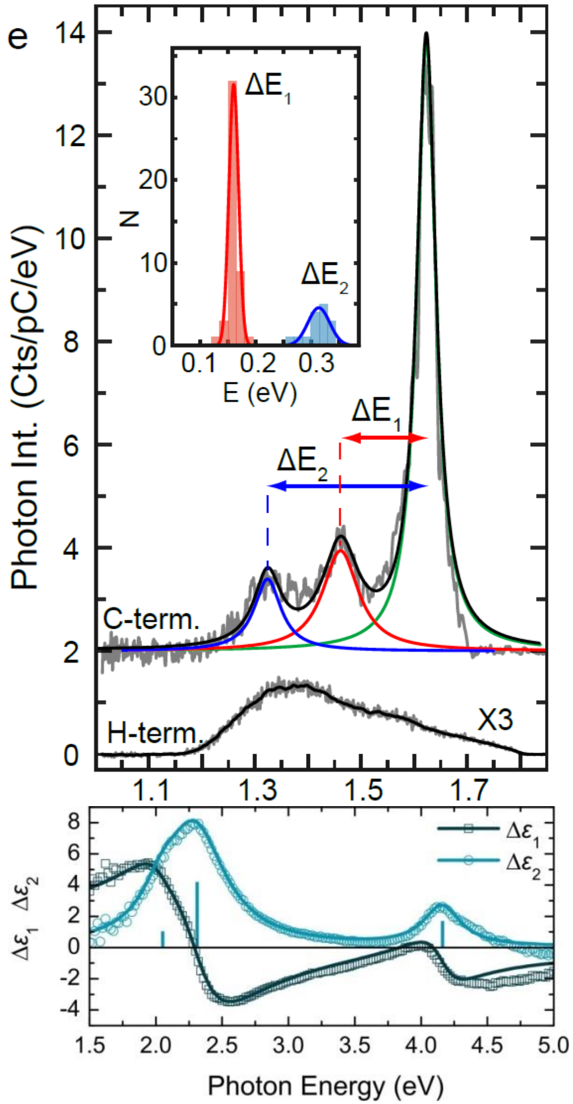


- **H-terminated GNR**
  - ✓ Broad and featureless spectrum as for the junction without GNR (plasmonic emission)
- **C-terminated GNR**
  - ✓ sharp peak at ~1.6 eV + redshited vibronic replicas (~160 meV)
  - ✓ extrapolating to zero bias: peak at ~1.16 eV << optical gap of 7-AGNR (~2 eV)

M. Chong, N. Afshar-Imani, F. Scheurer, C. Cardoso, A. Ferretti, D. Prezzi, and G. Schull, NL 18, 175 (2018)



STM-induced Light Emission



➔PL activated by coupling between STM tip and GNR terminus

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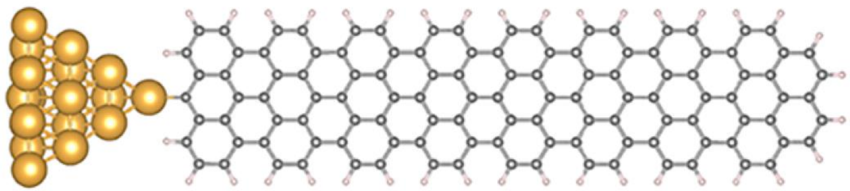
Insights from Ab-initio Simulations



✓ Capture key feature for the description of realistic systems

- Finite length GNRs
- Atomistic description of the contact with STM tip – **DFT framework**
- Inclusion of many-body effects to properly describe optical properties and allow comparison with spectroscopic measurements – **GW-BSE approach**

