Theoretical Spectroscopy of Graphene Nanoribbons

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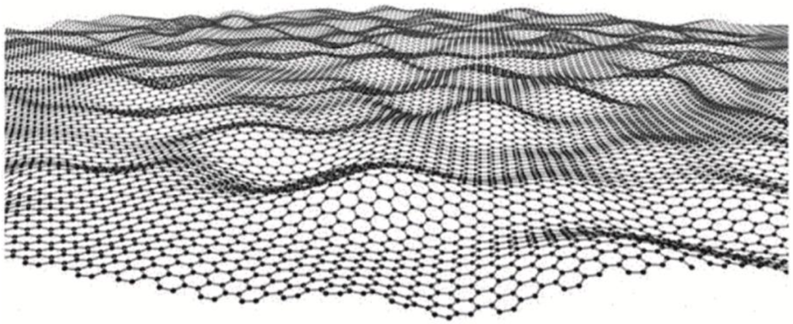
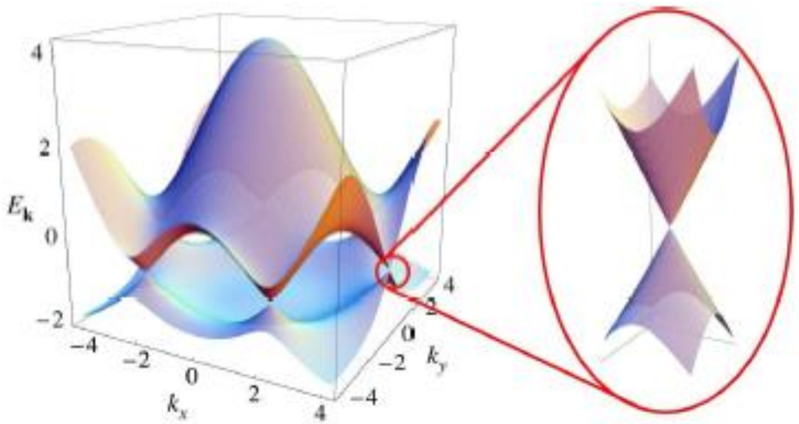
MODENA, ITALY

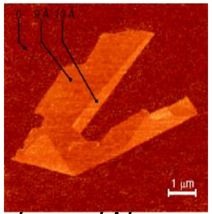
Graphene



special properties
of extended graphene

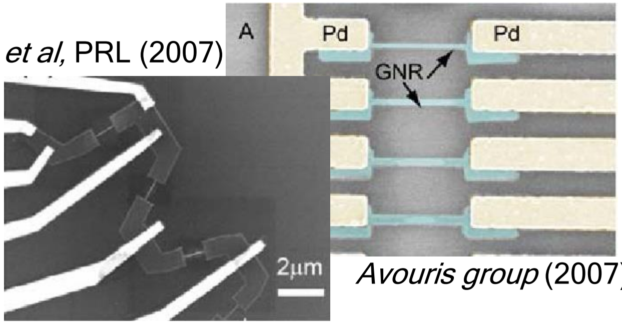


and …gap opening through
graphene nanostructuring



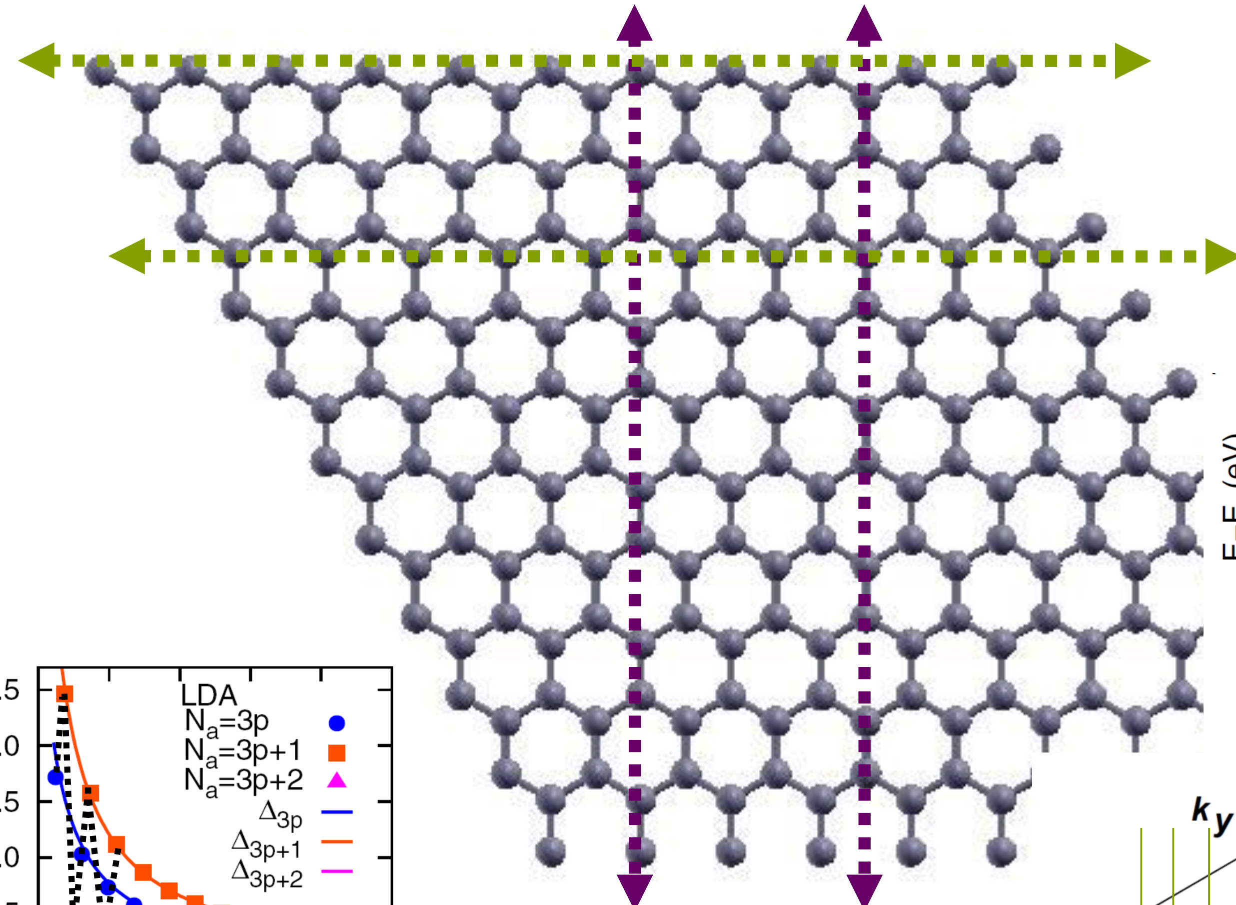
Geim and Novosolev, Nat. Mat. (2007)

Han et al, PRL (2007)

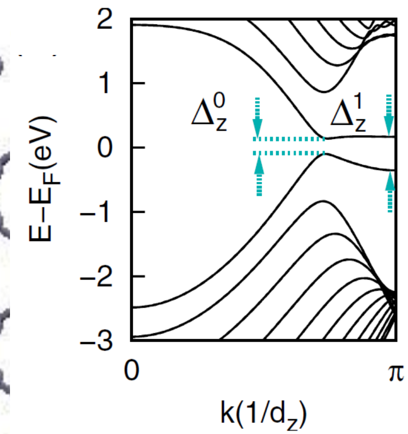


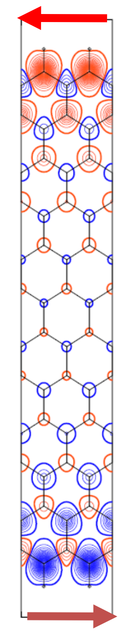
Avouris group (2007)

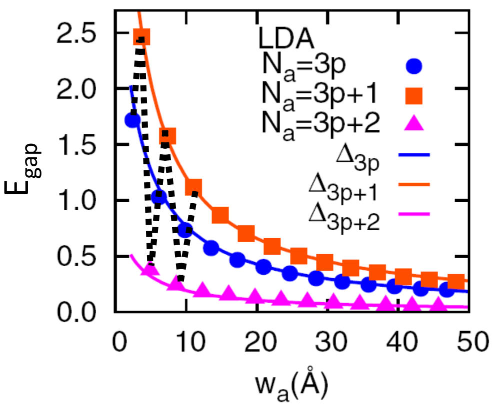
Edges



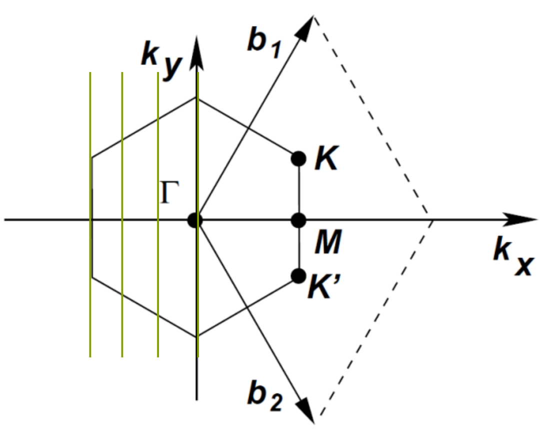
ZIGZAG
semiconductor
→ magnetic







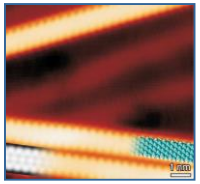
ARMCHAIR
semiconductor
oscillating gap vs width



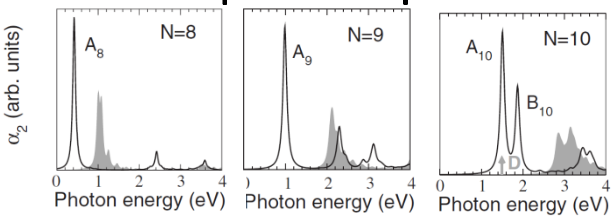
Graphene nanoribbons

- ***Fundamental properties***

  - 1D confinement effects

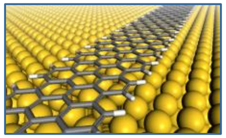


Optical absorption

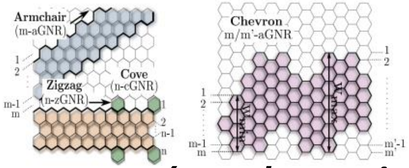


- ***Simulation of electronic, optical, vibrational spectroscopies → REAL LIFE!***

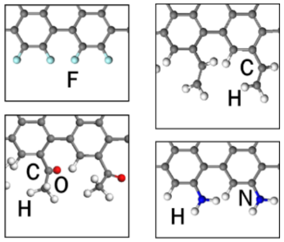
  - Substrate effects

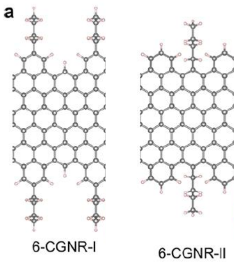


  - Edge-shape effects



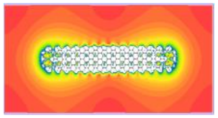
  - Impact of functionalization groups (and position)





  - Structural distortions

  - Finite-size effects

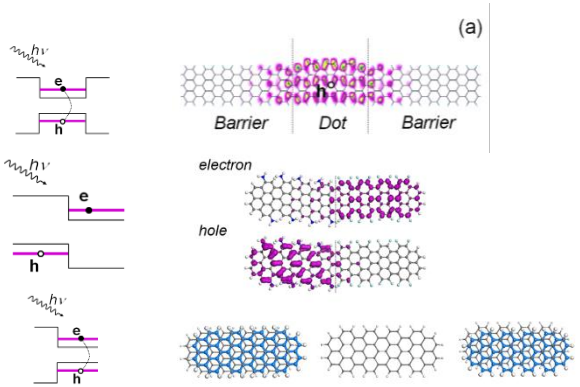


- ***Designing new structures, e.g. :***

  - Width modulation

  - Edge functionalization

  - π-π aggregation



Methods

Density Functional Theory (DFT) for ground state properties

- **Structural properties** (for 100-1000 atoms, errors of a few % on lattice parameters)
  - ✓ Surfaces & interfaces: adsorption energies – delicate parameter, depends on the description of van der Waals forces
  - ✓ Molecules/polymers: they might need more advanced xc functionals to be well reproduced, see e.g. torsion angles …
- **Vibrational properties** (within 10-50 cm^{-1})
  - ✓ Phonon calculations based on Density Functional Perturbation Theory (DFPT)*
  - ✓ Raman Intensities calculated according to Placzek approximation**

WARNING DFT fails:

- **Electronic properties**: strong underestimation of the band gap (> 30-50%)
- **Optical properties**: energies may be captured due to error cancellations; nature of optical excitation is however not correct (no bound states)

QUANTUM ESPRESSO

*S.Baroni Rev.Mod.Phys 73 515-562 (2001)

**M.Lazzeri et al. PRl 90 036401 (2003)

P. Giannozzi et al., JPCM (2009); JPCM (2017)

Methods

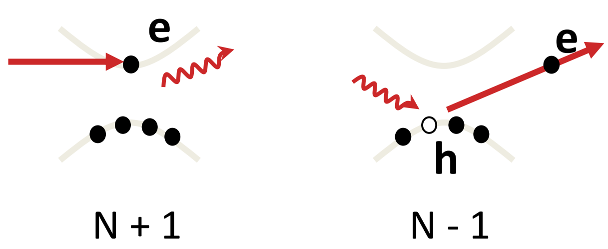
⇒ **Many-Body Perturbation Theory (MBPT)** for excited-state properties

- **<u>Electronic properties</u> within GW**

$\Sigma = GW$

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}} + V_{\text{Hartree}} + \Sigma_{\text{xc}}(\varepsilon) - \varepsilon\right]\psi(\mathbf{r}) = 0$$

Quasiparticle corrections within
GW* approximation



SIMULATED SPECTROSCOPIES:
STS,
PES, IPES, ARPES,
...

* *Hedin (1965); Hybertsen & Louie, PRB (1986)*

Methods

⇒ **Many-Body Perturbation Theory (MBPT)** for excited-state properties

- **Optical properties** within Bethe-Salpeter equation

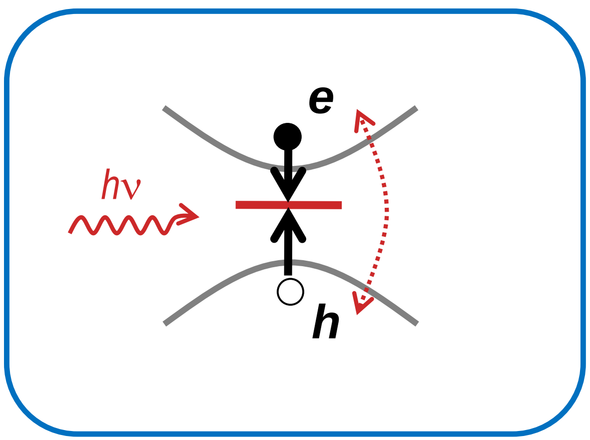
$$[(E_{ck} - E_{vk})\delta_{cc'}\delta_{vv'}\delta_{kk'} + K_{cvk,c'v'k'}]\Psi^{(n)}_{c'v'k'} = \Omega_n \Psi^{(n)}_{cvk}$$

Bethe-Salpeter equation

$$\phi^{(n)}(\mathbf{r}_e, \mathbf{r}_h) = \sum_{cvk} \Psi^{(n)}_{cvk} [\psi_{vk}(\mathbf{r}_h)]^* \psi_{ck}(\mathbf{r}_e)$$

Mixing of single particle transitions

$$\Omega_n \neq E_{ck} - E_{vk}$$



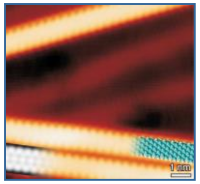
SIMULATED SPECTROSCOPIES:
OPTICAL ABSORPTION, RESONANT RAMAN, REFLECTANCE DIFFERENCE SPECTROSCOPY, …

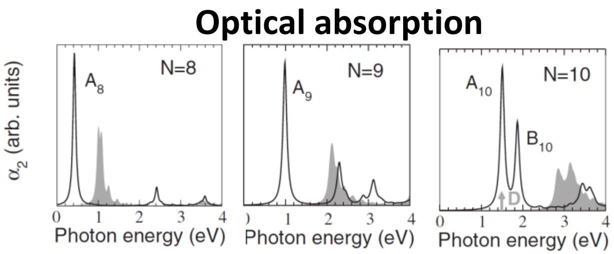
Yambo ©

Graphene nanoribbons

- ***Fundamental properties***

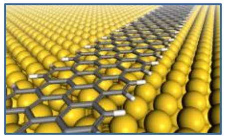
➡ *1D confinement effects*





- ***Simulation of electronic, optical, vibrational spectroscopies → REAL LIFE!***

  - *Substrate effects*



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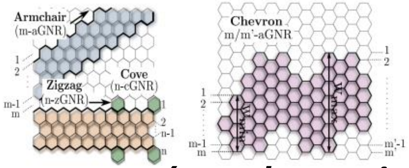
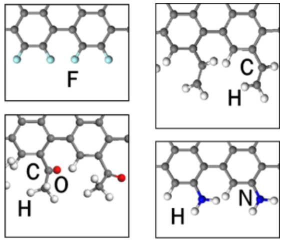
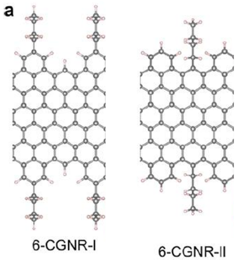


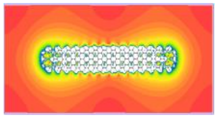
  - *Impact of functionalization groups (and position)*





