IPCMS Institut de Physique et Chimie des Matériaux de Strasbourg

Université de Strasbourg

Atomic-scale fluorescence of a molecule

Master 1 Internship presentation

BELLAHSENE Amar and **FRANCHOIS Lilian**

Supervisor : **Guillaume Schull**

IPCMS - STM team

QMat QUANTUM SCIENCE AND NANOMATERIALS

Institut de Physique et Chimie des Matériaux de Strasbourg
Unité Mixte de Recherche 7504, Campus de Cronenbourg

PhD students

K. Vasilev

Post-doc

A. Roslawska

S. Jiang

T. Neuman

K. Kaiser

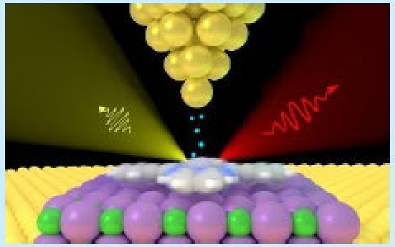
STM group

L. Limot

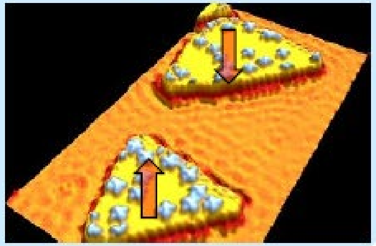
G. Schull

F. Scheurer

Atomic-scale Photonics



Atomic-scale Magnetism



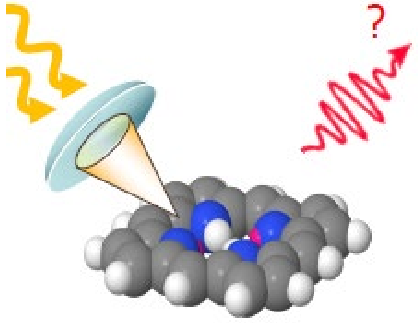
3 UHV LT-STM

http://www-ipcms.u-strasbg.fr/stmipcms/

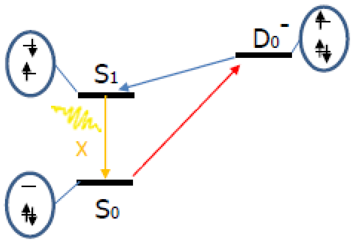
cnrs

Introduction

Fluorescence from single molecules



Scheme of the light emission of a molecule



Example of light excitation process in a molecule

Problematic

- How could we probe experimentally the electronic and optical properties of a single molecule?
- And in what extent could we reach the sub-nanometre scale?

I. STM – induced Fluorescence on Graphene nanoribbons (GNRs)

II. STM – PhotoLuminescence enhancement

Question

- What are the properties of the graphene nanoribbons (GNRs) ?

I. STM – induced Fluorescence on Graphene nanoribbons (GNRs)

a. **Graphene nanoribbons (GNRs) for quantum electronics**

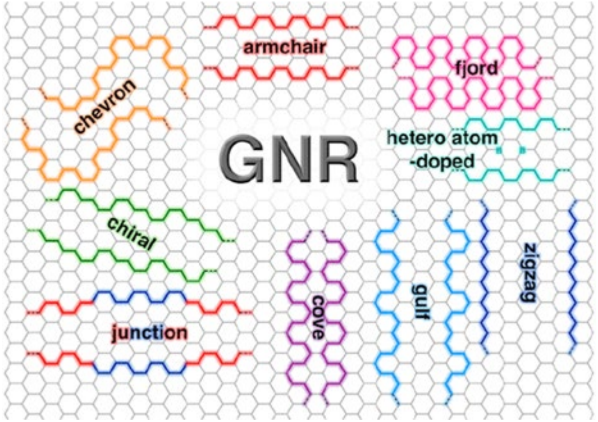
b. STM – ElectroLuminescence (STM-EL)

