CNR NANO
ISTITUTO NANOSCIENZE CONSIGLIO NAZIONALE DELLE RICERCHE

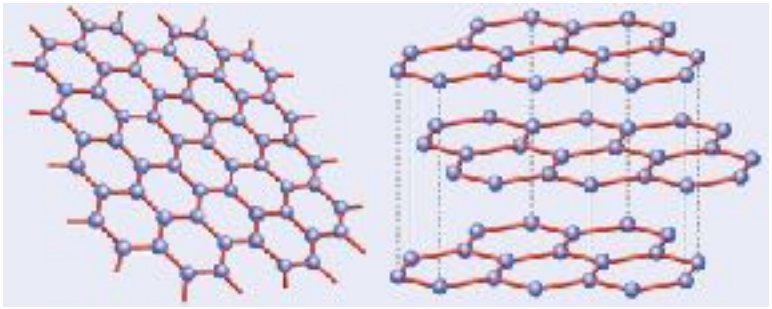
Istituto Nanoscienze
S3 center, Modena, Italy

Electron and Optical properties of Graphene Nanoribbons

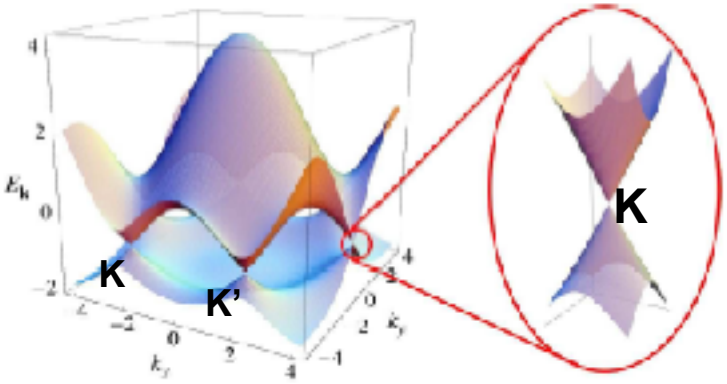
Andrea Ferretti

04 Dec 2017

electronics & optics



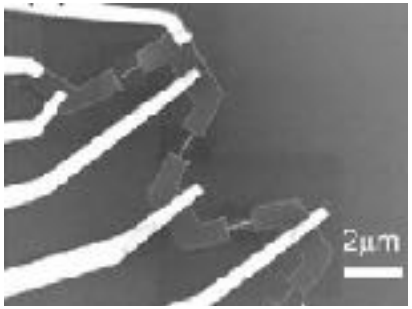
Geim and Novosolev, Nat. Mat. (2007)
Castro Neto et al., RMP (2009)



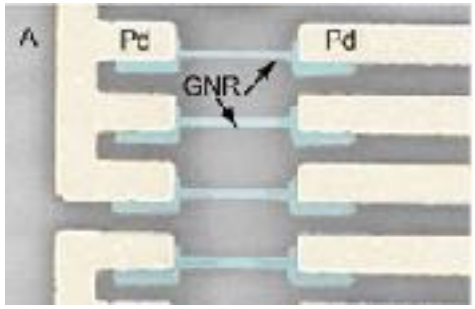
- *Semimetal* or zero gap semiconductor
- *Linear dispersion* around K (K')

Graphene Nanoribbons (GNRs)

Gap Opening?



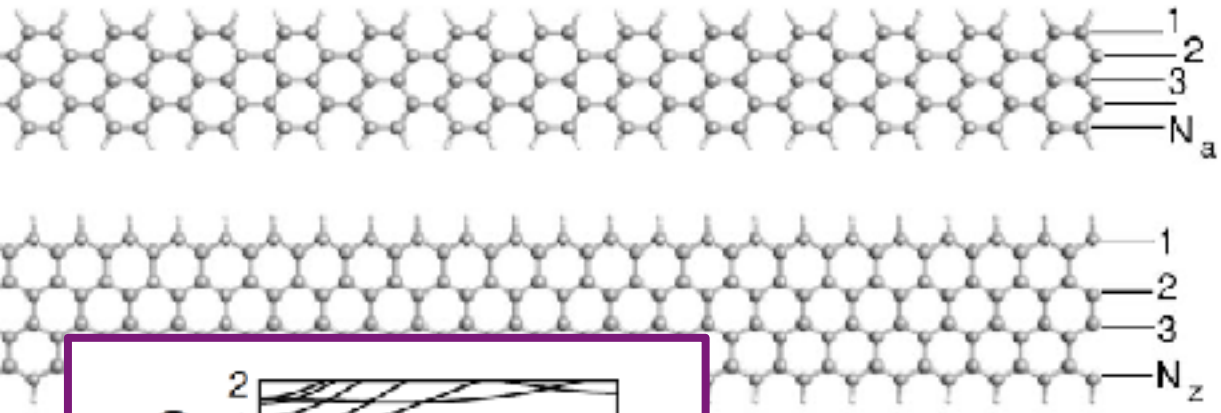
Han et al, PRL (2007)



Chen et al,
cond-mat/0701599v1 (2007)

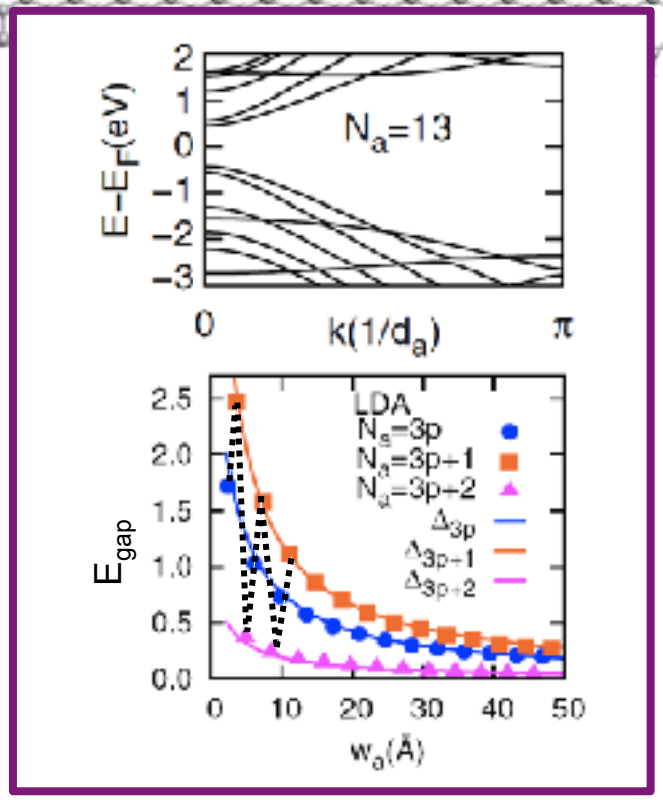
CNRNANO

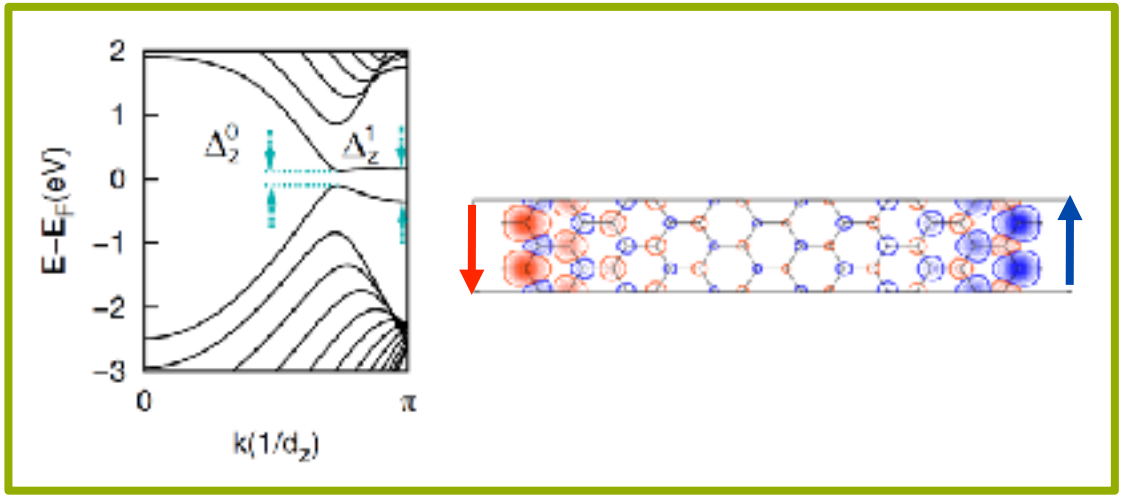
edge properties



Armchair edges
- Always semiconductors
- Oscillating energy gap

Zig-zag edges
- Semiconductors
- Magnetic ordering





Son et al., PRL (2006); Pisani et al., PRB (2007)

atomically-precise GNRs

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

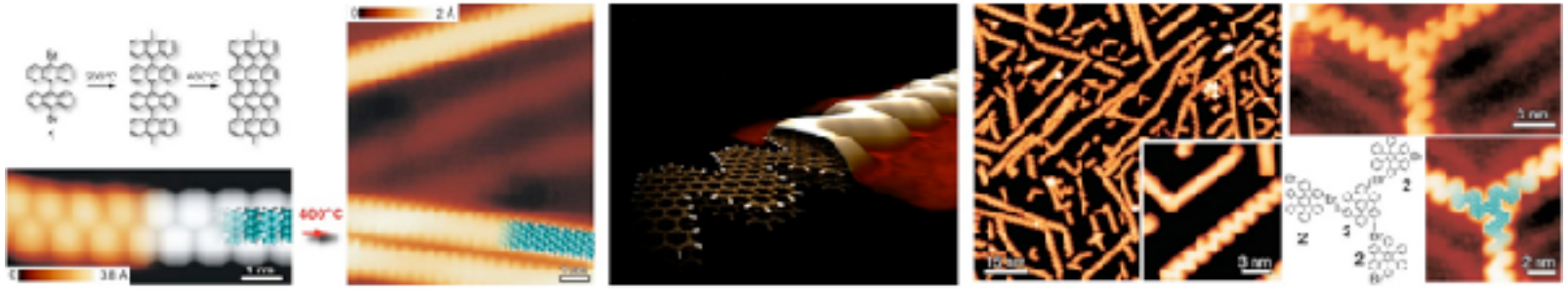
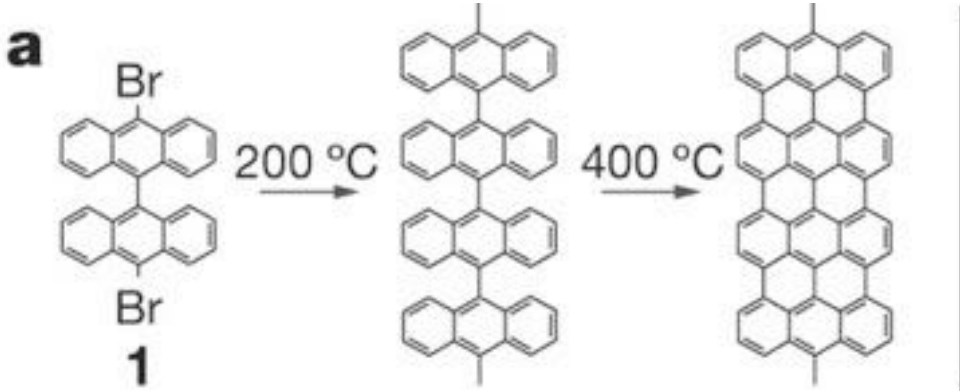


FIGURE 1. Graphene nanoribbons with nanometer width and atomically-controlled edges are self-assembled on metal substrates. STM images show several non-trivial geometries obtained by choosing appropriate precursors. After Cai et al, Nature 466, 470 (2010).



molecular precursor

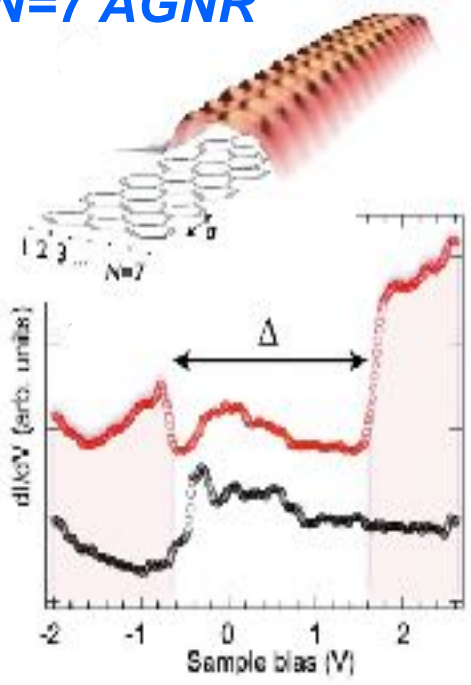
polymer

ribbon

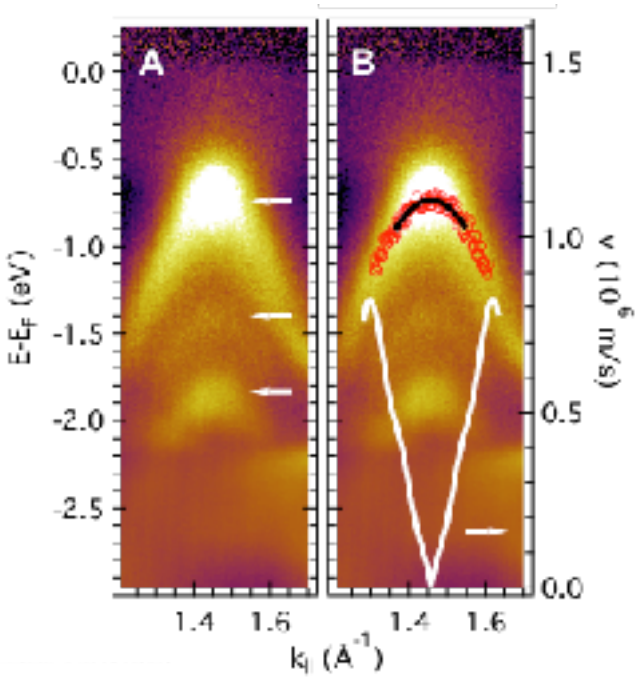
CNRNANO

exp: ARPES & STS

N=7 AGNR

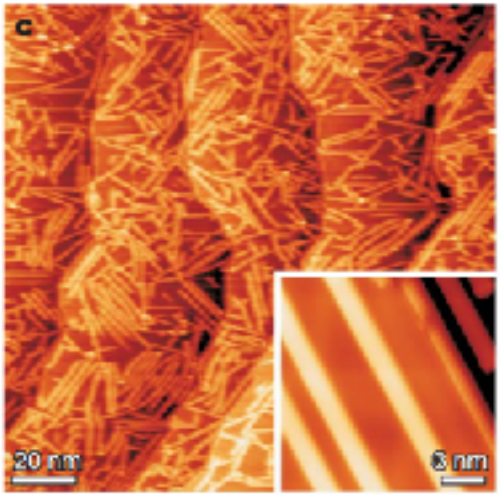


STS
GNR@Au(111)
E_{gap} = 2.3 ± 0.1 eV



ARPES
aligned GNR@Au(788)
parabolic dispersion,
$m^*=0.21\ m_0$

N7-GNRs@Au(111)