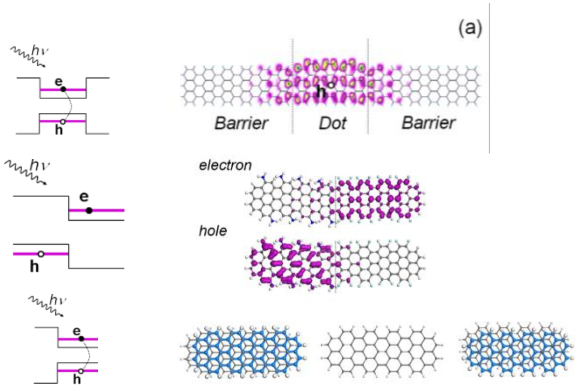
  - *Structural distortions*

  - *Finite-size effects*



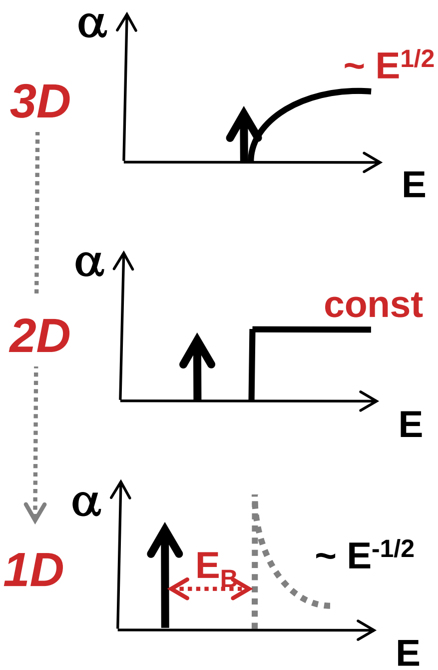
- ***Designing new structures, e.g. :***

  - *Width modulation*
  - *Edge functionalization*
  - *π-π aggregation*



Addressing optical excitations in low-D

Ideal low-D systems

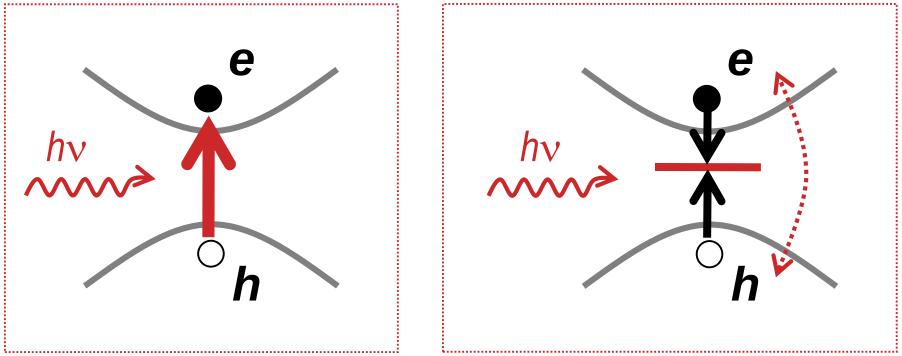


$E_B \rightarrow \infty$ for ideal **1D**

Suppression vHs

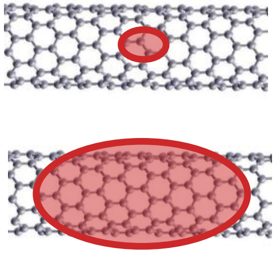
What about quasi-1D real systems?

→ Which nature of optical excitations?
Single-particle picture or excitons?

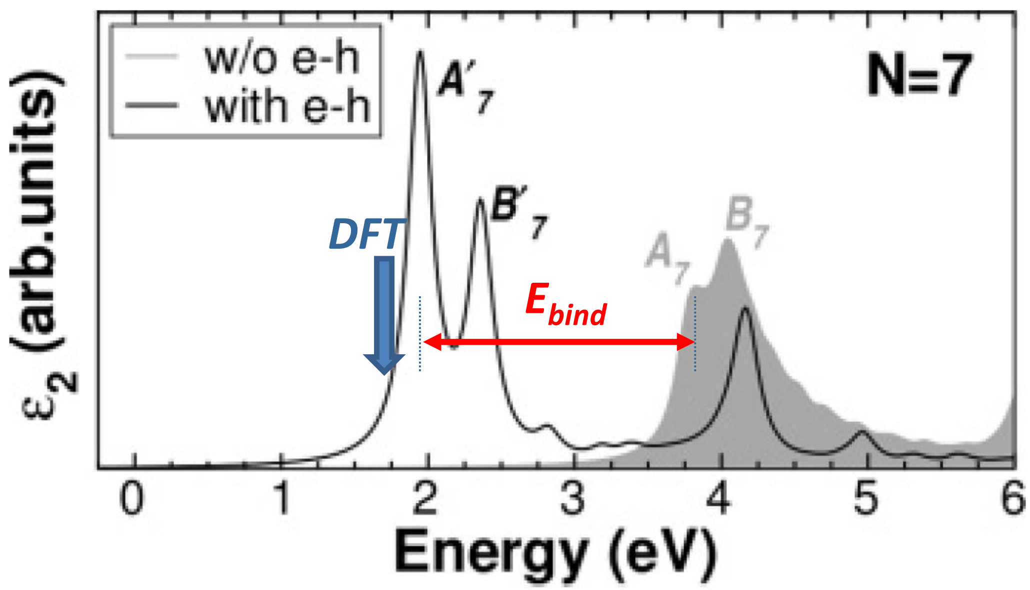


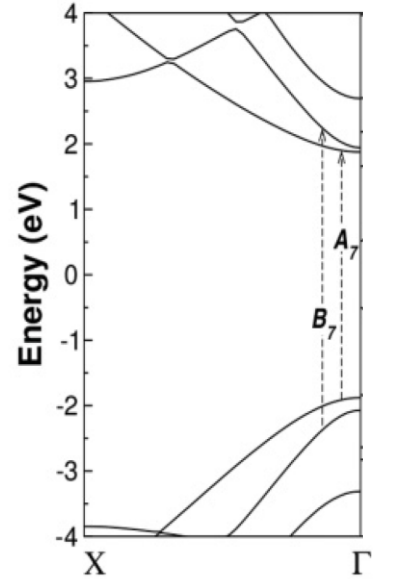
→ Magnitude of e-h interaction (E_B)?

→ Which kind of exciton?

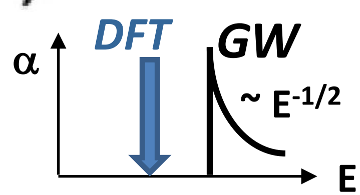


Many-body effects in GNRs



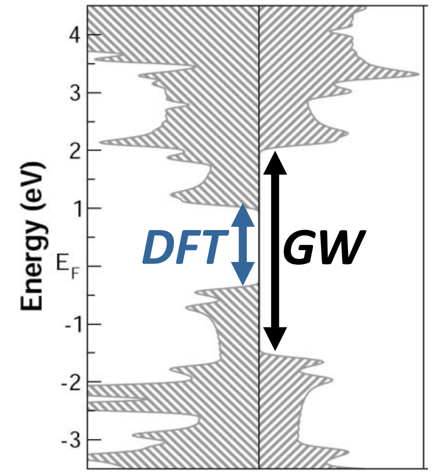


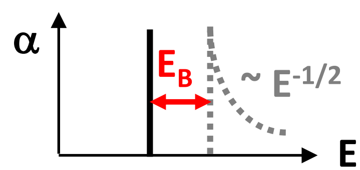
Without e-h (*GW*-RPA):



•$\mathbf{E^{-1/2}}$ singular behaviour in single-particle spectra

•Large QP corrections to E_{GAP} (GW vs. DFT)





With e-h (BSE):

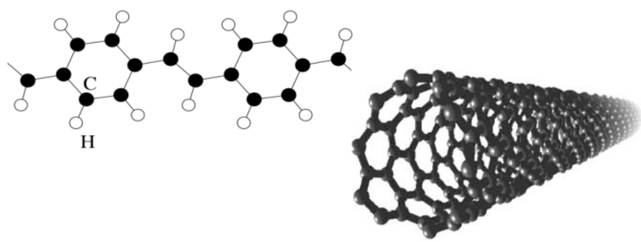
•Individual **excitonic** peaks below the continuum onset

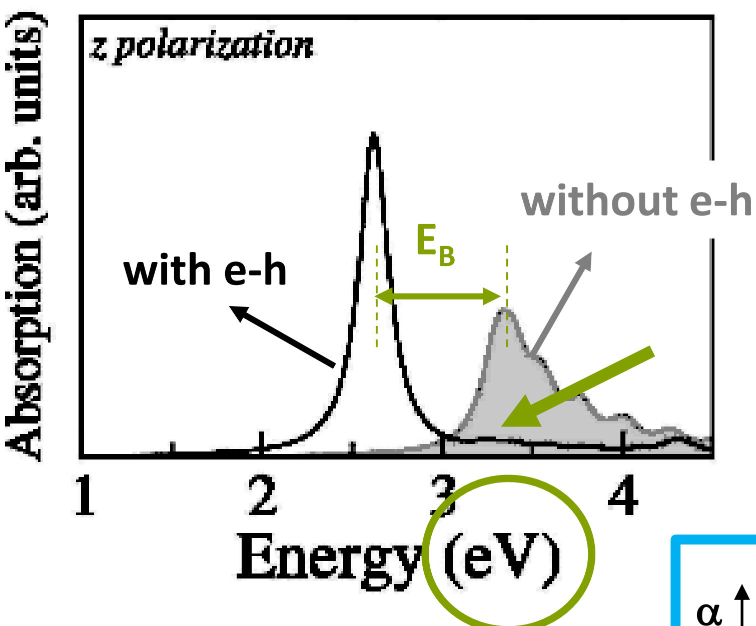
•Suppression of 1D van-Hove singularities

1D Confinement

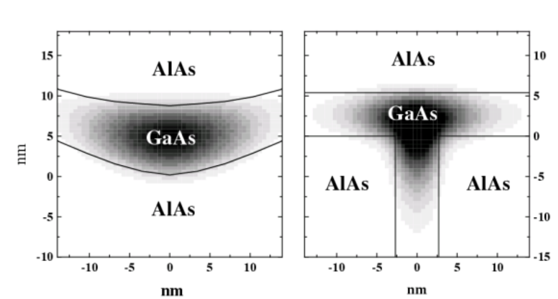
Confinement Effects in other 1D sysyems

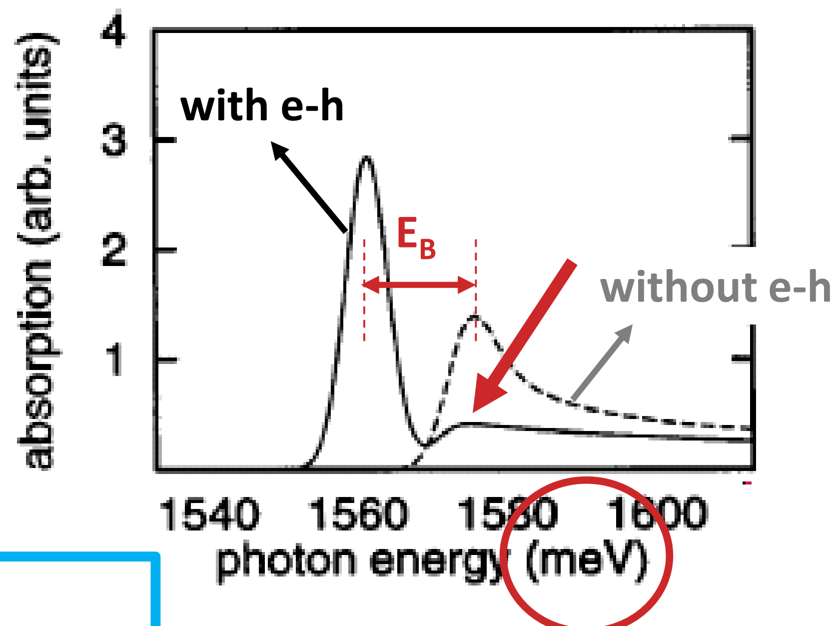
Polymers, Nanotubes

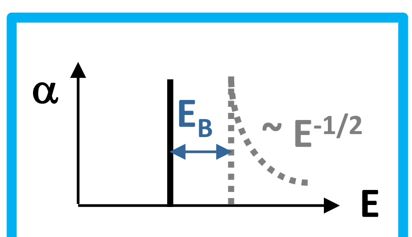




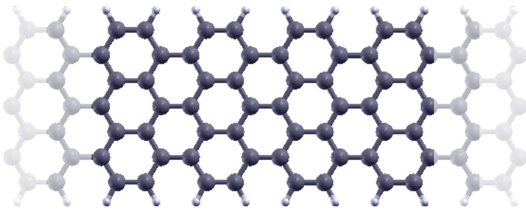
Quantum wires

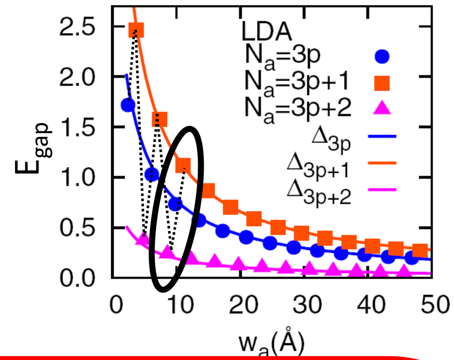






Optical Excitations



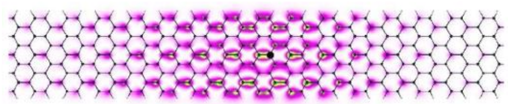


- **Strong excitonic effects**

  E_{bind} ~ 1 eV

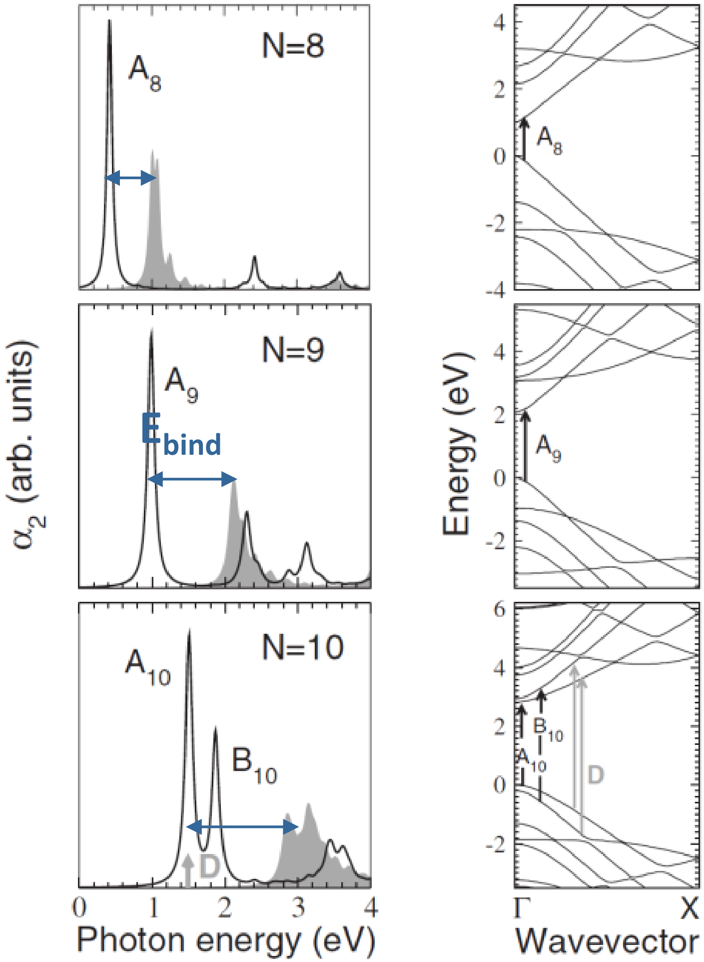
- **Wannier-like** bound excitons

  a_0 ~ 1 nm

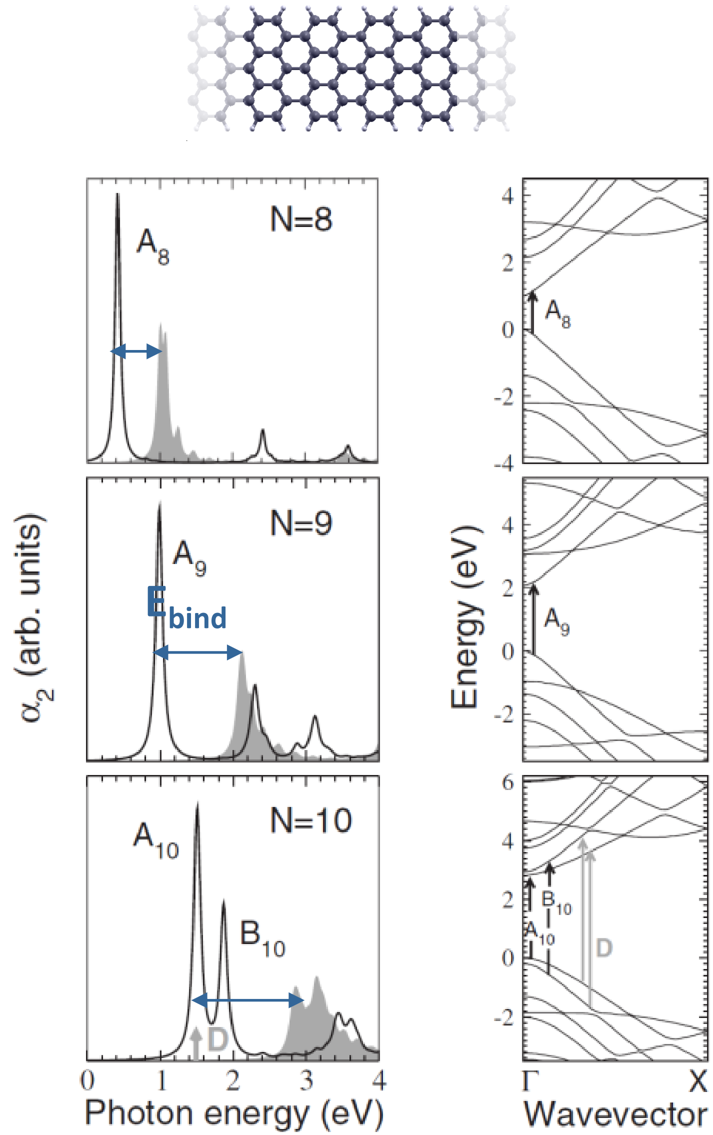


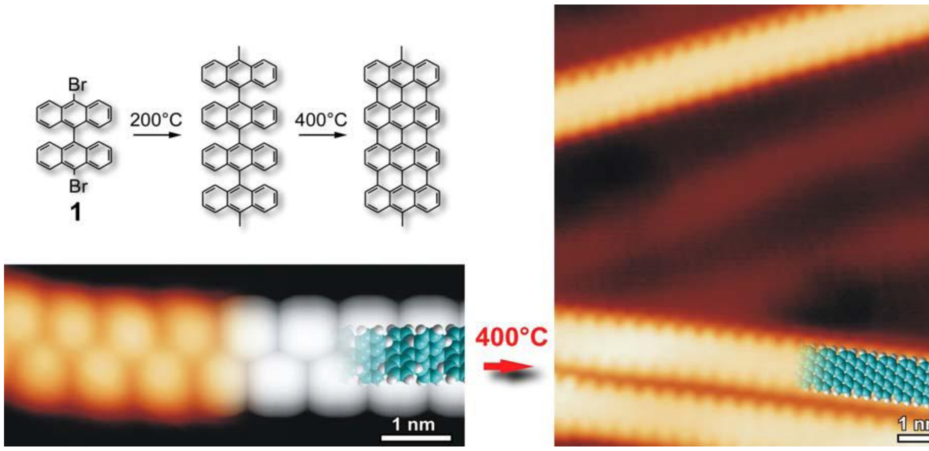
- **Family dependence** for $\mathbf{E_B}$ → ***Tunability***

