MOLECULAR ELECTRO-OPTO-SPINTRONICS

Mainz 15-18 Oct 2019

Graphene-based molecular devices for spin and photon detection

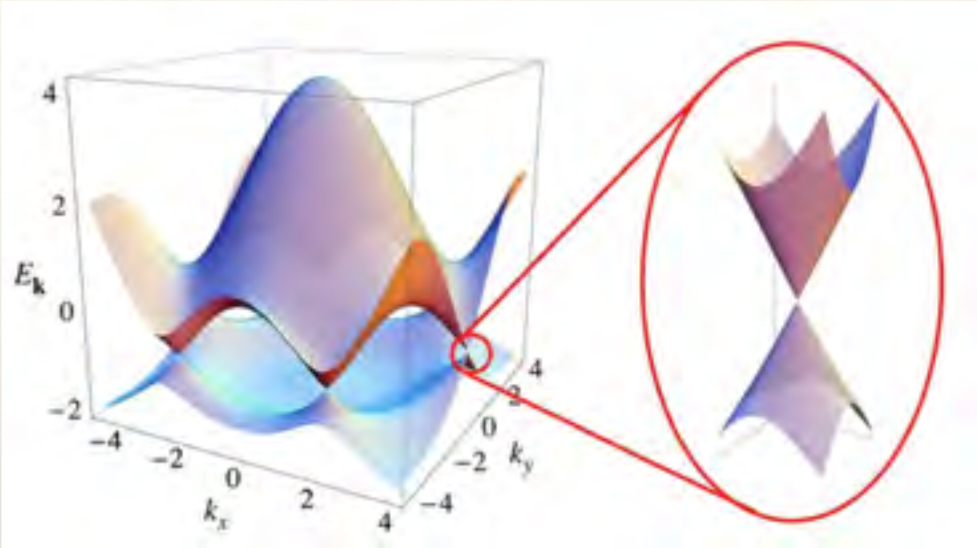
Marco Affronte

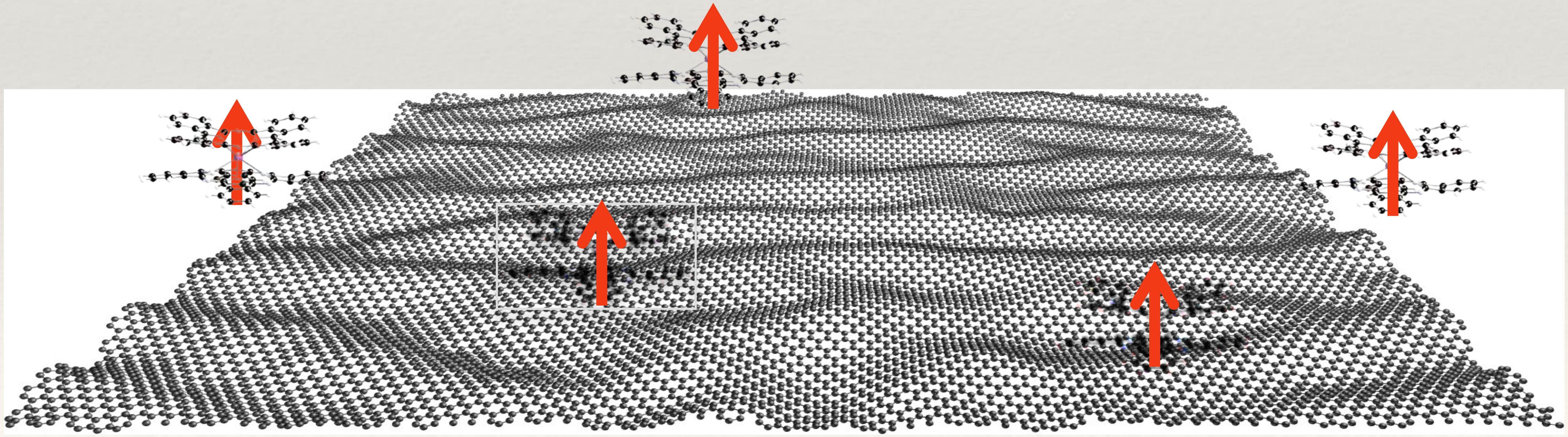
UNIMORE
UNIVERSITÀ DEGLI STUDI DI MODENA E REGGIO EMILIA

CNRNANO MODENA S3

graphene as platform for electronic devices

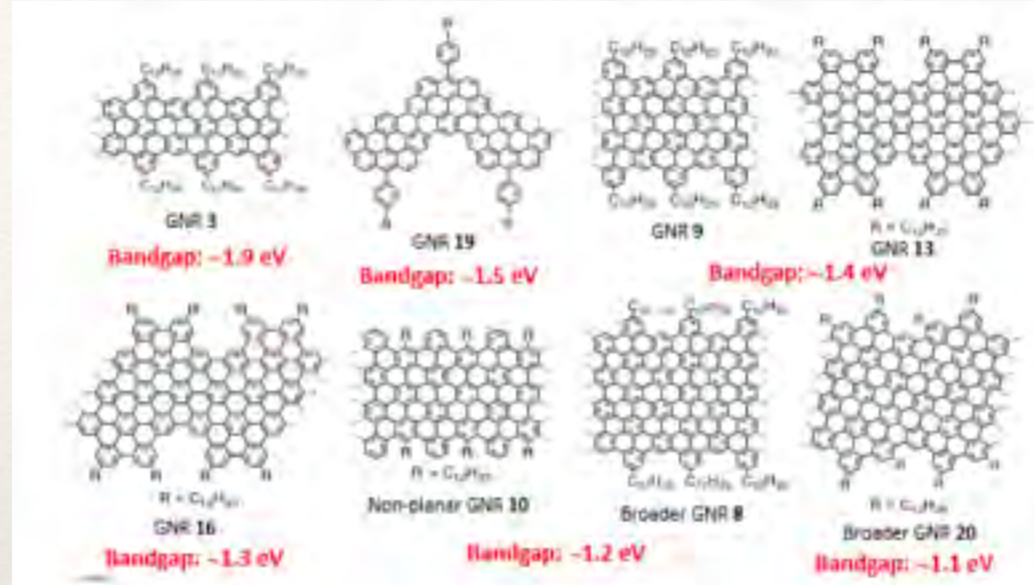
- graphene as conducting layer with tuneable charge polarity
- zero band-gap
- intrinsic magnetism (?)
- electrical contacts for molecular electronics (?)

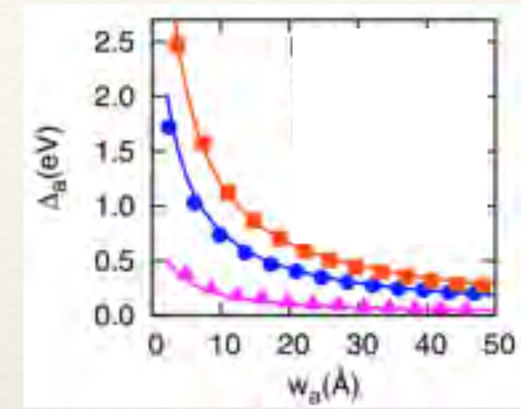




how add functionalities?

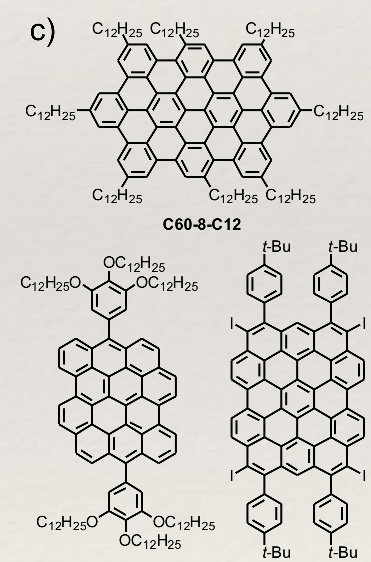
Graphene Nano-Ribbons (GNR)

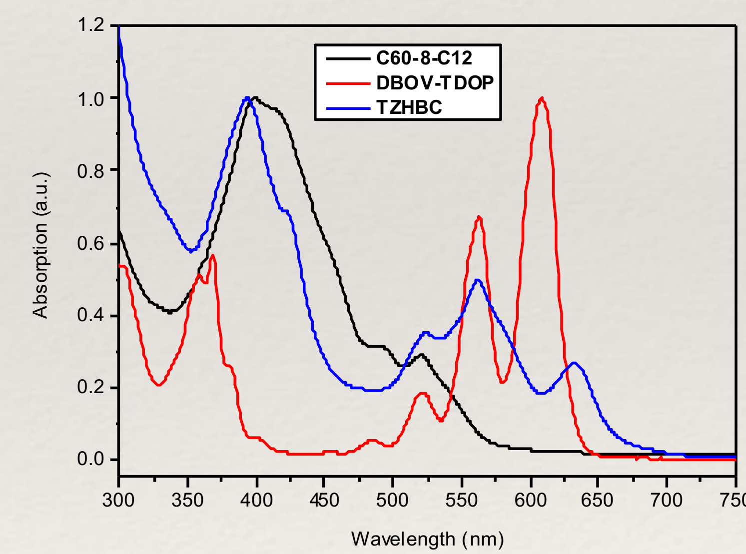




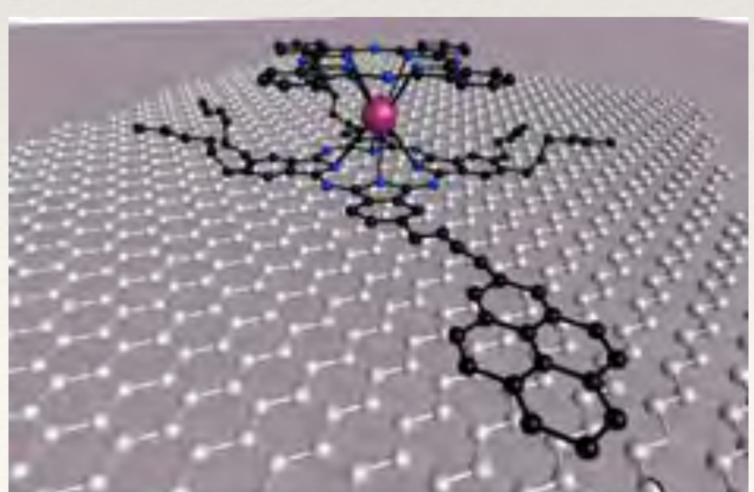
PRL vol. 97, no. 21, pp. 1–4, 2006.

Graphene Quantum Dots (GQD)

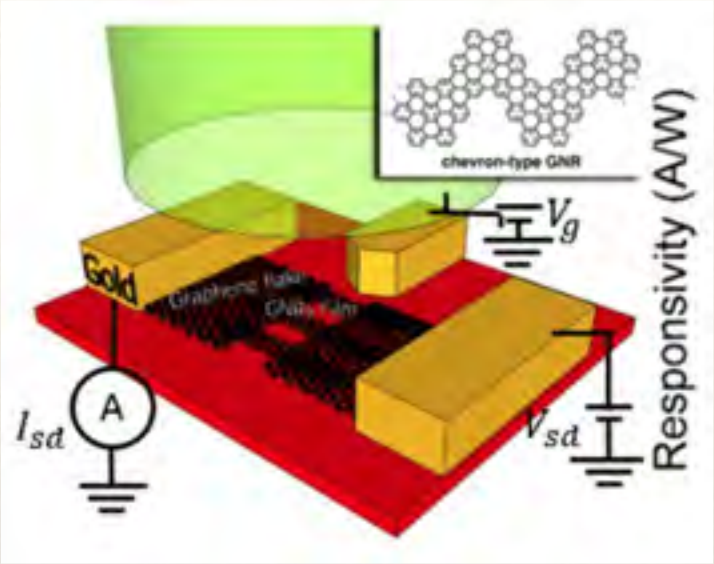




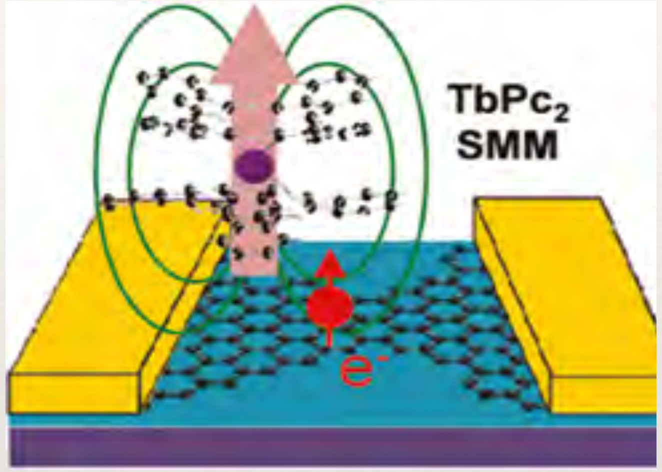
Molecular Spins



graphene based nano-architectures

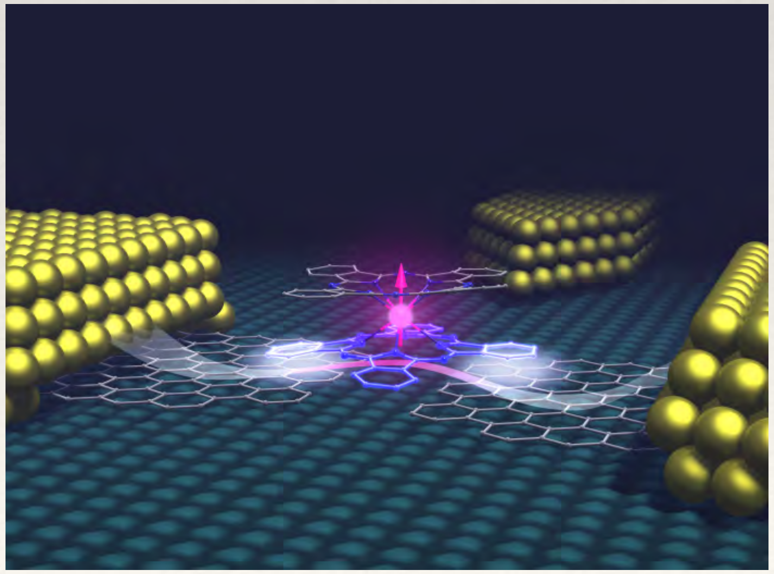


molecular spin valve

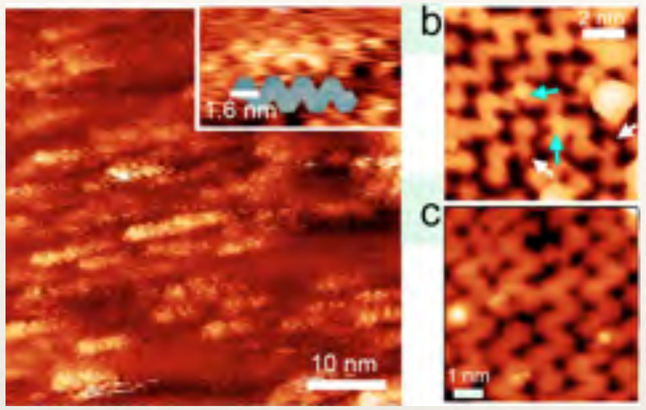


- **all-carbon molecular electronics**
  - graphene based electrodes
  - deposition of GNR/GQD
  - opto-electronic devices

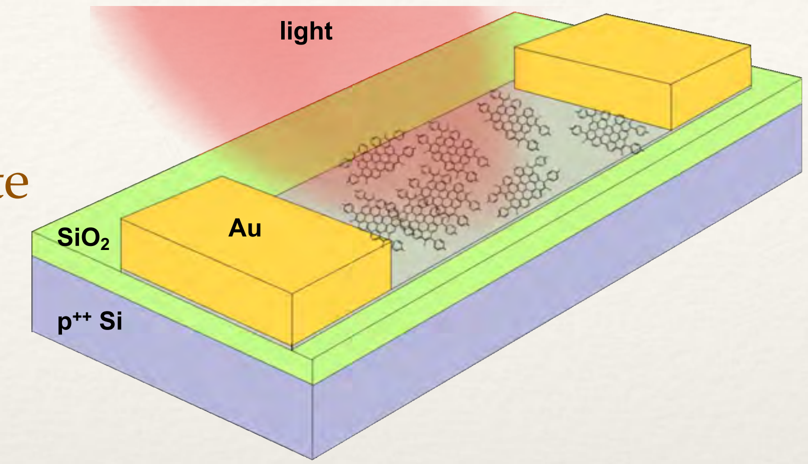
single-molecule spin transistor



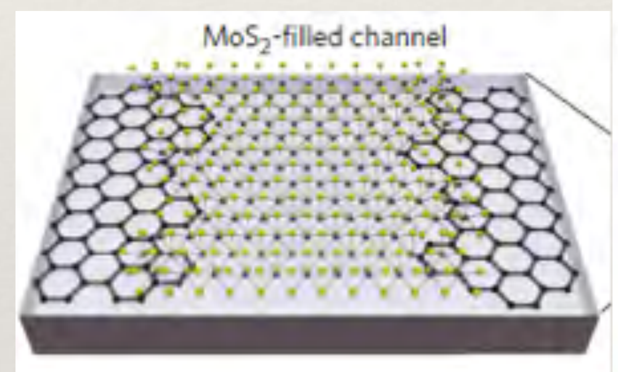
open issues



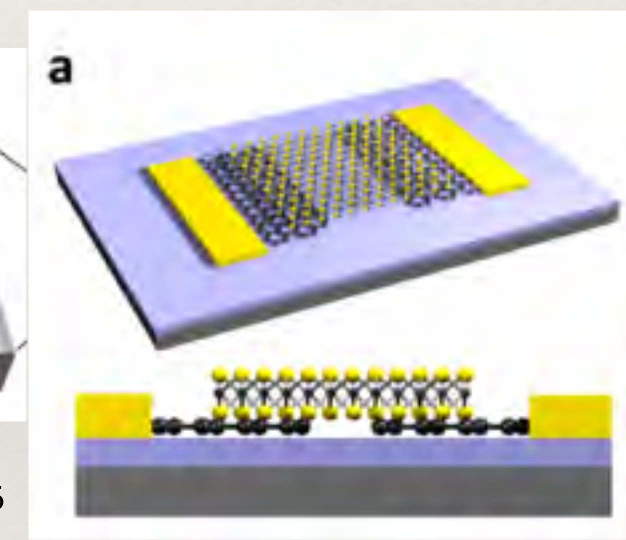
transfer from metal
to insulating substrate