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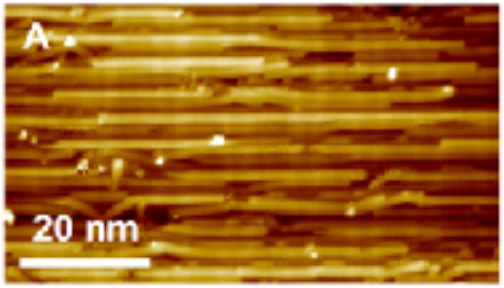


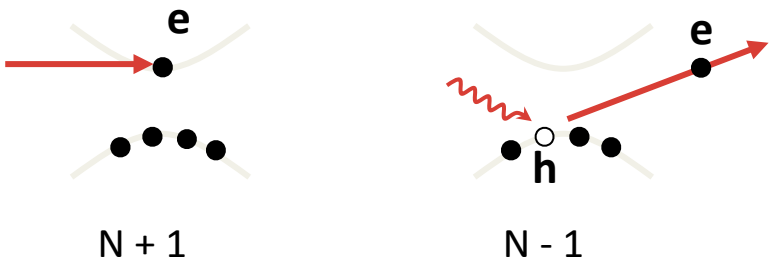
P. Ruffieux, J. Cai, N. C. Plumb, L. Patthey, D. Prezzi, **AF**, E. Molinari, X. Feng, K. Müllen, Carlo A. Pignedoli, and R. Fasel, ACS Nano **6**, 6930 (2012).

methods: DFT + GW + BSE

Electron and hole QP states:

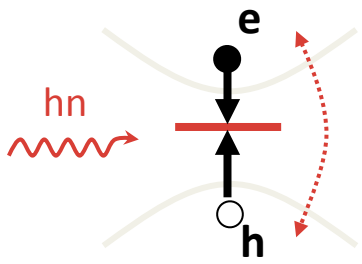
- Ground state within **Density Functional Theory (DFT)**
- Quasiparticle corrections: **GW approximation**

STS
ARPES



Optical excitations

- Electron-hole interaction included through the **Bethe-Salpeter equation**



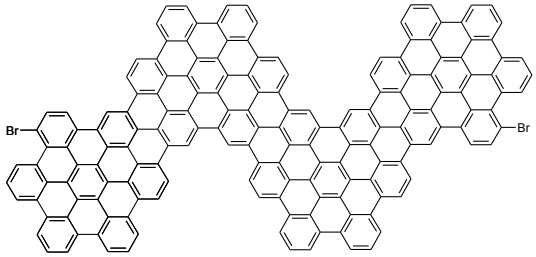
OPTICAL ABS
EELS

outline

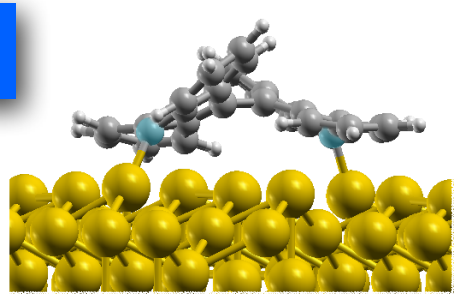
- **Armchair GNR**

  - Electronic and Optical properties

- **Chevron GNR**



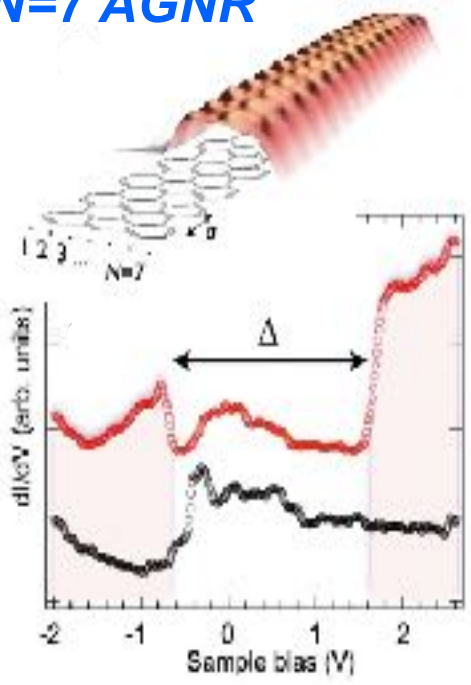
- **Armchair GNR: termini**



- **Armchair GNR: growth**

exp: ARPES & STS

N=7 AGNR



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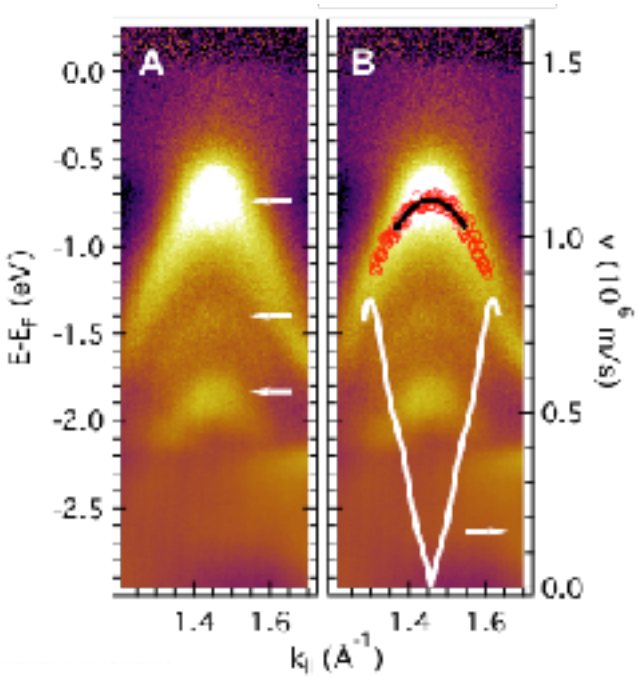

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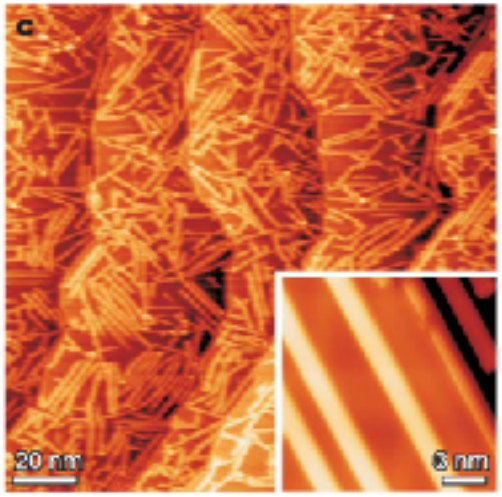

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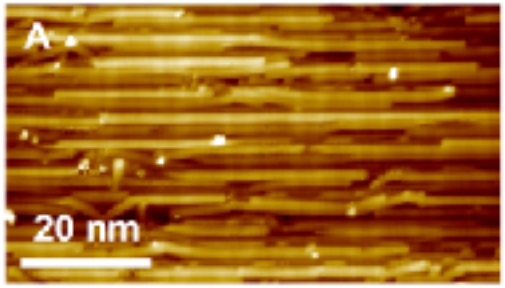

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optical properties

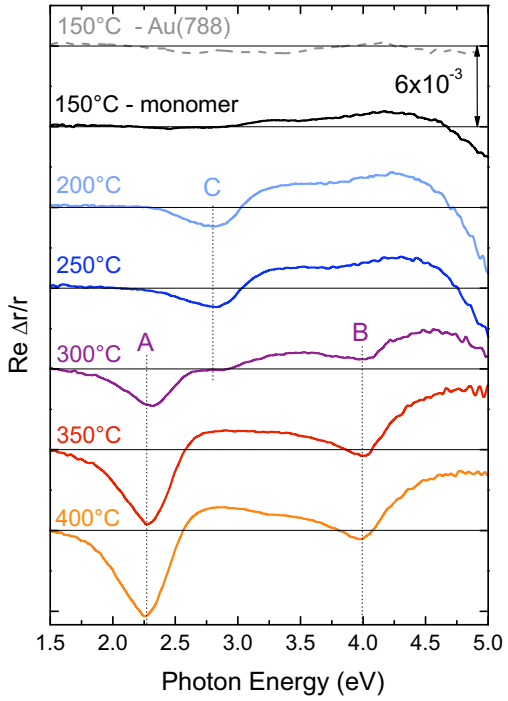
Reflectance Difference Spectroscopy (RDS)

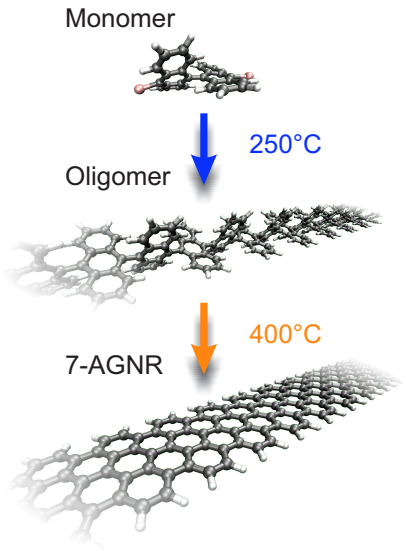
N7-GNRs@Au(788)

Measurement of optical in-plane anisotropy during GNR growth

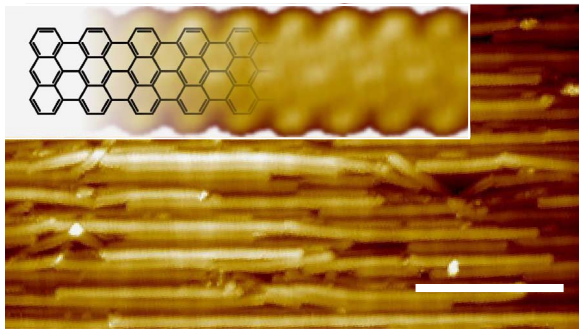
$$\frac{\Delta r}{r} = 2\frac{r_x - r_y}{r_x + r_y} = 2\frac{r_{[1\bar{1}0]} - r_{[001]}}{r_{[1\bar{1}0]} + r_{[001]}}$$

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

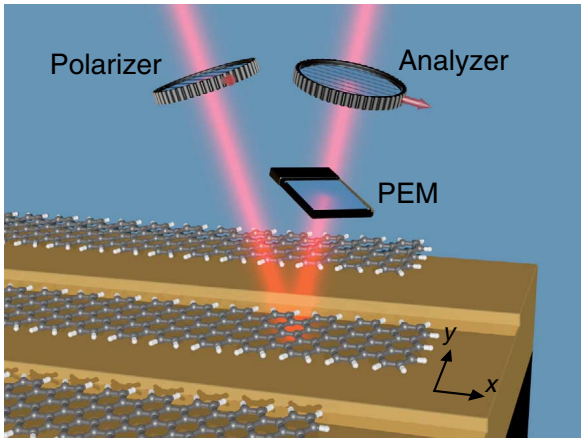




b



a



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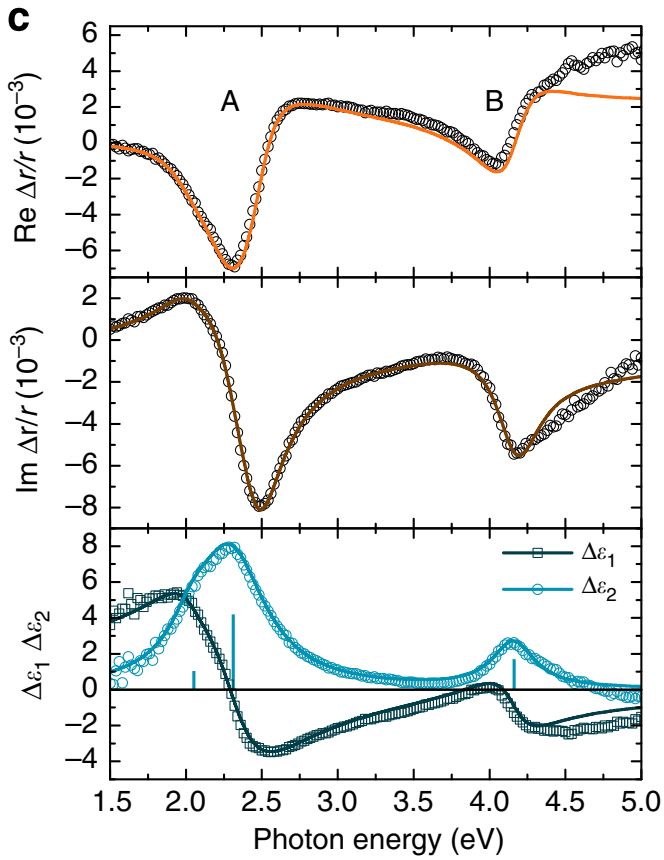
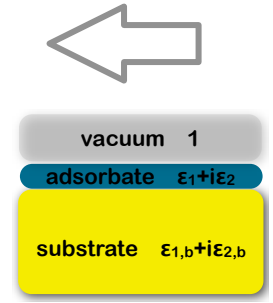
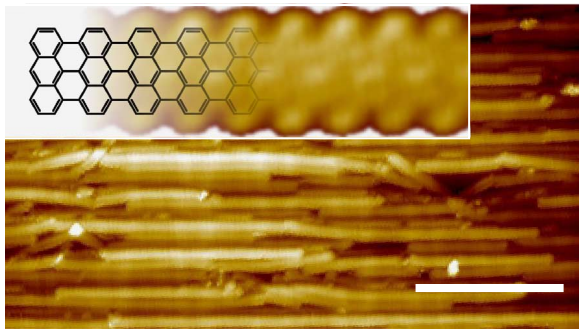
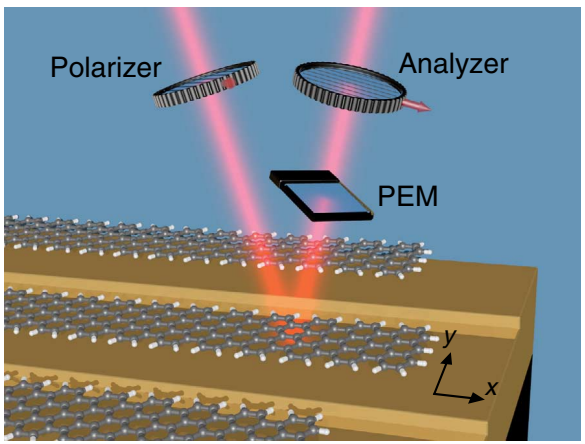