c. State of the art: 7-GNRs Fluorescence signal

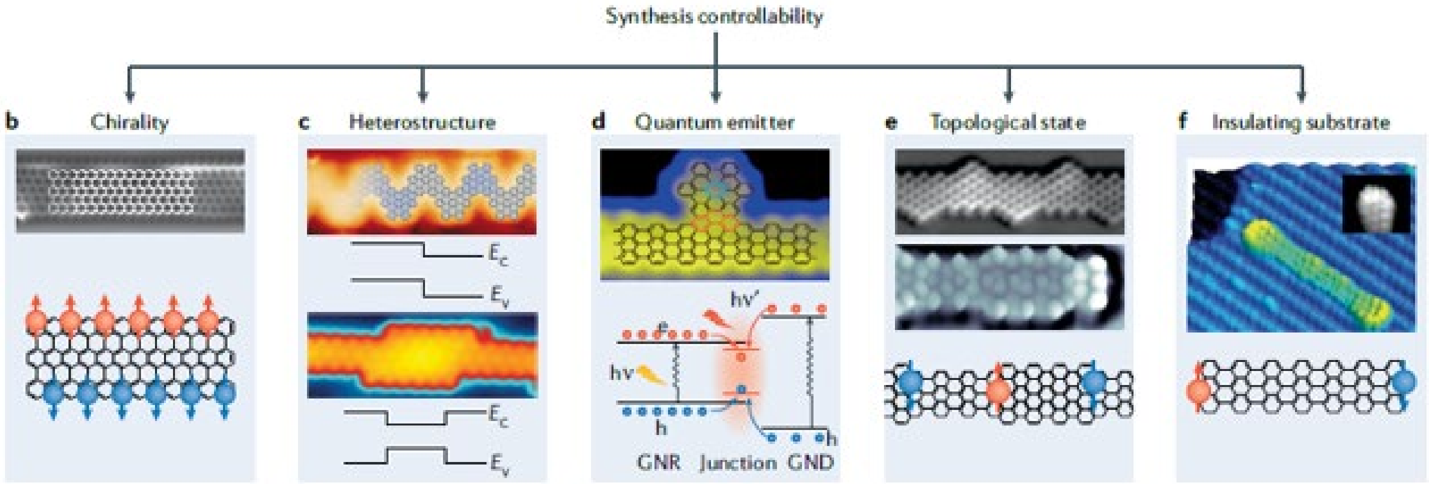
d. Our Experiment: 9-GNRs in STM junction

Graphene nanoribbons (GNRs) for quantum electronics

Interesting electronic properties



- **family of 1D materials -** graphitic lattice structure
- Properties :
  - high **mobility**
  - **current-carrying** capability
  - **Sizeable bandgap**
- Candidates for **quantum electronic applications**

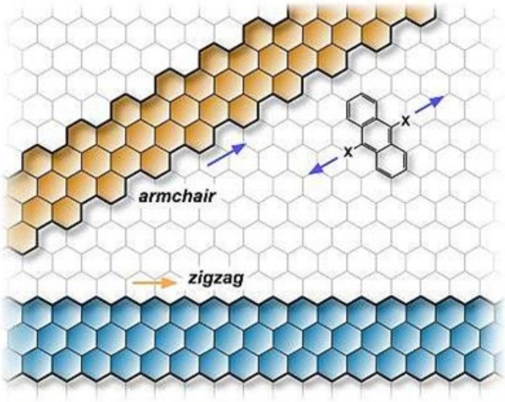


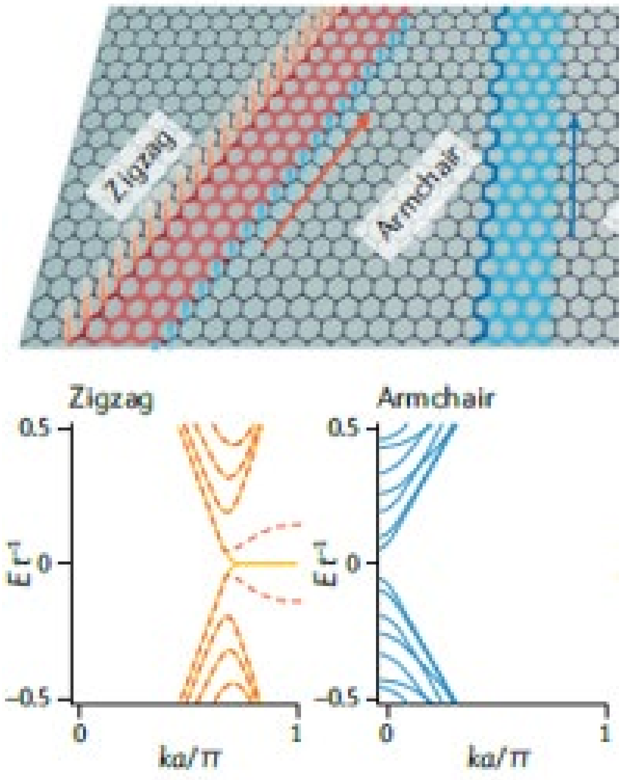
Synthesis controllability of graphene nanoribbons - Wang et al. Nature Perspectives 2021