efficient molecular contact



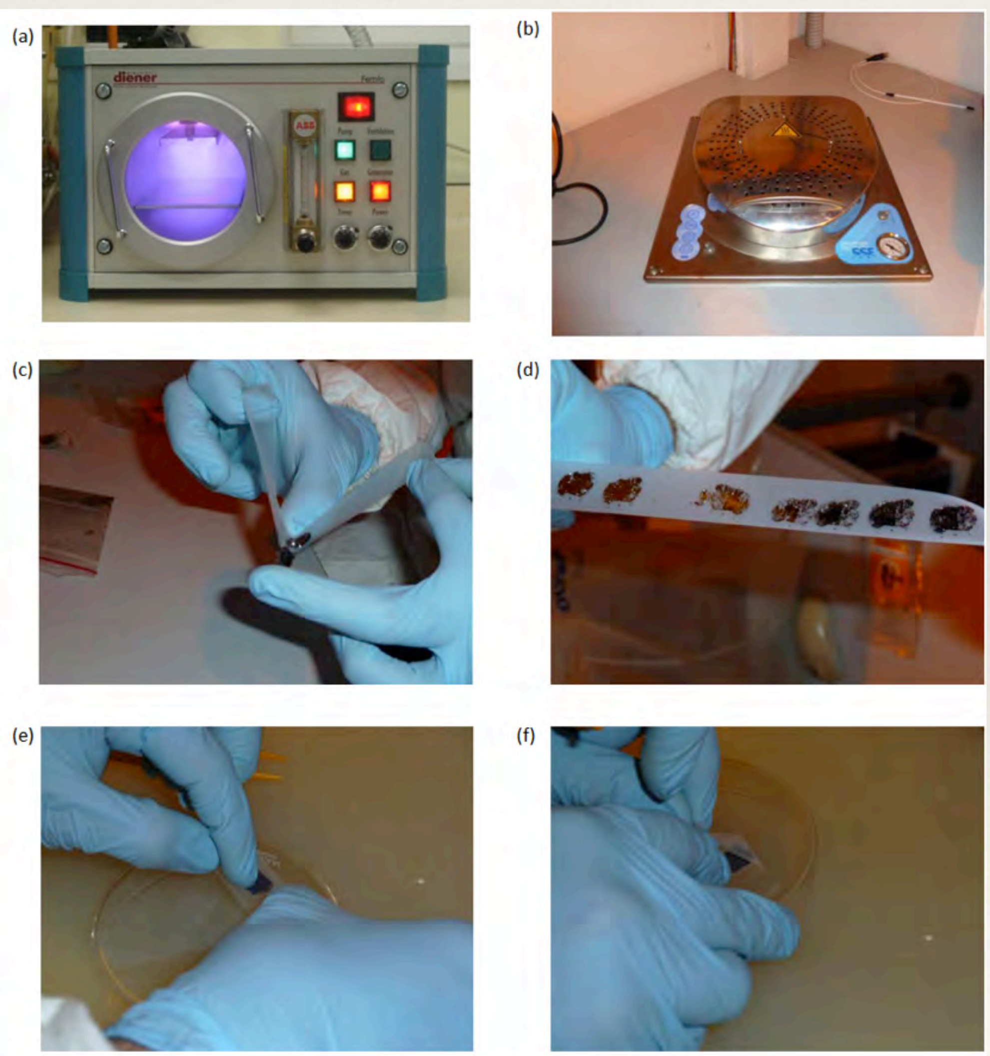
Y. Liu et al., Nano Lett. 2015
M. Zhao et al., Nature Nano, 2016



strategy for fabrication of molecular scale devices

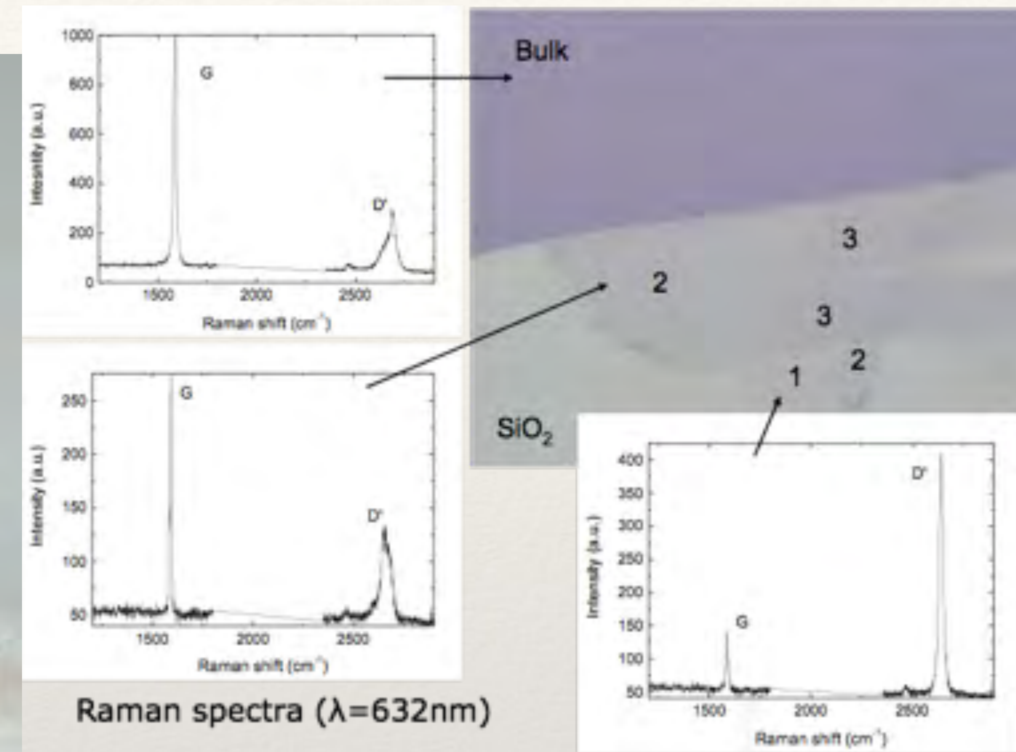
size / quantum effects when device works at molecular scale

fabrication of graphene devices: exfoliated graphene



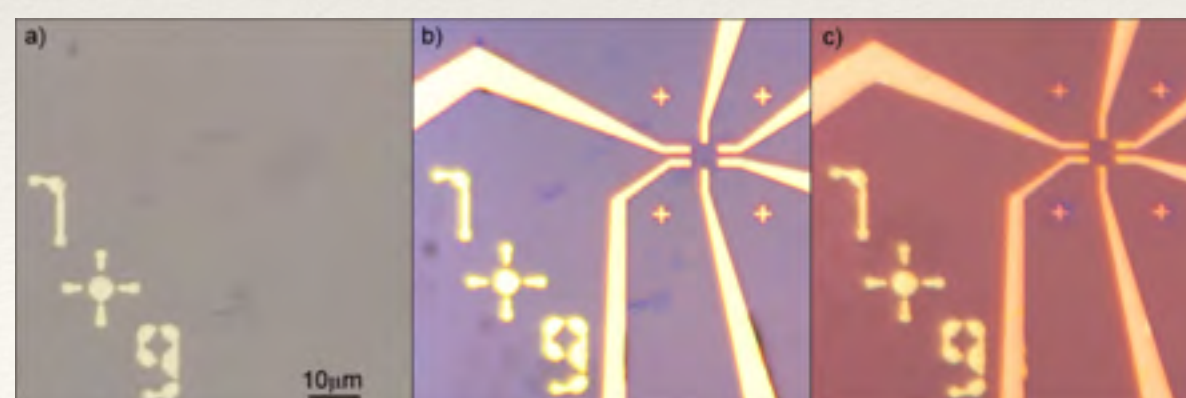
production by scotch tape-method

localisation on SiO substrate by optical microscope



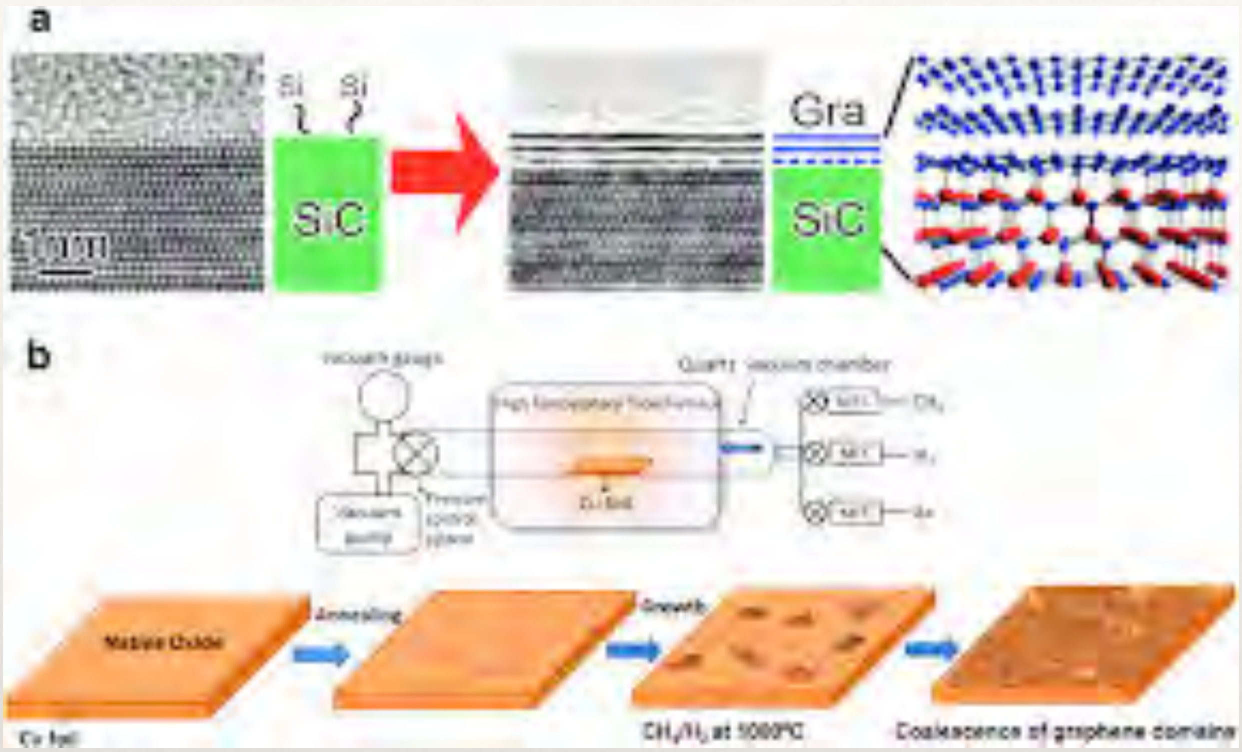
characterization by Raman spectroscopy

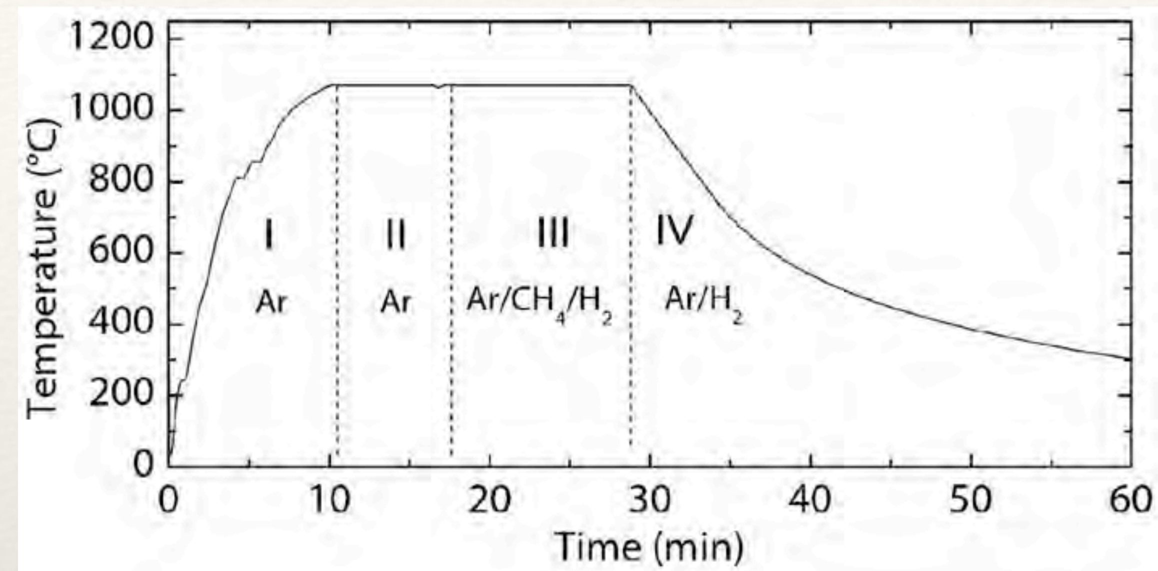
electrical contacts



graphene on C-SiC by CVD

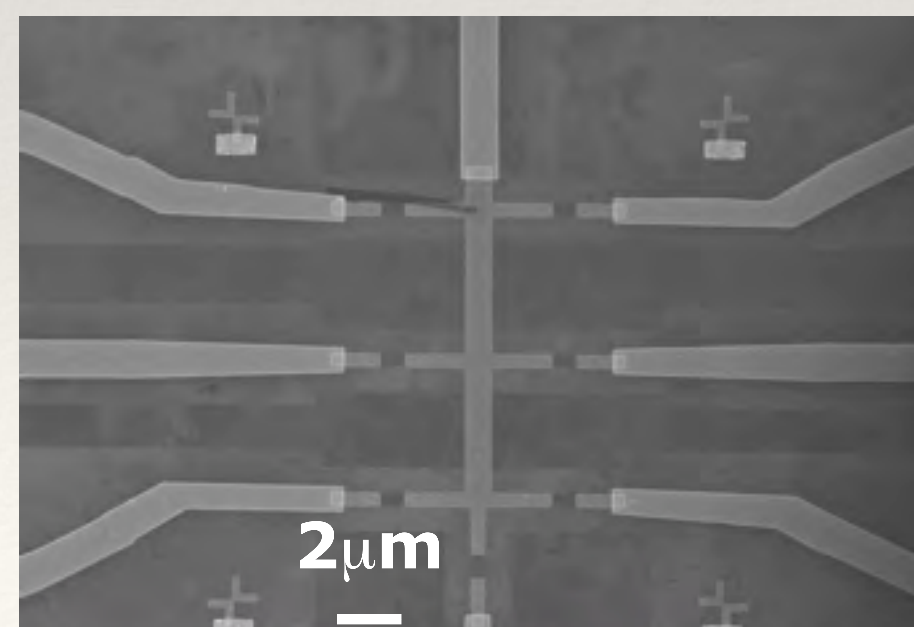
from C. Colletti , L. Martini IIT Pisa(IT)





graphene was obtained in reactor via thermal decomposition, achieved by heating the samples in an Ar atmosphere at = 1420°C and = 780 mbar for 90 minutes.

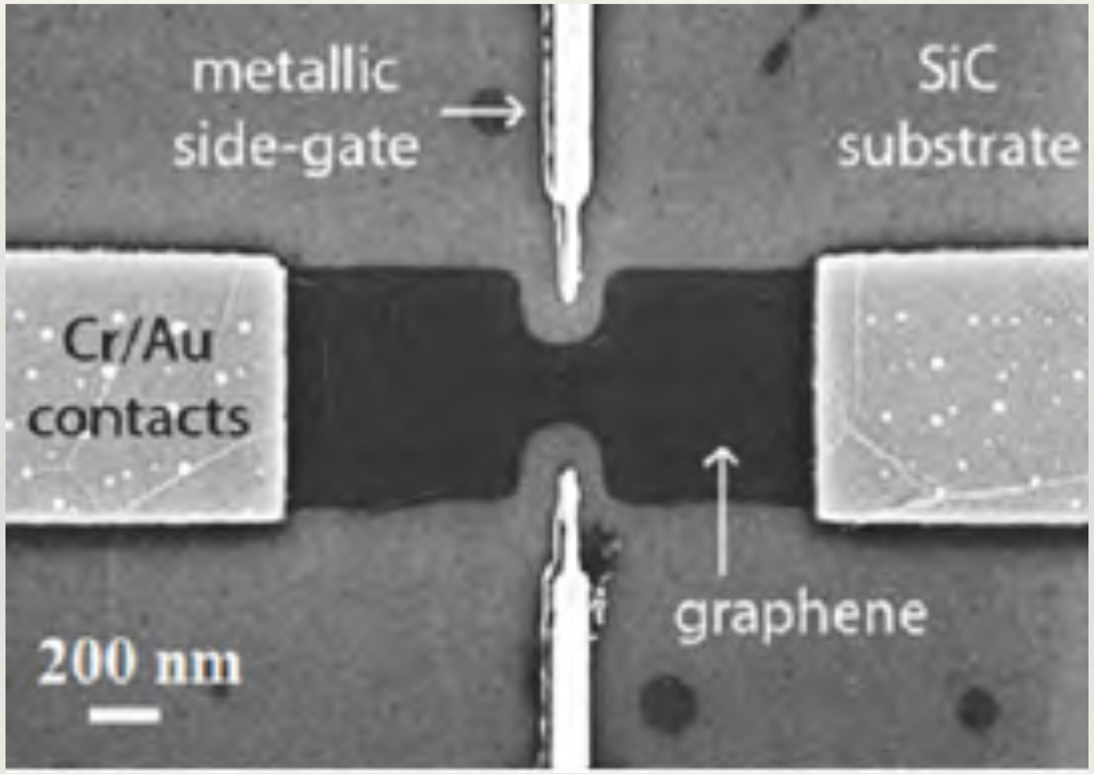
graphene over large surface allows realisation of multiple devices



Electron Beam Lithography

EBL is used to:

- pattern graphene
- fabricate metal contacts

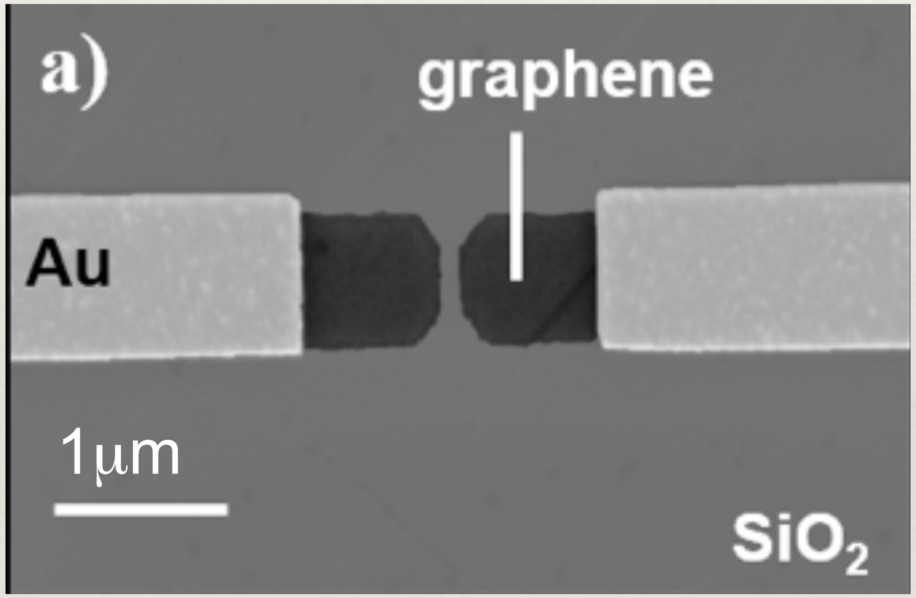
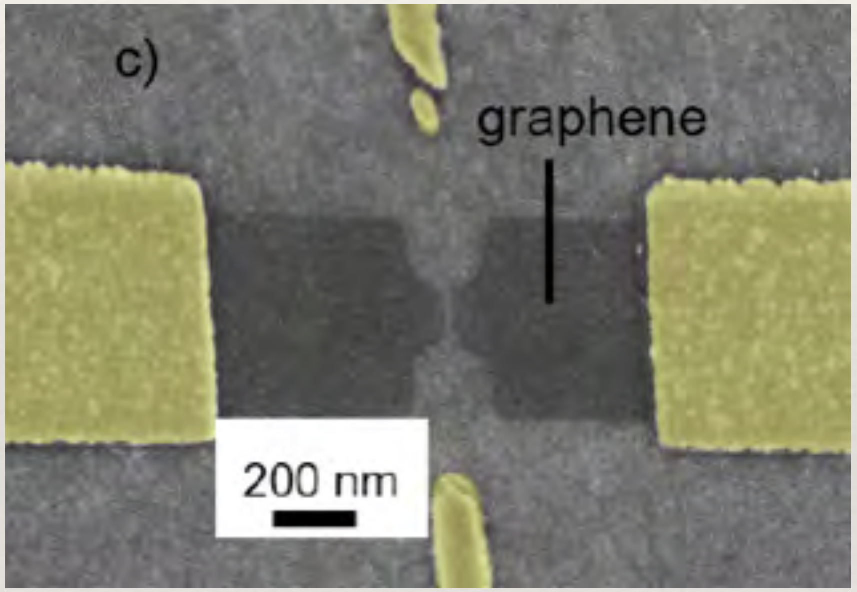
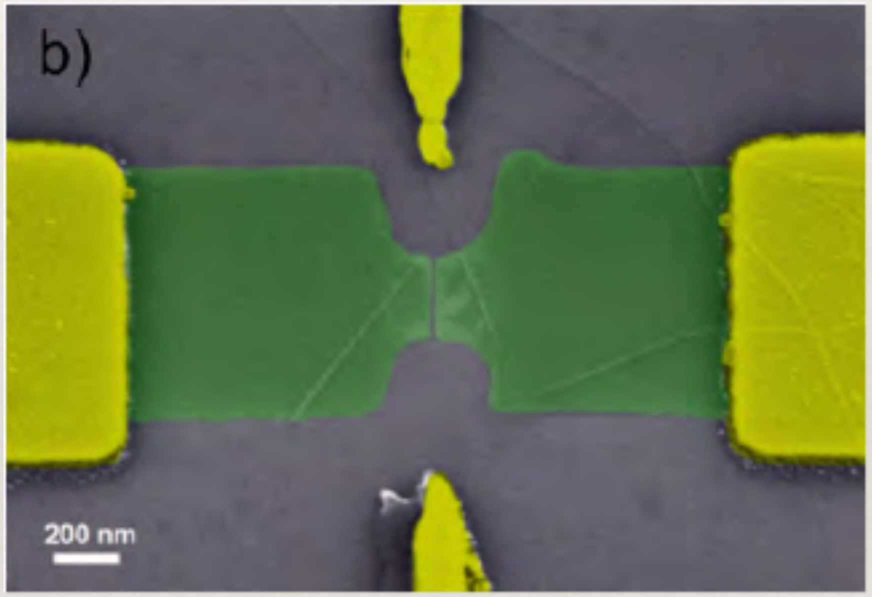


1. A thin film (300 nm) of poly(methyl-methacrylate) (PMMA) 950K was deposited on the wafer by having the spin-coater rotate at 4000 rpm for 1 minute.
2. The substrate was annealed at 115°C for 15 minutes in order for the PMMA solvent to evaporate without glass transition of the polymer.
3. The array of markers was patterned by EBL (consisting of a Sigma Zeiss SEM connected to a Raith pattern generator), using a beam aperture of 30micron and irradiating the resist with a dose of 240 microC/cm^2.
4. After the lithography, the pattern was developed by immersion in methyl-isobutyl-ketone (MIBK) for 2 minutes, which dissolves the areas exposed to the electron beam (the PMMA being a positive resist).
5. The development was stopped by plunging the substrate in isopropanol for 30 seconds.

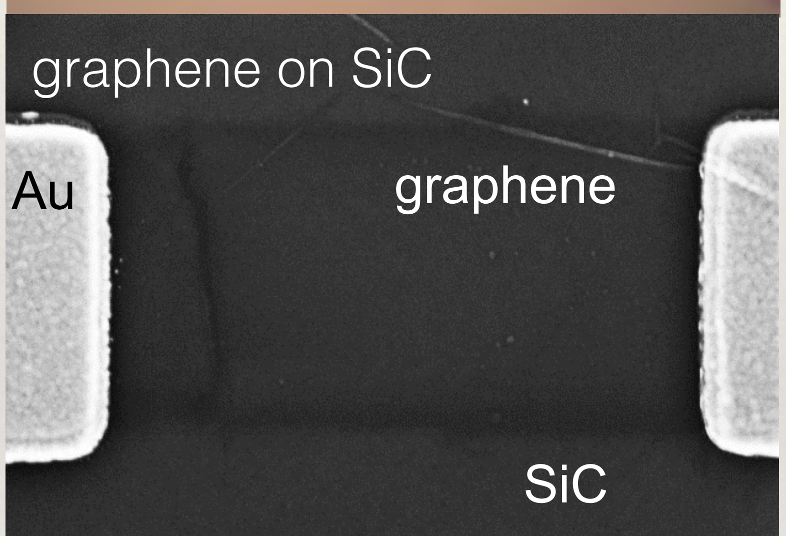
After resist development, the RIE was performed at a pressure = 10 mTorr with a constant oxygen flow rate of 20 sccm. The RF field was applied at 50 W over a time interval ranging from 10 to 20 seconds, which was sufficient to etch away all the uncovered graphene areas leaving behind graphene flakes with the desired final shape

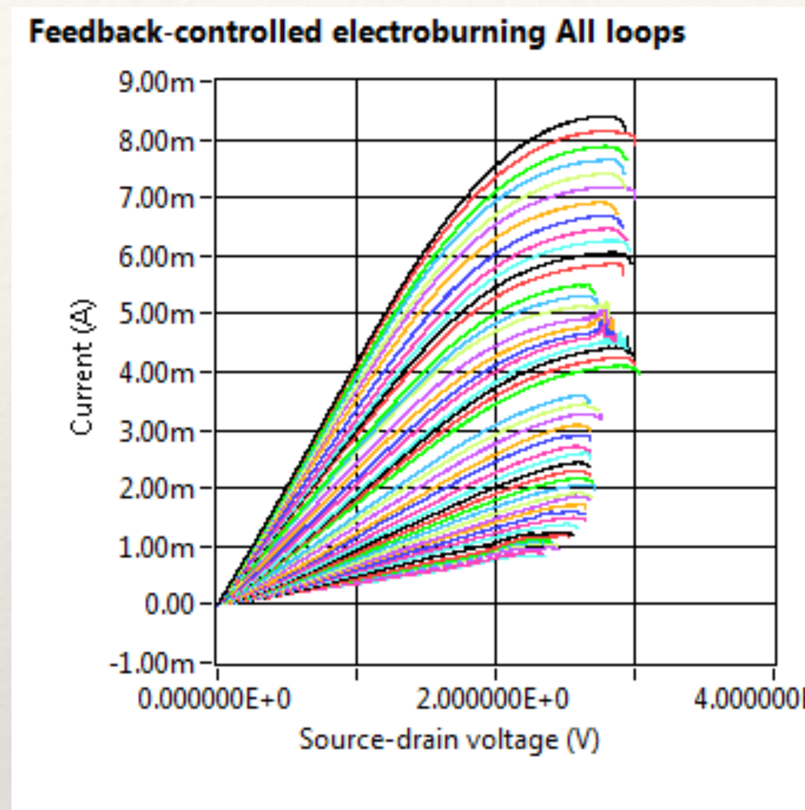
A. Candini et al., Beilstein J. Nanotech. **6,** 711 (2015)

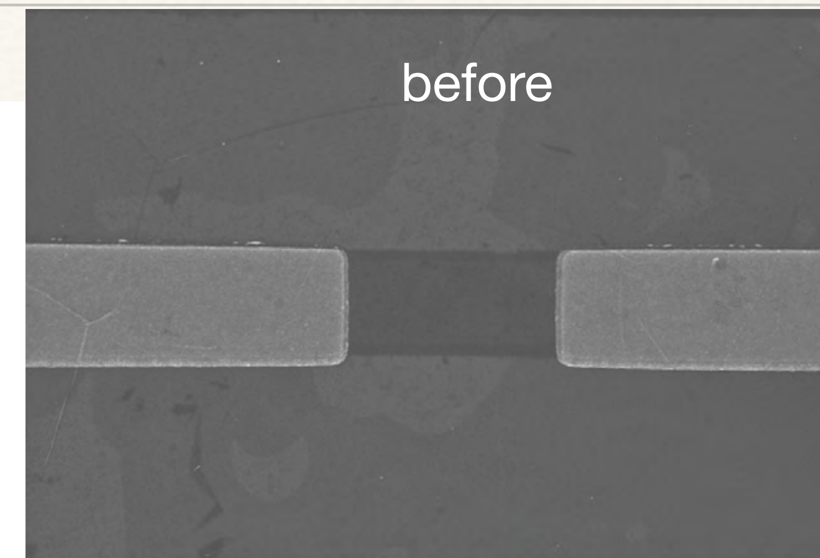
graphene electrode: different type of junctions

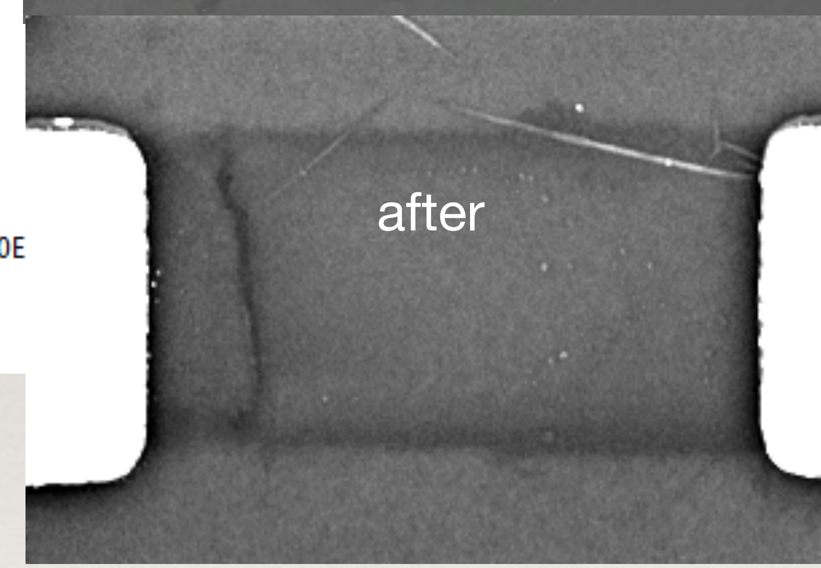
Lithography - fabricated	one shot Electroburning	Controlled Electroburning
		
down to ~50 nm	10 – 20 nm	1 – 5 nm

graphitic electrodes by electro-burning



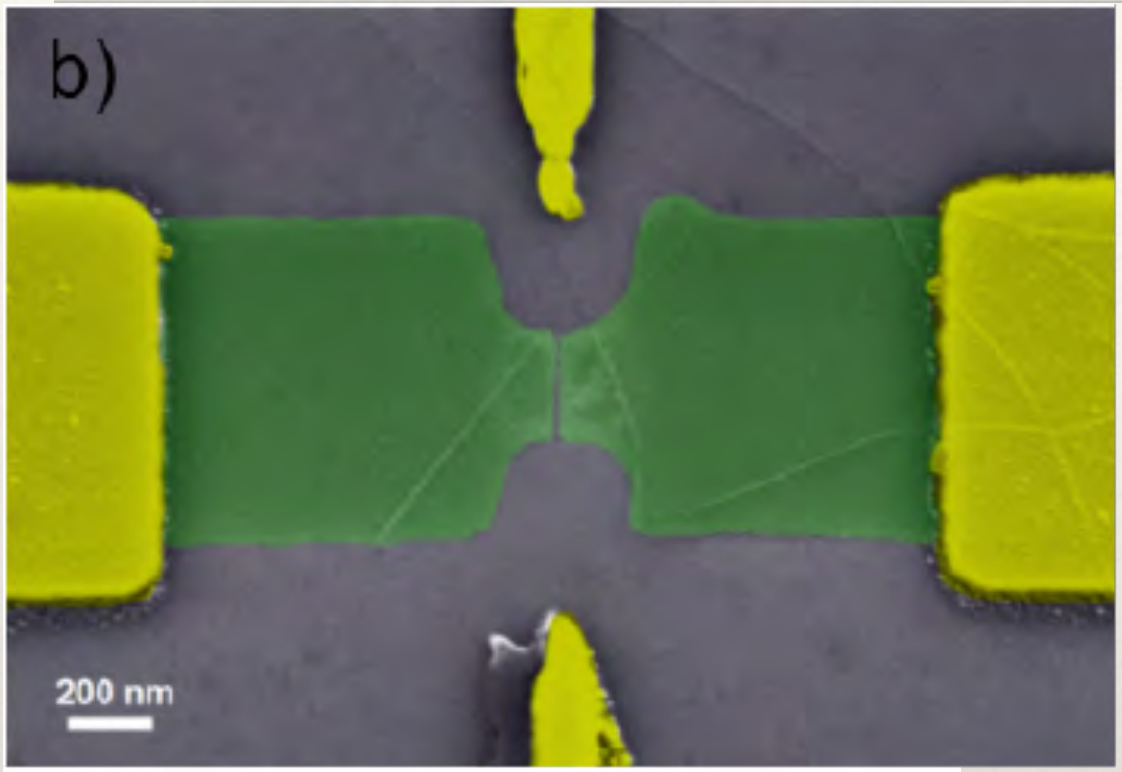




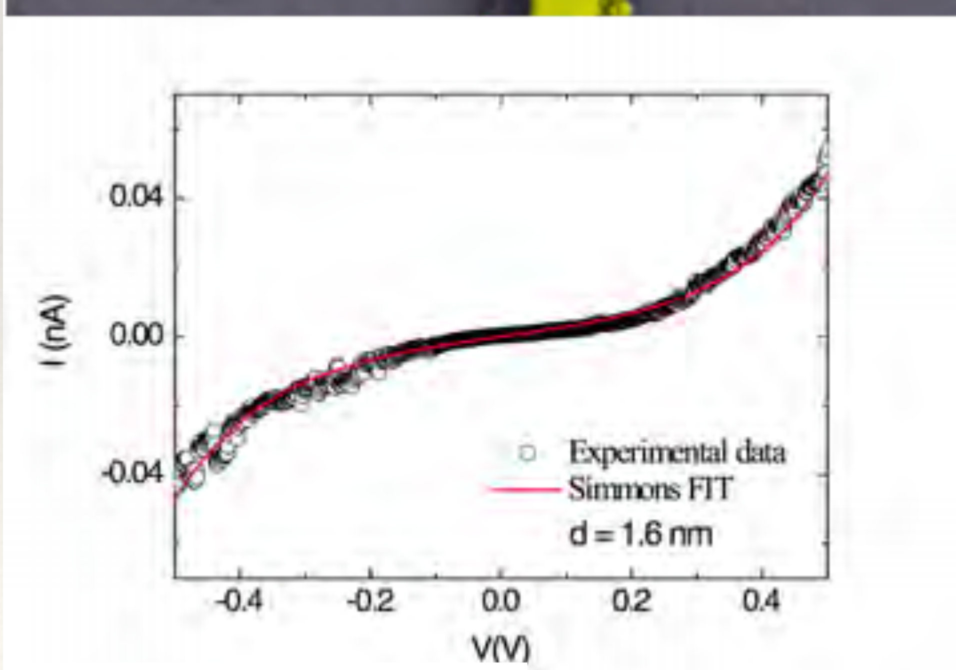


A. Candini, N. Richter, C. Coletti, F. Balestro, W. Wernsdorfer, M. Kläui and M. Affronte , *"Optimization of the electroburning process for few-layer graphene electrodes"*Beilstein J. Nanotechnol. **2015,** 6, 711–719.