  N=3p+1: doublet of optically active excitations + dark state

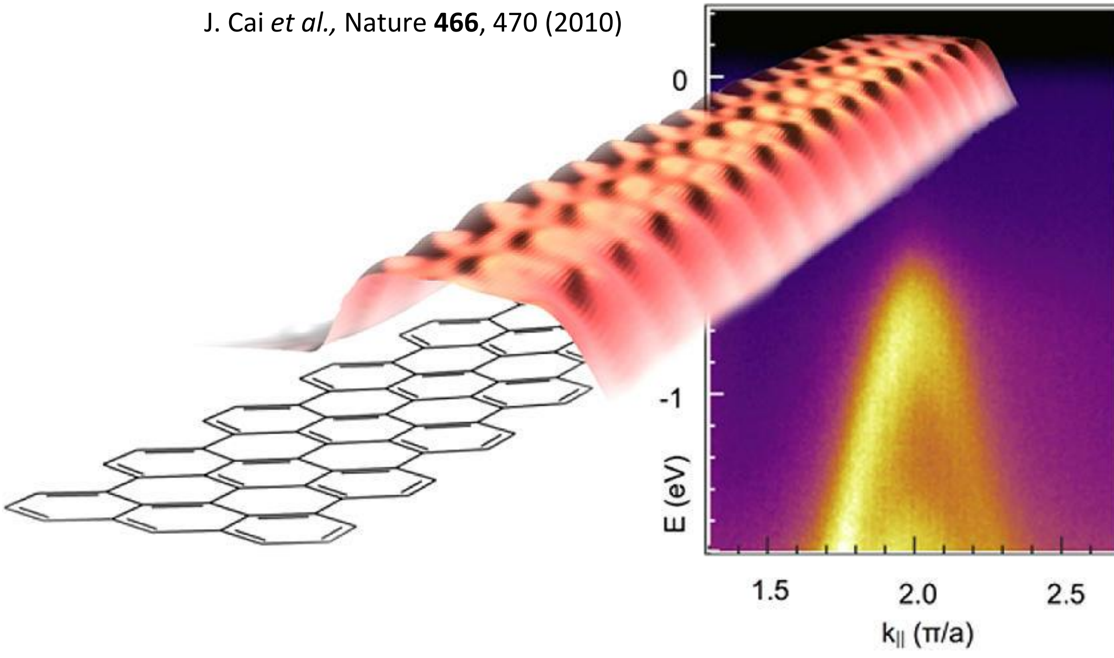


atomically precise ribbons were then produced!



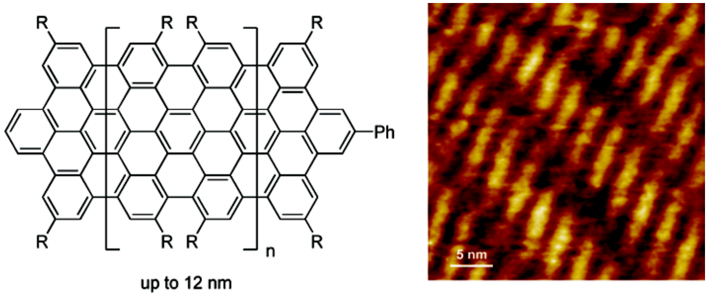


J. Cai *et al.*, Nature **466**, 470 (2010)

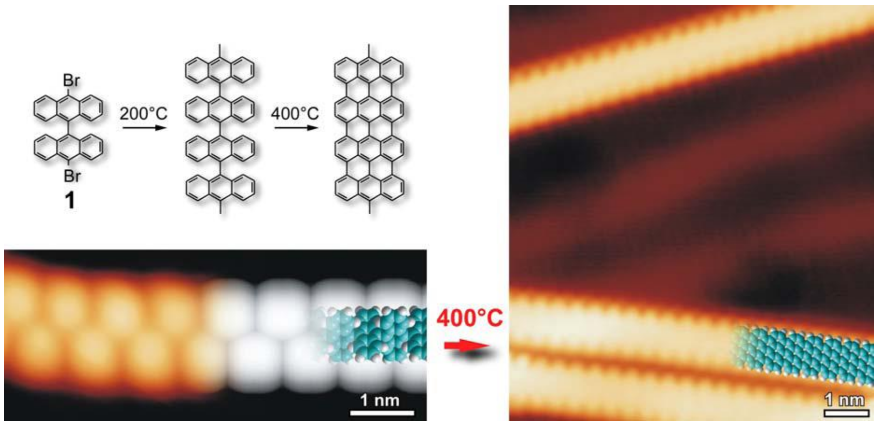


GNRs: Bottom-up Production Techniques

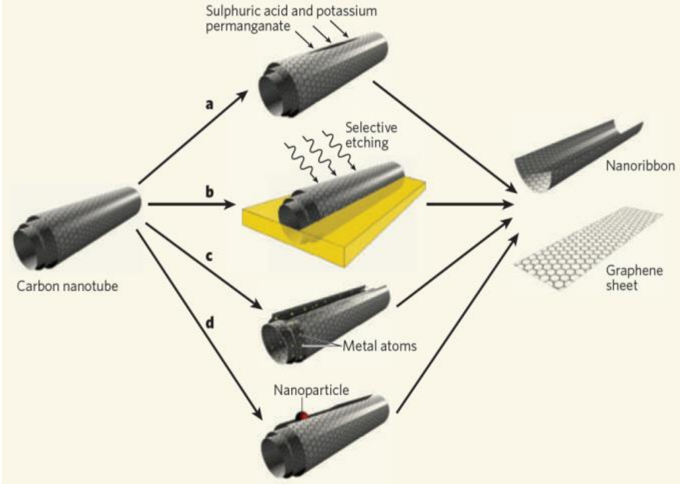
Controlled Synthesis of GNRs: ***nm-wide structures, edge control***



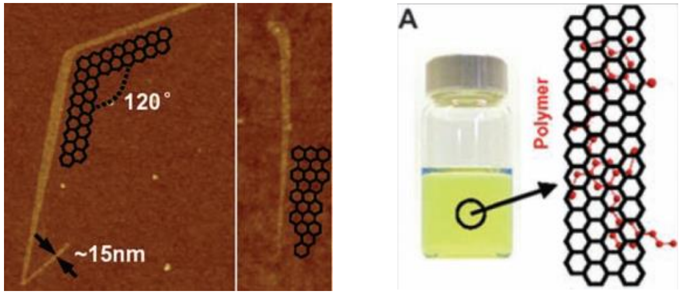
X. Yang *et al.,* JACS **130**, 4216 (2008)



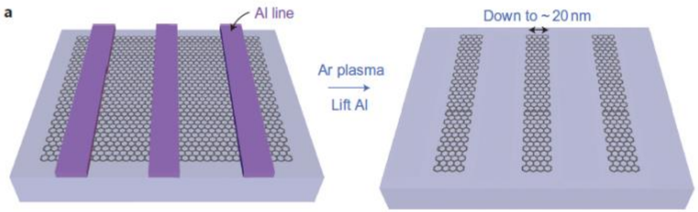
J. Cai *et al.,* Nature **466**, 470 (2010)



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

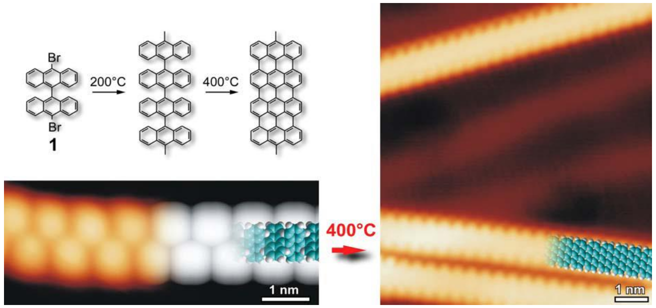


Science **319**, 1229 (2008)

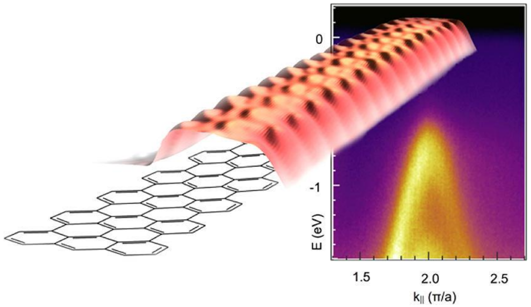


Wang & Dai Nature Chem. **2**, 661 (2010)

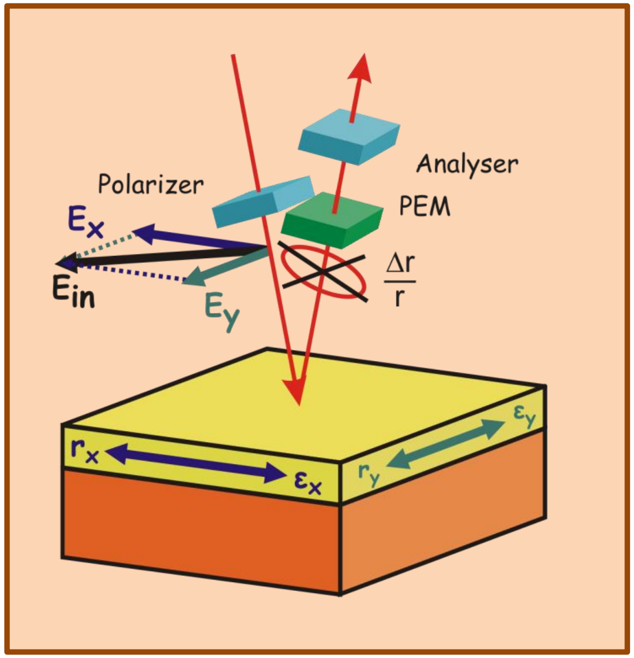
Not only atomically precise GNRs (2010)… but also optical measurements became available (2014)!



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



Reflectance Difference Spectroscopy: Measuring optical in-plane anisotropy during GNR growth



R. Denk *et al.,* Nature Comm. **5**, 4253 (2014)

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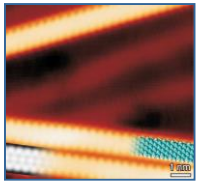
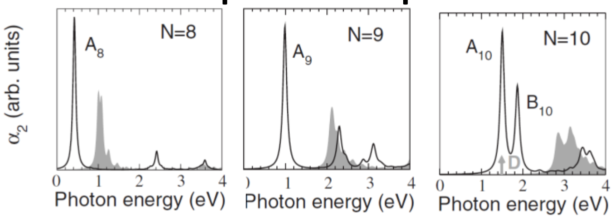
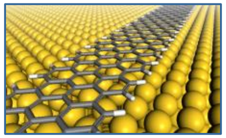


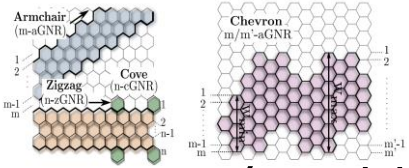


- ***Simulation of electronic, optical, vibrational spectroscopies → REAL LIFE!***

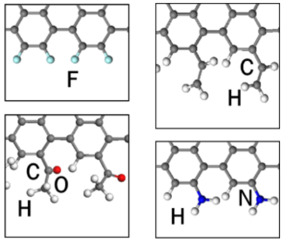
  - Substrate effects

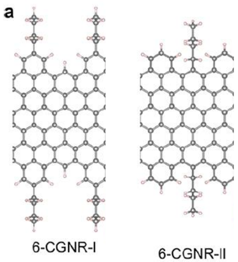


  - Edge-shape effects



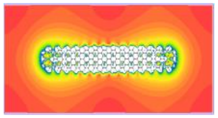
  - Impact of functionalization groups and position





  - Structural distortions

  - Finite-size effects

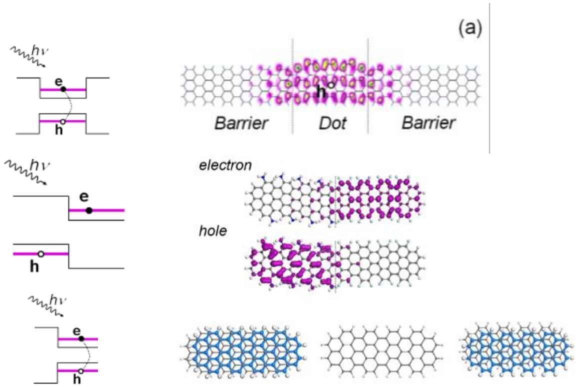


- ***Designing new structures, e.g. :***

  - Width modulation

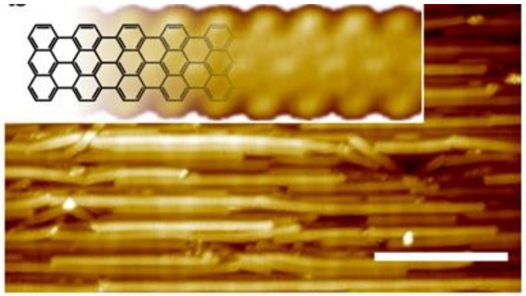
  - Edge functionalization

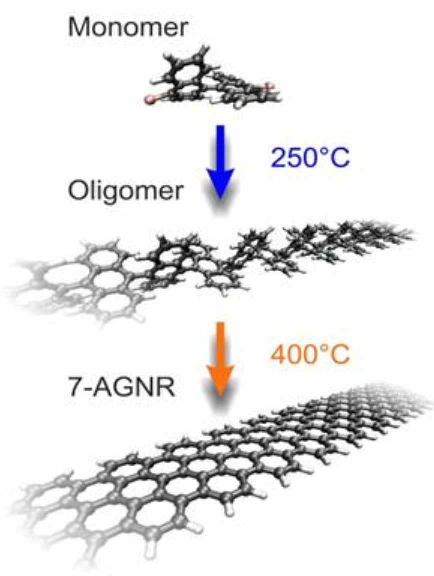
  - π-π aggregation



Optical properties

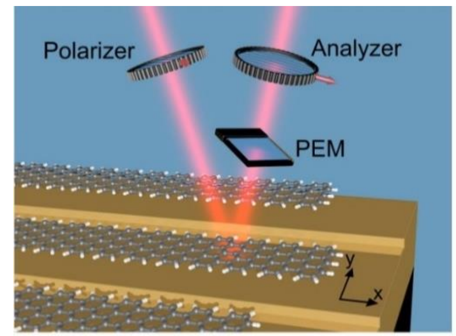
Precursors deposited on Au(788)