3-phase model





NATURE COMMUNICATIONS | DOI: 10.1038/ncomms5253

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

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

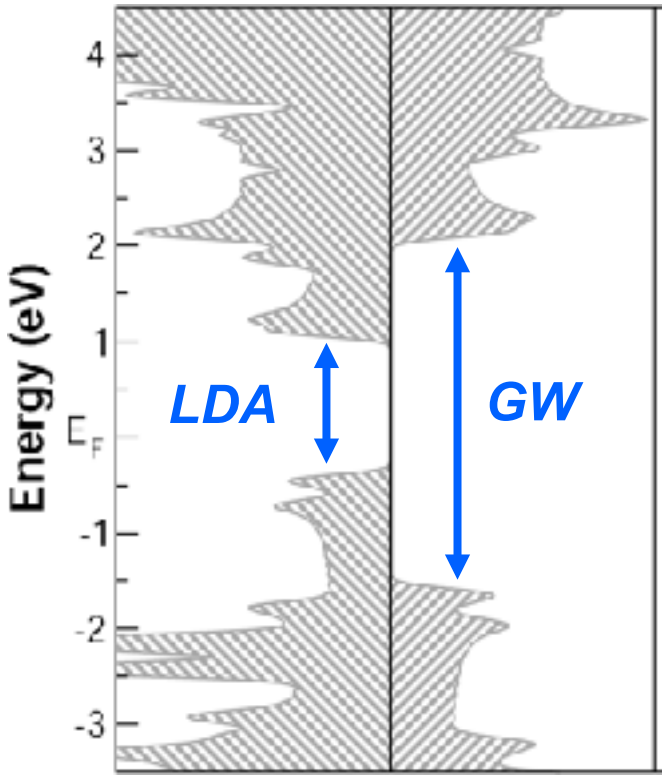
7-AGNR, armchair GNRs of width $N=7$; BSE, Bethe–Salpeter equation; IC, image charge; PA, polyanthrylene; RDS, reflectance difference spectroscopy; STS, scanning tunnelling spectroscopy.
The experimentally determined transport band gap (STS) of 7-AGNRs and the intermediate PA oligomers adsorbed on the Au substrate compared with the fundamental *GW* band gap including IC corrections. For the first optical transitions, the experimental values are related to the *GW* band gap corrected by the exciton binding energies E_b[11/22], as determined within the *GW*-BSE scheme.

theory: electronic structure

theory: isolated AGNRs

Electron and hole QP states:

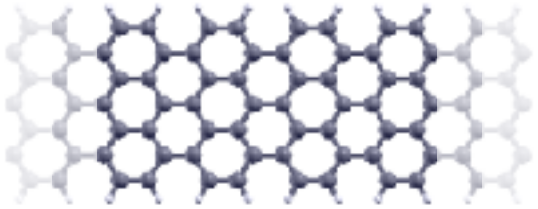
- Ground state within **Density Functional Theory** (DFT)
- Quasiparticle corrections: **GW approximation**



- Large quasi-particle corrections to E_{gap}:

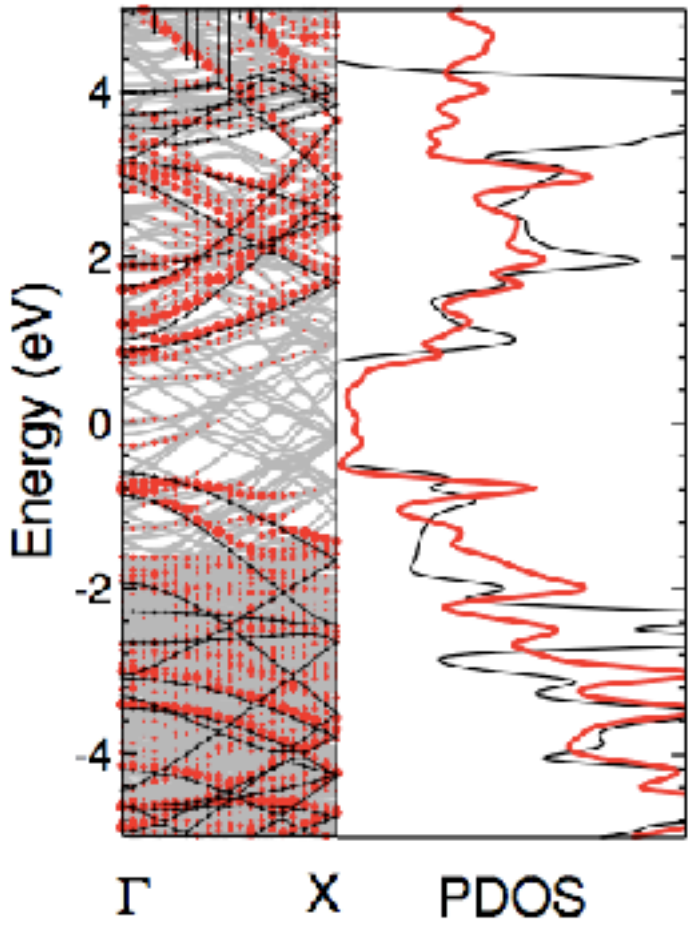
E_{LDA} = 1.6 eV → E_{GW} = 3.7 eV

- Confinement → increase e-e interaction
- Weak Screening



N=7

AGNR @ Au(111)



DFT electronic structure:

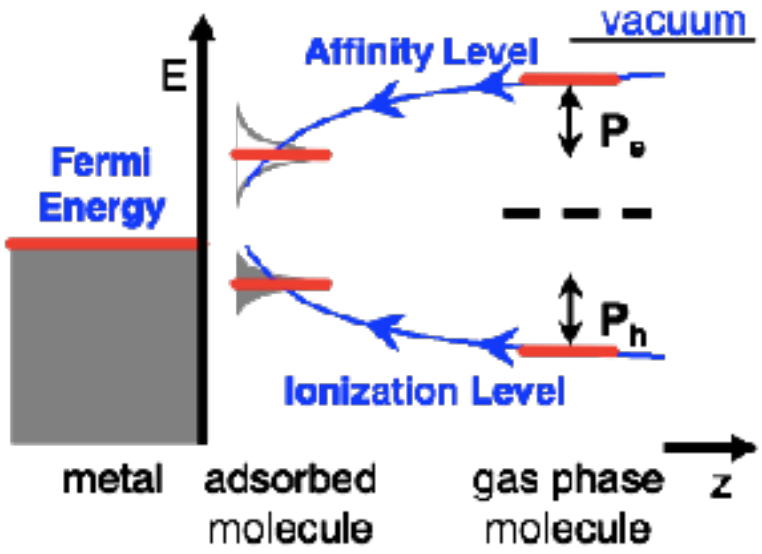
- AGNR bands at Au(111) (**red**) very similar to gas phase (**black**)
- Minimal hybridization effects
- Substrate effects mostly due to surface polarizability

⇩

we correct for the presence of the substrate by using an **image charge model**

including the substrate

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



L estimated from

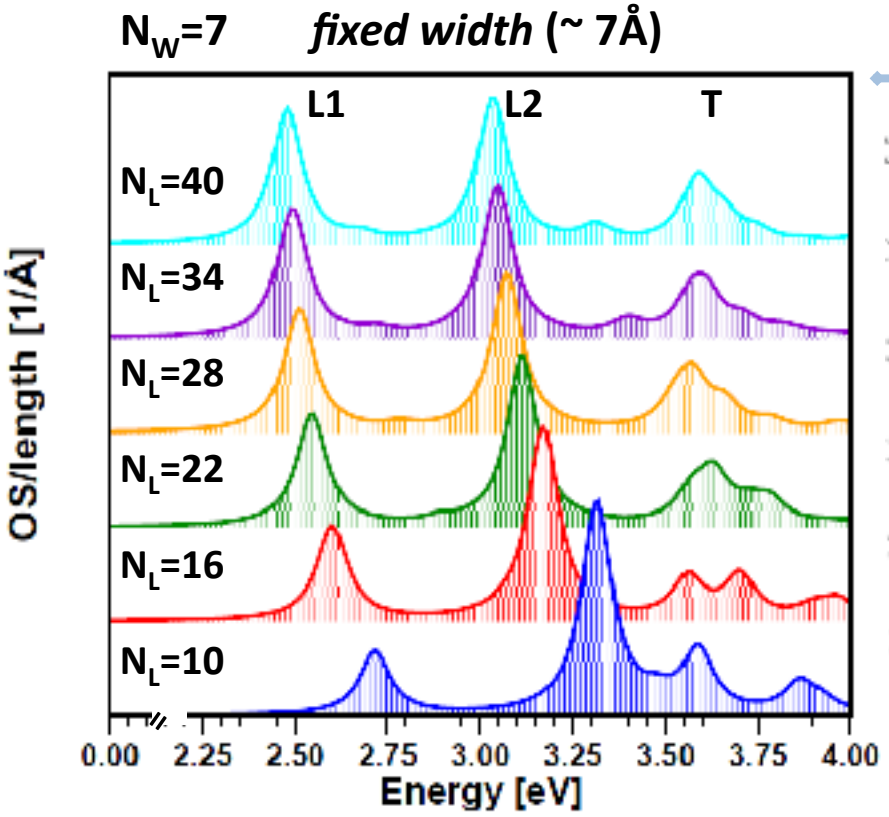
exciton wavefunction (BSE)
&
optical saturation length
(excitons in finite ribbons)

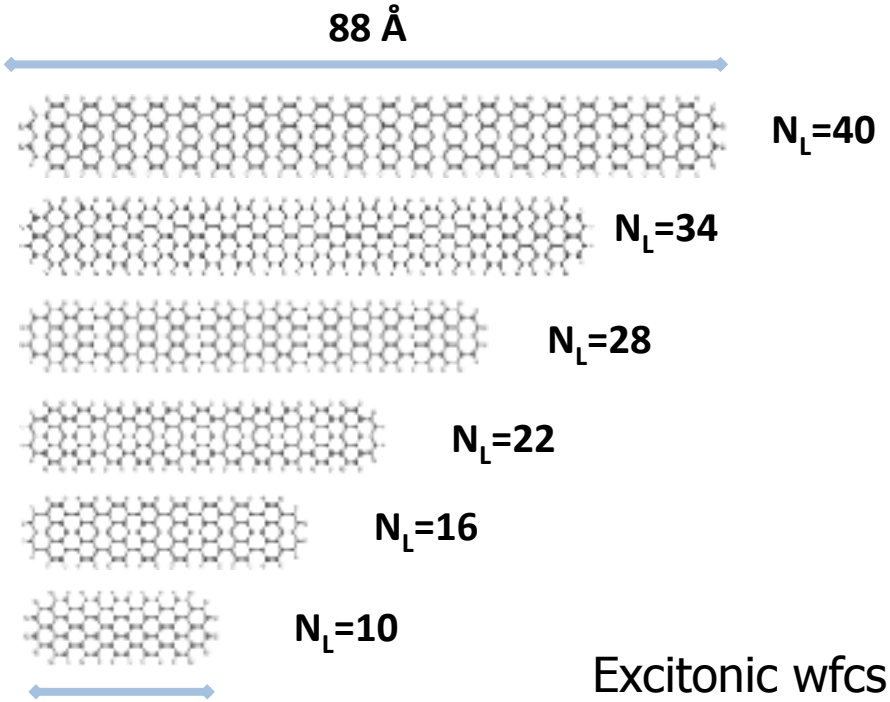
Image charge model

- 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 define an **effective (screening) length L** of the excitation charge distribution

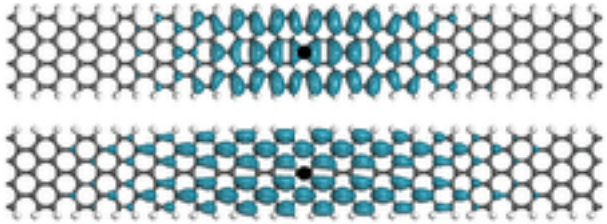
L ~ 30-60 Å for N7-ANGR

optical saturation





Excitonic wfcs



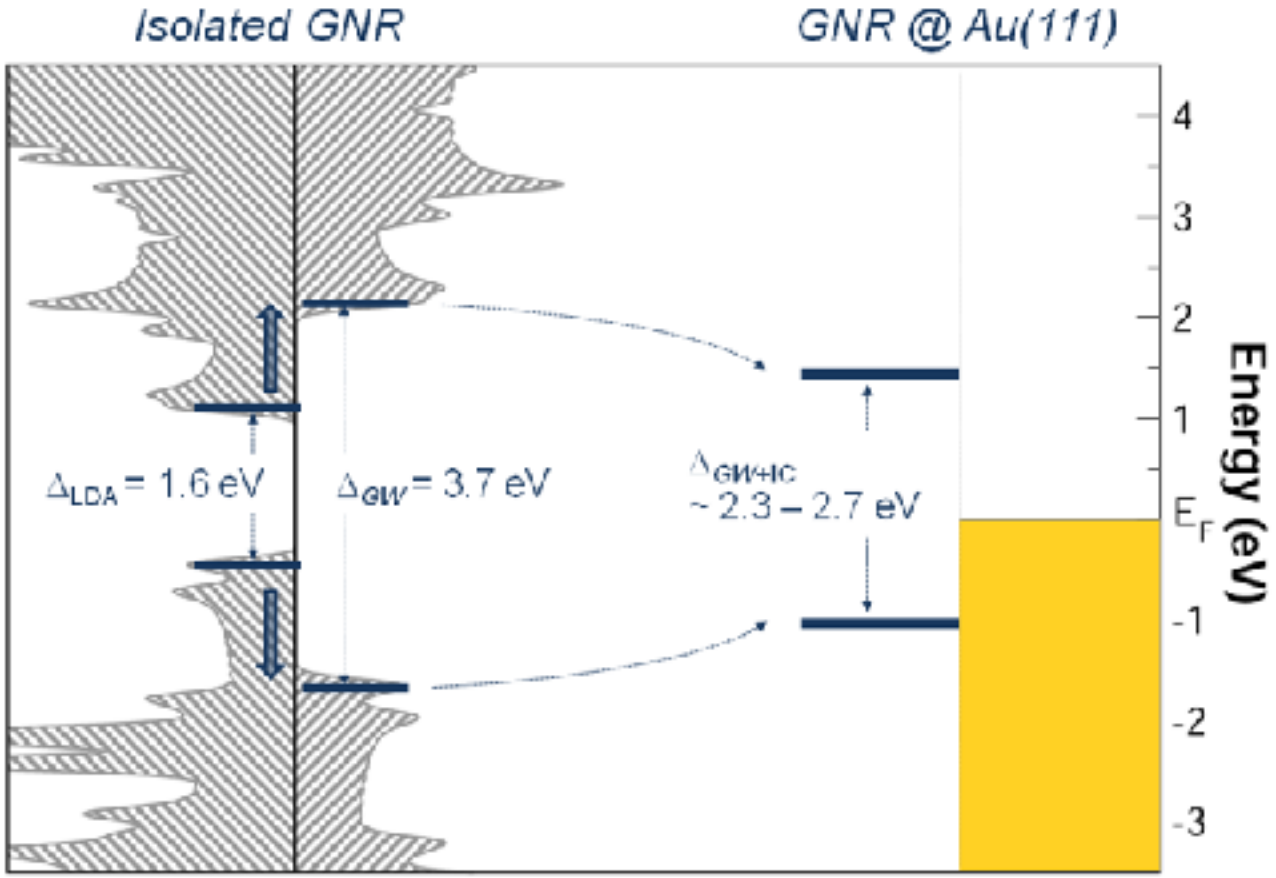
red shift of **L1** at increasing length
saturation below N ~ 40

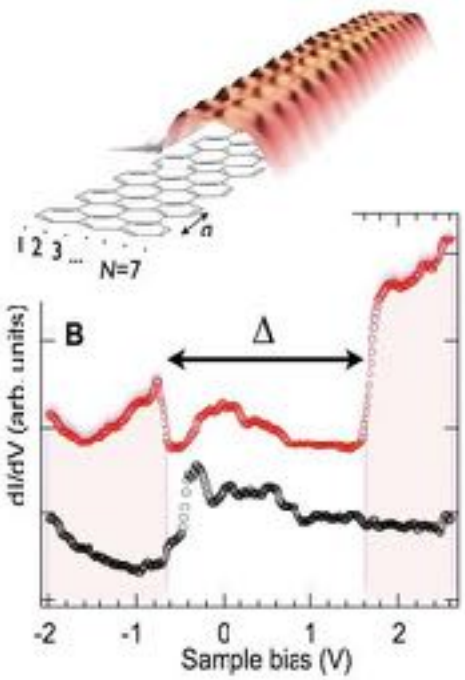
L ~ 30-60 Å for N7-ANGR

Cocchi et al, J. Phys. Chem. Lett. **3**, 924 (2012)

see also: D.Varsano, A.Marini, A. Rubio, PRL **101**, 133002 (2008)

substrate effect





To be compared with: STS on GNR@Au(111)