QUANTUMESPRESSO

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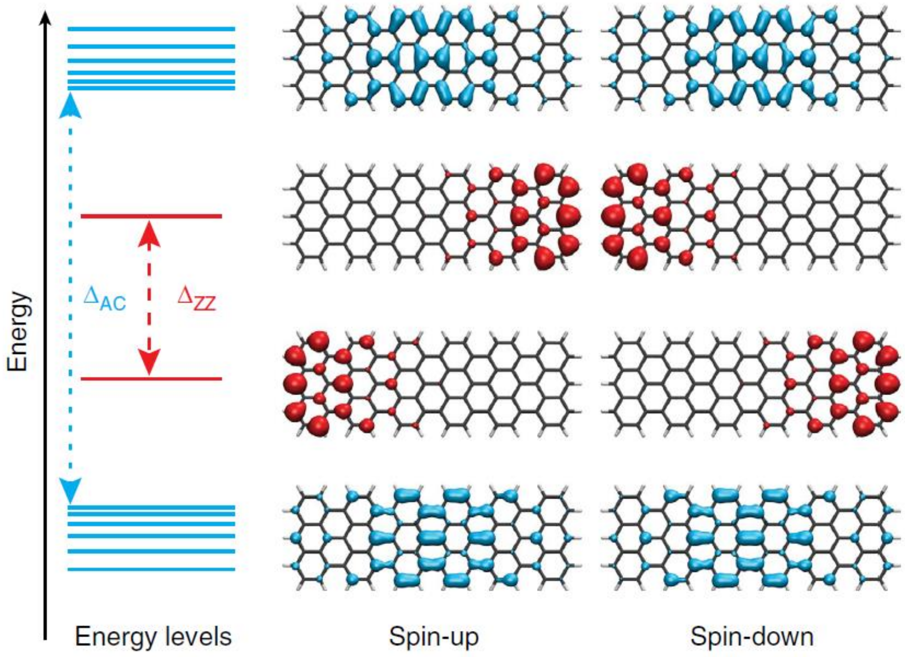
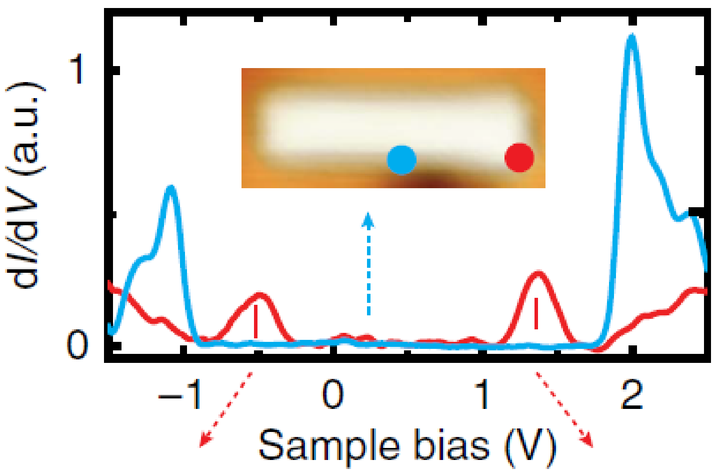
M. Chong, N. Afshar-Imani, F. Scheurer, C. Cardoso, A. Ferretti, D. Prezzi, and G. Schull, NL 18, 175 (2018)

Finite-Length Effects
From First Principles

➔ **Anything special at the terminus?** Antiferromagnetic order, Tamm-like states localized at the zigzag termini within the gap defined by bulk delocalized states



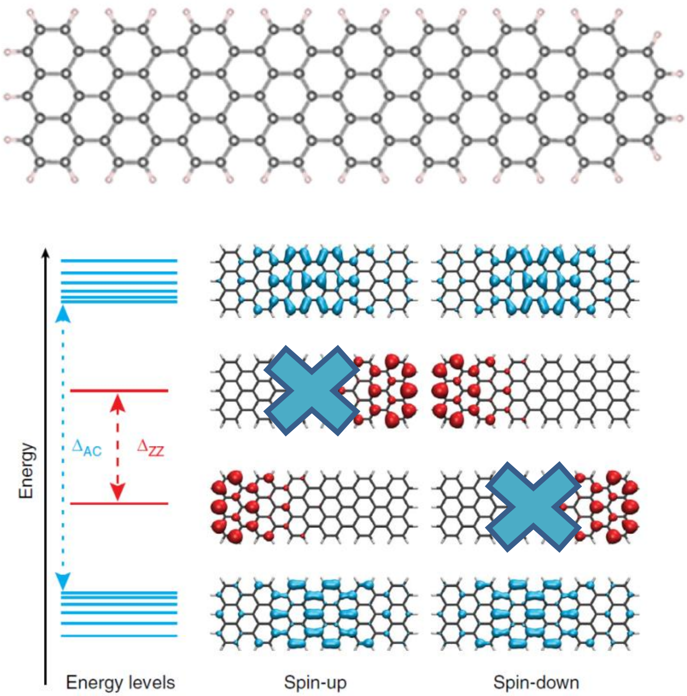


Finite length effects never taken into account in the evaluation of optical properties