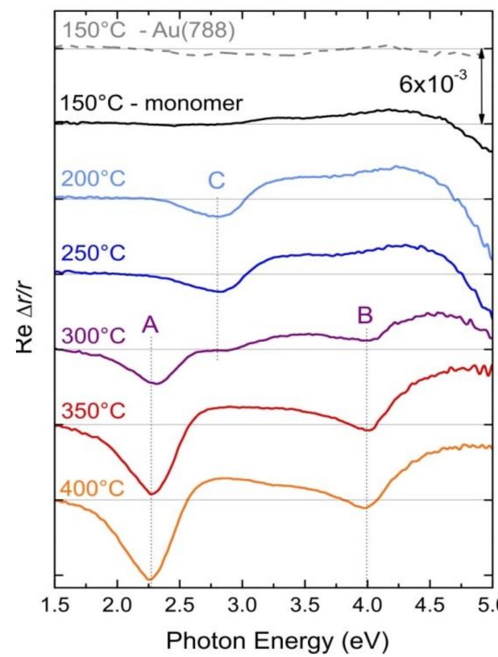




Reflectance Difference Spectroscopy

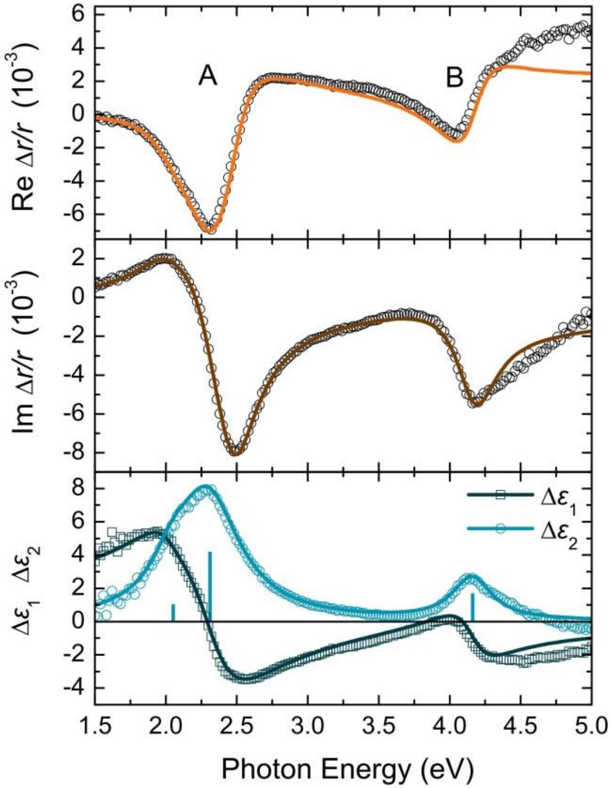
$$\frac{\Delta r}{r} = 2\frac{r_x - r_y}{r_x + r_y} = 2\frac{r_{[1\bar{1}0]} - r_{[001]}}{r_{[1\bar{1}0]} + r_{[001]}}$$



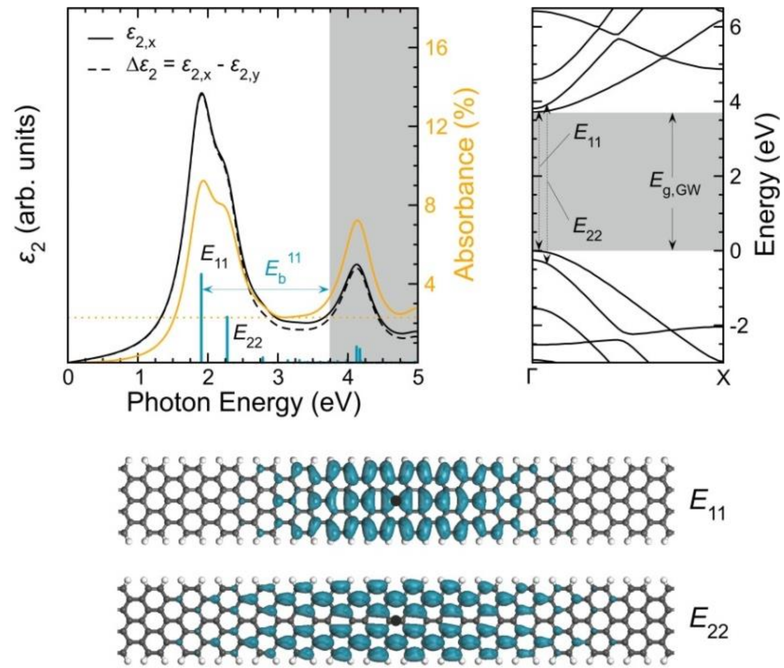


Optical properties of GNRs: Exp vs. Theo

RDS experiment



Theory

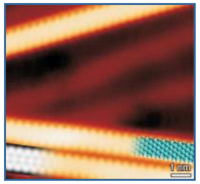


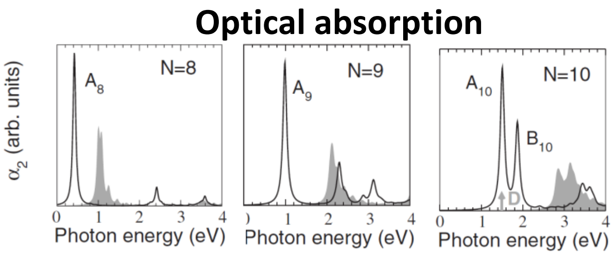
- Optical properties dominated by excitons
- Very good agreement theo↔exp ⇒ negligible substrate effects
- Large absorbance

Graphene nanoribbons

- ***Fundamental properties***

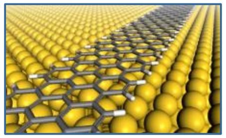
  - *1D confinement effects*



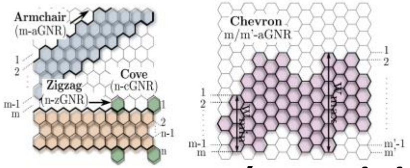


- ***Simulation of electronic, optical, vibrational spectroscopies → REAL LIFE!***

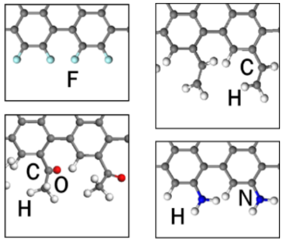
  - *Substrate effects*

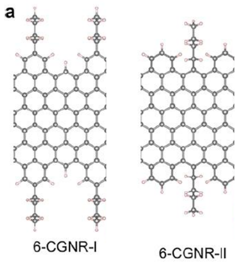


  - *Edge-shape effects*



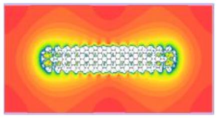
  - *Impact of functionalization groups and position*





  - *Structural distortions*

  - *Finite-size effects*



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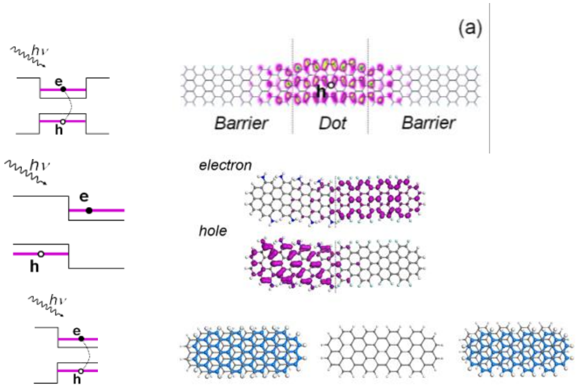
  - *Width modulation*
  - *Edge functionalization*
  - *π-π aggregation*

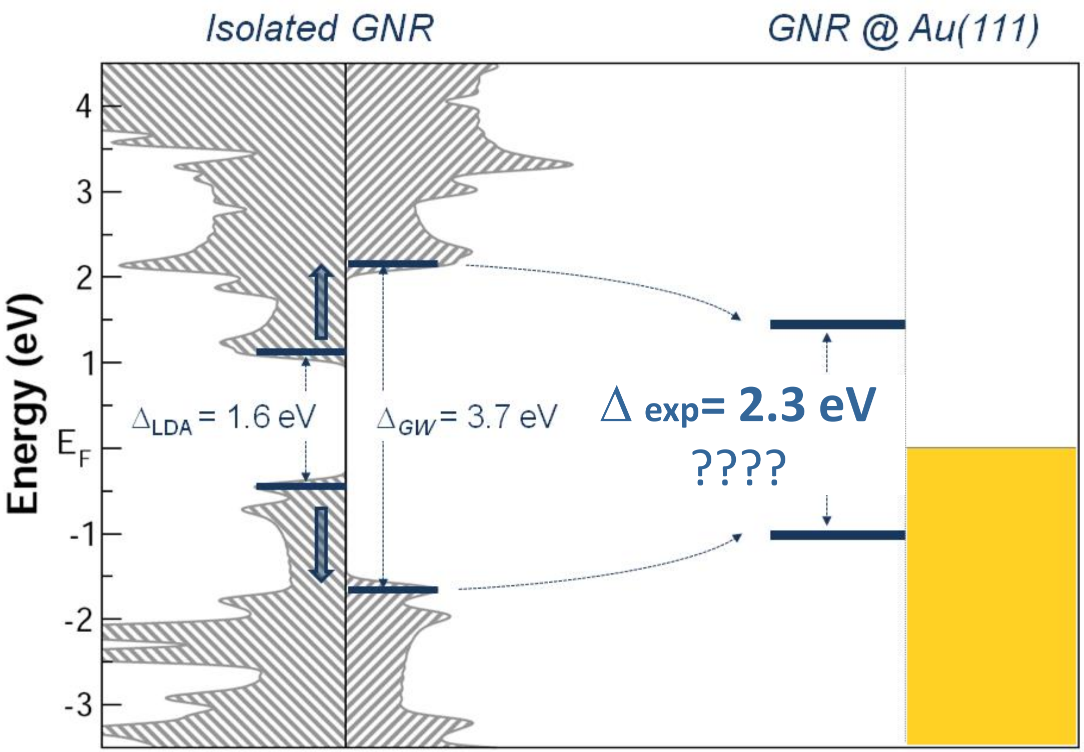


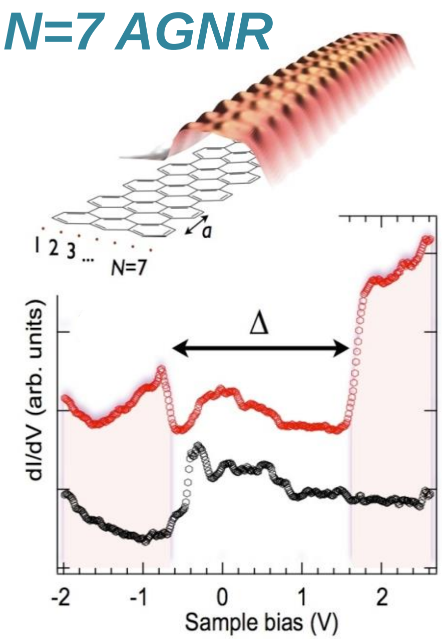
Which interpretation?

Table 1 | Electronic and optical properties of 7-AGNRs and PA oligomers.

	GW	Exp. (STS)
Transport band gap (eV)		
7-AGNR	3.7	2.3
PA oligomer	5.3	3.7
		Exp. (RDS)
Optical band gap (eV)		
7-AGNR		2.1/2.3
PA oligomer		3.0

Electronic band structure: substrate effects





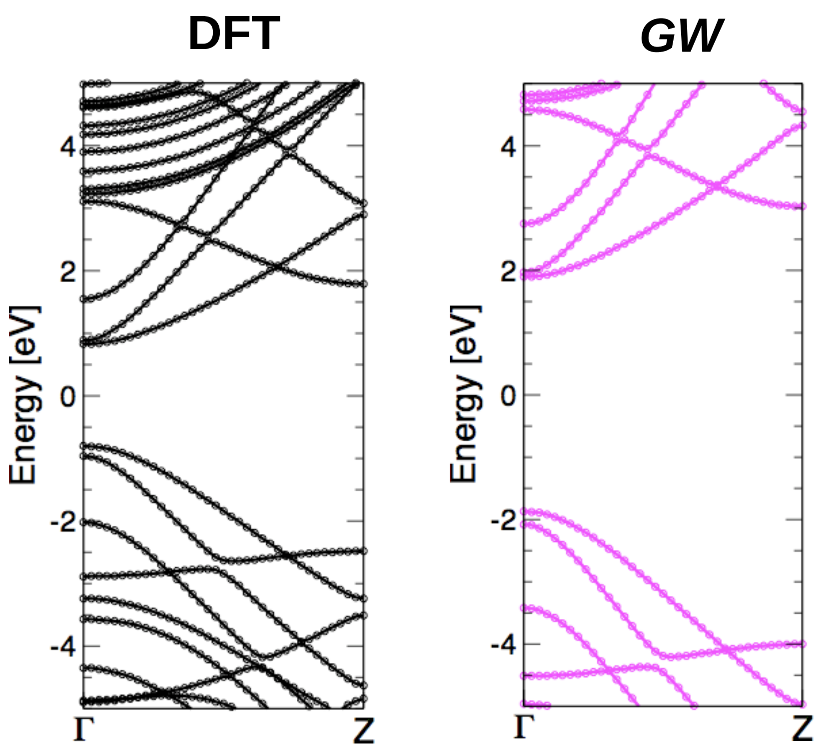
STS

GNR@Au(111)

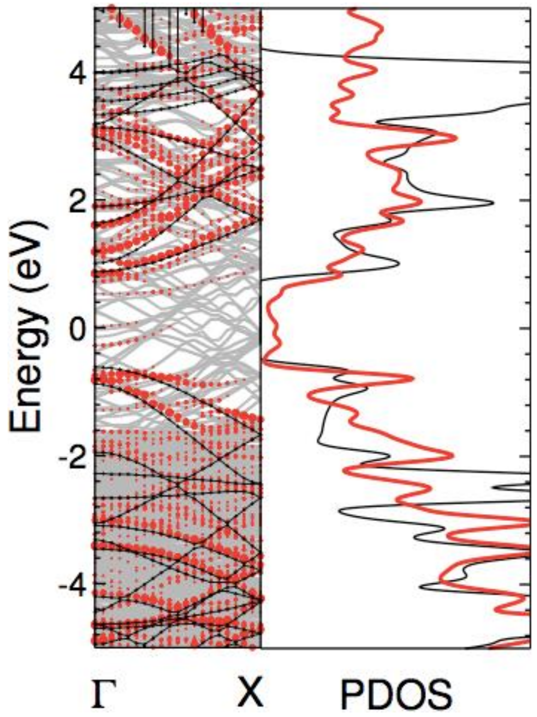
E_{gap} = 2.3 ± 0.1 eV

Electronic band structure: substrate effects

GAS-PHASE 7-AGNR



7-AGNR WITH AU SUBSTRATE



large quasi-particle corrections to the energy gap E_{LDA} = 1.6 eV → E_{GW} = 3.7 eV

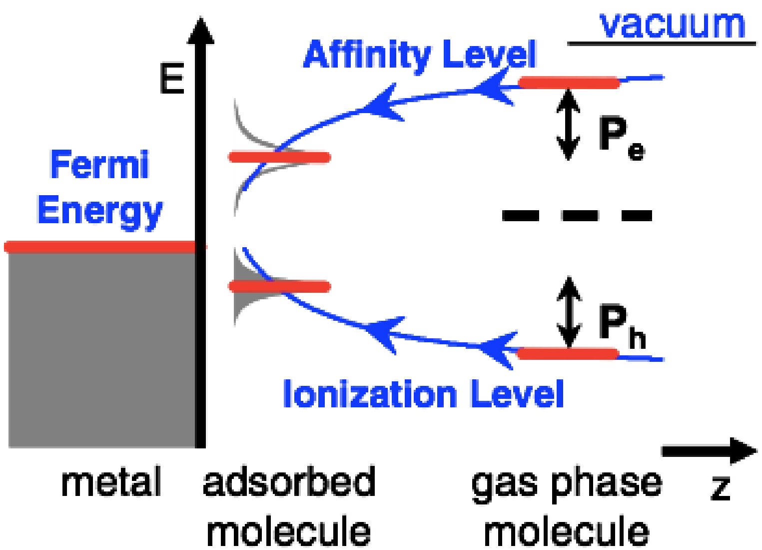
- confinement increases e-e interaction
- weak screening

A-GNR bands at Au(111) (**red**) very similar to gas phase (**black**)

- minimal hybridization effects
- substrate effects mostly due to surface polarizability → Image Charge Model!