E_{gap} = 2.3 ± 0.1 eV

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

NATURE COMMUNICATIONS | DOI: 10.1038/ncomms5253

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				
				Exp. (RDS)
Optical band gap (eV)				
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theory: optical properties

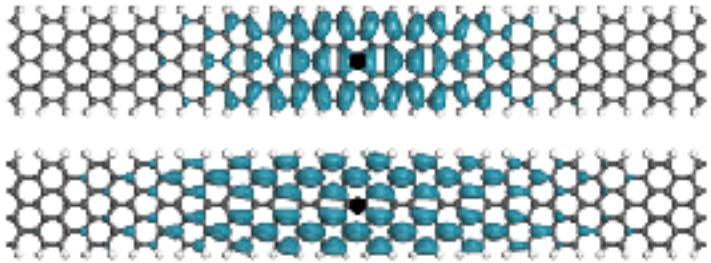
optics of isolated AGNRs

Optical excitations N7 AGNR

- Electron-hole interaction included through the solution of the **Bethe-Salpeter equation**

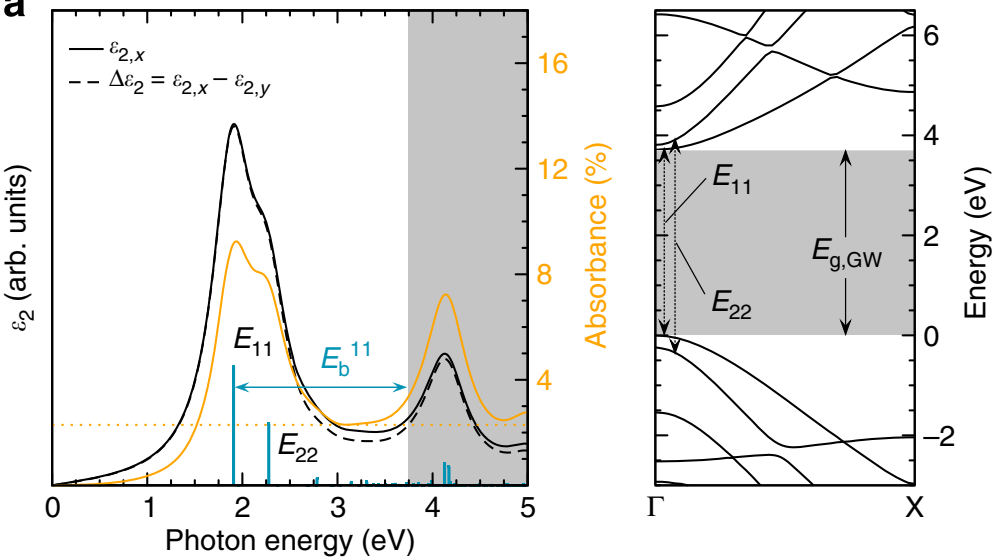
see also:
D. Prezzi et al, Phys. Rev. B **77**, 041404 (2008)
L. Yang et al, Nano Lett. 7, 3112 (2007)

1.91 eV first peak
mainly HOMO -> LUMO



2.28 eV second peak
mainly HOMO-1 -> LUMO+1

EXC Binding Energy: 1.8/1.4 eV



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Optical band gap (eV)				
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PA oligomer				

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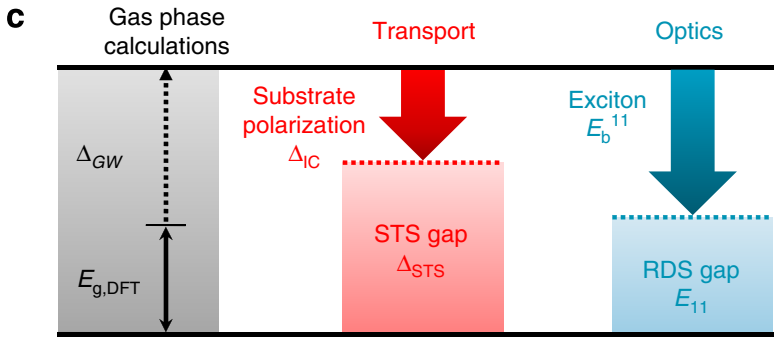
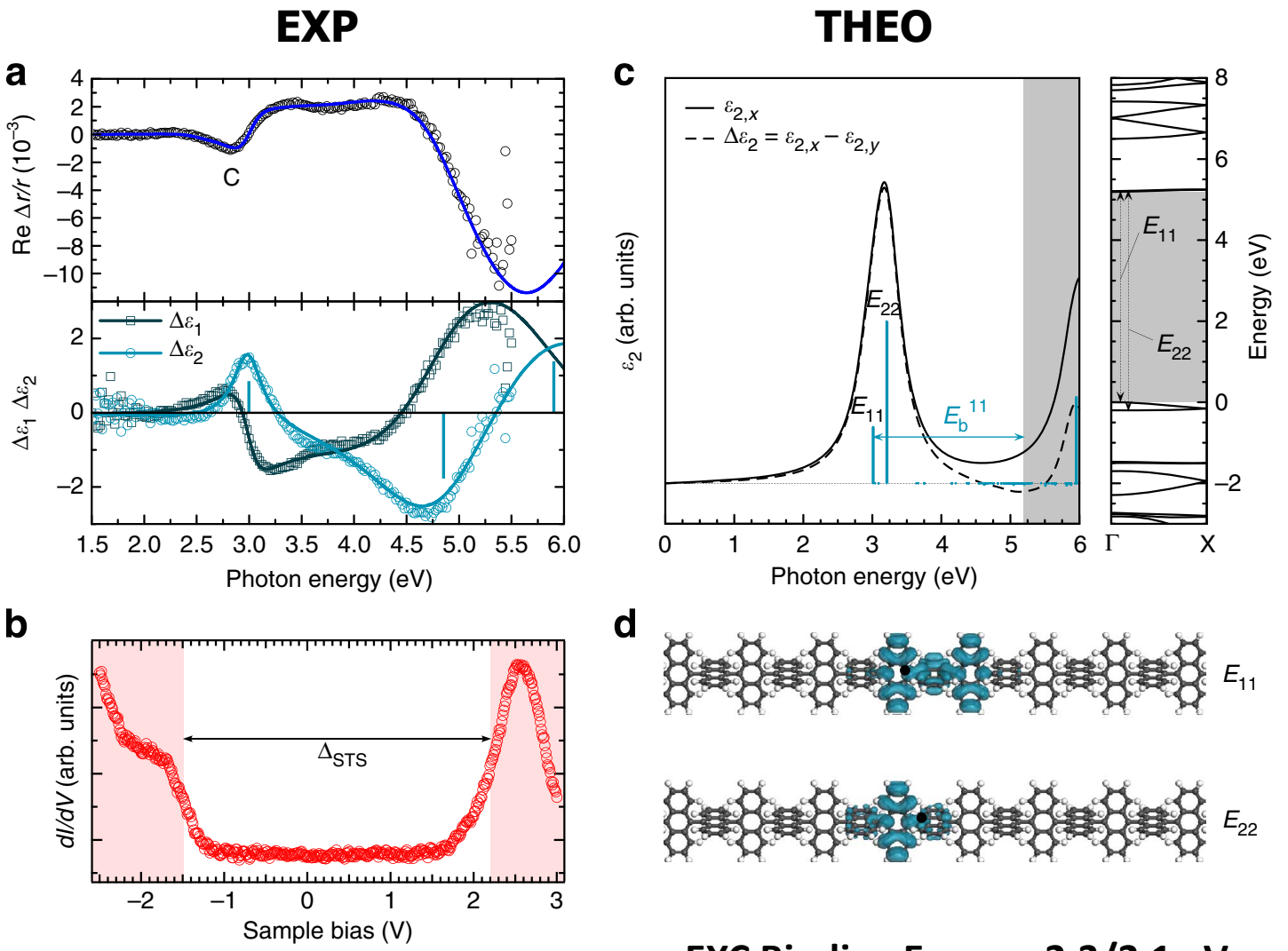


poly-anthryl



EXC Binding Energy: 2.3/2.1 eV

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

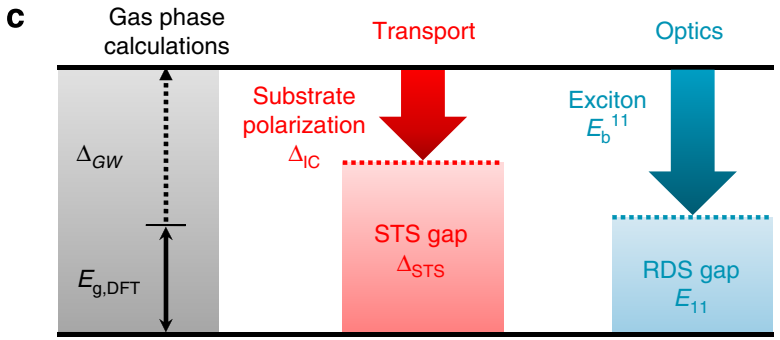
R. Denk et al., Nat Comm **5**, 4253 (2014)

NATURE COMMUNICATIONS | DOI: 10.1038/ncomms5253

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

7-AGNR, armchair GNRs of width $N = 7$; BSE, Bethe–Salpeter equation; IC, image charge; PA, polyanthrylene; RDS, reflectance difference spectroscopy; STS, scanning tunnelling spectroscopy. The experimentally determined transport band gap (STS) of 7-AGNRs and the intermediate PA oligomers adsorbed on the Au substrate compared with the fundamental *GW* band gap including IC corrections. For the first optical transitions, the experimental values are related to the *GW* band gap corrected by the exciton binding energies $E_b^{11/22}$, as determined within the *GW*-BSE scheme.



summary

- **From model to real systems**

  prediction of fundamental properties by MBPT (GW + BSE)

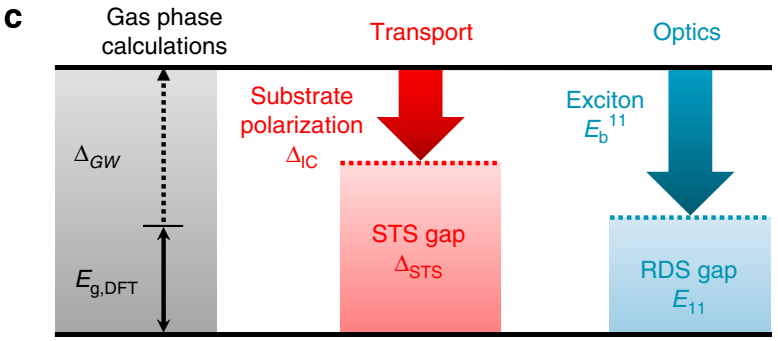
- **Substrate effects**

  electronic properties are markedly modified by the substrate
  IC corrections ~ 1eV

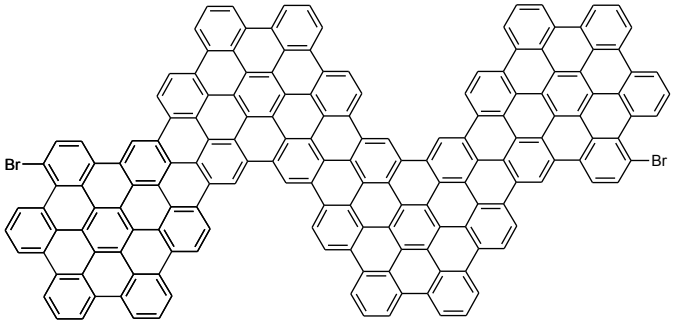
  corrections to **optical excitations** are less relevant or negligible