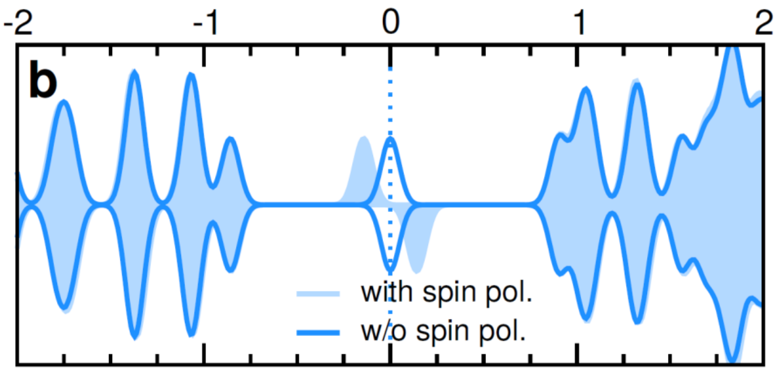
Wang et al., Nature Commun. 7, 11507 (2015)

Finite-Length Effects
From First Principles

➔ **Asymmetric** finite 7-AGNR to <u>remove termini-termini interaction</u>

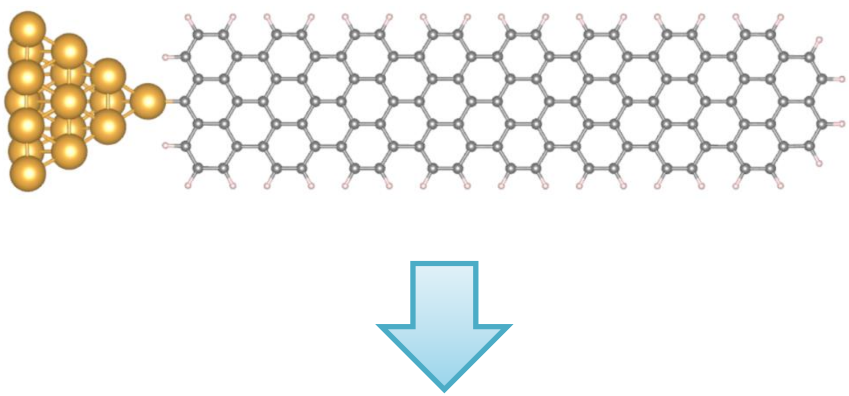


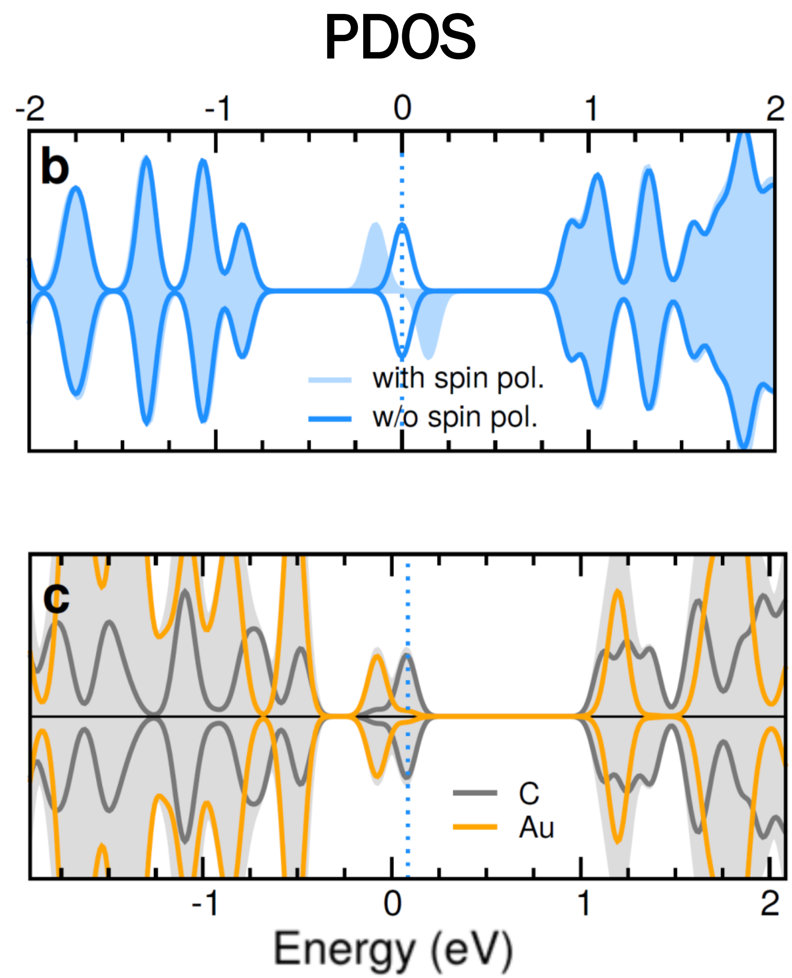
PDOS



Contact with STM tip
From First Principles

➔ Contact with a gold cluster mimicking the tip



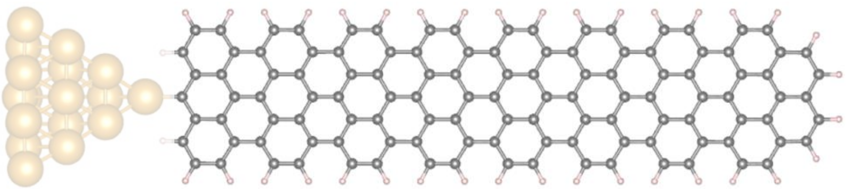


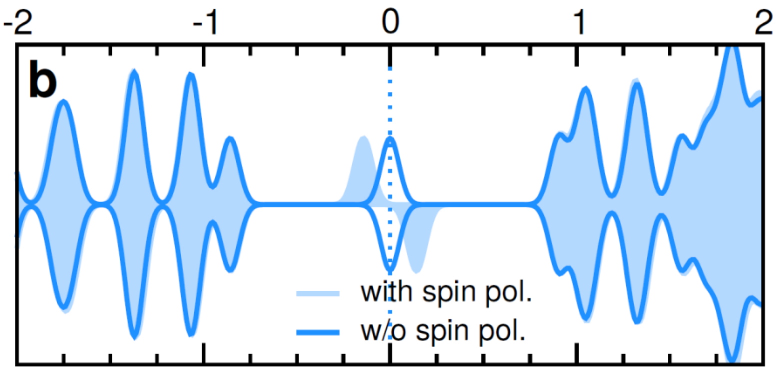
- ✓ The presence of gold makes the system **paramagnetic**
- ✓ End-localized states located close to the Fermi level

Optical properties
From First Principles

➔ Use the **<u>isolated</u>** finite-length GNR with **<u>spin unpolarized</u>** GS as starting point for the calculation of the optical properties

PDOS





- Inclusion of <u>many-body effects</u> to properly describe optical properties and allow comparison with spectroscopic measurements – **GW-BSE approach**