electro-burnt graphene junctions

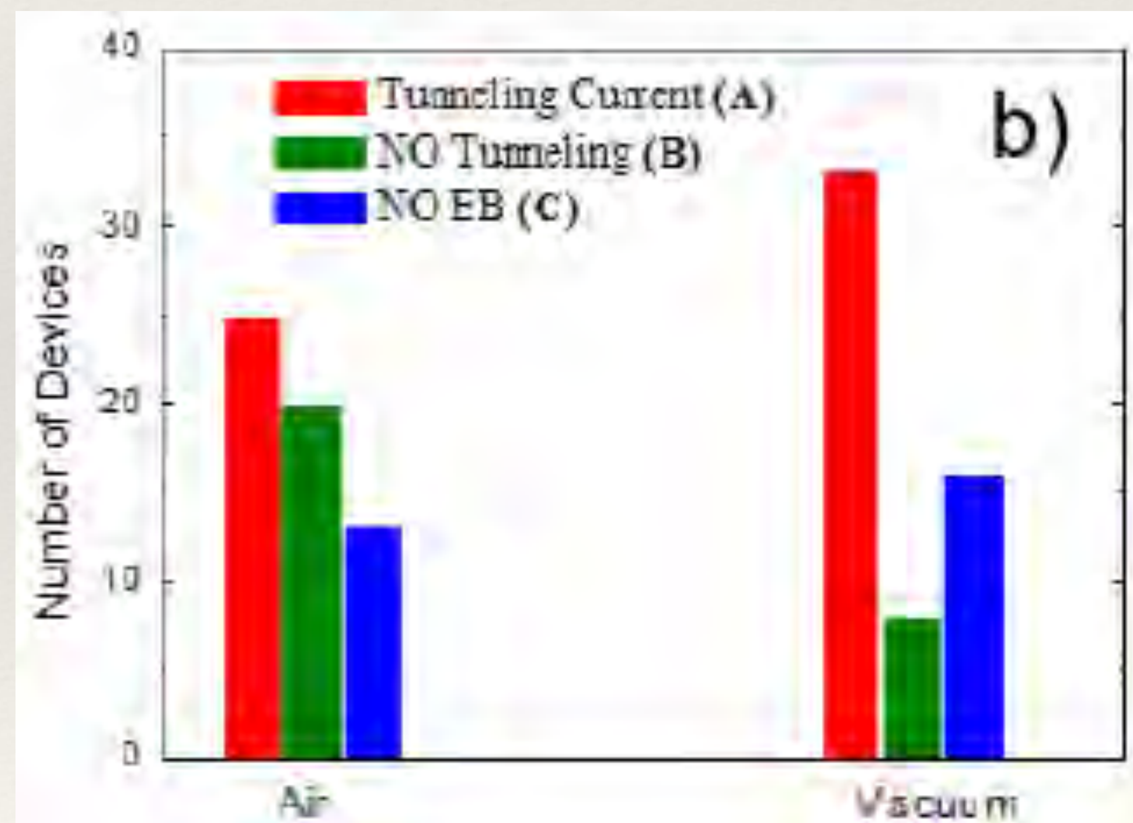


Single molecule devices as ultimate device downscaling



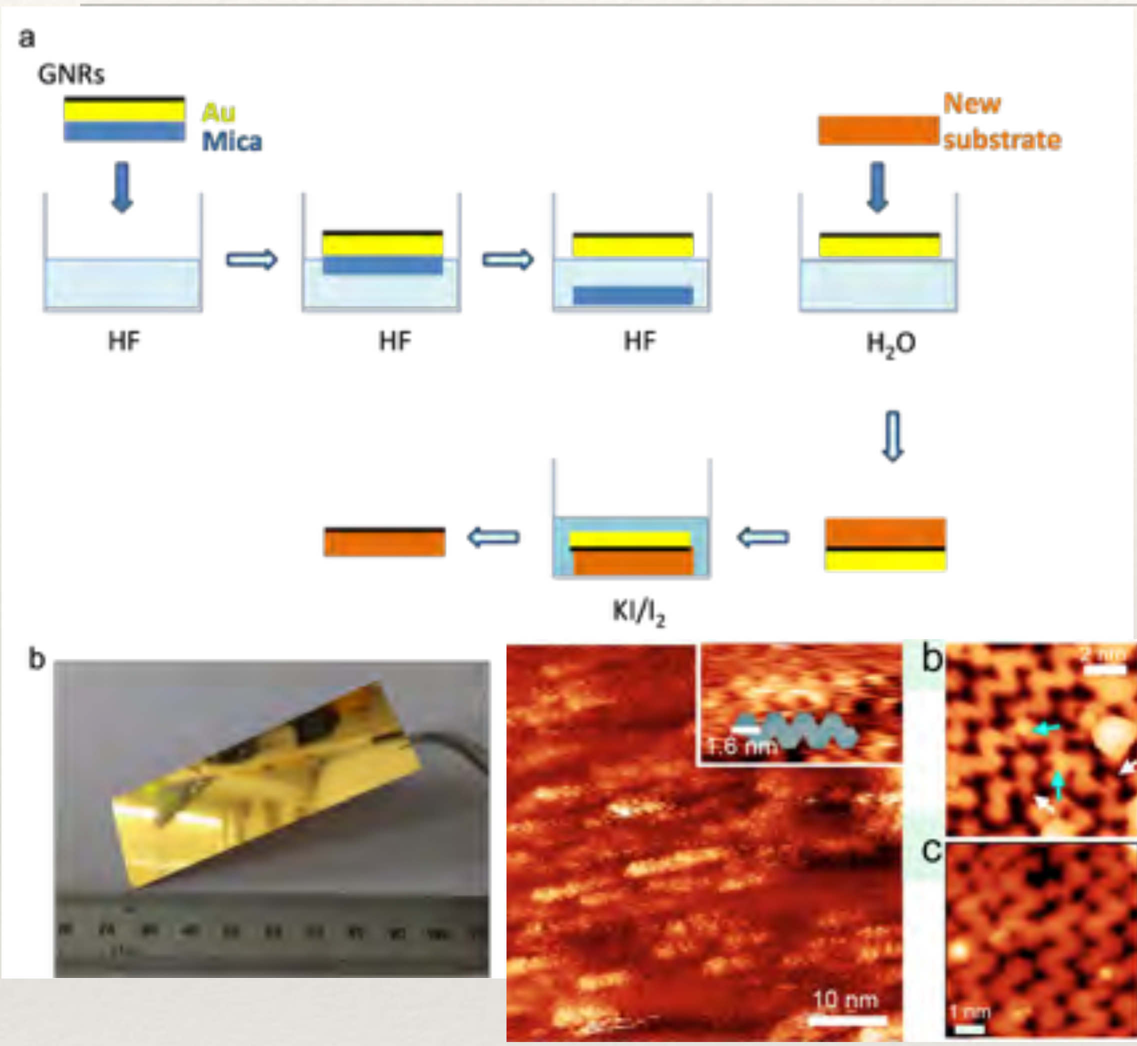
d = 1.6 nm

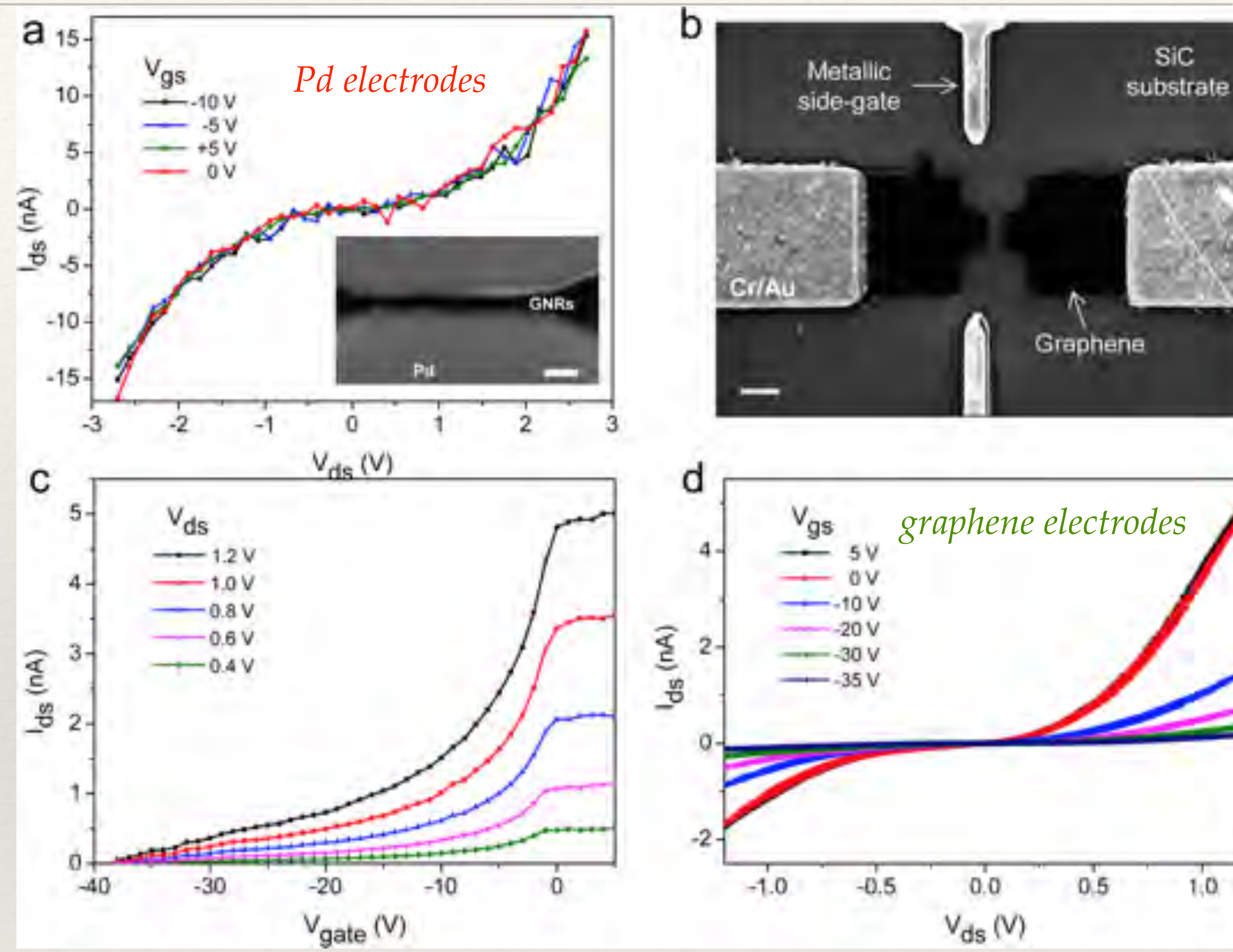
Yield ~80% in vacuum



A. Candini et al., Beilstein J. Nanotech. **6,** 711 (2015)

Field Effect Transistor made of GNRs by CVD

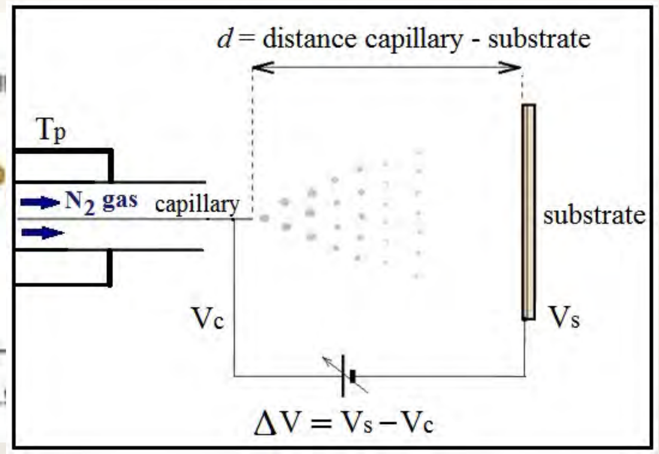


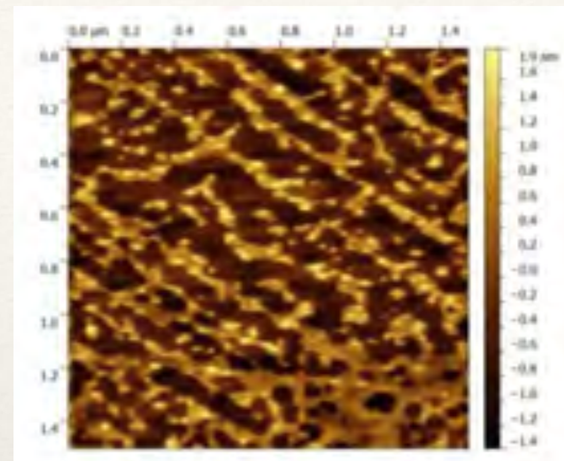


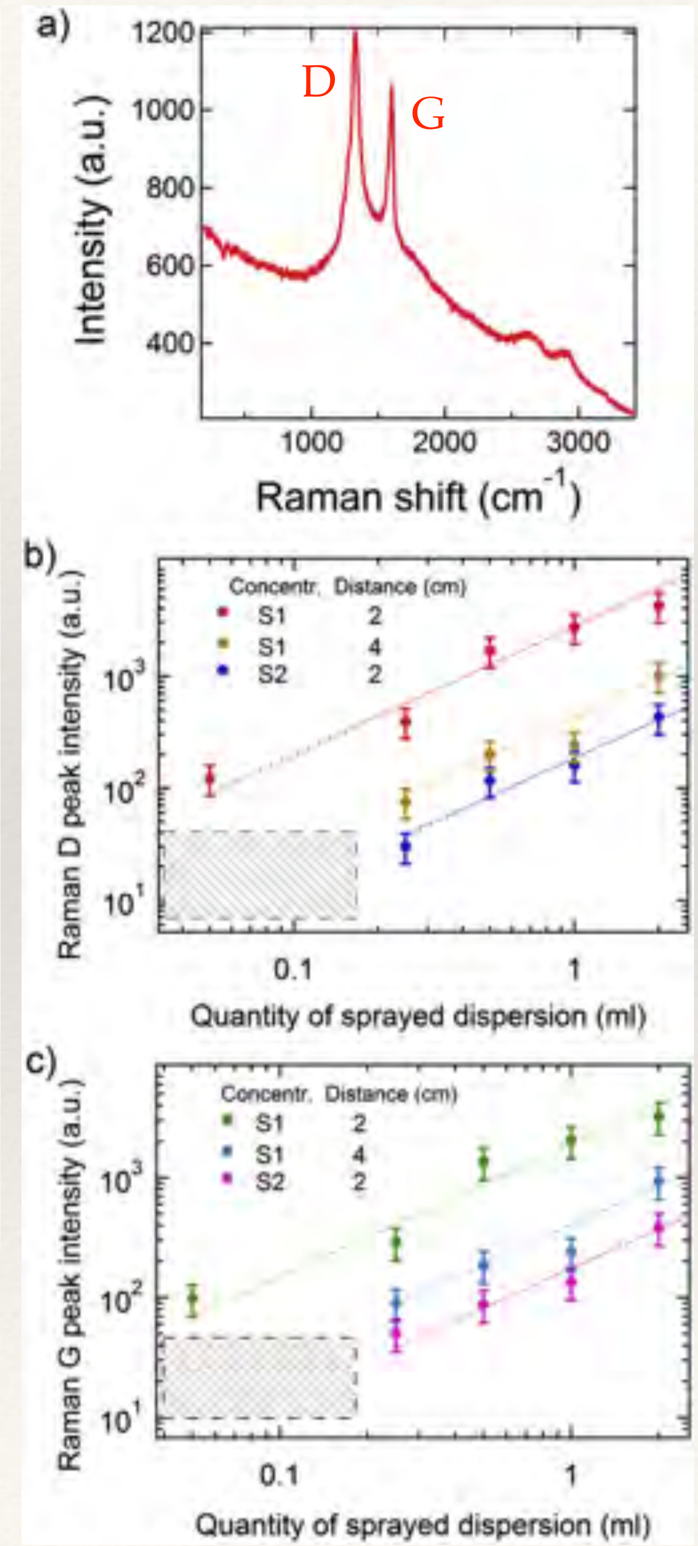
on/off ratio>6000

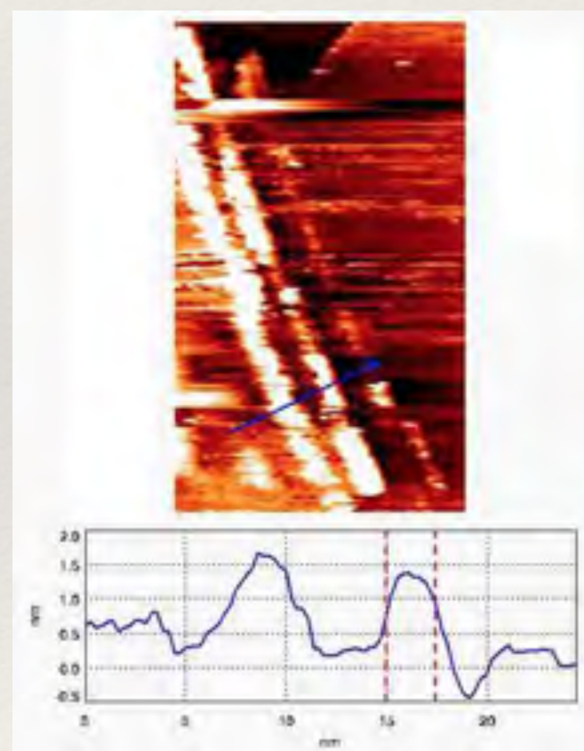
Precision synthesis of graphene nanoribbons by ambient-pressure chemical vapour deposition
***J. Am. Chem. Soc.*, 2016, 138 (47), pp 15488–15496**