Electronic band structure: substrate effects

J. Neaton et al., PRL 97, 216405 (2006)



L estimated from exciton wavefunction (BSE)

&

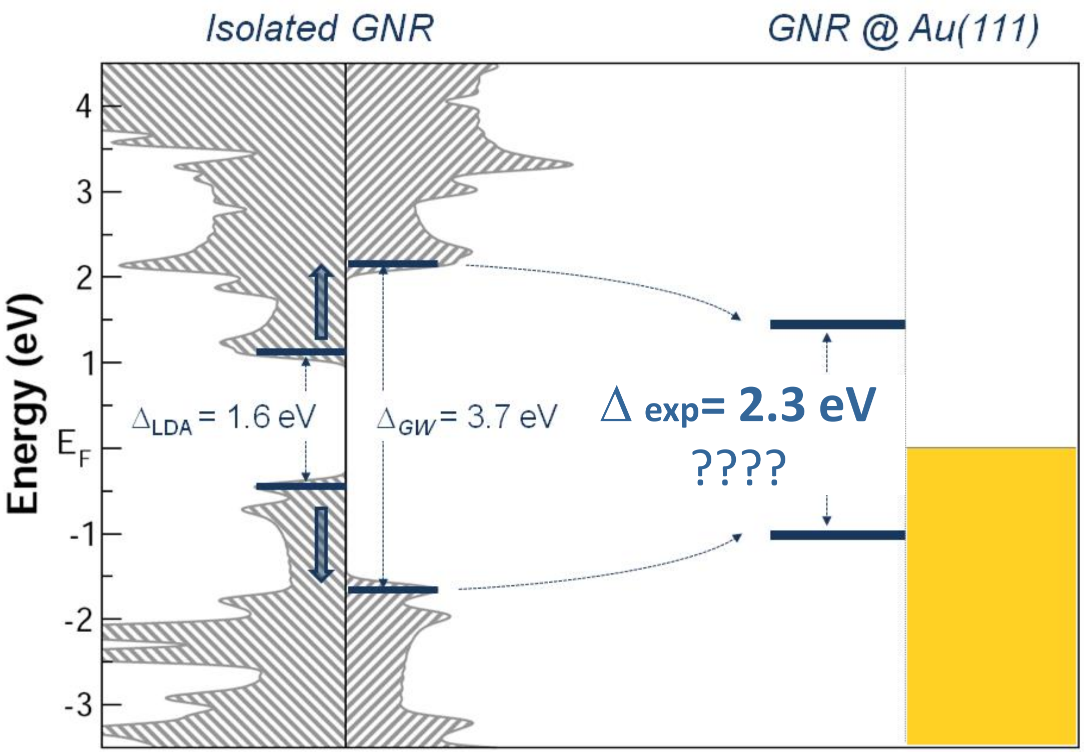
optical saturation length (excitons in finite ribbons)

Image charge model

- takes into account the polarization induced by the charged excitation of the system
- for finite systems, the charge distribution of the frontier orbitals (HOMO or LUMO) is described in terms of localized charges
- for extended systems, we need to define an effective (screening) length L of the excitation charge distribution

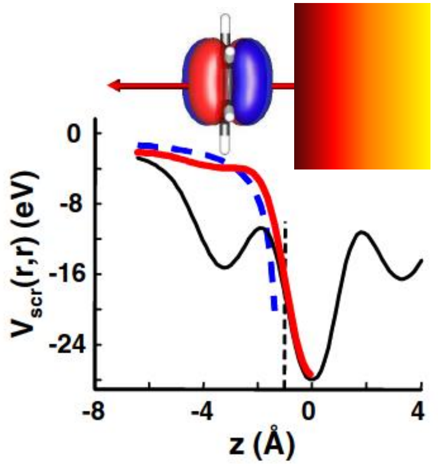
L ~ 30-60 Å

Electronic band structure: substrate effects



Effect of the metallic substrate

→The gap is reduced as an effect of the ***substrate polarization*** [See Neaton et al, PRL 97, 216405 (2006) – Fig. below]



Quasiparticle corrections

+ *Image Charge model*

Δ_{GW+IC} = 2.3 – 2.7 eV

Electronic and optical properties

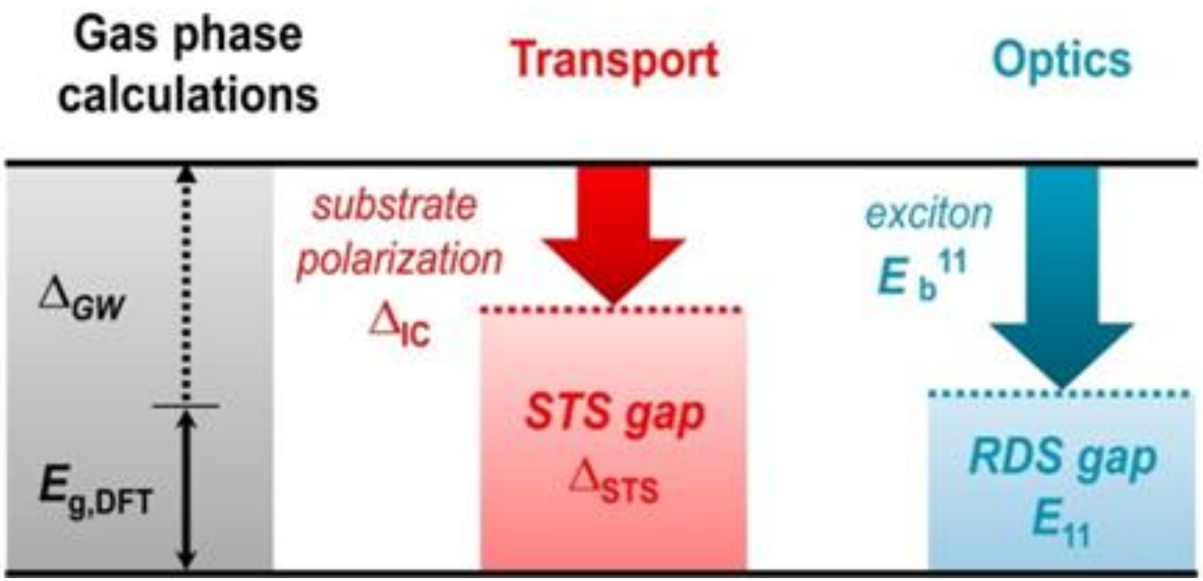


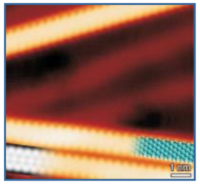
Table 1 | Electronic and optical properties of 7-AGNRs and PA oligomers.

	GW	**IC corr.**	**GW + IC corr.**	**Exp. (STS)**
Transport band gap (eV)				
7-AGNR	3.7	1.0–1.4	2.3–2.7	2.3
PA oligomer	5.3	1.0–1.4	3.9–4.3	3.7
		$E_b^{11/22}$	**GW + BSE**	**Exp. (RDS)**
Optical band gap (eV)				
7-AGNR		1.8/1.4	1.9/2.3	2.1/2.3
PA oligomer		2.3/2.1	3.0/3.2	3.0

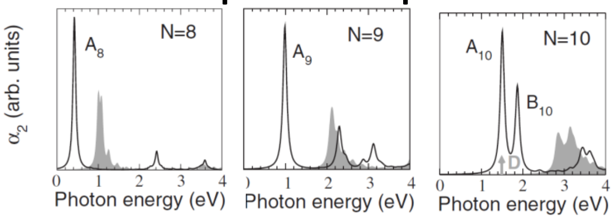
Graphene nanoribbons

- ***Fundamental properties***

  - 1D confinement effects

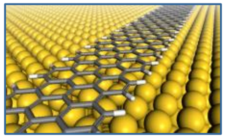


Optical absorption

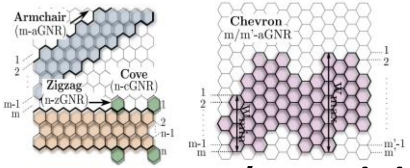


- ***Simulation of electronic, optical, vibrational spectroscopies → REAL LIFE!***

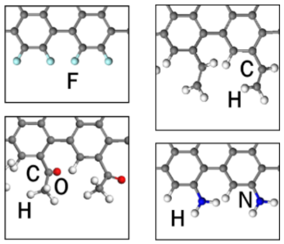
  - Substrate effects

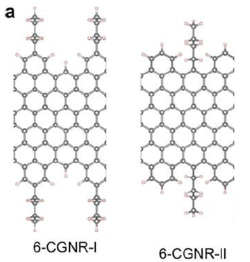


  - Edge-shape effects



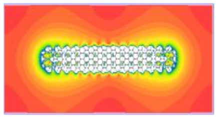
  - Impact of functionalization groups and position





  - Structural distortions

  - Finite-size effects



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  - Width modulation

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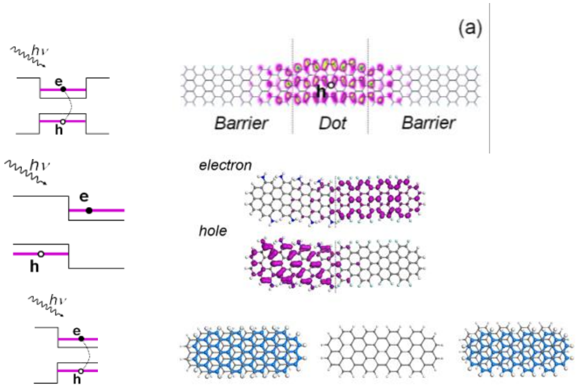
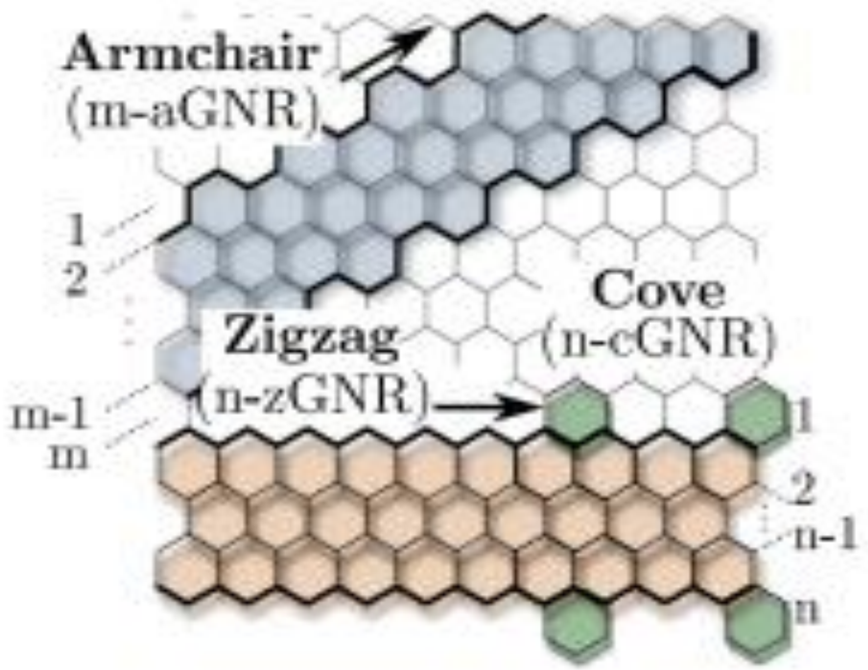
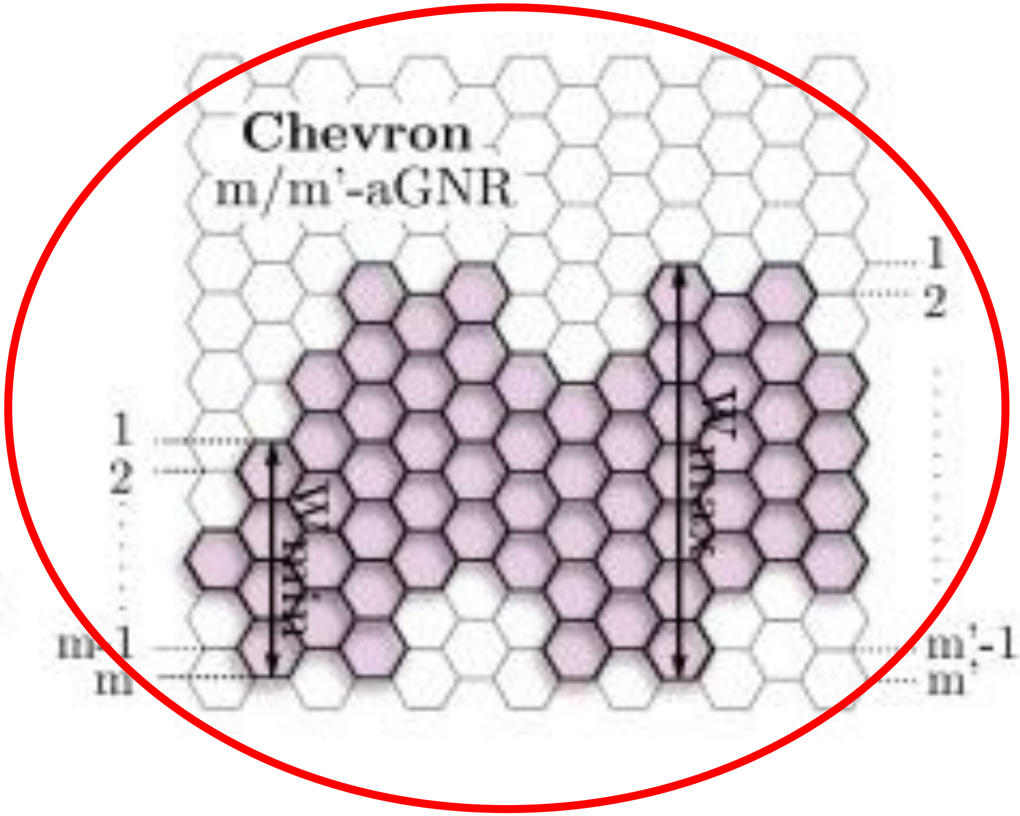
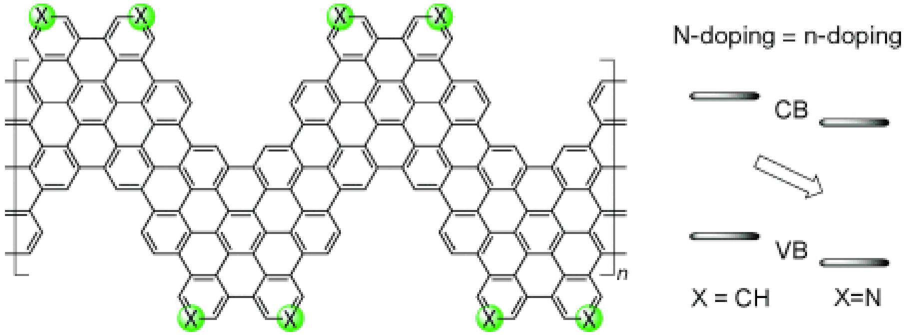
  - π-π aggregation



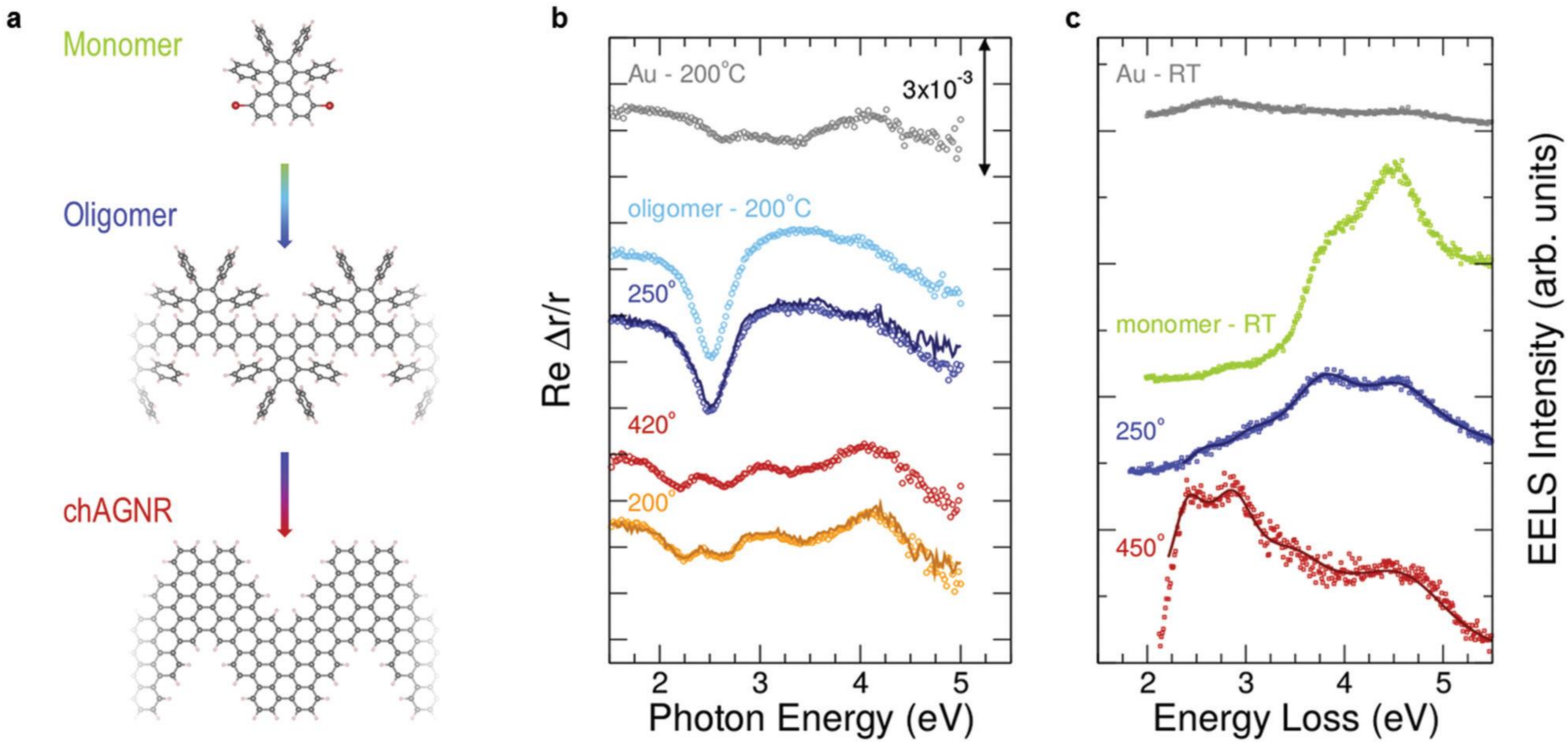
Several possible edge shapes beyond straight-edge aGNRs and zGNRs!