- **Exciton build-up**

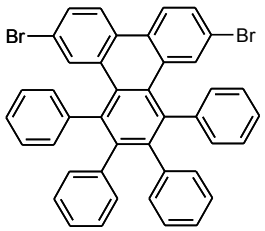
  from polymer precursors to GNRs



chevron ribbons

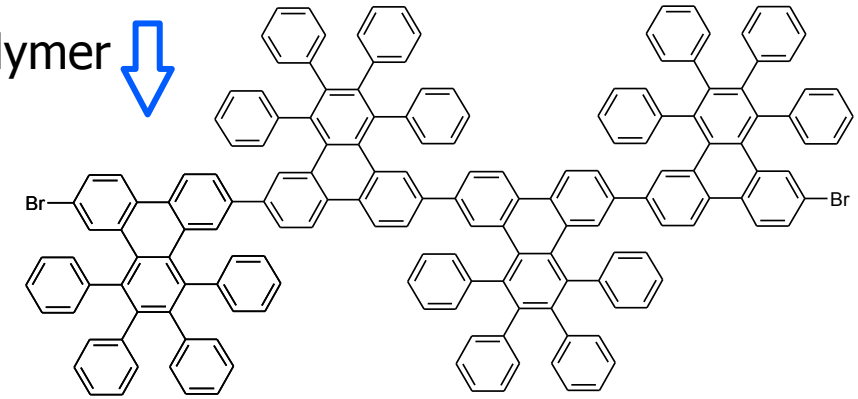


growth

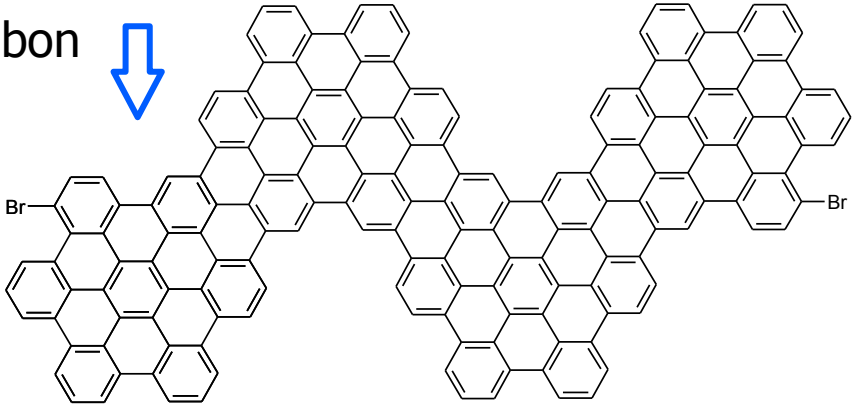


precursor

polymer



ribbon



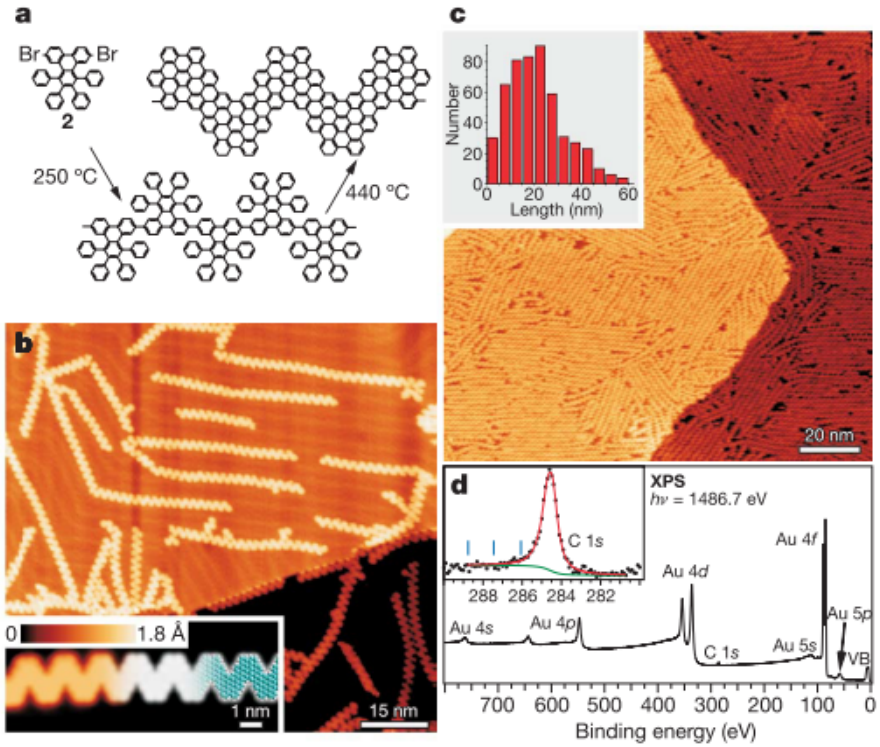
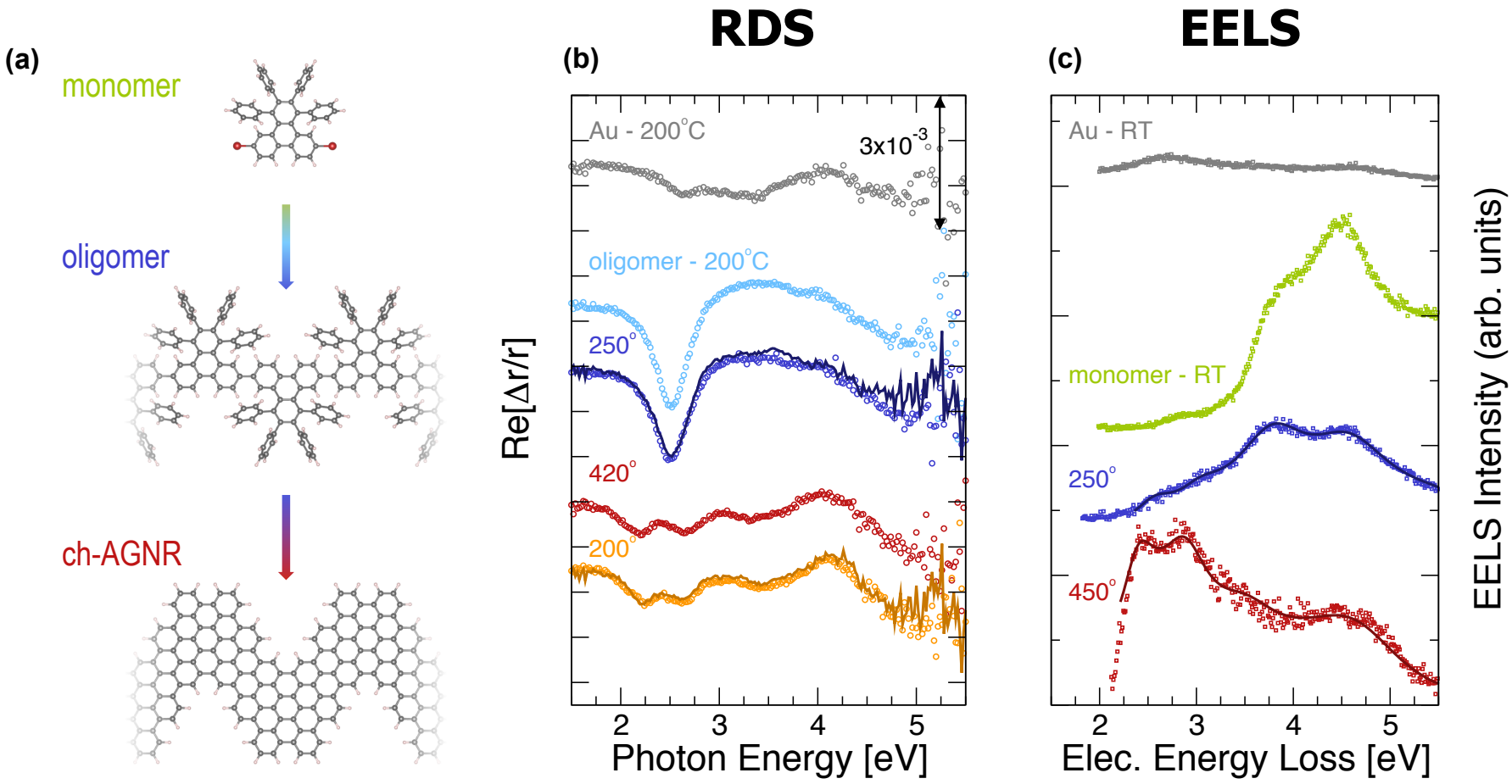


Figure 3 | Chevron-type GNRs from tetraphenyl-triphenylene monomers.

J. Cai et al, Nature **466**, 470 (2010);
J. Cai et al, Nature Nanotech **8** (2014)

The **same reaction pattern**
as for N7-AGNR

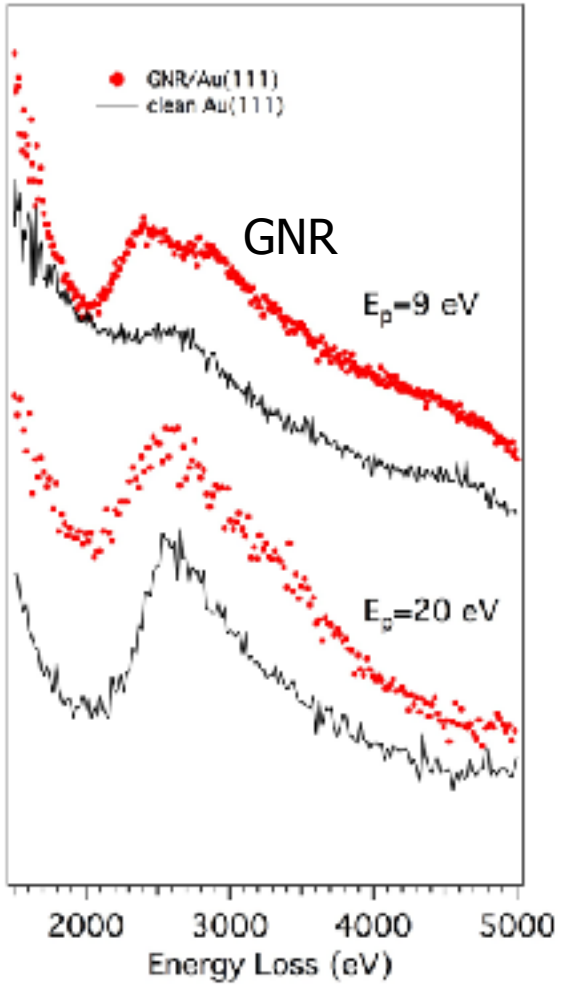
dielectric response



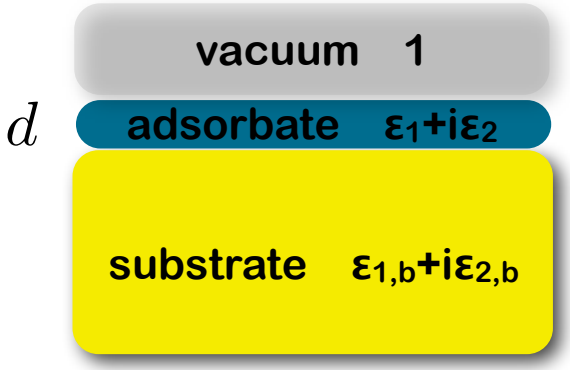
dielectric response

- attention needs to be paid to the **surface plasmons**
- primary electrons with E=20 eV lead to gold dominated signal
- At E=9 eV, EELS signal displays the molecular features

EELS



3 phase model



$$\epsilon(\omega) = 1 + \sum_m \frac{A_m}{E_m^2 - \omega^2 - iE_m\Gamma_m}$$

$$\epsilon = \epsilon_1 + i\epsilon_2 \qquad \Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$$

anisotropy

$$\epsilon^b = \epsilon_1^b + i\epsilon_2^b$$

bulk

RDS

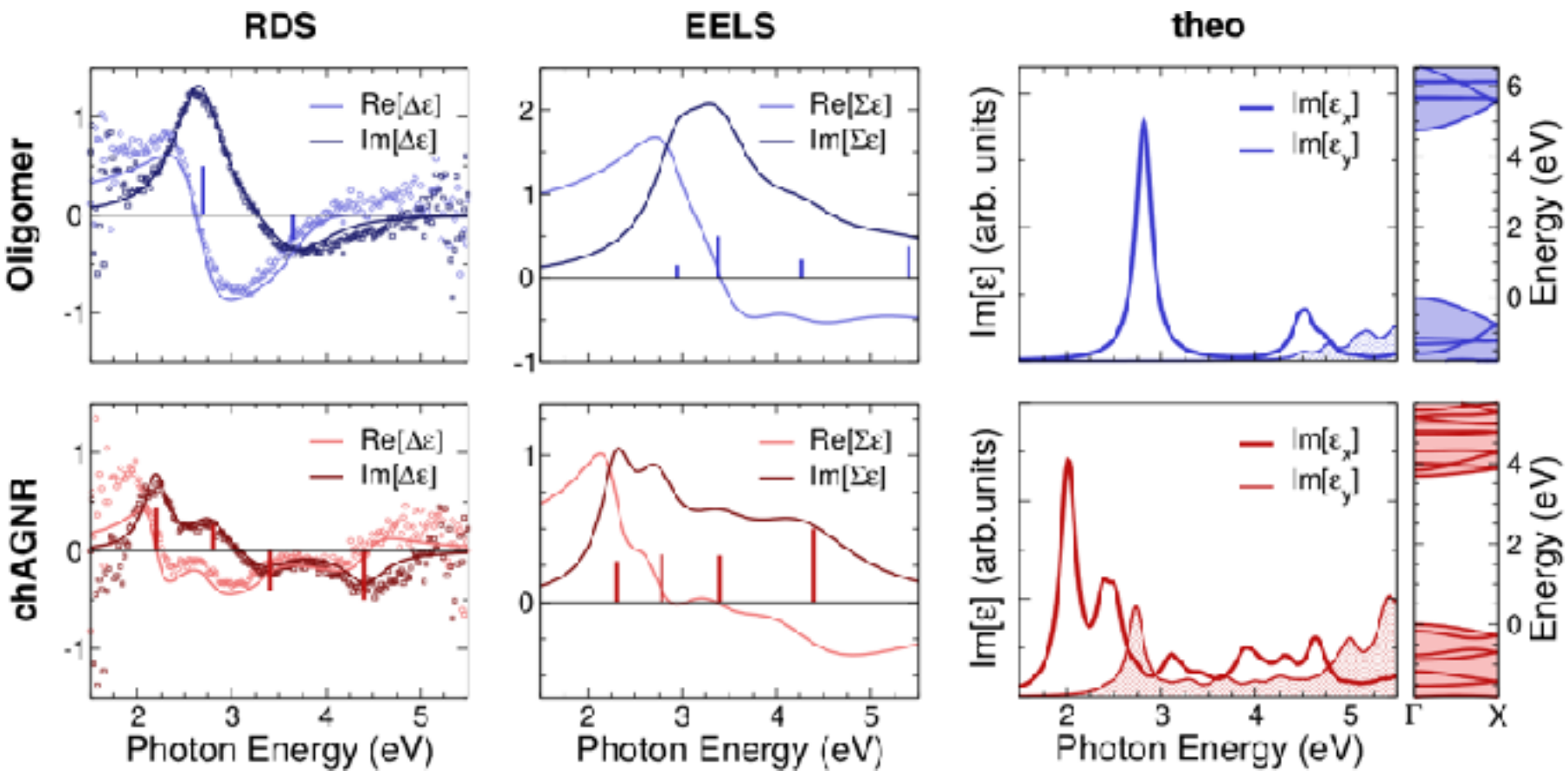
$$\frac{\Delta r}{r} = -\frac{4\pi i d}{\lambda}\frac{\Delta\epsilon}{\epsilon_b - 1} = \frac{4\pi d}{\lambda}\left[\frac{\Delta\epsilon_2(\epsilon_1^b - 1) + \Delta\epsilon_1\epsilon_2^b}{(\epsilon_1^b - 1)^2 + (\epsilon_2^b)^2} - i\frac{\Delta\epsilon_1(\epsilon_1^b - 1) + \Delta\epsilon_2\epsilon_2^b}{(\epsilon_1^b - 1)^2 + (\epsilon_2^b)^2}\right]$$

EELS

$$L(\omega) = \mathrm{Im}\left\{\frac{-1}{\tilde{\epsilon}(q_{\parallel},\omega) + 1}\right\} \qquad \tilde{\epsilon}(q_{\parallel},\omega) = \epsilon(\omega)\left[\frac{1 + \Delta(\omega)\exp(-2q_{\parallel}d)}{1 - \Delta(\omega)\exp(-2q_{\parallel}d)}\right]$$

$$\Delta(\omega) = \frac{\epsilon^b - \epsilon}{\epsilon^b + \epsilon}$$

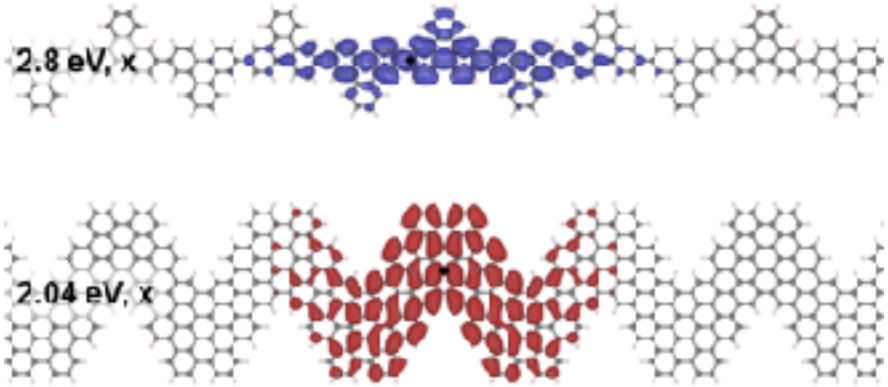
dielectric response

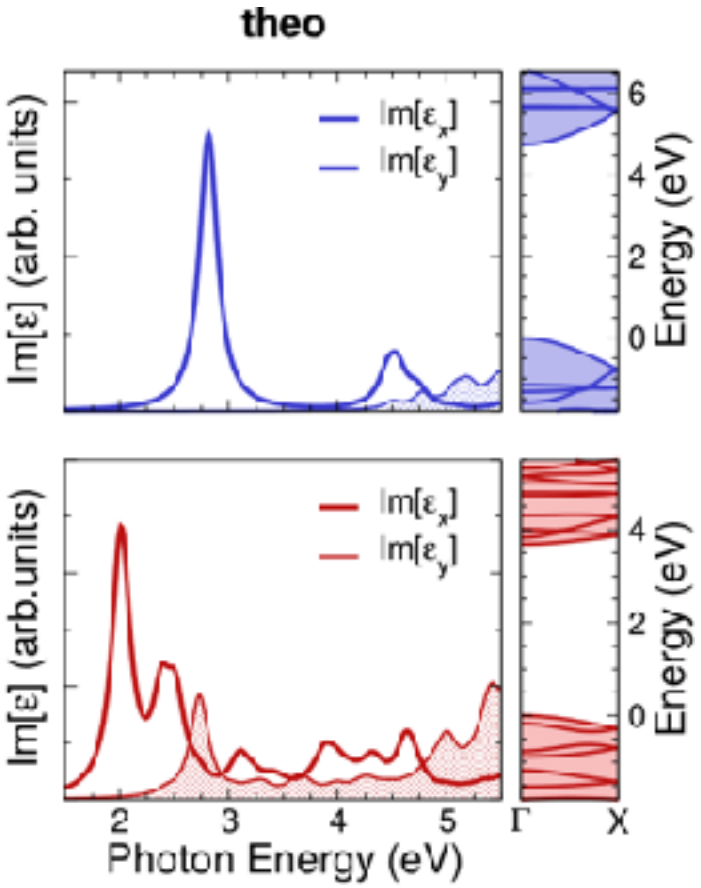


dielectric response

Excitation energies [eV]