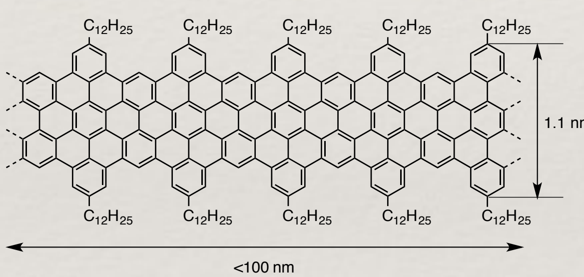
electro-spray deposition of GNR

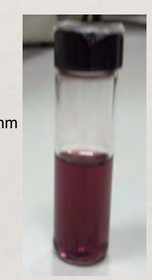








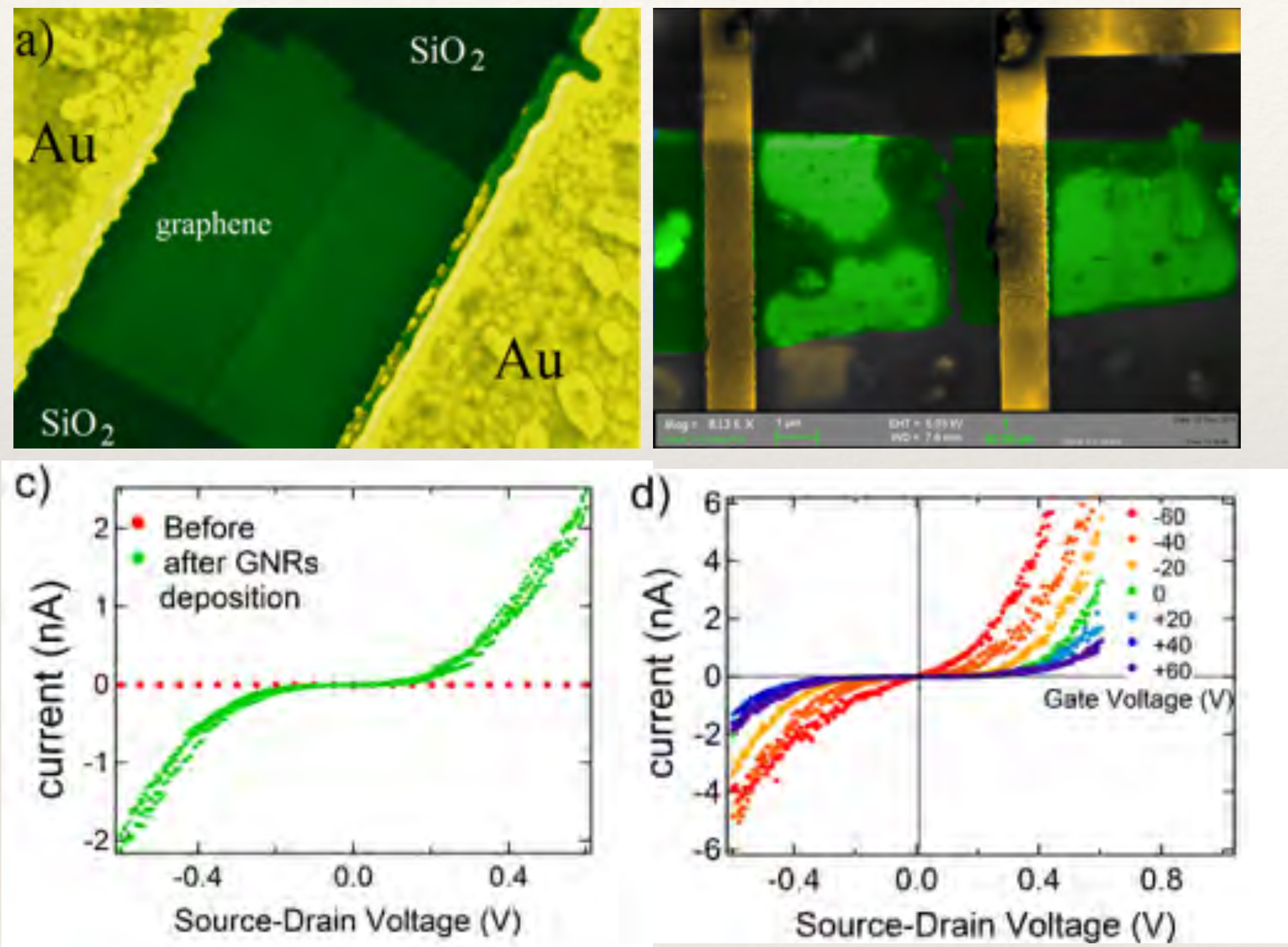




GNR9 in
Tetrahydrofuran (THF) + acetonitrile

Fabrication of Three Terminal Devices by ElectroSpray Deposition of Graphene Nanoribbons.
P. Fantuzzi, L. Martini, A. Candini, V. Corradini, U. del Pennino, Y. Hu, X. Feng, K. Müllen, A. Narita,
M. Affronte ***Carbon 104 (2016) 112-118***

electro-spray deposition of GNR



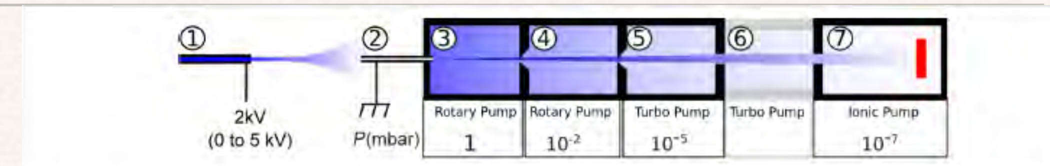
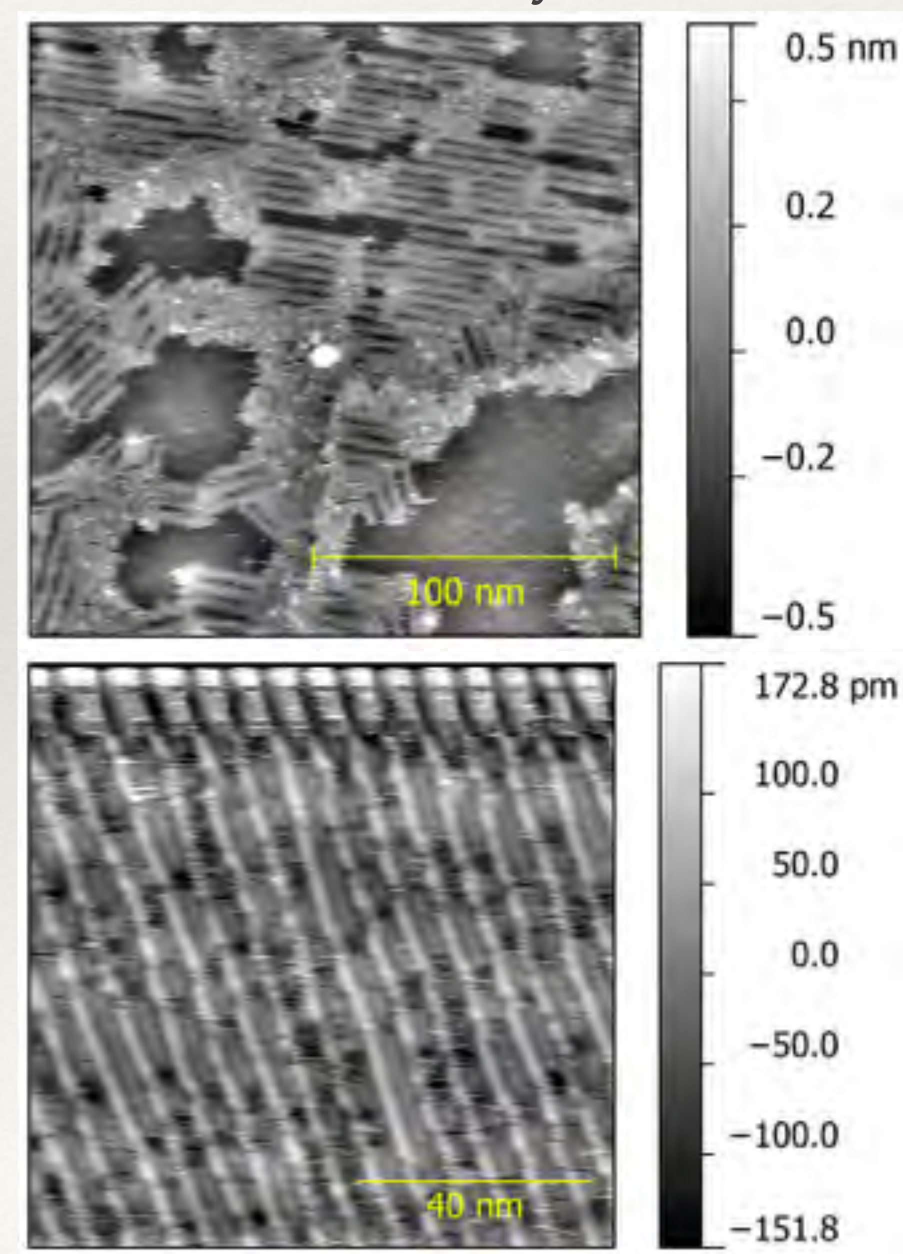


Figure 1: Scheme of the commercial ESI setup [33] (1 to 5) connected to the UHV chamber (7), i.e., sample preparation chamber. The additional vacuum chamber (6) was added to further enhance the performance of the deposition system.

A. Hinaut & E. Meyer in Basel



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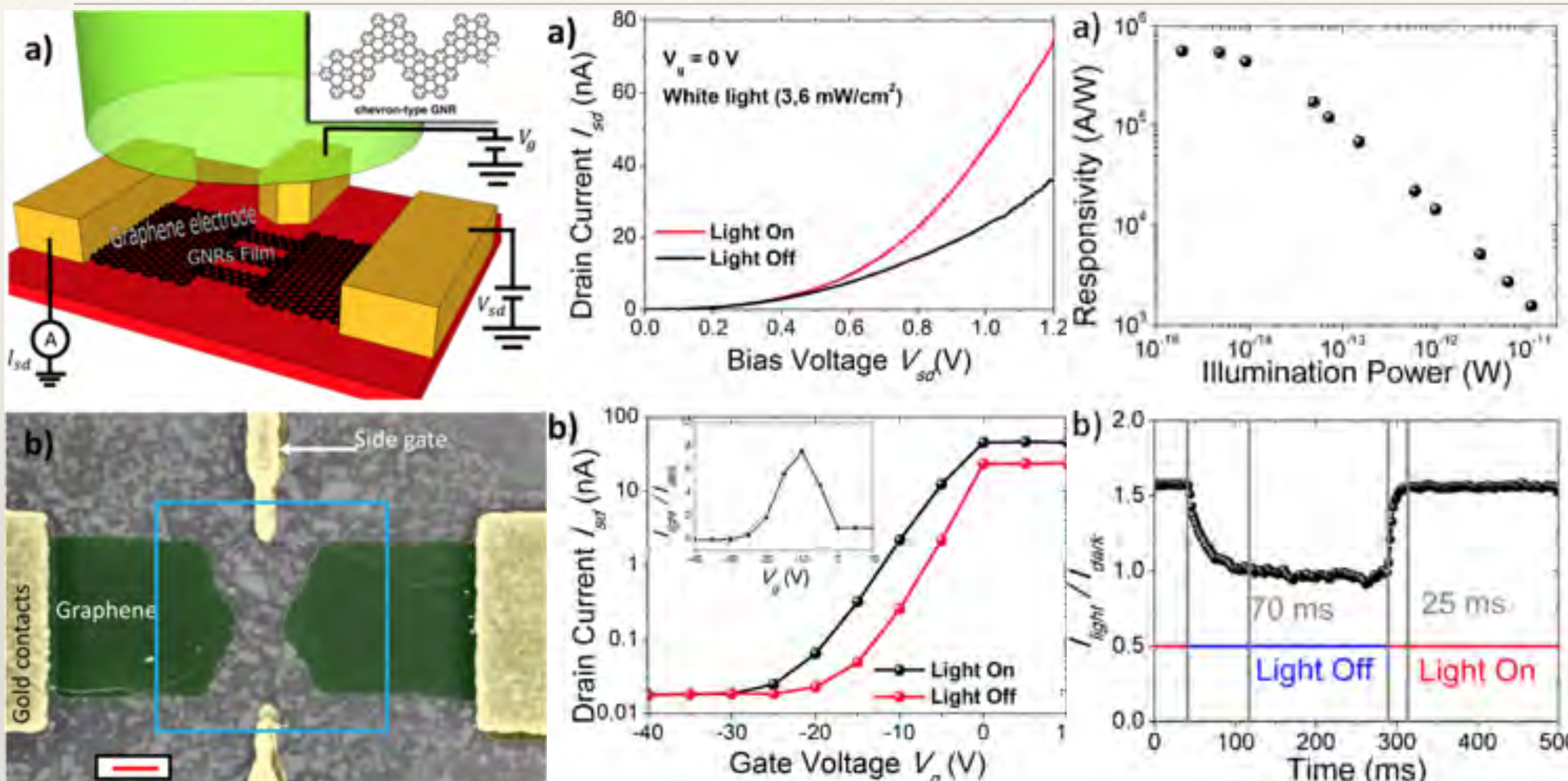
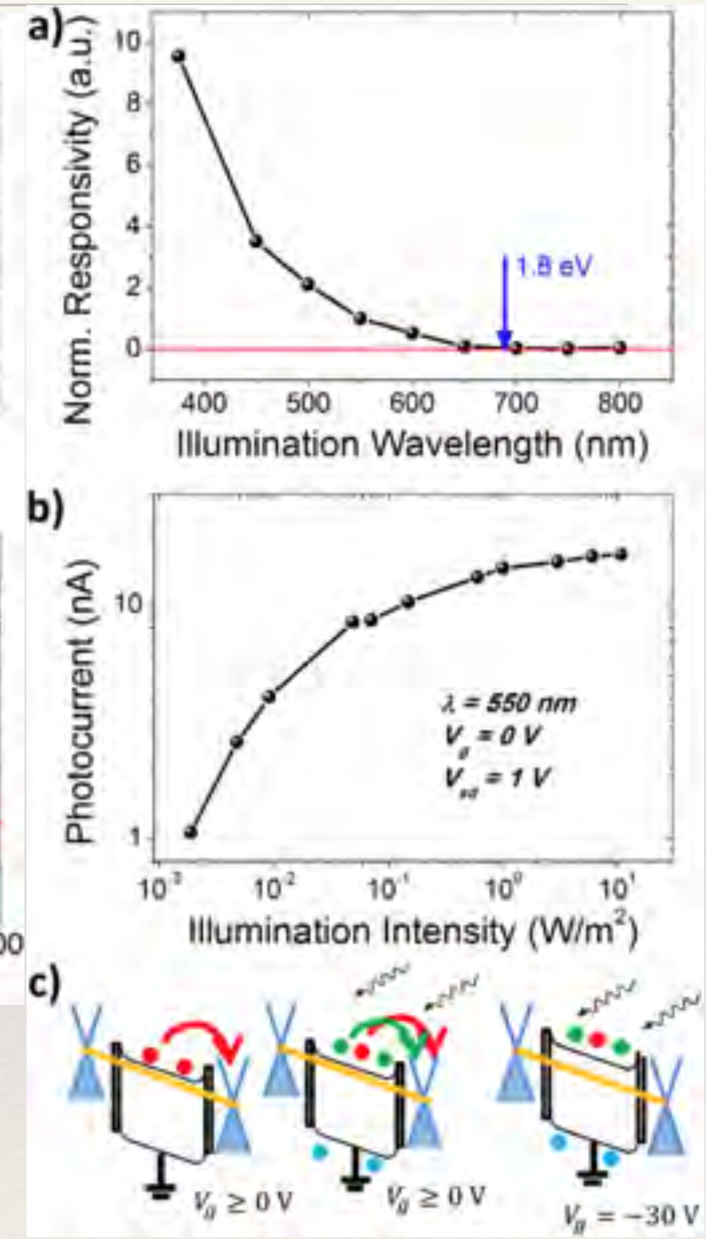
CVD-GNR/graphene: optoelectronic properties



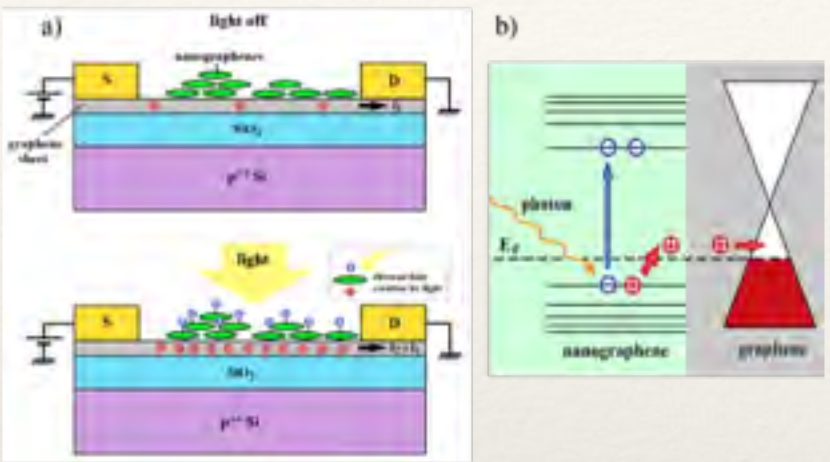


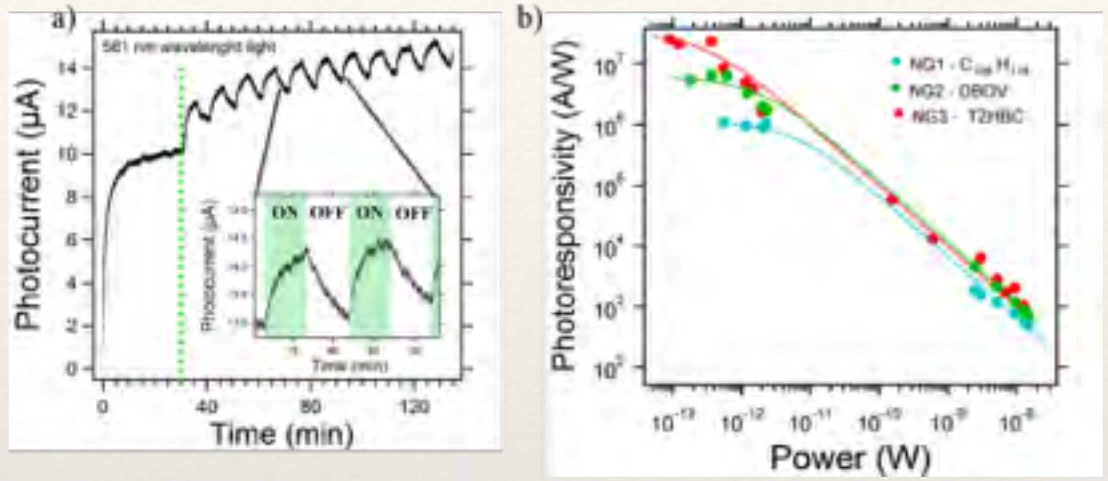
high photoresponsivity of 5×10^5 A/W

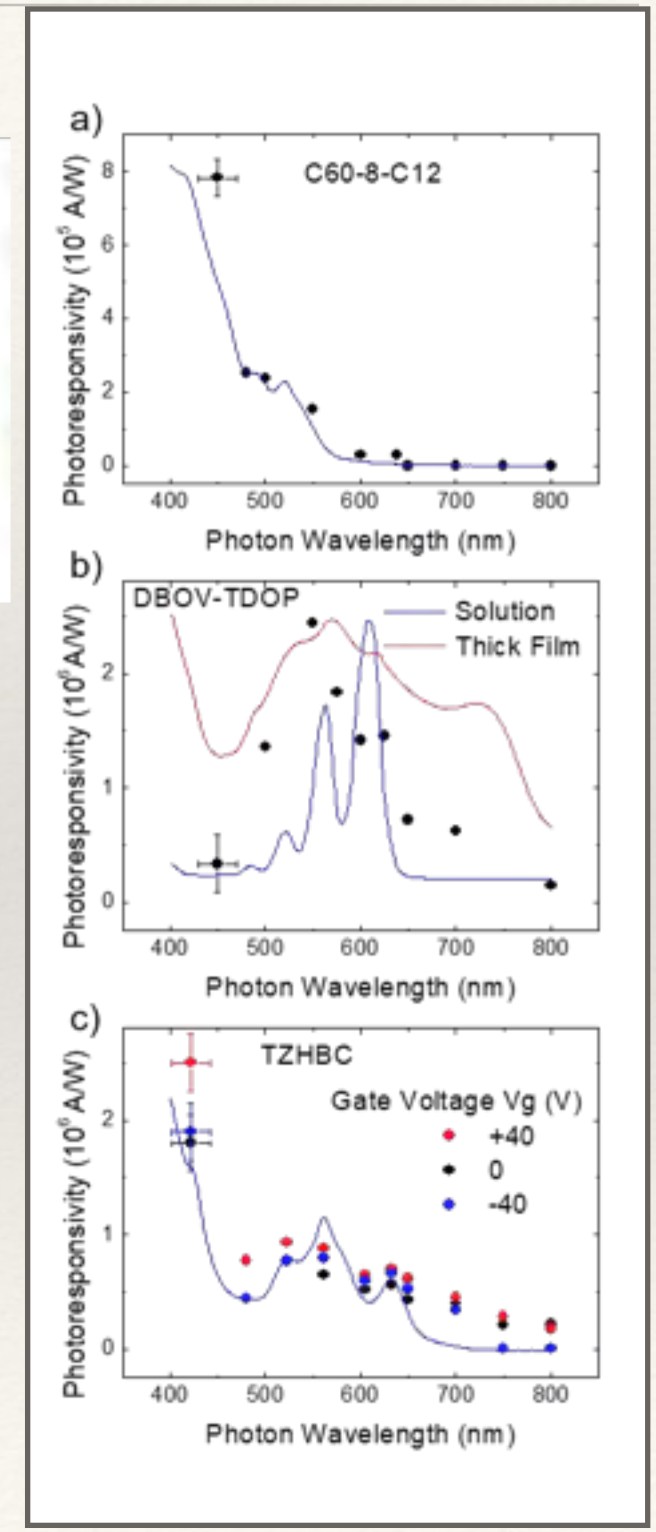
High Photoresponsivity in Graphene Nanoribbon Field Effect Transistor Devices Contacted With Graphene Electrodes Andrea Candini, Leonardo Martini, Zongping Chen, Neeraj Mishra, Domenica Convertino, Camilla Coletti, Akimitsu Narita, Xinliang Feng, Klaus Müllen, and Marco Affronte.