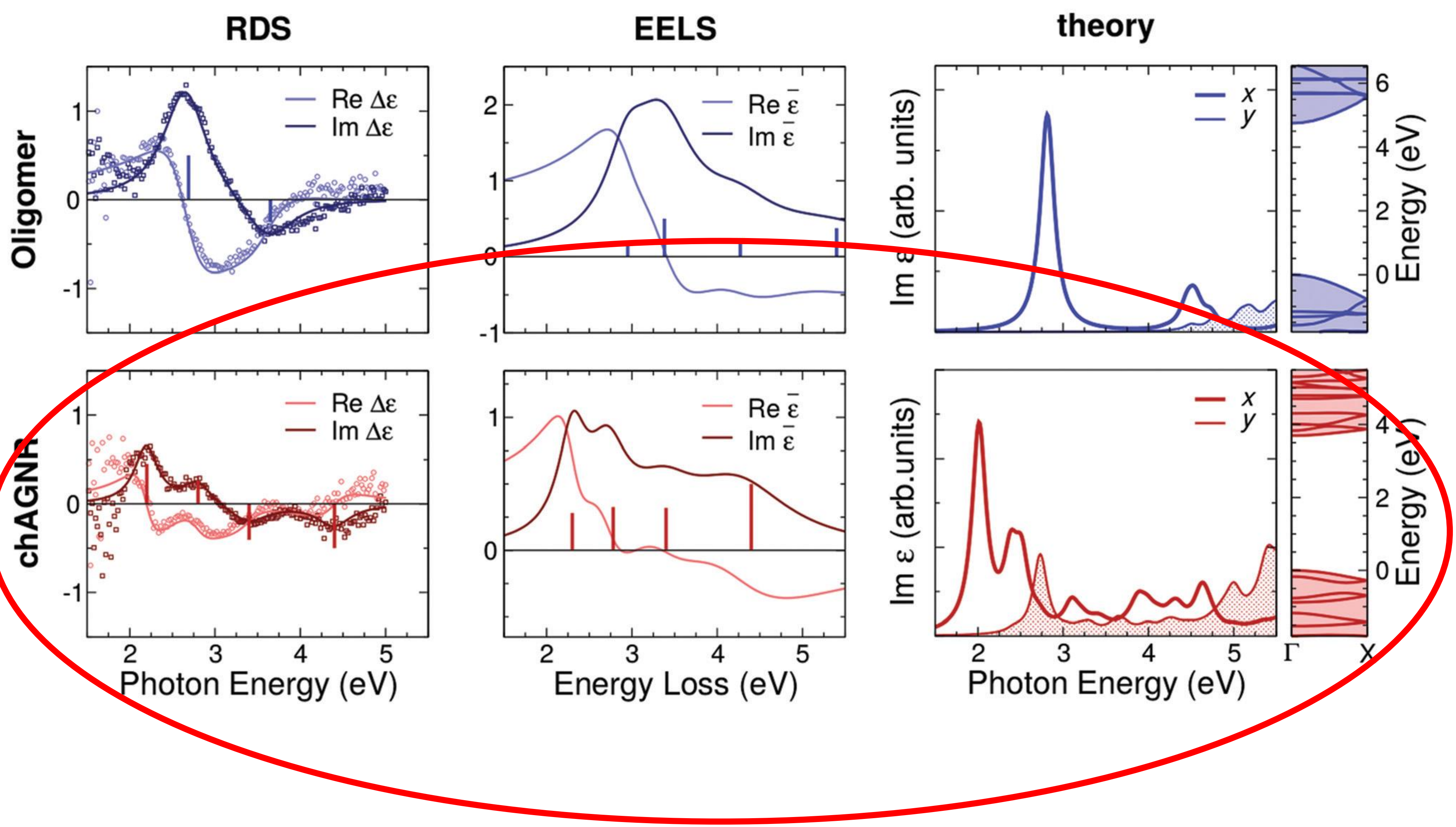
Chevron-like armchair GNRs



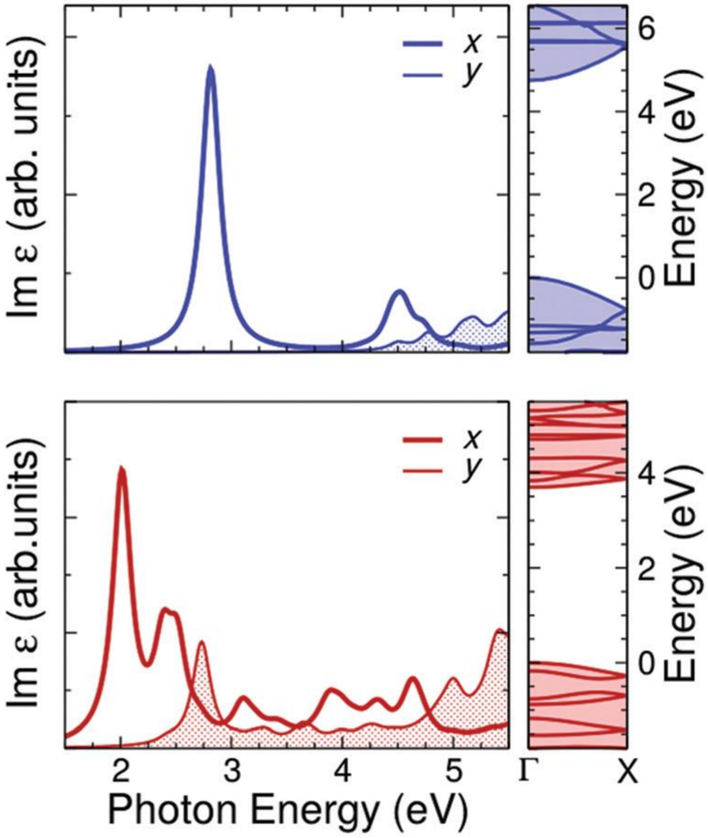
- *Still strong 1D fingerprints?*

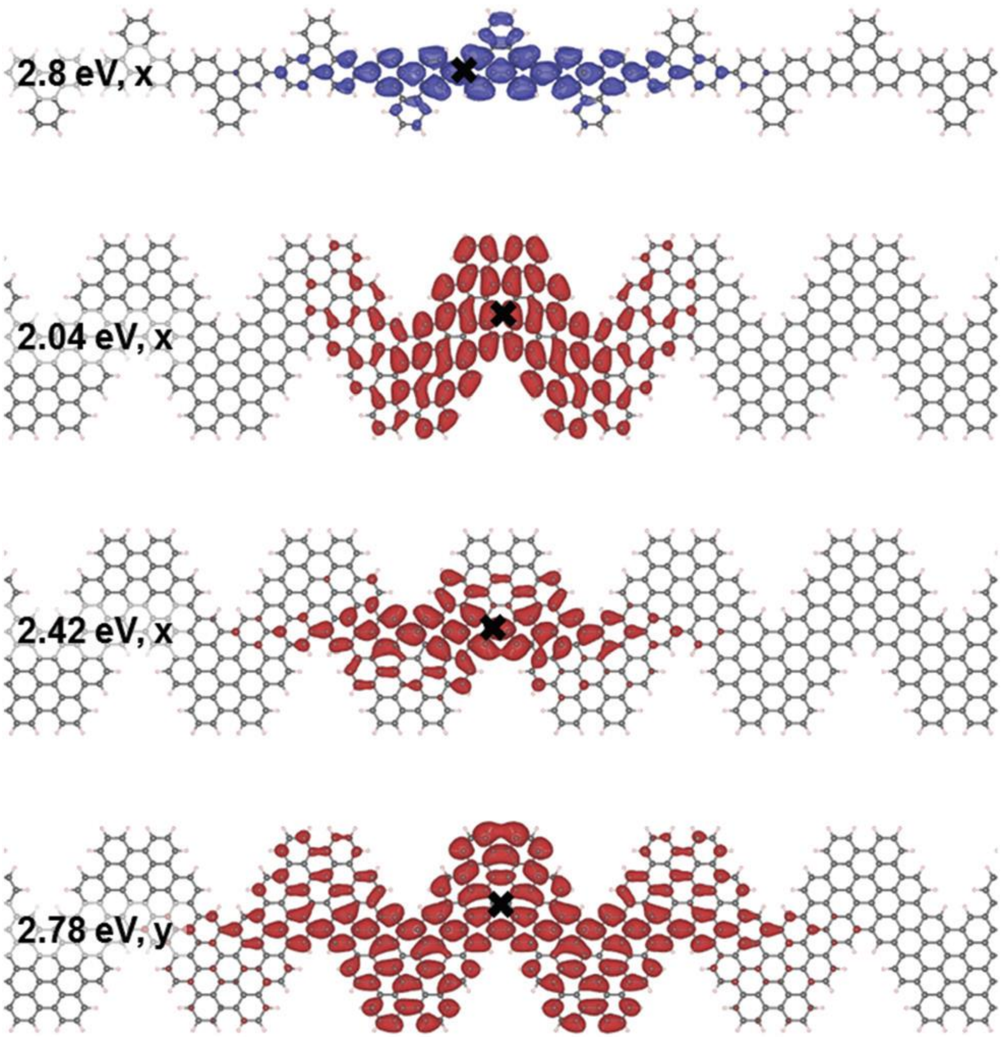
- *Different spectroscopies in comparison*

Theo vs. Exp for Chevron oligomers and GNRs



Rationale from MBPT for chevron oligomers and GNRs





Graphene nanoribbons

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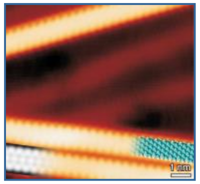
  - 1D confinement effects



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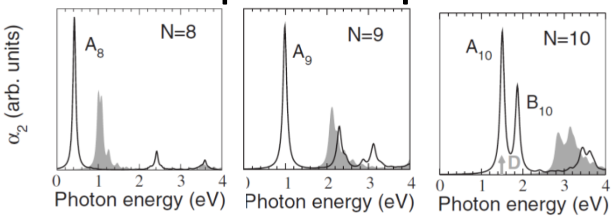
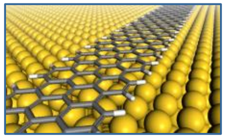


- ***Simulation of electronic, optical, vibrational spectroscopies → REAL LIFE!***

  - Substrate effects



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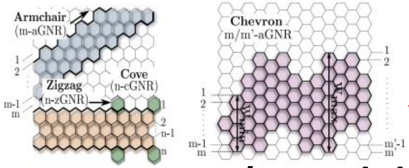

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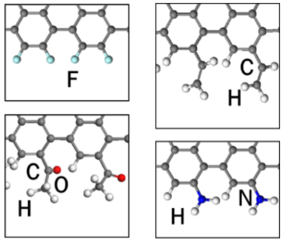

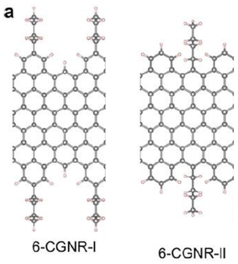

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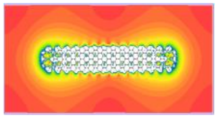

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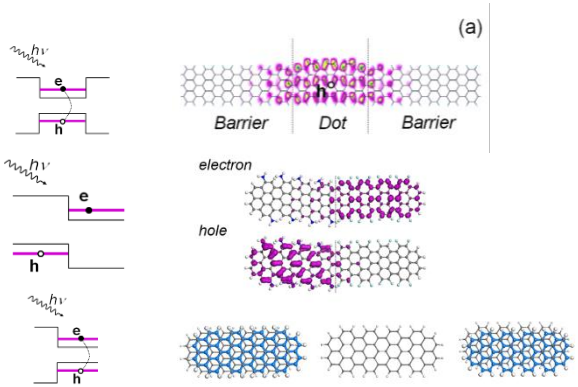
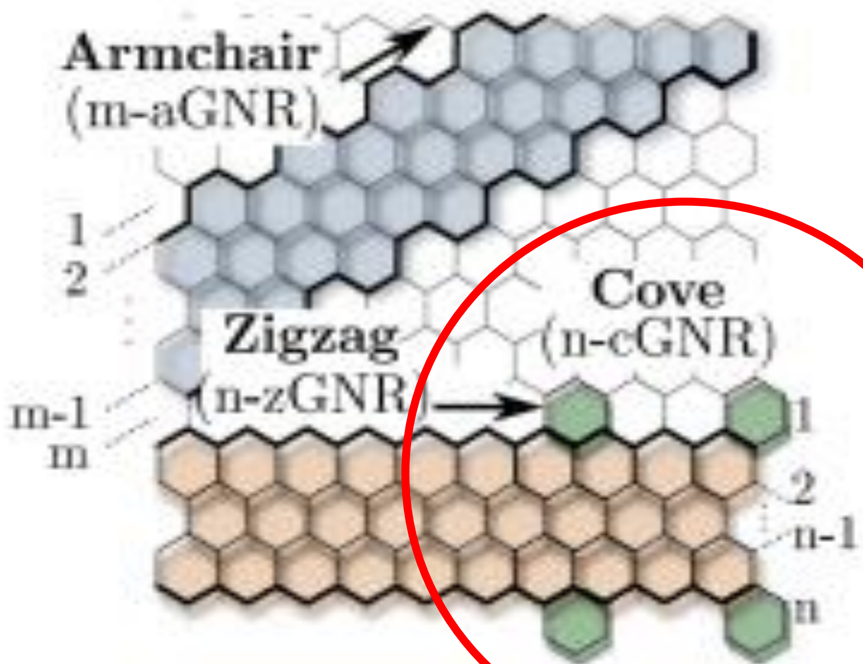
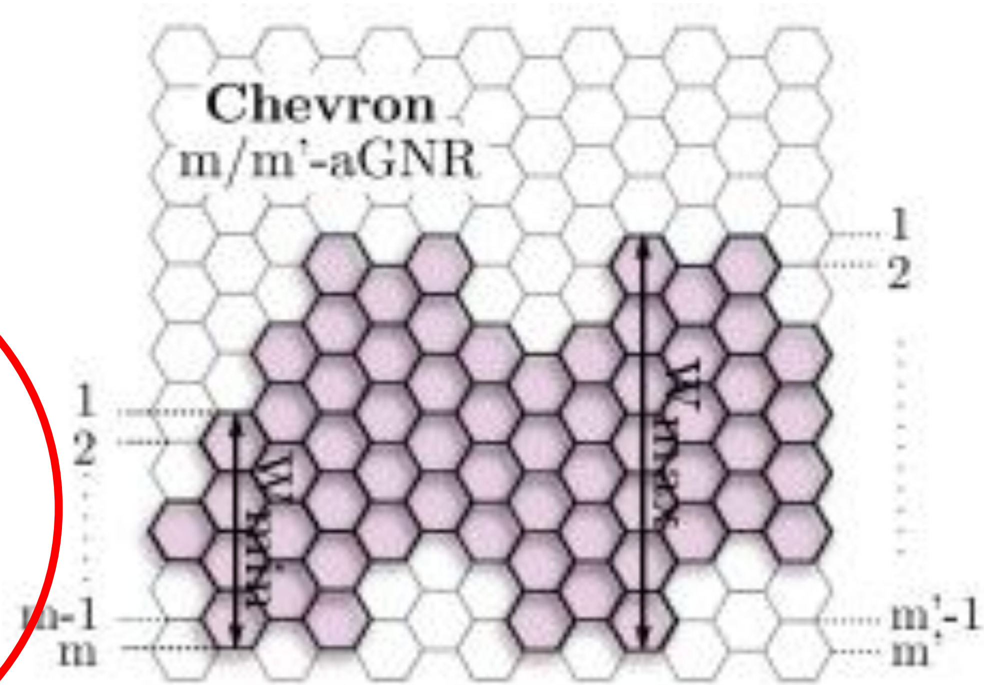
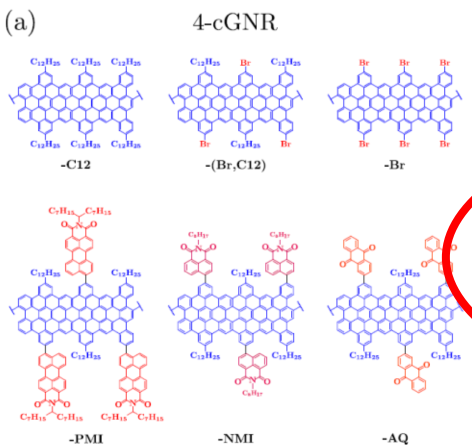
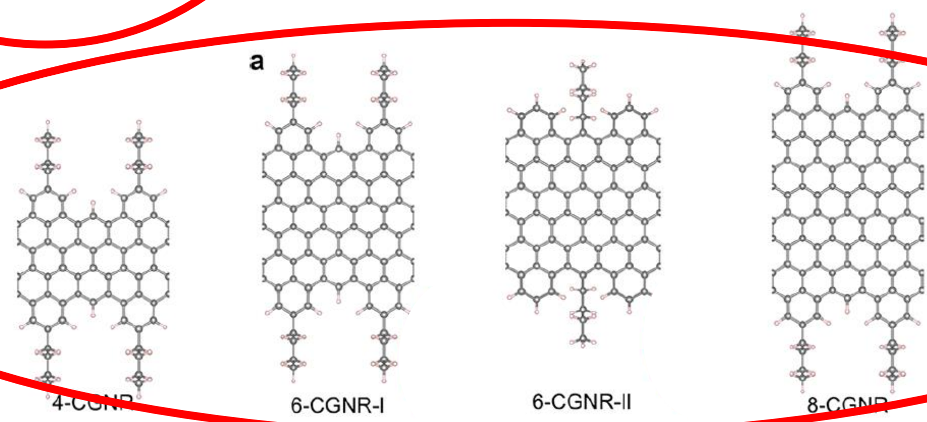


Several possible edge shapes beyond straight-edge aGNRs and zGNRs!