	E1	E2	E3	E4
EELS	2.305	2.780	3.400	4.400
RDS	2.200	2.800	3.400	4.400
THEO	2.05	2.5	2.8	





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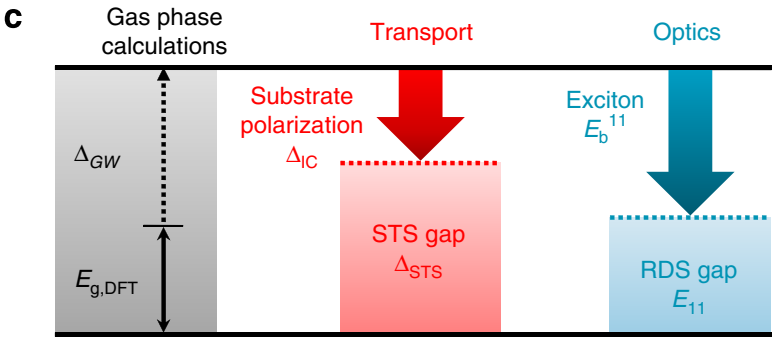


acknowledgements

Coworkers:

THEO **S. Wang, D. Prezzi, A. Ruini, E. Molinari** – **S3-CNR-NANO & UniMoRe**
C. Cardoso, D. Varsano

EELS **V. De Renzi**, **A. Lodi-Rizzini,** R. Biagi – **UniMoRe & S3-CNR-NANO**

RDS **P. Ruffieux**, J. Cai, C. A. Pignedoli, R. Fasel – **EMPA, Zurich**
STS

ARPES **R. Denk**, M. Hohage, P. Zeppenfeld – **Linz University**

N.C. Plumb, L. Patthey – **Swiss Light Source, Villigen**

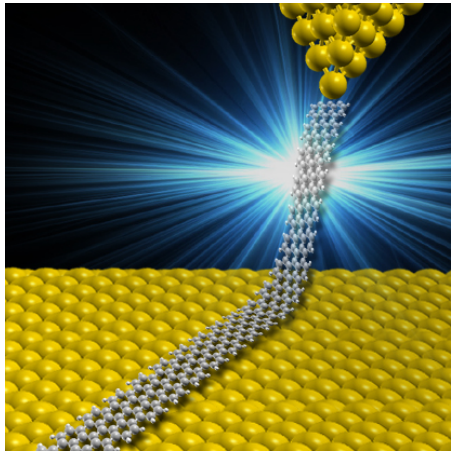
X. Feng, K. Müllen – **Max Planck Institut, Mainz**

Related papers:

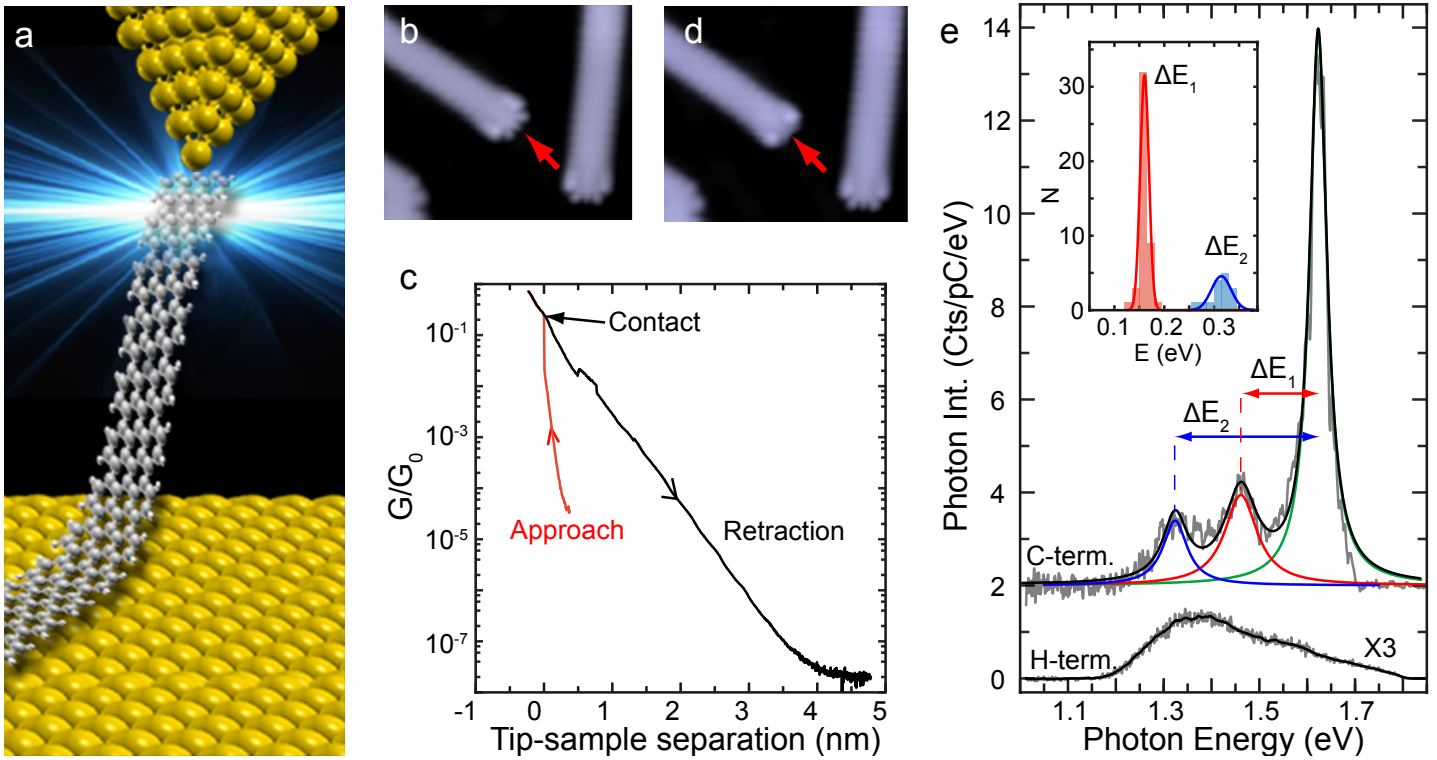
R. Denk et al, Nanoscale **9**, 18326 (2017)

STM-induced

GNR luminescence



experiments



- clear experimental evidence of tip-induced **photoluminescence** from **suspended ribbons**
- tip needs to be in chemical contact with the ribbon (C-term.)
- excitation energy significantly smaller than extended GNR => **GNR termination**

free standing termini

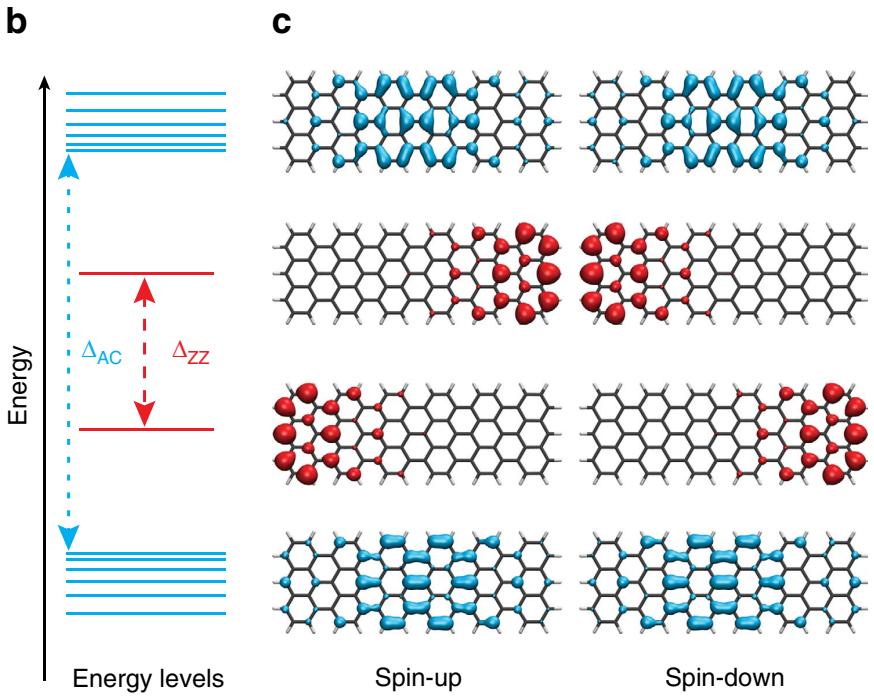
ARTICLE

Received 28 Sep 2015 | Accepted 4 Apr 2016 | Published 16 May 2016

DOI: 10.1038/ncomms11507 OPEN

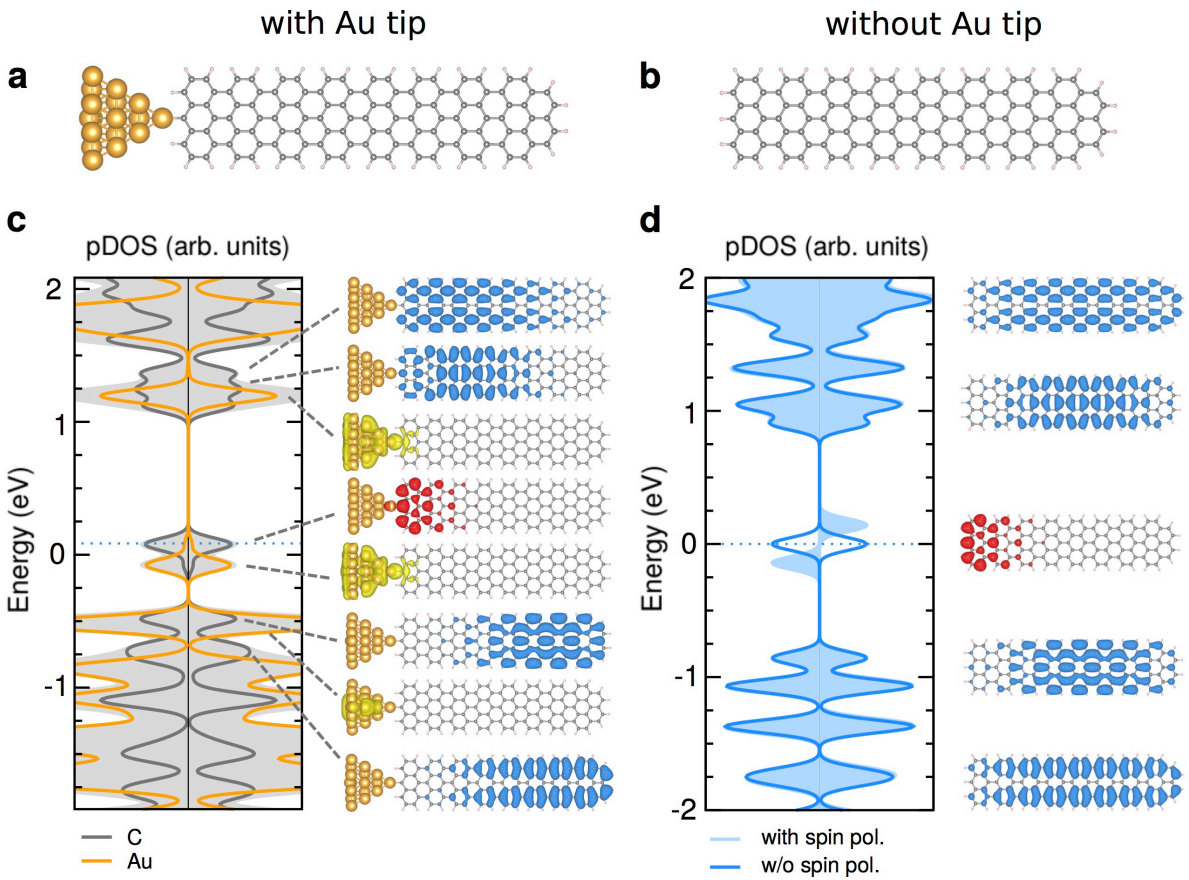
Giant edge state splitting at atomically precise graphene zigzag edges

Shiyong Wang[1,*], Leopold Talirz[1,*], Carlo A. Pignedoli[1,2], Xinliang Feng[3], Klaus Müllen[3], Roman Fasel[1,4] & Pascal Ruffieux[1]