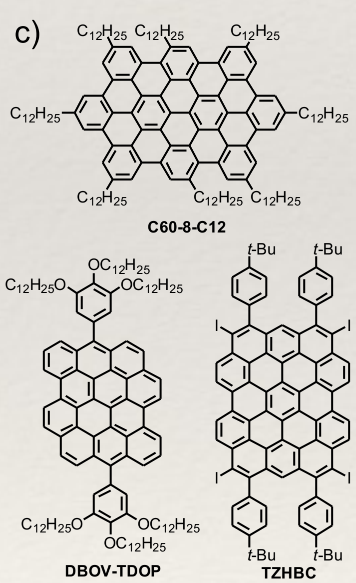
J. Phys. Chem. C, (2017), 121 (19), pp 10620–10625

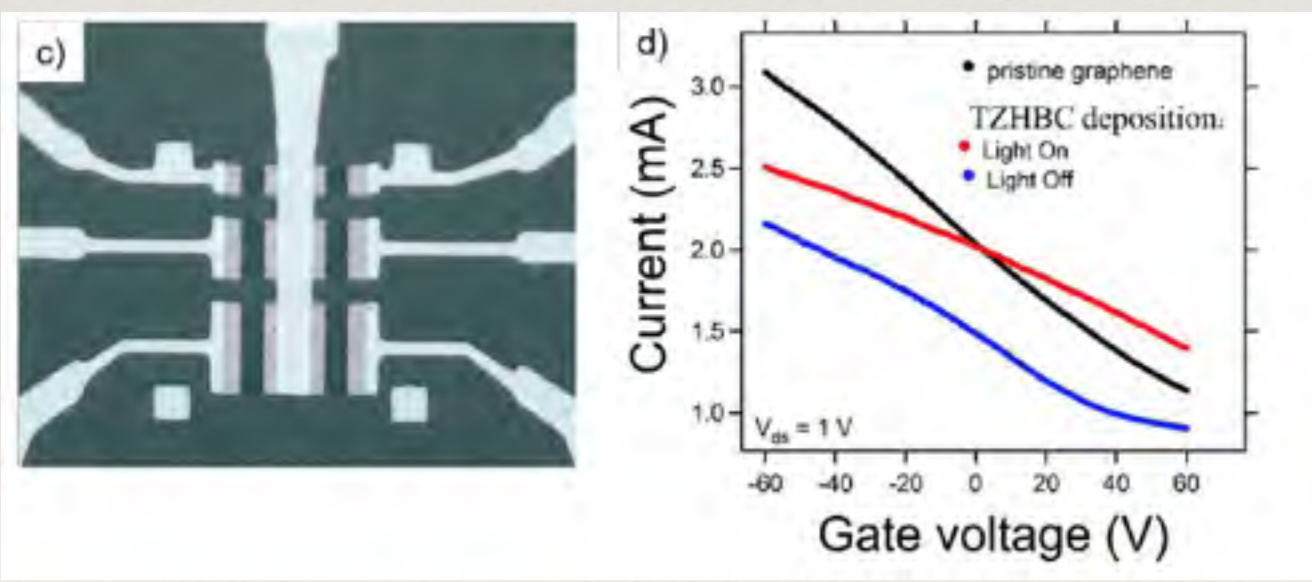
Photo-chromatic response of Graphene Quantum Dots







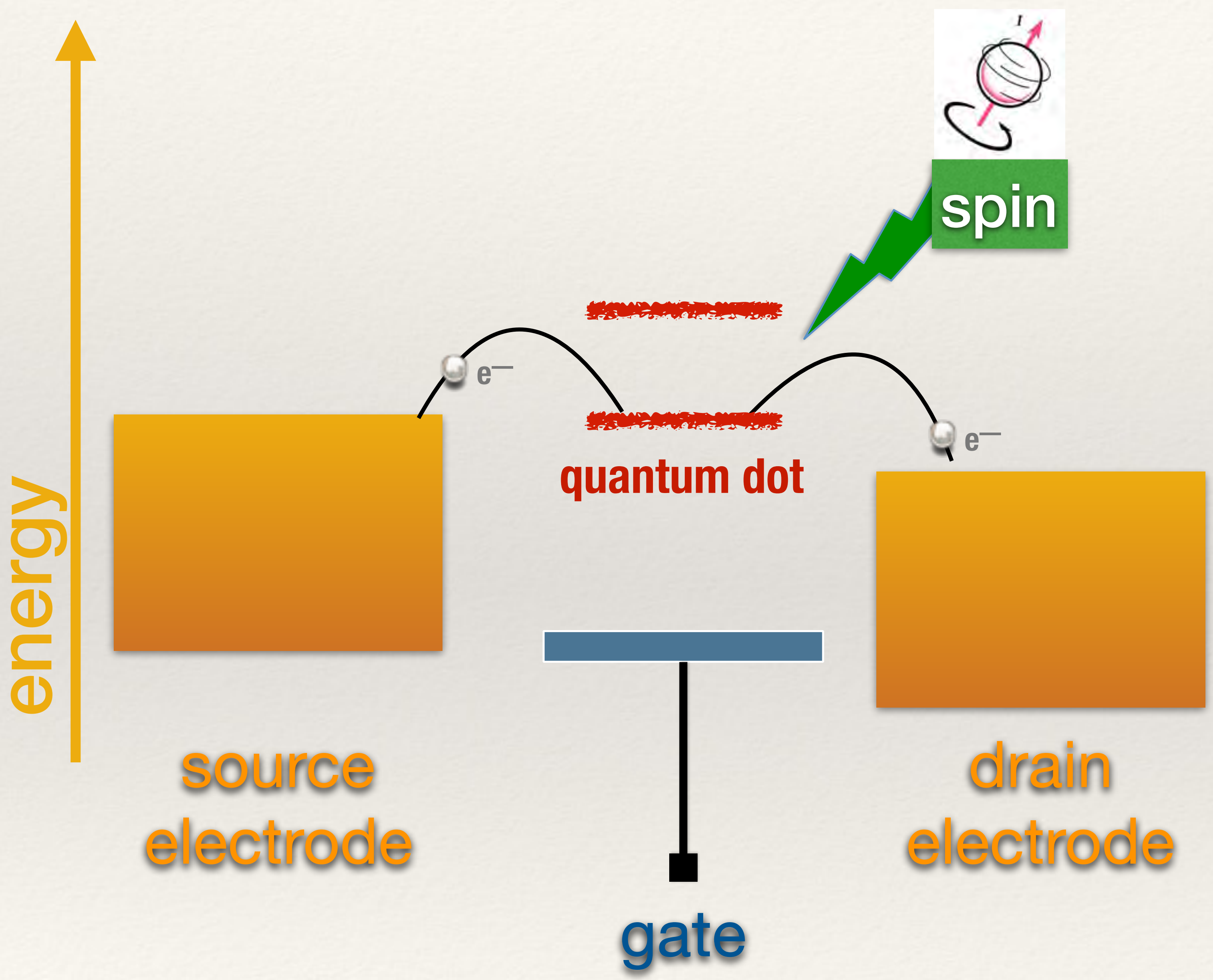




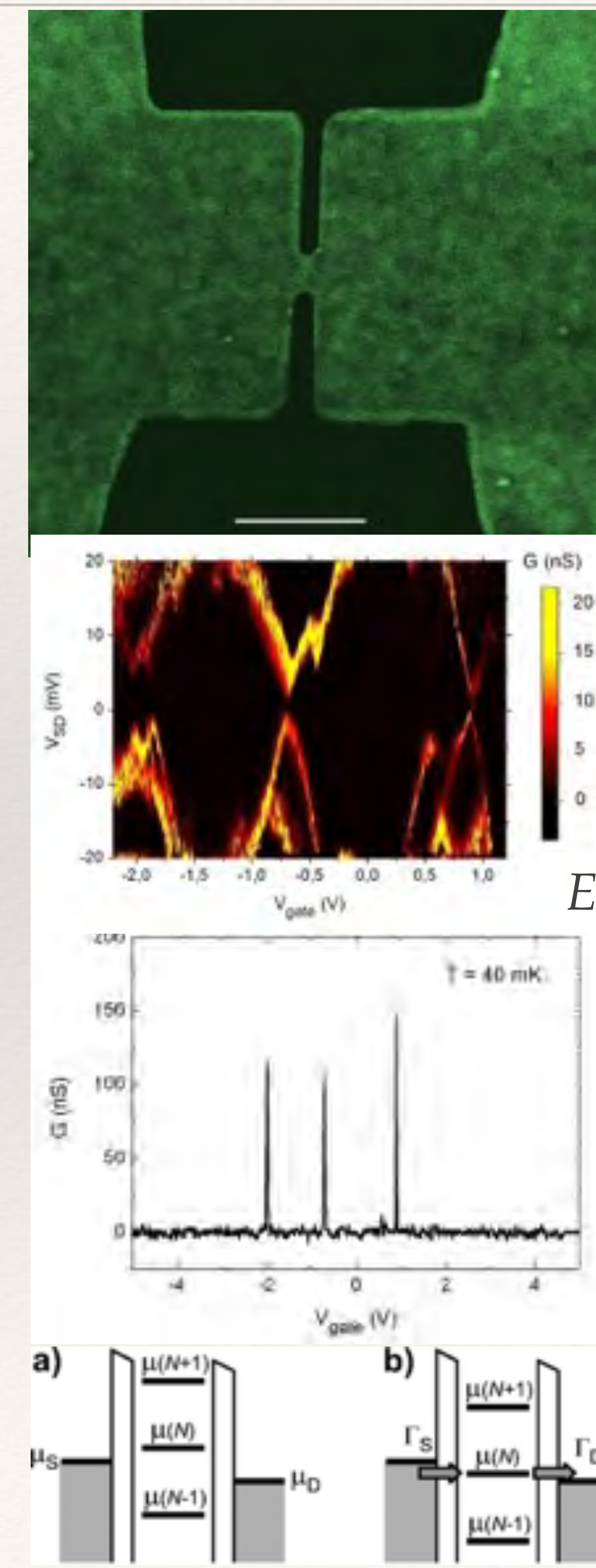
P. Fantuzzi, A. Candini, A. Narita, K. Mullen M. Affronte et al.