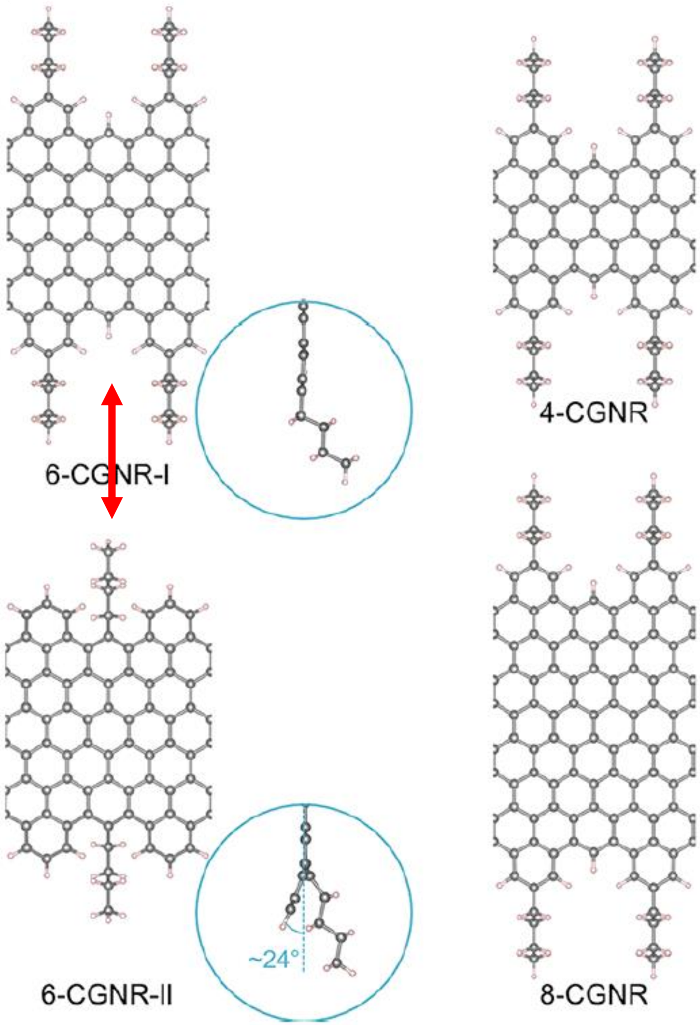


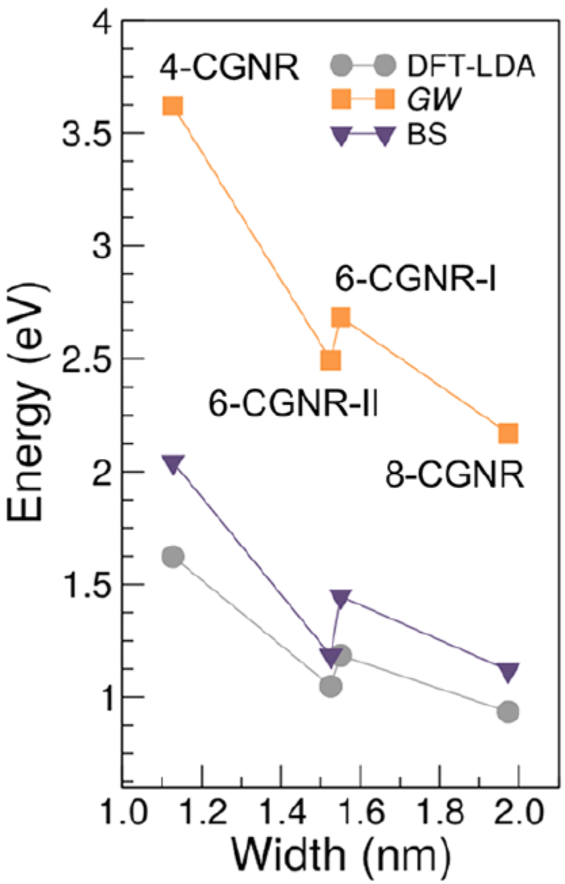




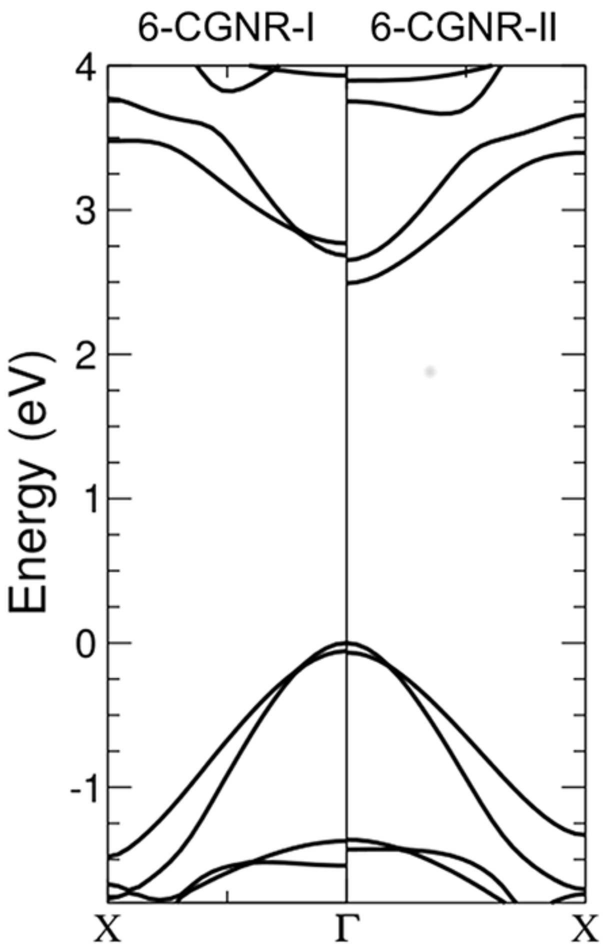


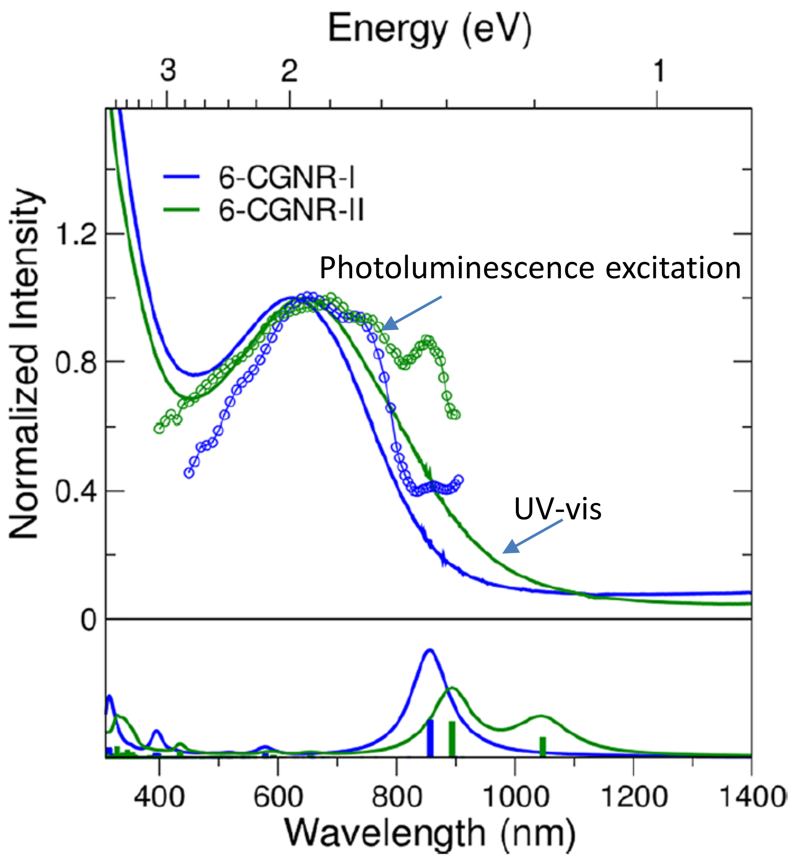
Cove-shaped GNRs





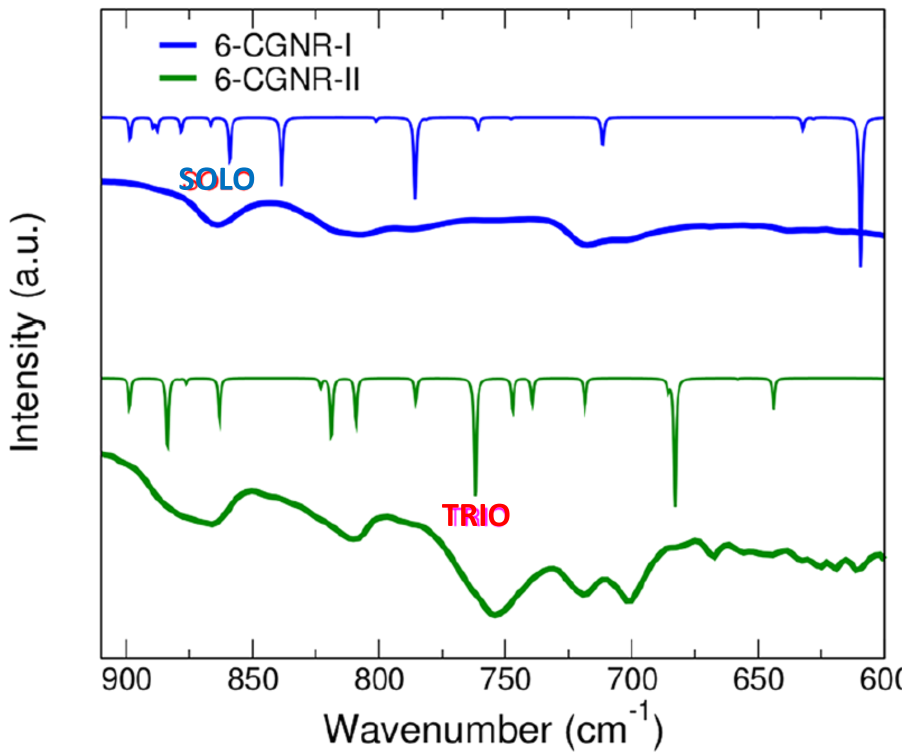
Electronic and optical properties of cove-shaped GNRs

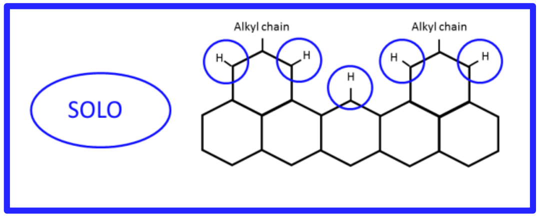


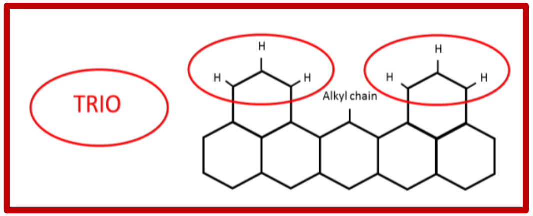


- The overall spectral feaures agree, two separate optical transitions for CGNR-II
- This behavior can be traced back to occurring band inversion
- Theoretical peaks are slightly red-shifted

Vobrational signatures for cove-shaped GNRs



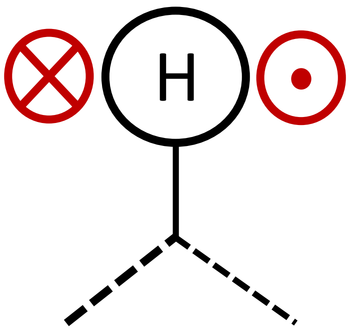


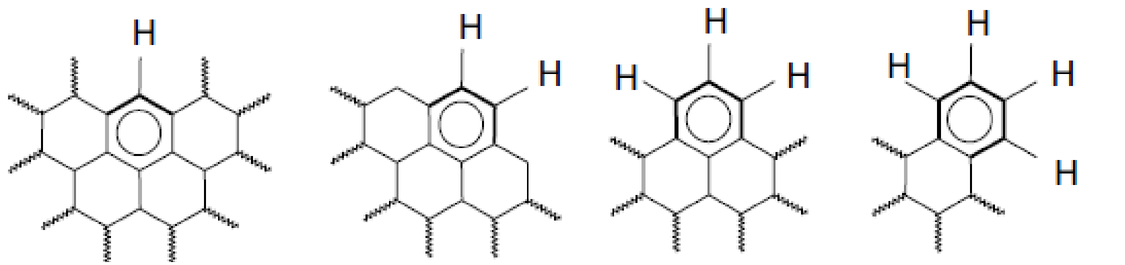


- The two structures can be fingerprinted through the TRIO mode
- The overall good agreement theo-exp supports the successful synthesis and the structural variation

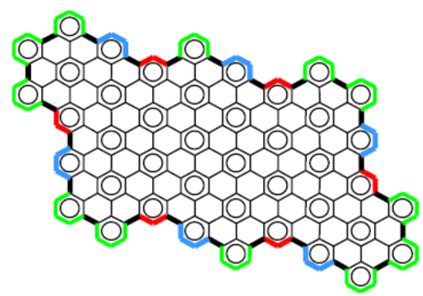
C-H wagging signatures in IR spectrum of nanographene

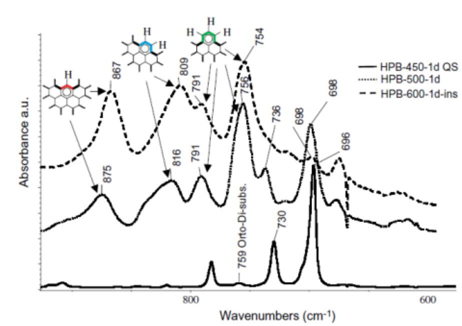
C-H Wagging





SOLO	DUO	TRIO	QUATRO
860-910 cm^{-1}	800-860 cm^{-1}	750-800 cm^{-1}	730-770 cm^{-1}

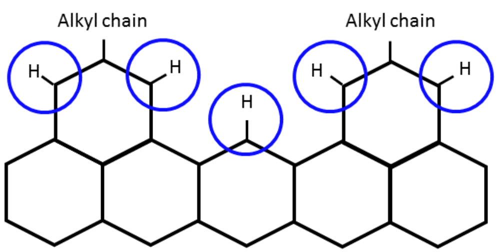




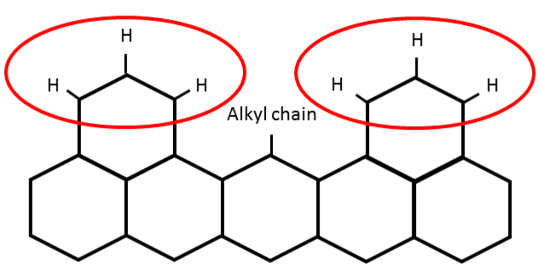
Centrone et al., Carbon 43, 1593 (2005)

In the CNR case:

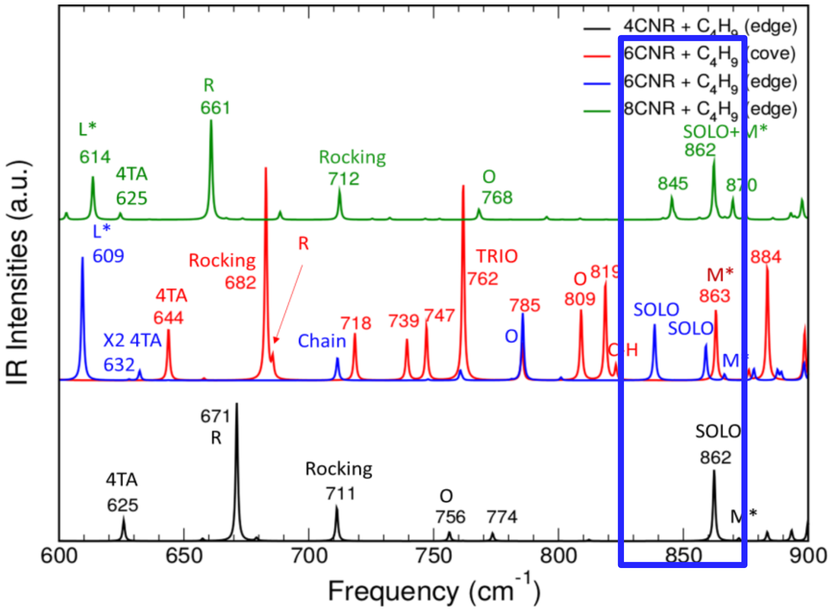
SOLO

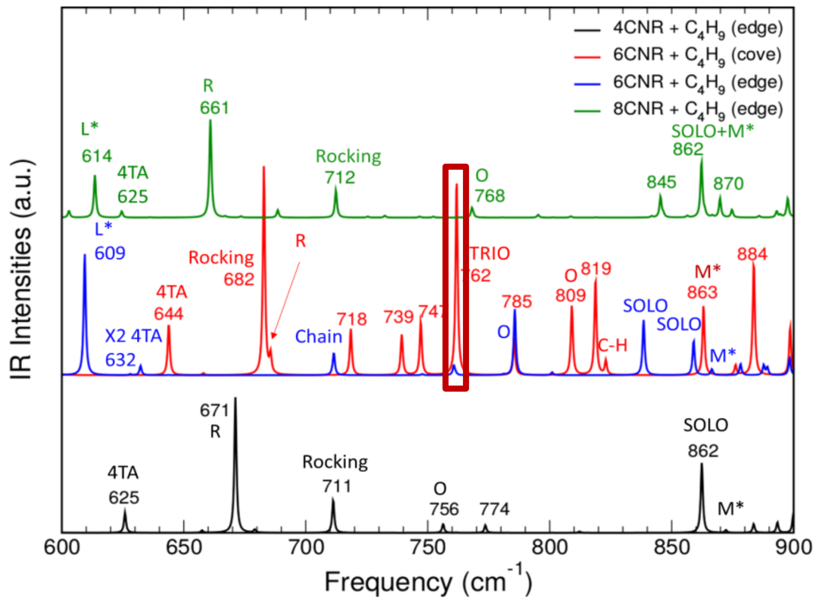


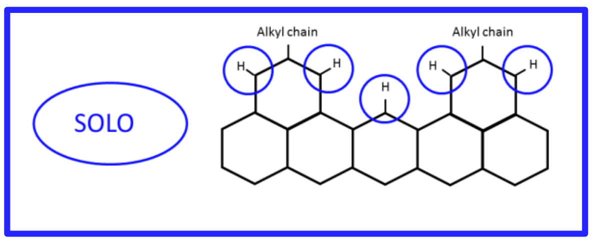
TRIO

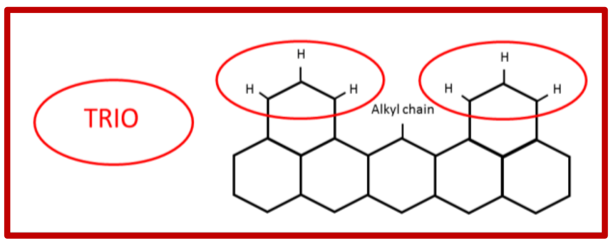


Vibrational IR signatures for cove-shaped GNRs







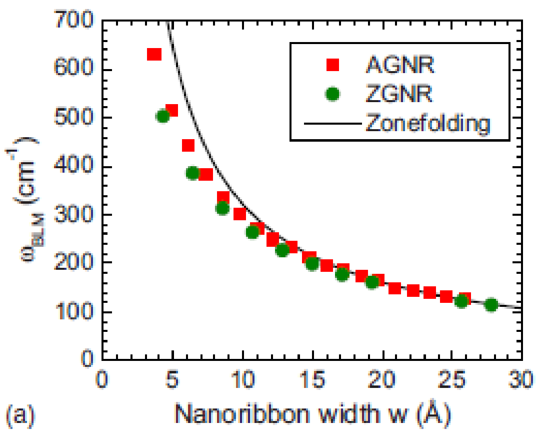


The peak at 863 cm^{-1} is connected to the wagging of C-H in SOLO position

The peak at 769 cm^{-1} is connected to the wagging of C-H in TRIO position

Raman fingerprints for GNRs

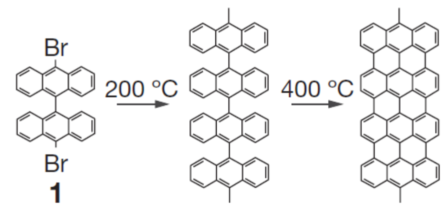
Theory

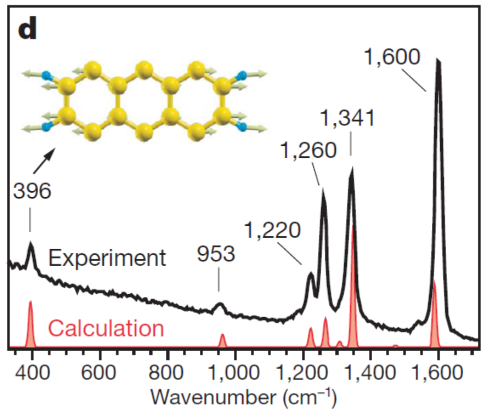


$$\omega_{\rm BLM} = \frac{a\pi}{w} = \frac{3222\ \text{Å cm}^{-1}}{w}.$$

Gillen et al, PRB 80, 155814 (2009); PRB 81, 205426 (2010)