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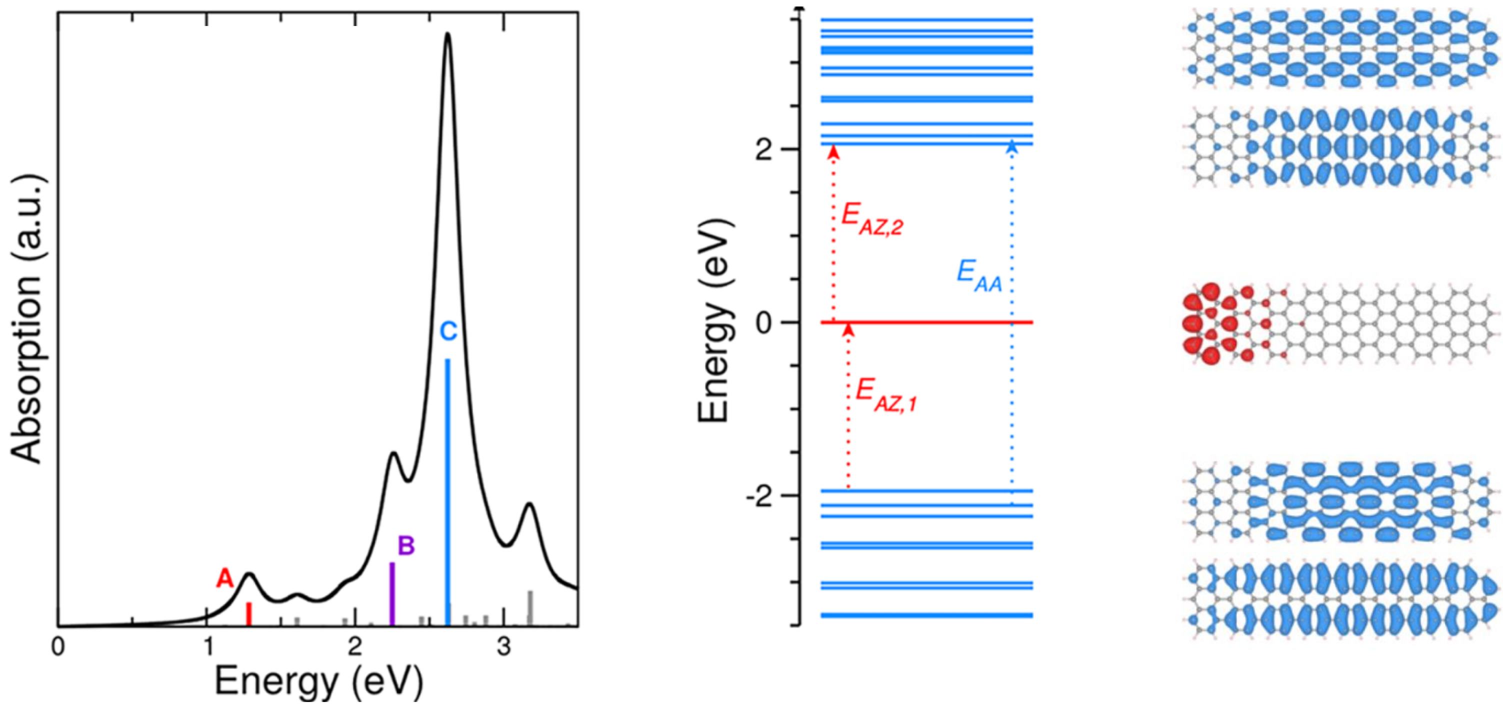
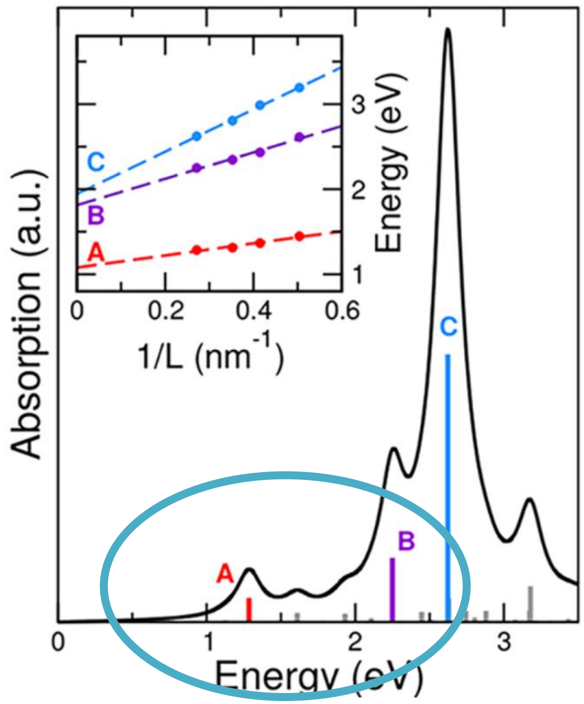
Finite-Length Effects & Optics
From First Principles



- Finite length gives rise to excitations involving transition between states localized at the GNR termini and delocalized bulk states

Finite-Length Effects & Optics
From First Principles

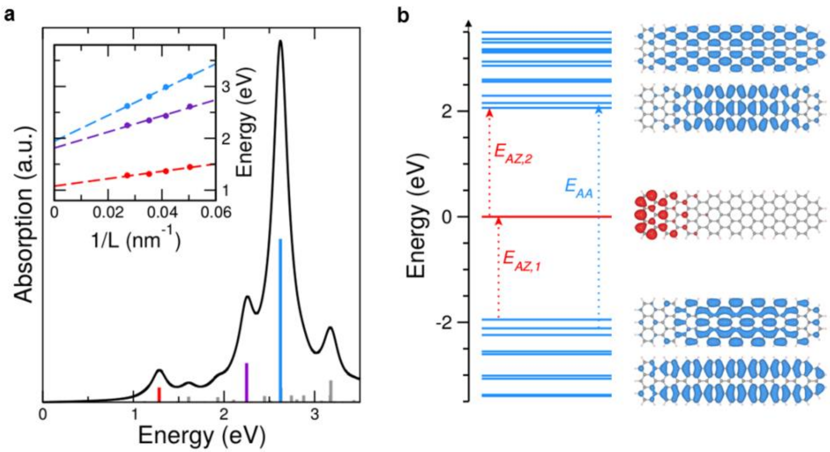


length (N)	Δ_{AA} - DFT (eV)	Δ_{AA} - GW (eV)	E_{AA} - BSE (eV)
8	2.2	4.6	3.2
10	2.0	4.3	3.0
12	1.9	4.2	2.8
16	1.8	4.0	2.6