DOI: 10.1021/acs.jpcc.9b05013

Read-out of molecular spins by QD



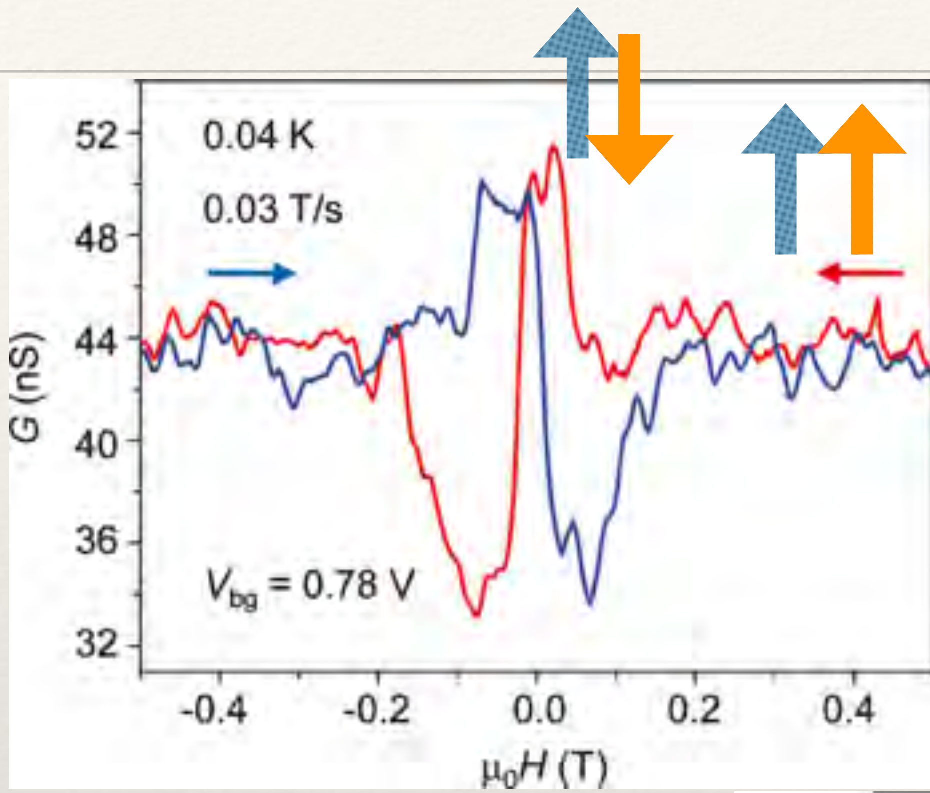
graphene nanoconstriction

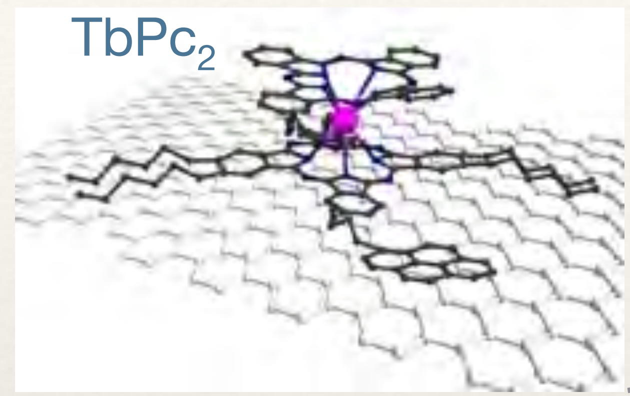


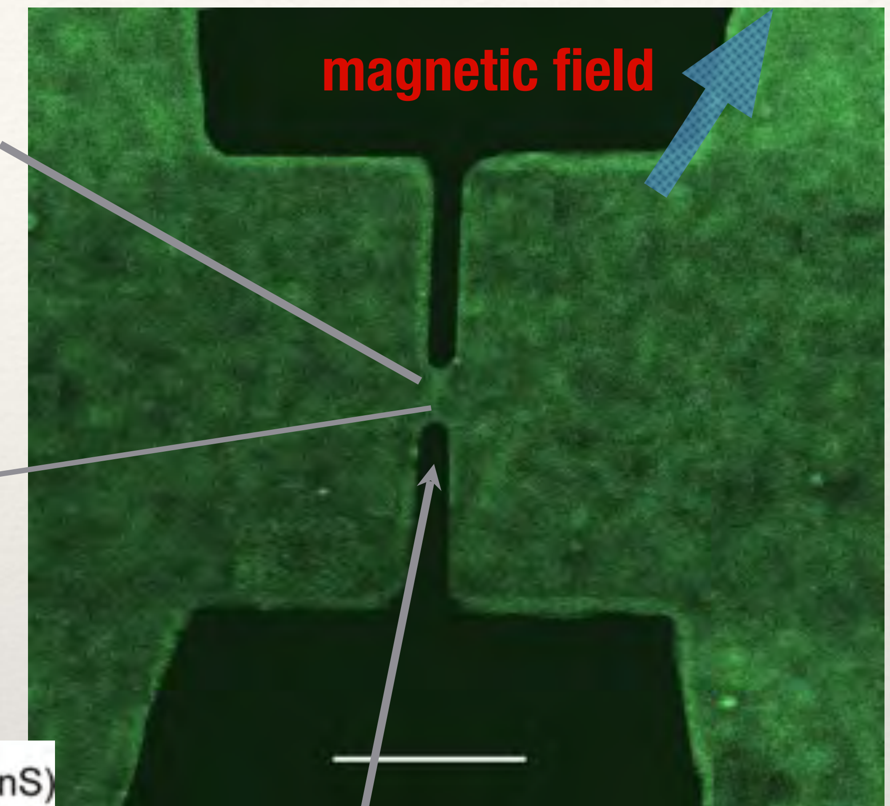
E_c=35meV

Molecular spin valve

A. Candini, S. Klyatskaya, M. Ruben, W. Wernsdorfer and M. Affronte
Nanoletters 11, 2634–2639 (2011)





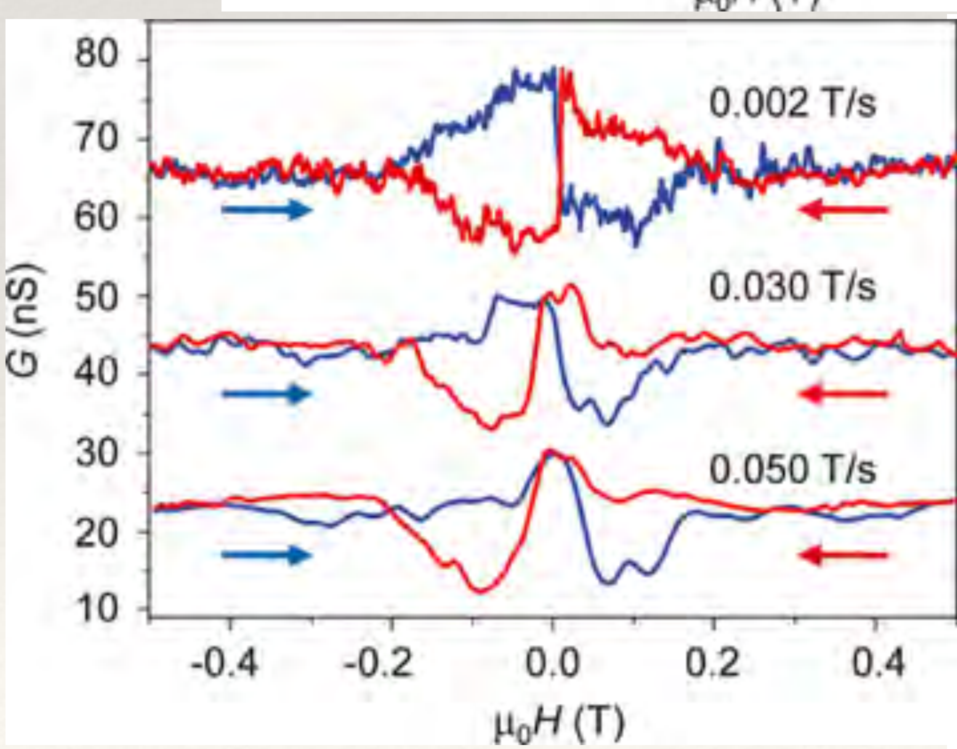


graphene nano-constriction

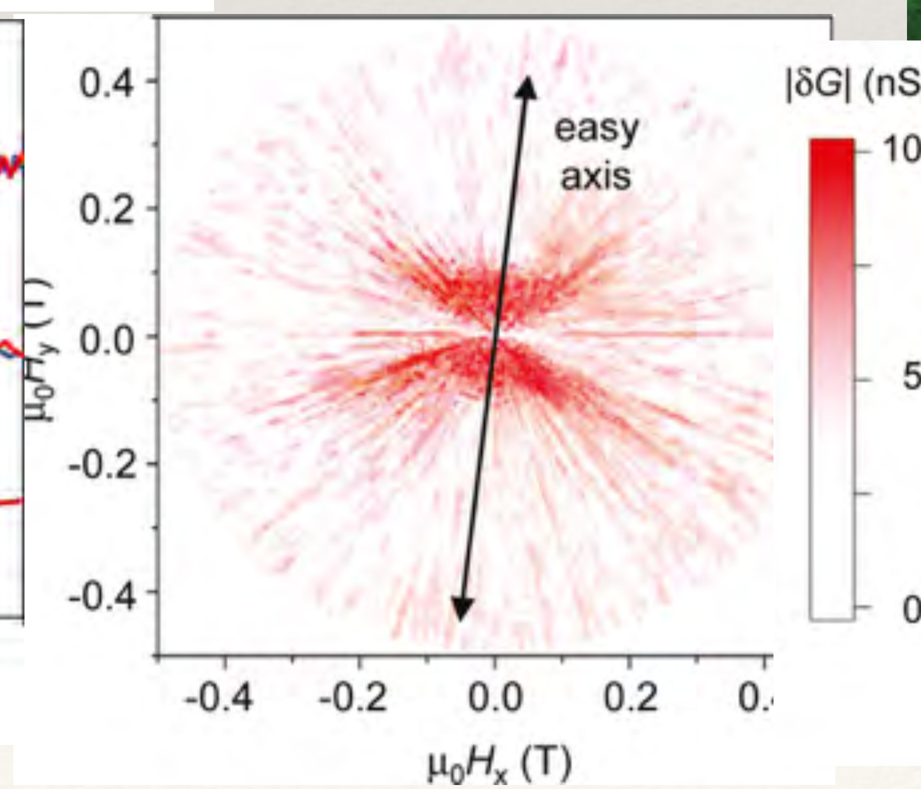
Estimation: ~10 molecules

base temperature: 30mK

sweep of magnetic field in 3D

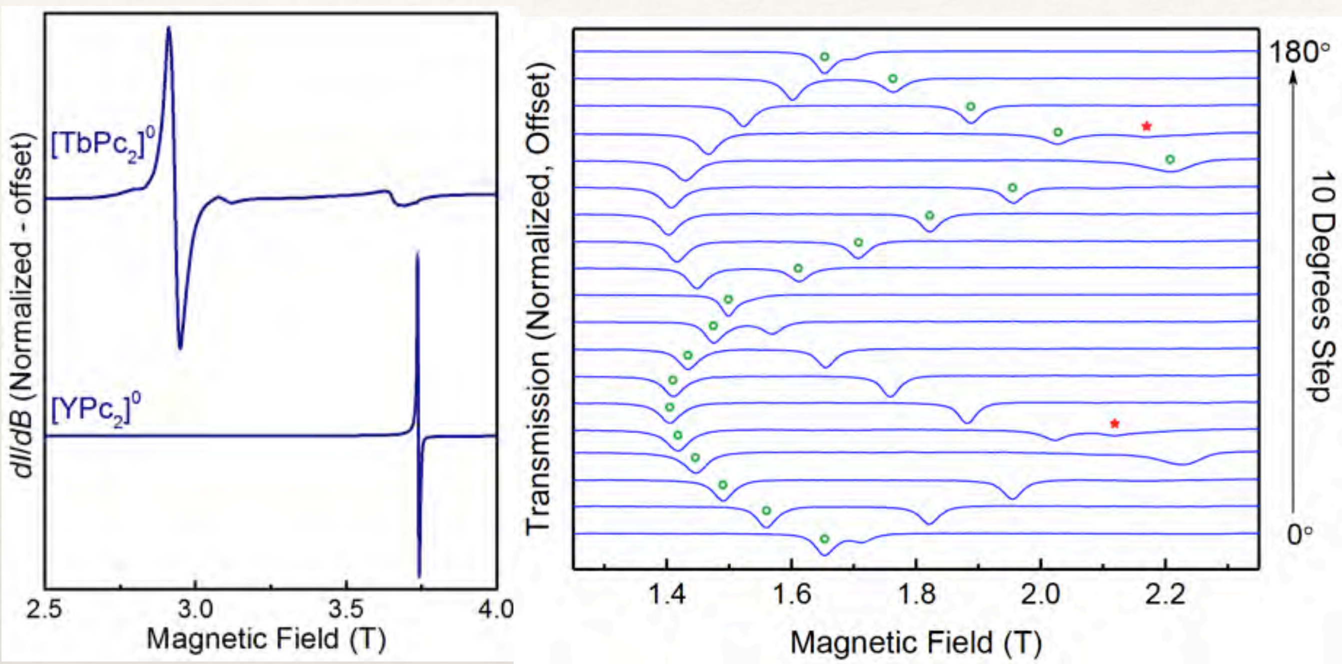


NO DEPENDENCE ON SWEEPING RATE

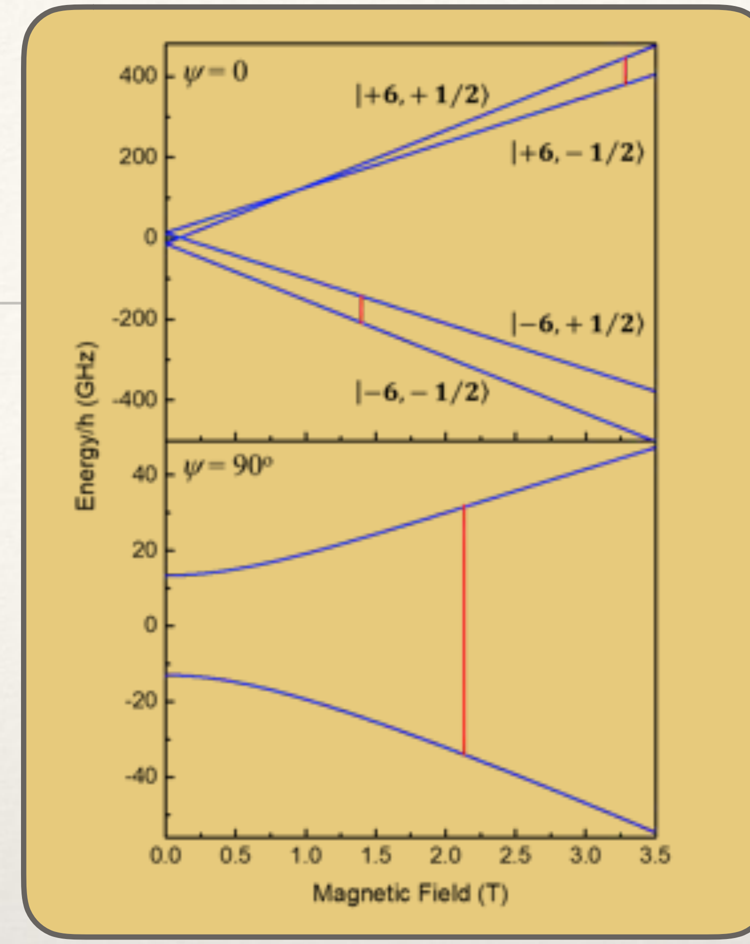


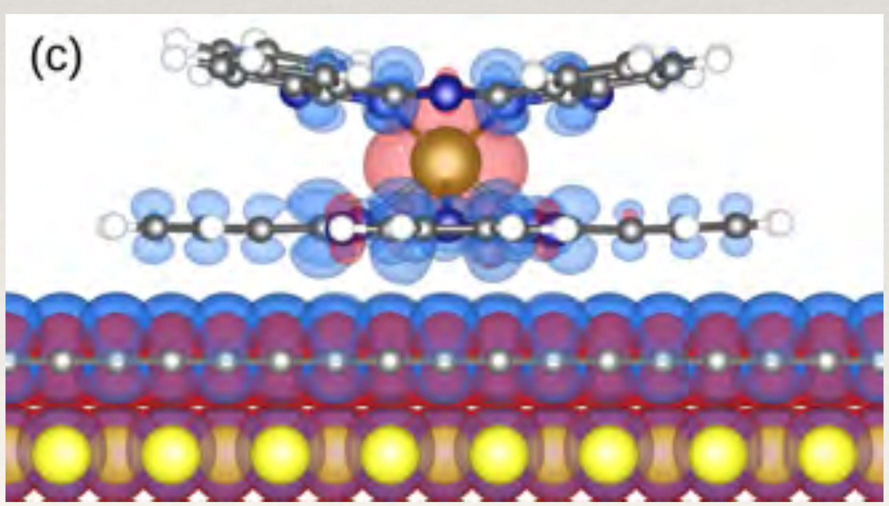
ANGULAR DEPENDENCE

molecule design:
role of radical in [$TbPc_2$]

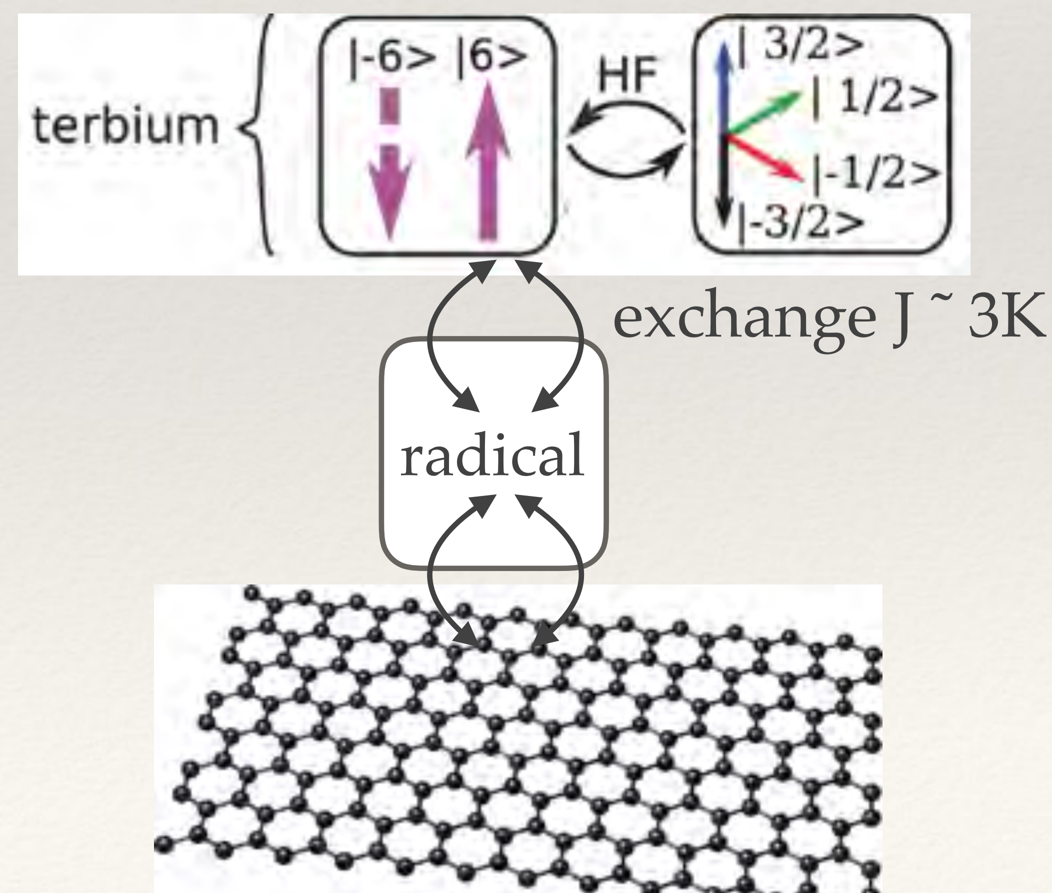


HF-EPR prove that radical spin and Tb magnetic moment are tightly coupled
Phys Rev, Materials **2**, 024405 (2018)

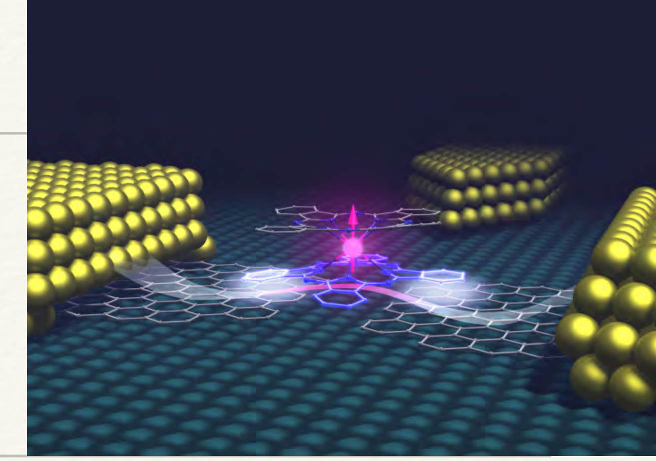


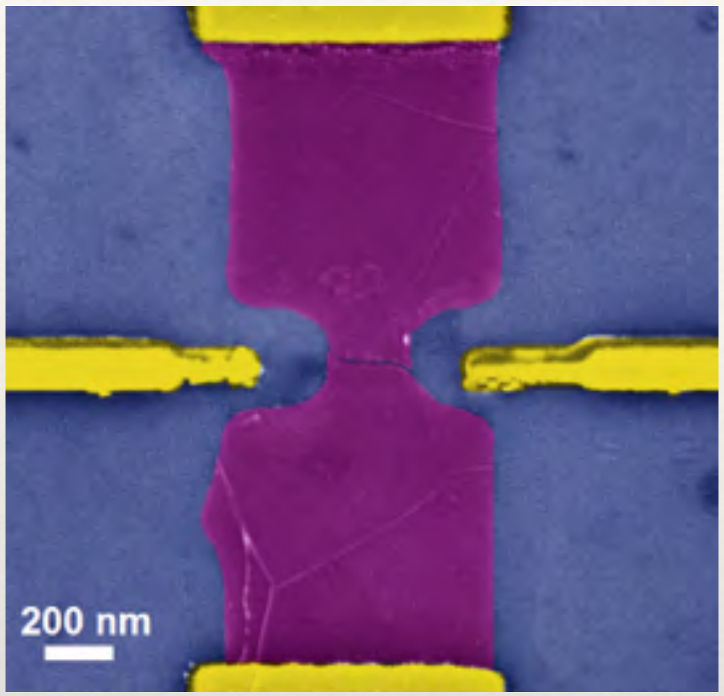


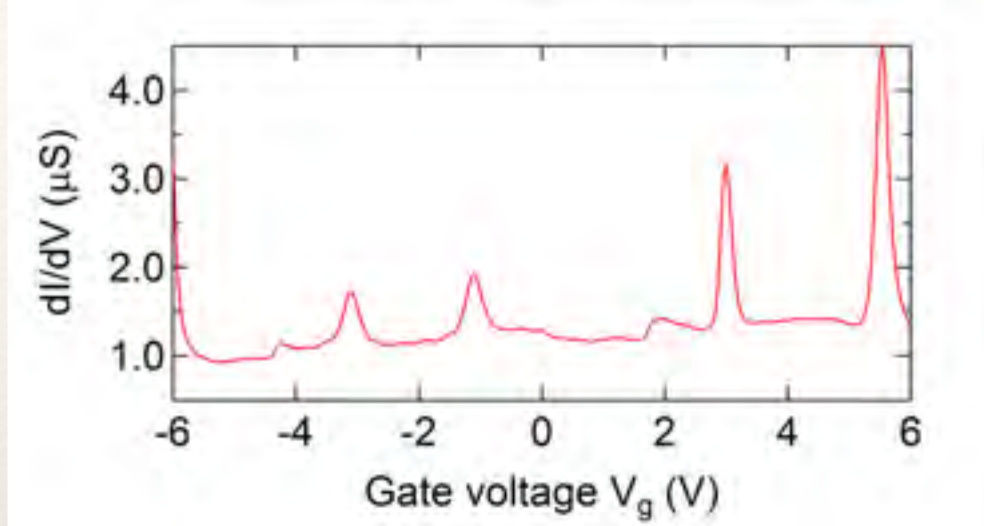
DFT calculations and XMCD experiments prove that radical play a key role for exchange coupling with bottom (graphene) layer
ACSnano 9353-9360 (2016).