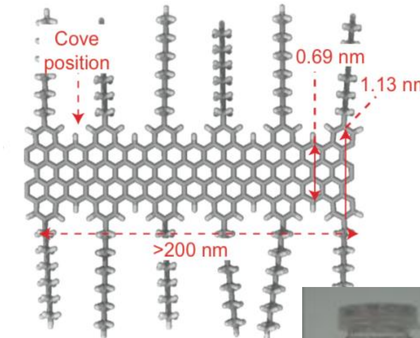
A-GNRs @ Au(111)

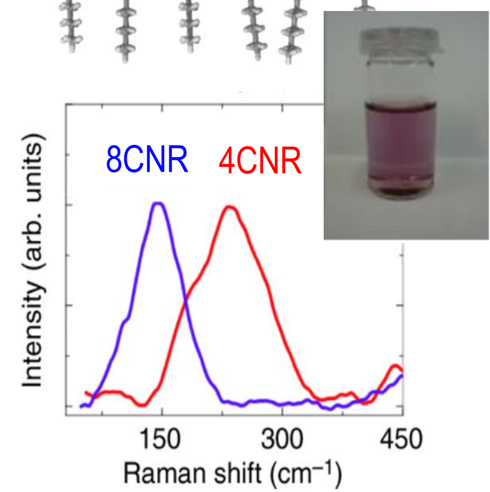




J. Cai *et al.*, Nature (2010)

CNRs in solution

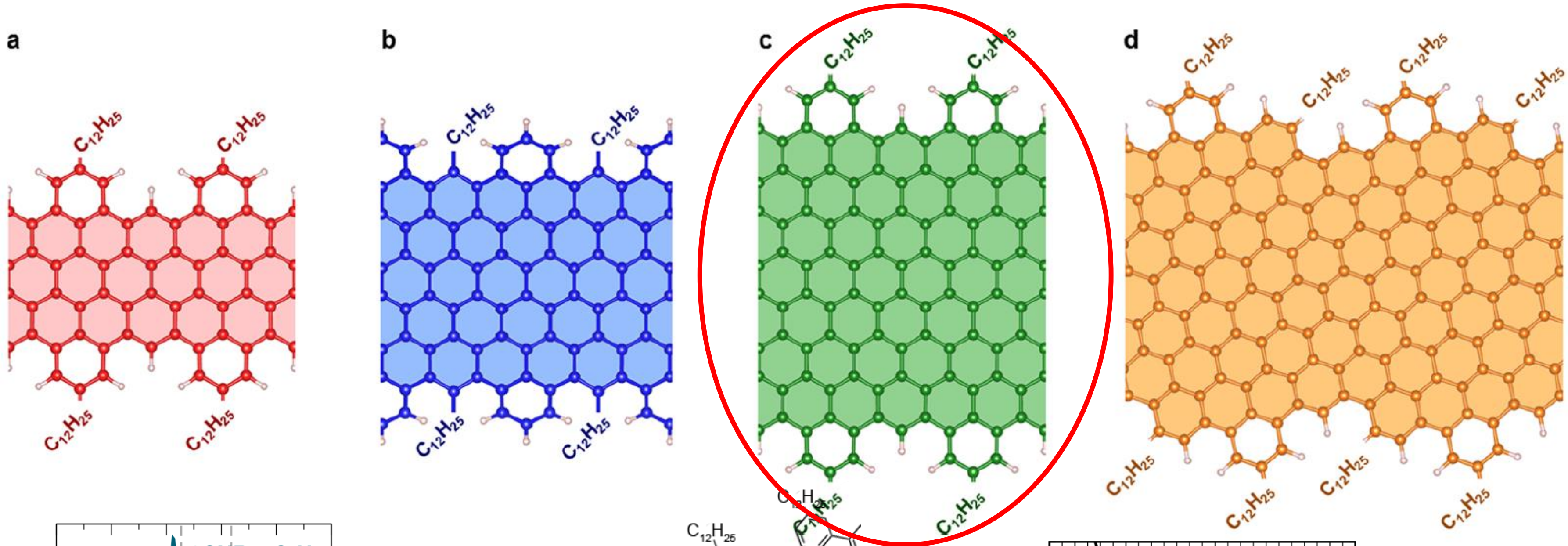


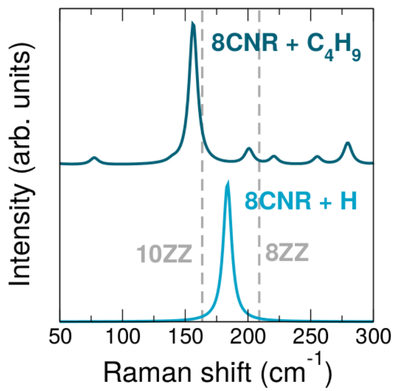


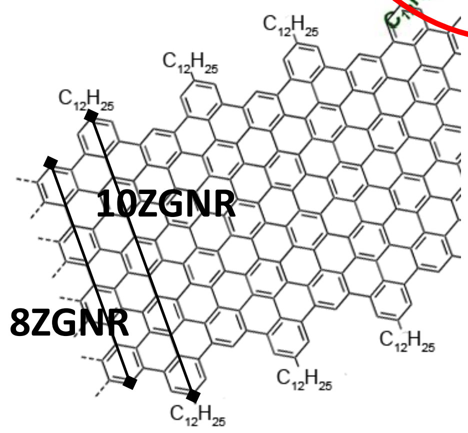
Narita et al. Nat. Chem. (2014)

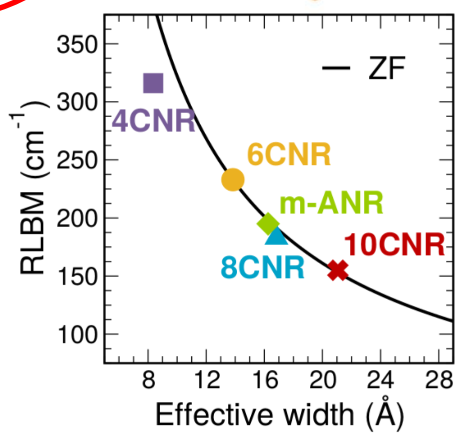
- Very good agreement for AGNRs @ Au
- Puzzling results for cove-shaped GNRs in solutions, such as:
  - BLM peak is not where expected
  - Unusual peak broadening

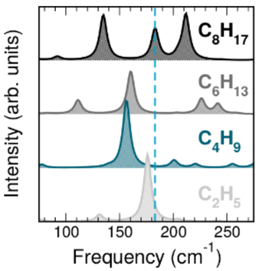
Raman fingerprints for cove-shaped GNRs











- Effective width should be considered for cove-shaped GNRs
- Coupling with alkyl side chains might further influence the BLM peak, which is red-shifted and broader

Graphene nanoribbons (from 2007)

- ***Fundamental properties***

  - 1D confinement effects

  - D. Prezzi,et al , "Optical properties of one-dimensional graphene polymers: the case of polyphenanthrene", *pssb* 244, 4124 (2007)
  - D. Prezzi, et al , "Optical properties of graphene nanoribbons: The role of many-body effects", *PRB* 77, 041404(R) (2008)

- ***Simulation of electronic, optical, vibrational spectroscopies***

  - Substrate effects

  - R. Denk,et al, "Exciton-dominated optical response of ultra-narrow graphene nanoribbons", *Nature Communications* 5, 4253 (2014)

  - Edge-shape effects

  - D. Rizzo,et al, "Multiwavelength Raman spectroscopy of ultranarrow nanoribbons made by solution-mediated bottom-up approach", *PRB* 100, 045406 (2019)
  - R. Denk,,et al, "Probing optical excitations in chevron-like armchair graphene nanoribbons", *Nanoscale* 9, 18326-18333 (2017).

  - Impact of functionalization groups

  - C. Cocchi,,et al, "Electronics and Optics of Graphene Nanoflakes: Edge Functionalization and Structural Distortions", *JPCC* 116, 17328 (2012)
  - I. A. Verzhbitskiy,et al, "Raman Fingerprints of Atomically Precise Graphene Nanoribbons", *Nano Letters* 16, 3442 (2016)

  - Structural distortions

  - C. Cocchi,et al, "Concavity Effects on the Optical Properties of Aromatic Hydrocarbons", *JPCC* 117,12909 (2013)
  - .B. Hu, et al, "Bandgap Engineering of Graphene Nanoribbons by Control over Structural Distortion", *J. Am. Chem. Soc.*140, 7803-7809 (2018)

  - Finite-size effects

  - C. Cocchi,et al, "Optical Excitations and Field Enhancement in Short Graphene Nanoribbons", *JPCL* 3, 924 (2012).
  - C. Cocchi,et al, "Anisotropy and Size Effects on the Optical Spectra of Polycyclic Aromatic Hydrocarbons", *Journal of Physical Chemistry A* 118, 6507 (2014)

- ***Designing new structures, e.g. :***

  - Width modulation

  - D. Prezzi, et al, "Quantum dot states and optical excitations of edge-modulated graphene nanoribbons", *PRB* 84, 041401(R) (2011)

  - Edge functionalization

  - C. Cocchi,et al, "Optical Properties and Charge-Transfer Excitations in Edge-Functionalized All-Graphene Nanojunctions", *JPCL* 2, 1315 (2011)
  - C. Cocchi, et al, "Designing All-Graphene Nanojunctions by Covalent Functionalization", *JPCC* 115, 2969 (2011)

  - π-π aggregation

  - M. De Corato, et al,"Optical Properties of Bilayer Graphene Nanoflakes", JPCC 118, 23219 (2014).

Conclusions

- *Ab initio methods provide a powerful tool for:*

  → ***understanding/predicting*** *fundamental physical properties*

  → *"in-silico" materials* ***design***

- *In the case of* ***GNRs****, simulation of spectroscopies allow :*

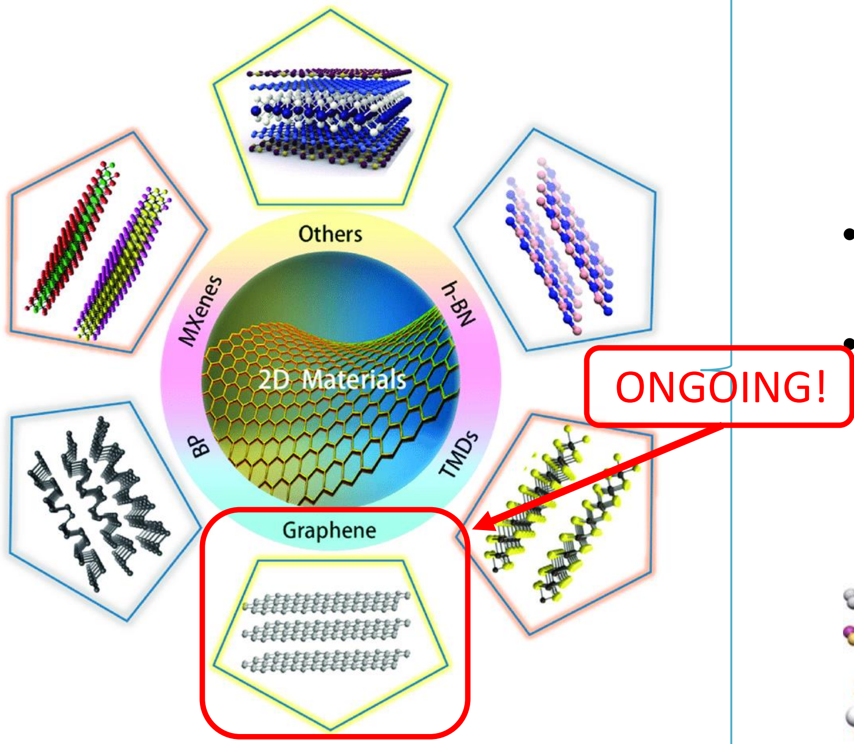
  → *Capturing several different* ***effects*** *for this very rich class of materials, such as quantum confinement, substrate, edge-shape, edge-functionalization, structural distortion,…, one can play with*

  → *Tunability means extraordinary versatility as next-generation semiconducting material for nano-electronics and -optoelectronics*

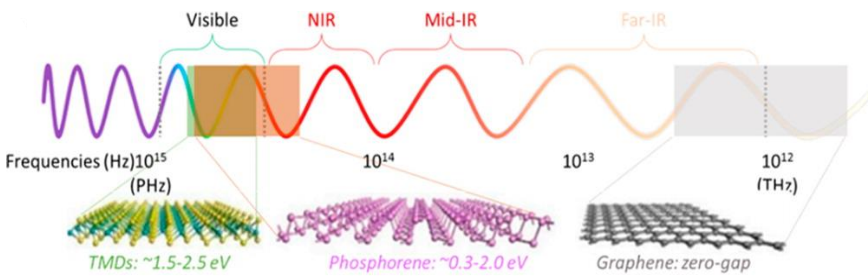
  → *Designing new, tunable graphene-nano-****heterostructures*** *through edge modulation, chemical functionalization and π-coupling*

- *Many open challenges … in many different directions!!!*

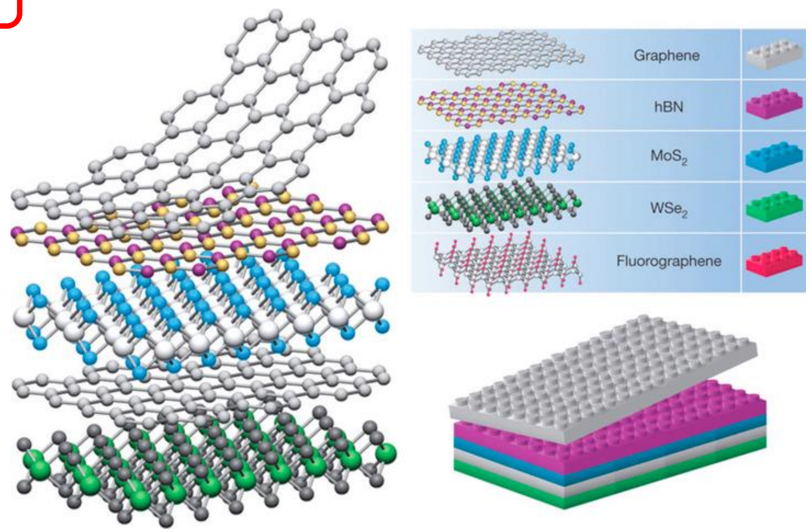
Designing new lowD materials



- Changing the elements



- Playing with heteroatoms and dimensionality
- Combining different 2D materials



Special thanks to:

THEO COWORKERS


Deborah Prezzi

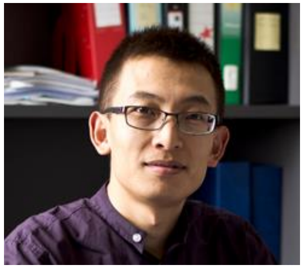

Andrea Ferretti


Daniele Varsano


Caterina Cocchi


Marzio De Corato


Marilia J. Caldas


Sudong Wang


Stefano Corni


Elisa Molinari

MAIN EXP COLLAB.


Valentina De Renzi


Aki Narita


Cinzia Casiraghi

… and to all of you for your attention!