Exp peak ~1.16 eV
Optical gap ~2 eV

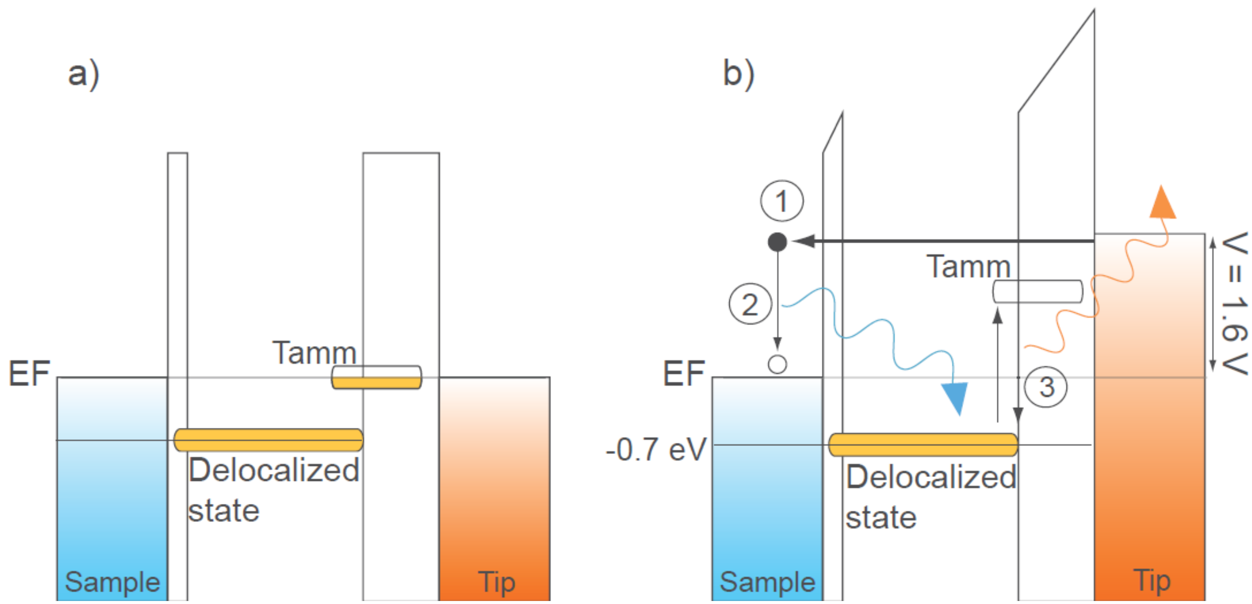
- Finite length gives rise to excitations involving transition between states localized at the GNR termini and delocalized bulk states
- Different length dependence of edge-related and bulk excitons
  → **extrapolation for comparison with exp observations**
- Several states below the optical gap for infinite system with low OS
  → **effects on the PL efficiency**

Emission mechanism



Plasmon-mediated mechanism:

- Inelastic electrons injected in the junction excite a LSP
- The LSP transfers its energy to the GNR which goes from ground S0 to excited states S1
- The GNR emits light by decaying from S1 to S0



Conclusions

- **Electronic & optical properties are governed by e-e interactions**

  → need to resort to beyond-DFT schemes to enable an accurate description & comparison with electronic and optical spectroscopy measurements

- **Full inclusion of the tip for describing STM-induced PL**

  → finite size effects, coupling with the end-localized states

NANO LETTERS
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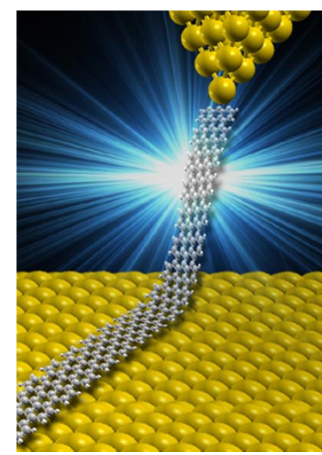
Nano Lett. 2018, 18, 175–181
Letter
pubs.acs.org/NanoLett

Bright Electroluminescence from Single Graphene Nanoribbon Junctions

Michael C. Chong,[†] Nasima Afshar-Imani,[†] Fabrice Scheurer,[†] Claudia Cardoso,[‡] Andrea Ferretti,[‡] Deborah Prezzi,[*,‡] and Guillaume Schull[*,†]



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Guillaume Schull