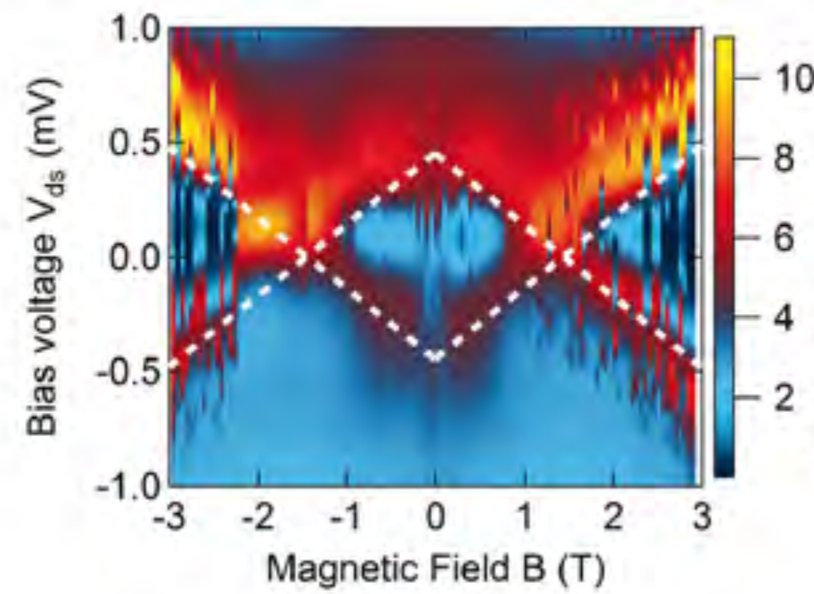


single molecule transistor with graphitic electrodes







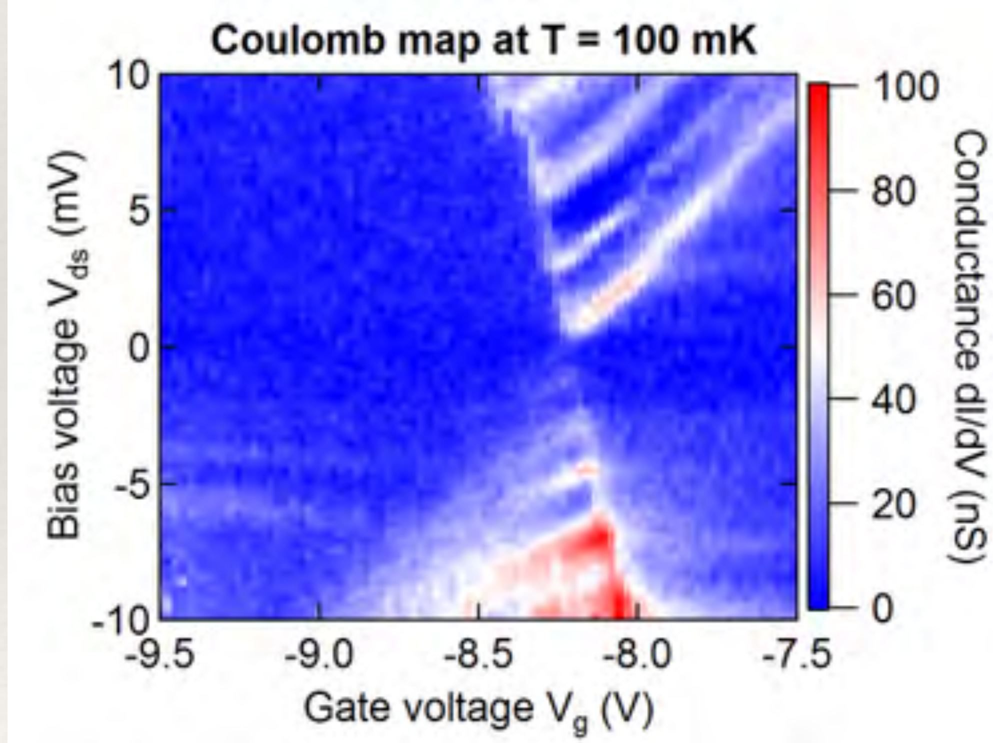


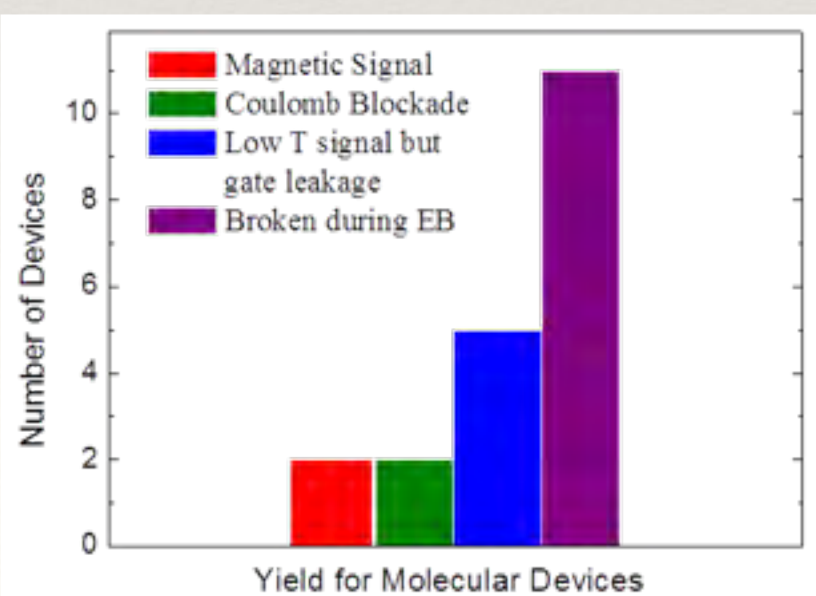
$$a g_J \mu_B J_z = k_B T_K + 2 g \mu_B B_c$$

Kondo resonance
AF coupling between s=1/2 and J_{Tb}

Procedure:

- Partial EB (air) (Res~10^5-10^6 Ω)
- Molecule deposition (drop casting)
- Cool down

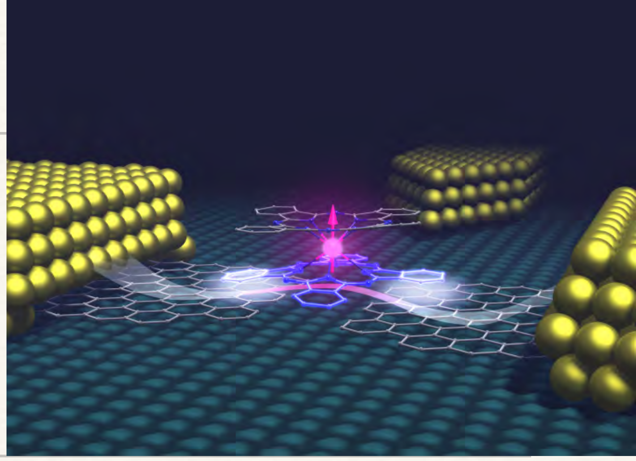


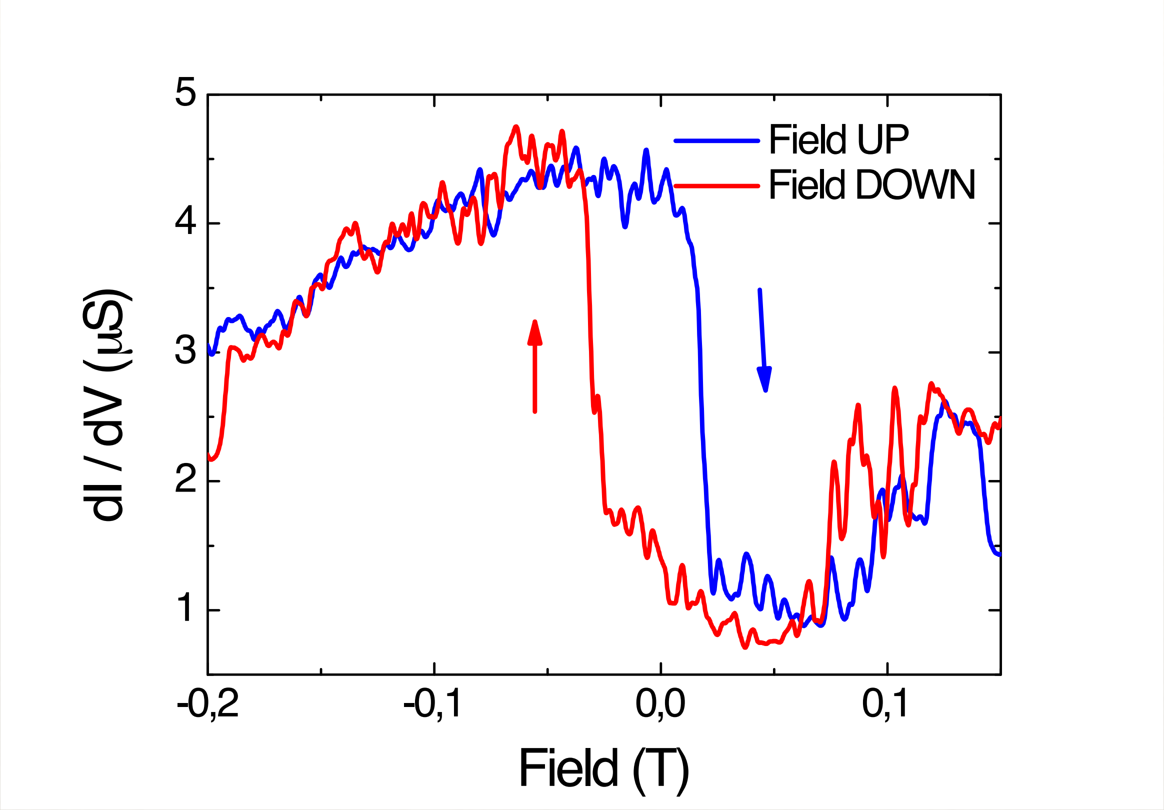


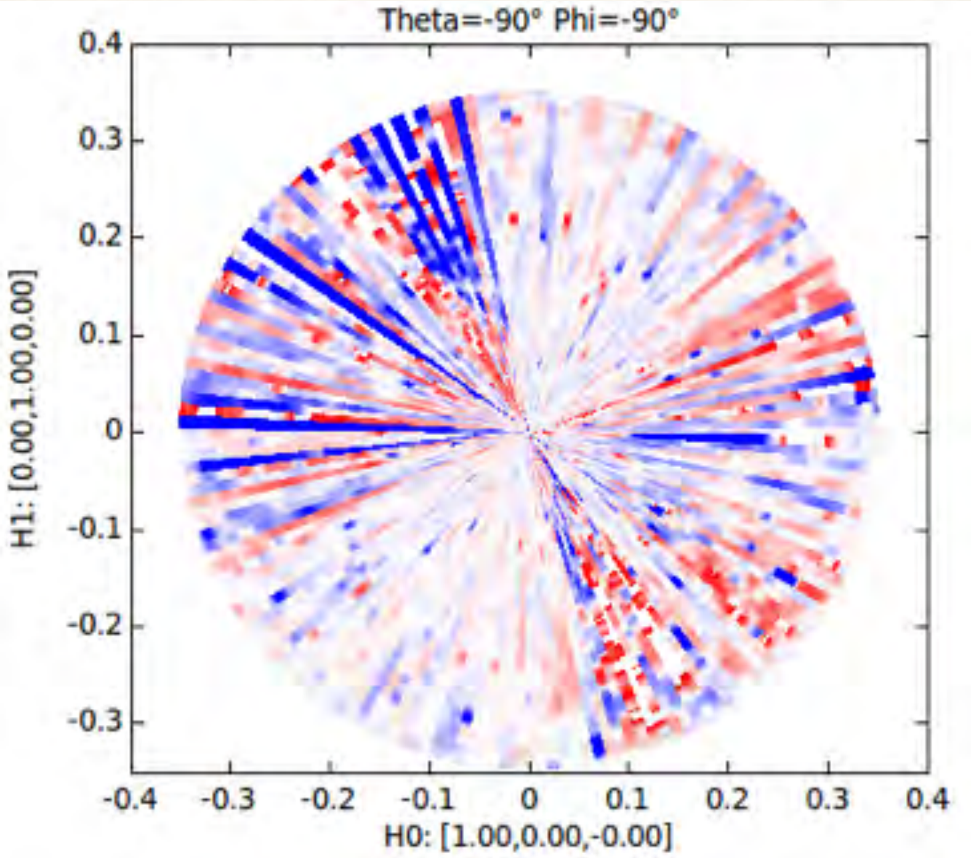
Stefano Lumetti PhD Thesis (2017)

MolSpin

Molecular $TbPc_2$ spin transistor with graphitic electrodes





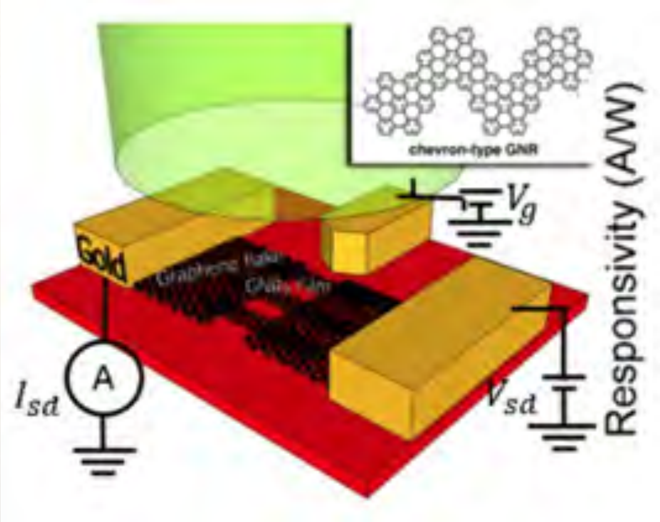


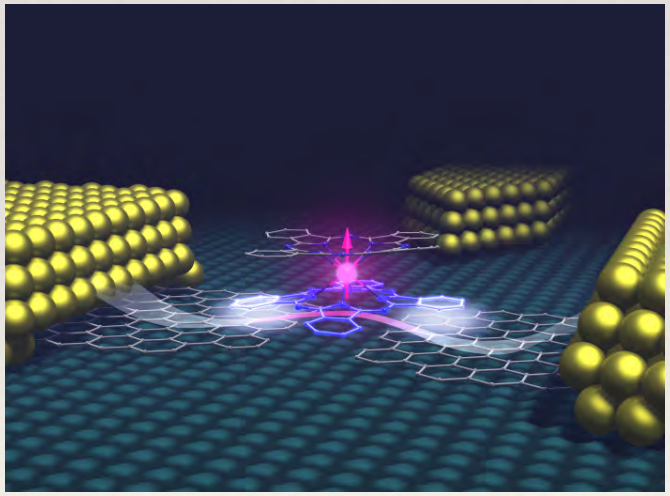
Addressing single molecular spin with graphene based nano-architectures. A.Candini, S. Lumetti, F. Balestro, W. Wernsdorfer, M. Affronte in ***Molecular Architectonics,*** Ed. Ogawa Takuji (2017) p.165, ISBN 978-3-319-57096-9 DOI: 10.1007/*978-3-319-57096-9*

Single-molecule devices with graphene electrodes S. Lumetti, A. Candini, C. Godfrin, F. Balestro, W. Wernsdorfer, S. Klyatskaya, M. Ruben and M. Affronte ***Dalton Transactions*, 2016, 45, 16570 – 16574**

conclusions

- transfer of GNR to insulating substrate
- all-carbon (opto-)electronic devices
- molecules with fingerprint
- QD read out of molecular spins





thank you!

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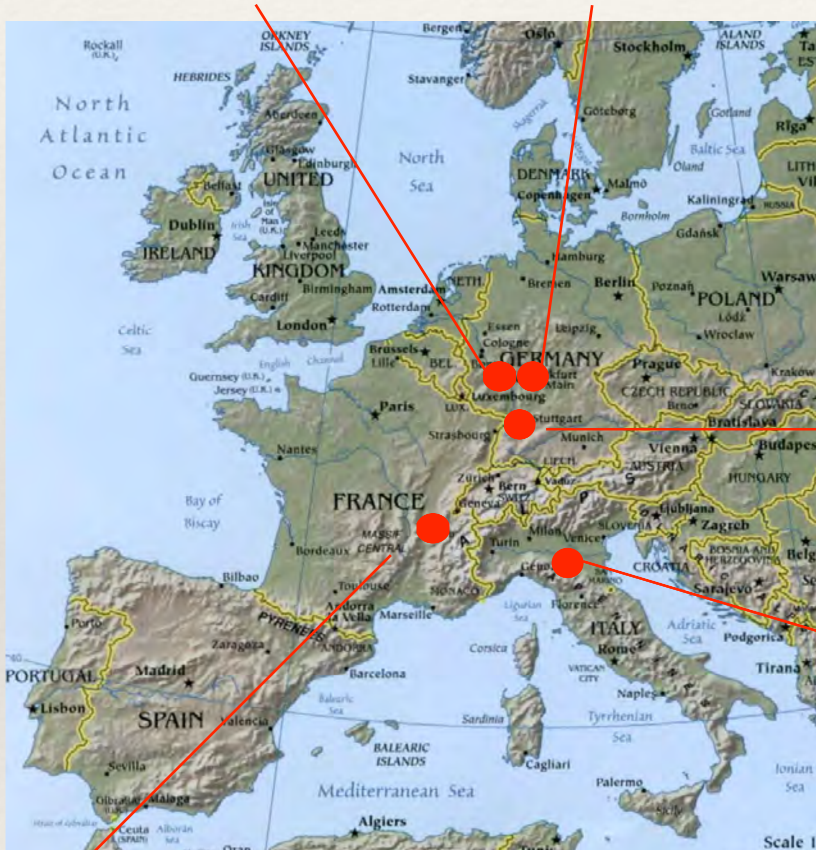
Dr. N. Richter

http://www.moquas.eu/

2013-17



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