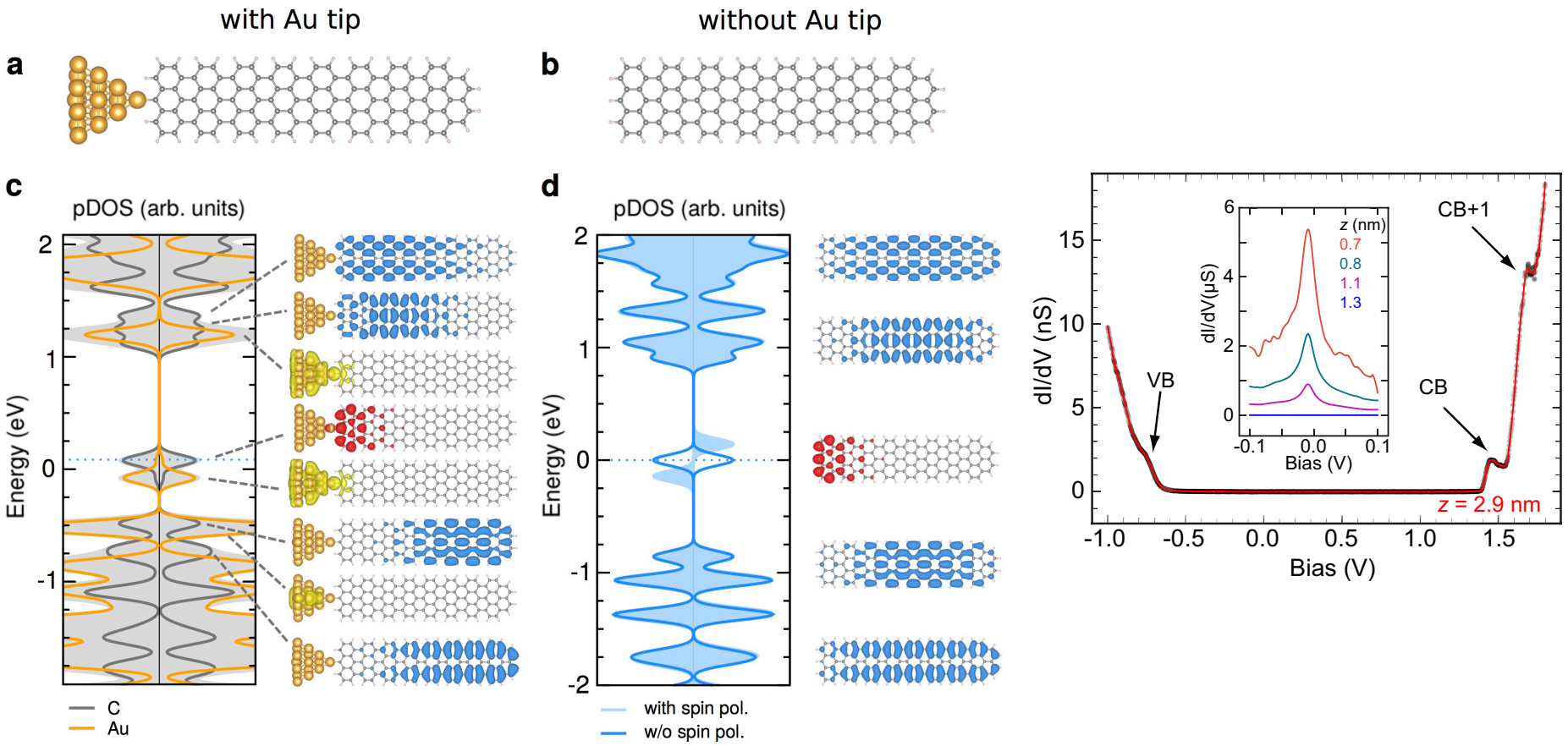
- Anti-ferromagnetic edge states when zig-zag termini are exposed
- GW gives a **gigantic splitting** as compared to DFT (0.3 eV -> 2.8 eV)
- bulk states are non-magnetic and resemble the case of extended GNR

tip effect from DFT



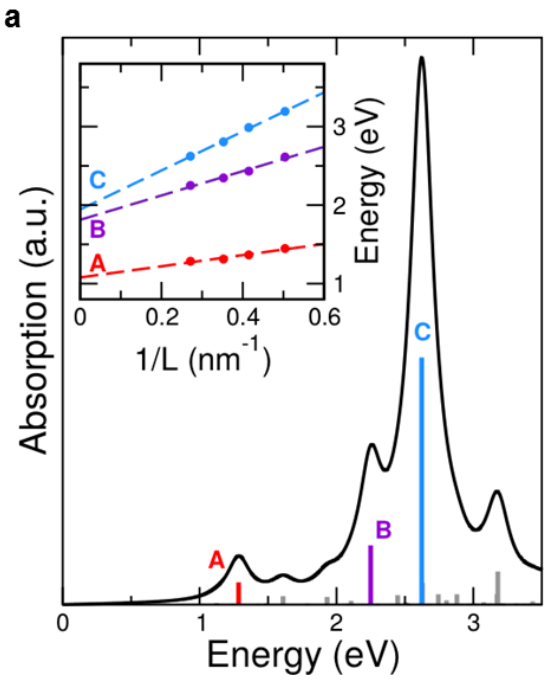
- gold tip restores a **non-magnetic ground state**
- antiferromagnetic states no longer found

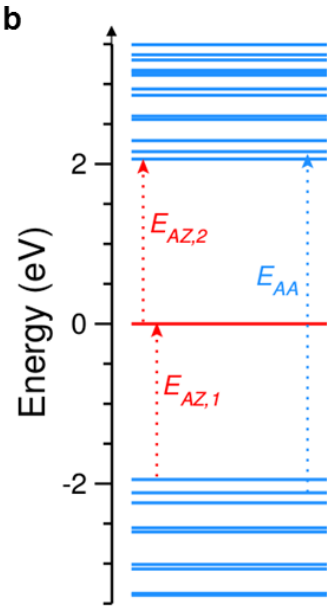
tip effect from DFT

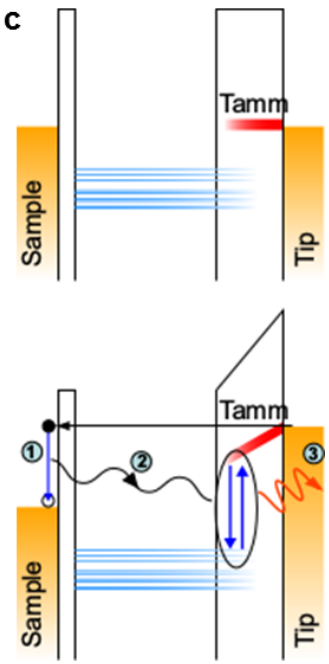


- gold tip restores a **non-magnetic ground state**
- no antiferromagnetic states found
- **experimentally confirmed** by STS

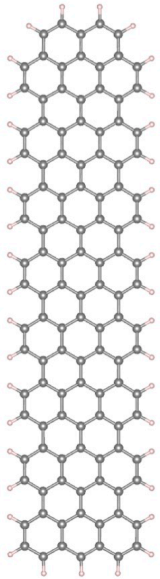
GNR optics







- **GW & BSE calculations** done without tip for several ribbon length
- computationally quite demanding (need HPC)
- relevant **excitations** involve the **states at the termini**
- **excellent agreement with experiments**



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Coworkers:

THEO **D. Prezzi, C. Cardoso** – **S3-CNR-NANO & UniMoRe**

STS **M. Chong,** N. Afshar-Imani, F. Scheurer,
G. Schull – **Uni Strasburg, CNRS**

Related papers:

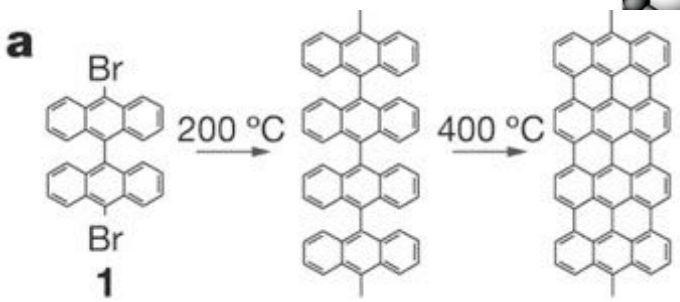
M. Chong et al, submitted (2017)

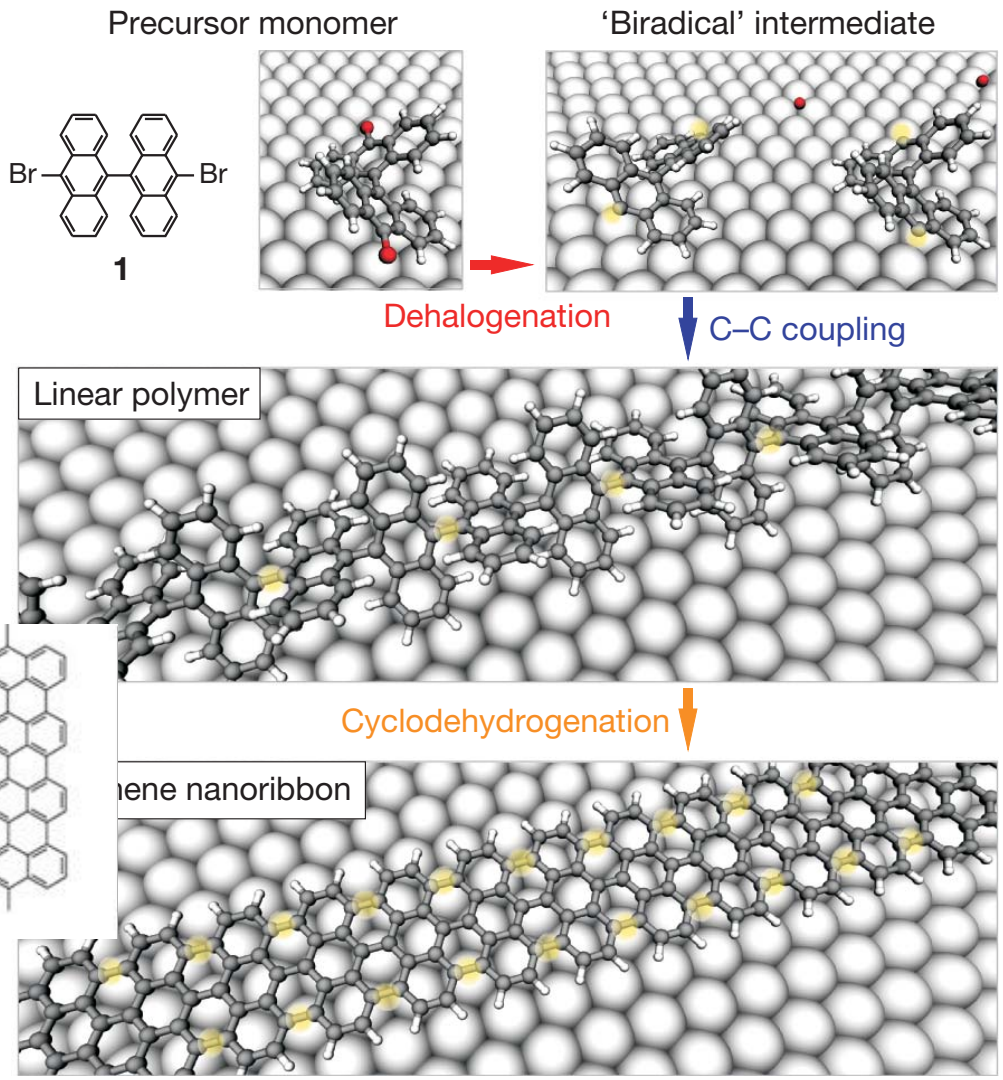
GNR growth on Au

GNR growth

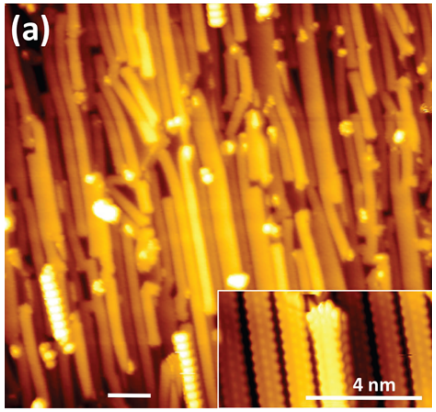
J. Cai et al, Nature **466**, 470 (2010)

- bottom up from molecular precursors
- two-step reaction
- catalyses by the surface

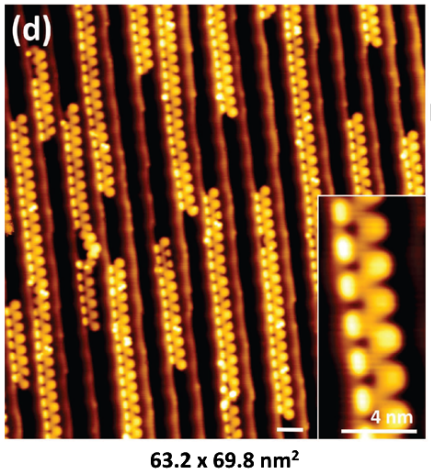




Au(110) & GNR alignment

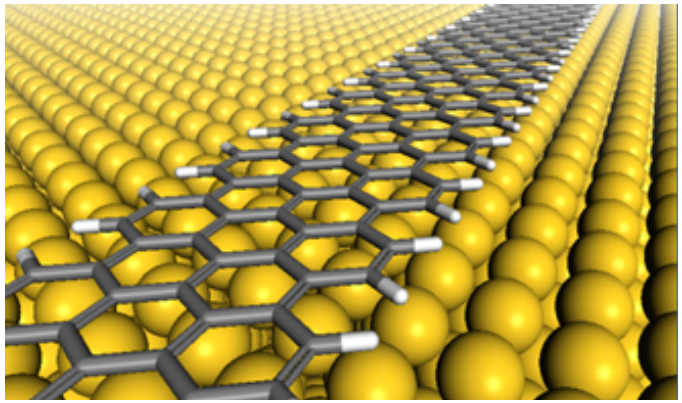


42 x 46 nm²

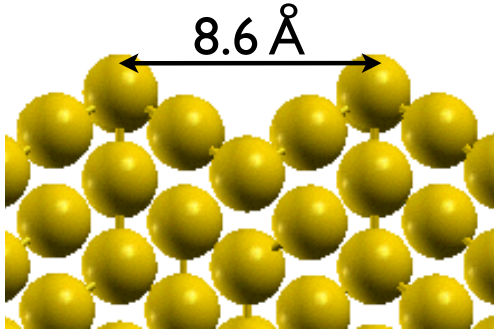


63.2 x 69.8 nm²

Linden et al. ,
PRL 108, 216801 (2012)



Au (788)



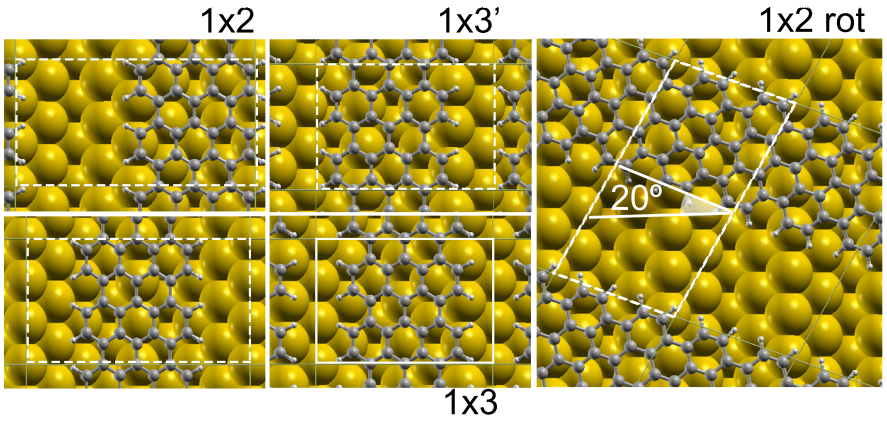
Au (110)
1x2 reconstruction

GNR @ Au(110)

EXTENDED SYSTEMS:

Plane-waves / ultrasoft pseudopotentials / DFT, as implemented in

QUANTUMESPRESSO



GNR and precursors on Au(110)

MOLECULES:

aug-cc-pVTZ basis set / CAM-B3LYP, as implemented in ORCA

Results compared with structural and spectroscopic measurements:

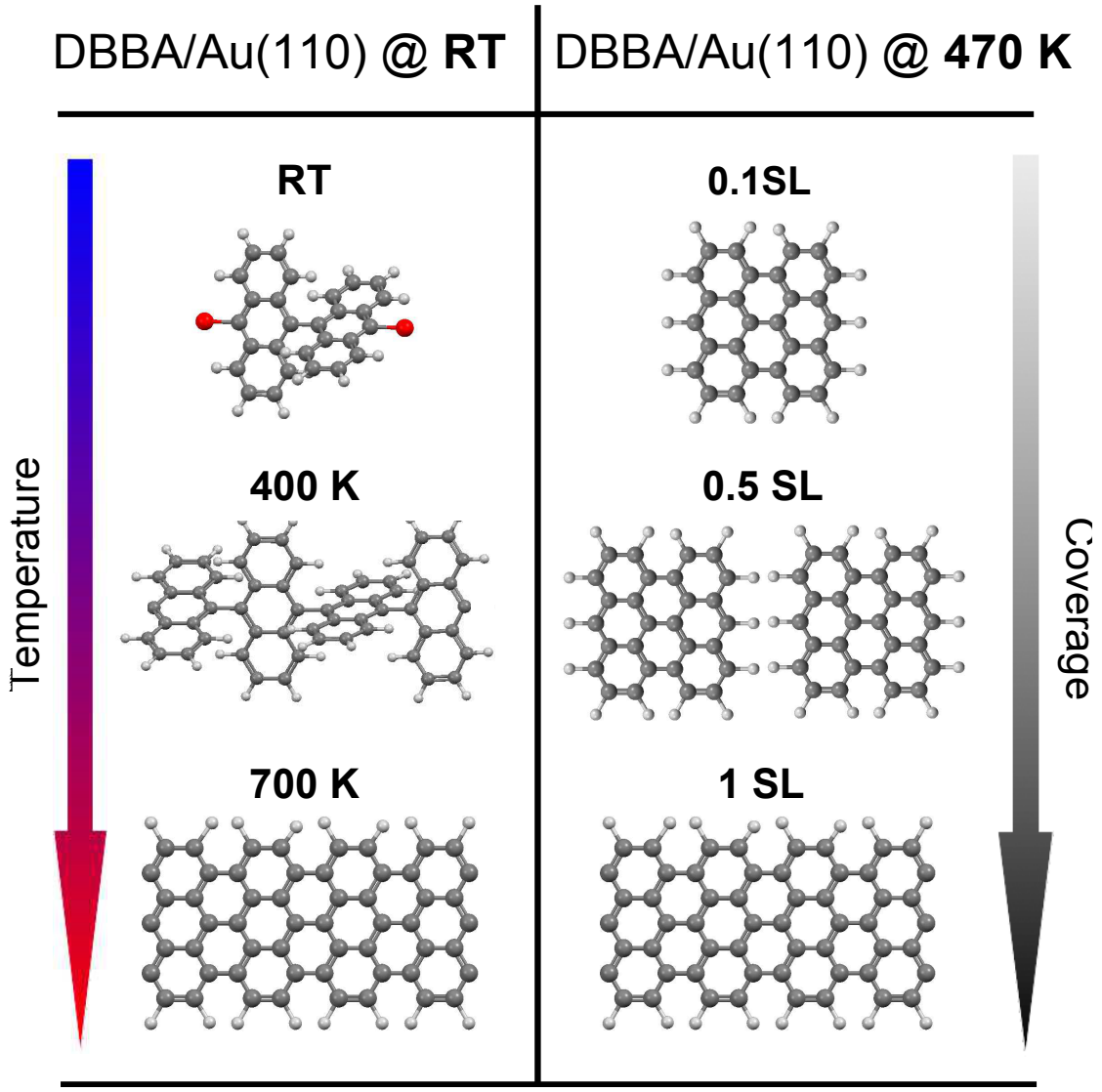
STM, XPS/UPS, NEXAFS.

GNR @ Au(110)

L. Massimi et al, JPCC **119**, 2427 (2015)

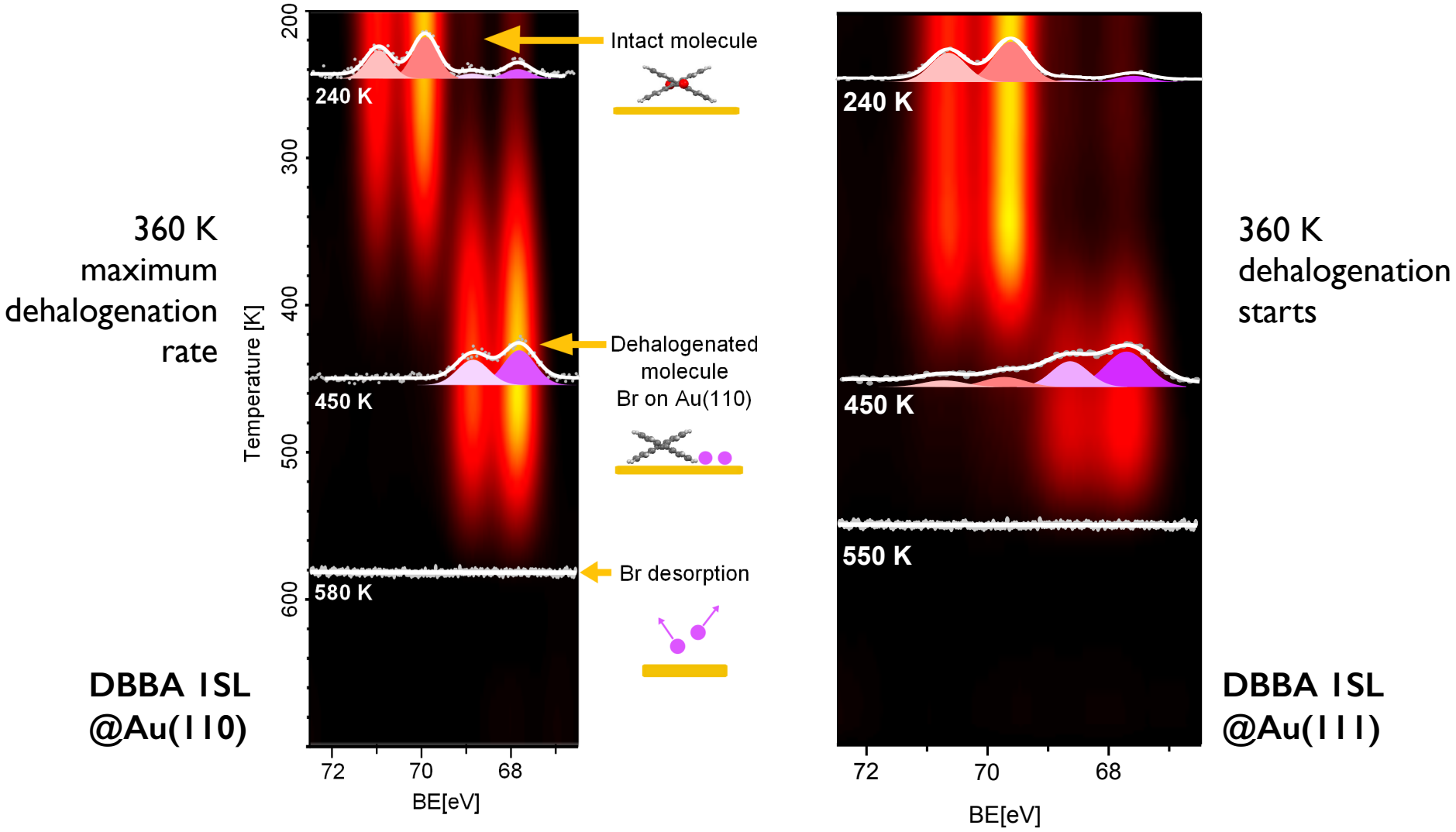
A. Della Pia et al, JPCC **120**, 7323 (2016)

low GNR yield, competing mechanisms



XPS: Br-3d core levels

L. Massimi et al, JPCC **119**, 2427 (2015)



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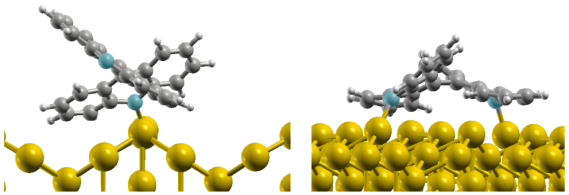
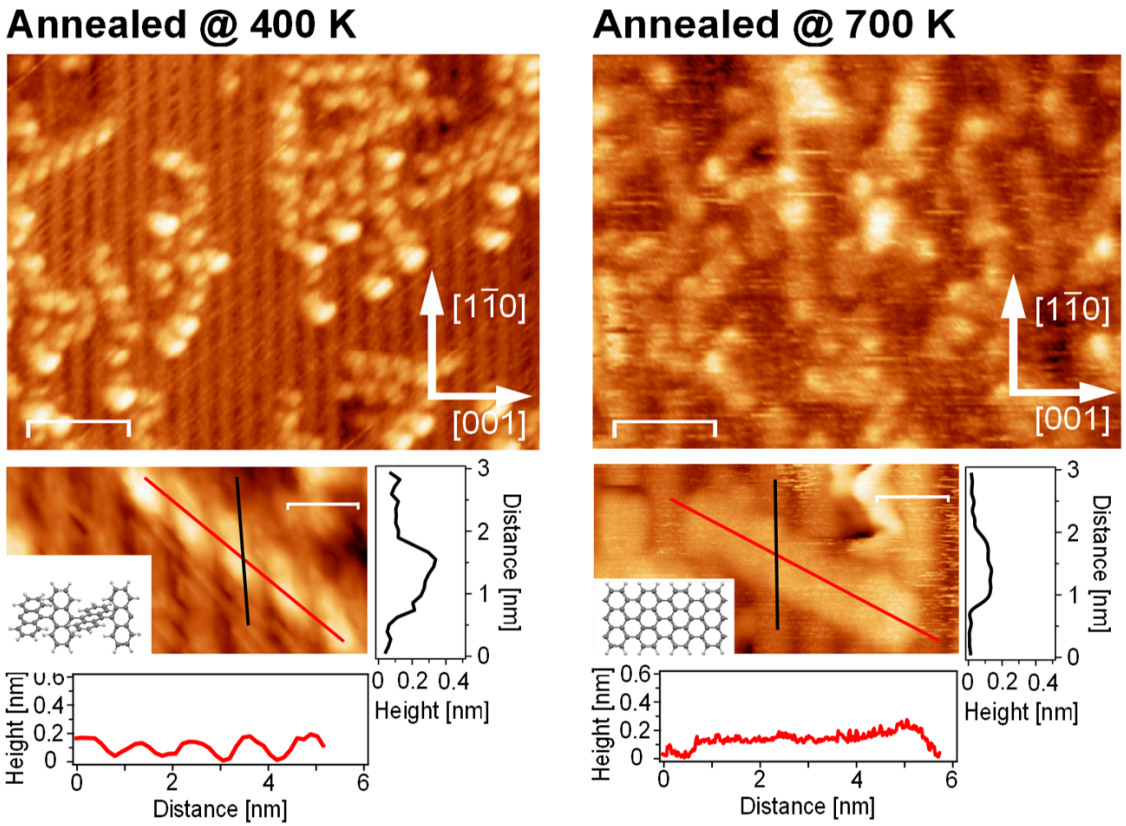


Figure 5. Optimized geometries computed within DFT for the debrominated DBBA. Left panel: molecule aligned along the Au rows, forming one bond with the surface. Right panel: the molecule rotated by 20° with respect to the direction perpendicular to the Au channels, showing the two bonds with the Au surface. The debrominated C atoms are in light blue.



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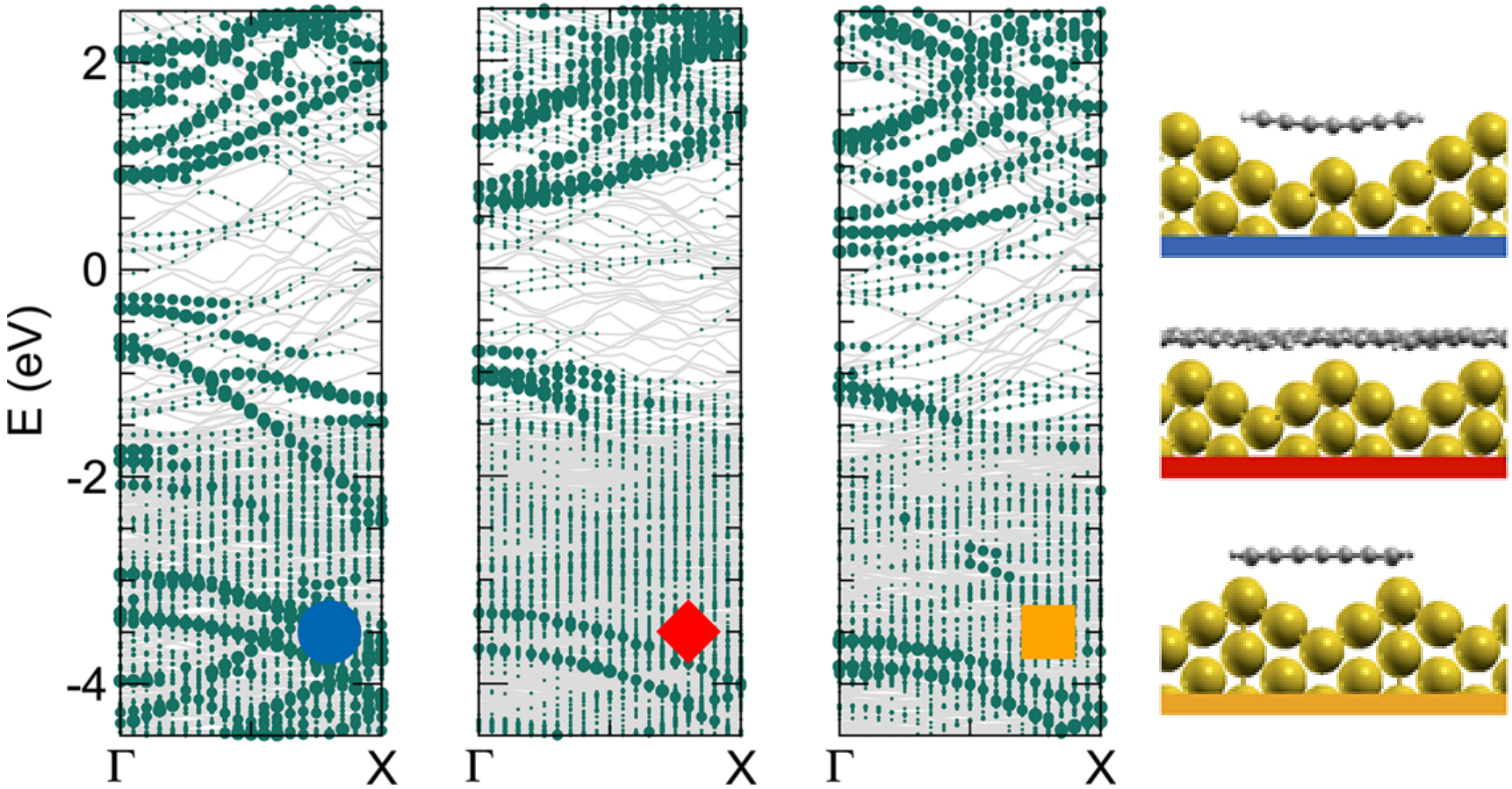
Electronic structure



summary

- **Au(110) studied as a driver for GNR alignment**

detailed characterization,
low GNR yield,
competing mechanisms present

delicate interplay of substrate-molecule interaction, corrugation & mobility

- **Substrate-molecule interaction**

catalyze the growth of GNR

stronger in Au(110) than Au(111)

electronic structure:
interaction strength experimentally characterised (UPS) and theoretically simulated.

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THEO C. Cardoso, D. Varsano, – S3-CNR-NANO & UniMoRe
D. Prezzi, E. Molinari

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O. Ourdjini, A. Della Pia,

M.G. Betti, C. Mariani

E. Cavaliere, L. Gavioli – Uni Catt. Brescia

thanks!


FUTURO
IN RICERCA


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