Graphene nanoribbons (GNRs) for quantum electronics

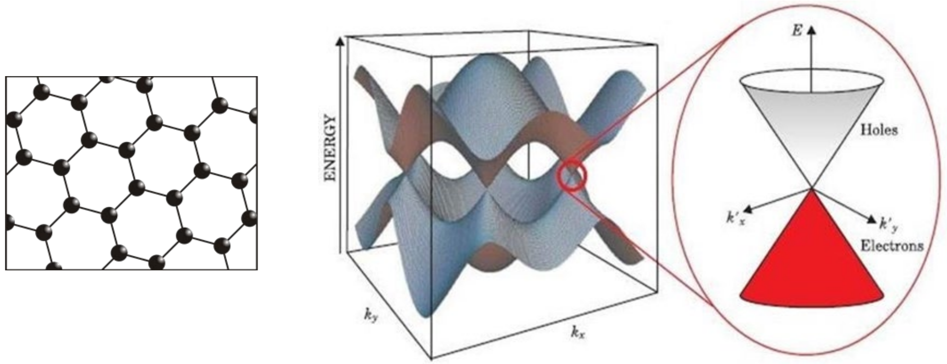
GNRs with optical Bandgap – Electronic structures

- **Zigzag GNRs - metallic**
  - Fermi level - **Conducting channels**
  - Topological states - **Localized emission**
- **Armchair GNRs – semiconductor**
  - **Bandgap - spatial confinement** of the electronic wavefunctions
  - **Delocalized emission** states





Electronic structures of GNRs- Wang et al Nature Perspectives 2021



Electronic structure of graphene 2D layer

Question

- What strategy is performed by the team to probe Single molecule Fluorescence?

I. STM – induced Fluorescence on Graphene nanoribbons (GNRs)

a. Graphene nanoribbons (GNRs) for quantum electronics

b. STM – ElectroLuminescence (STM-EL)

c. State of the art: 7-GNRs Fluorescence signal

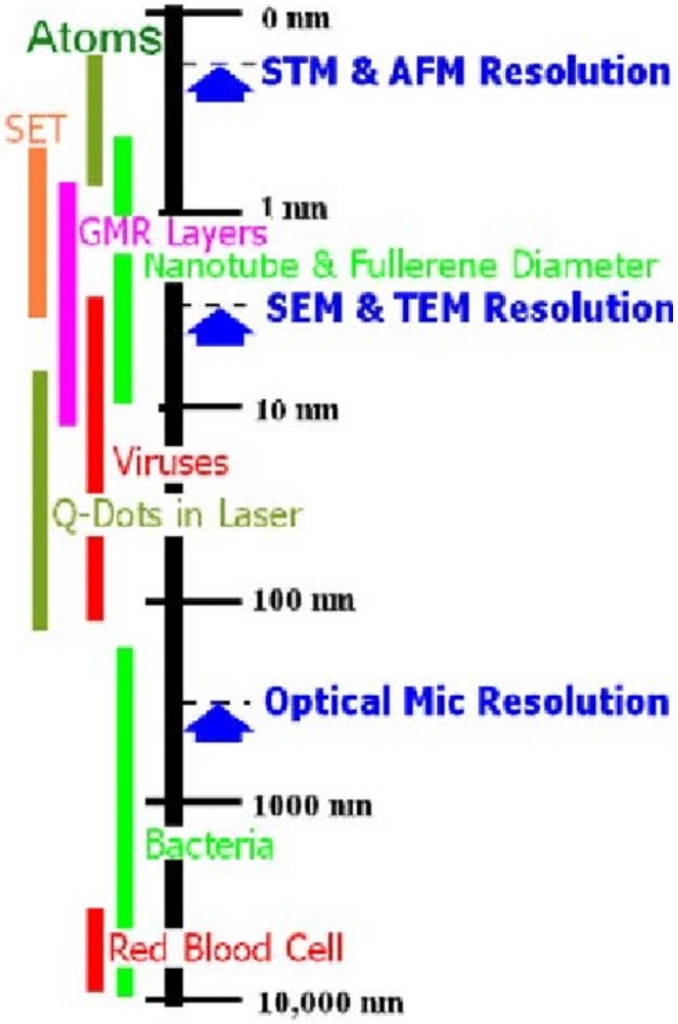
d. Our Experiment: 9-GNRs in STM junction

STM – ElectroLuminescence (STM-EL)

STM: an efficient way to probe single molecules

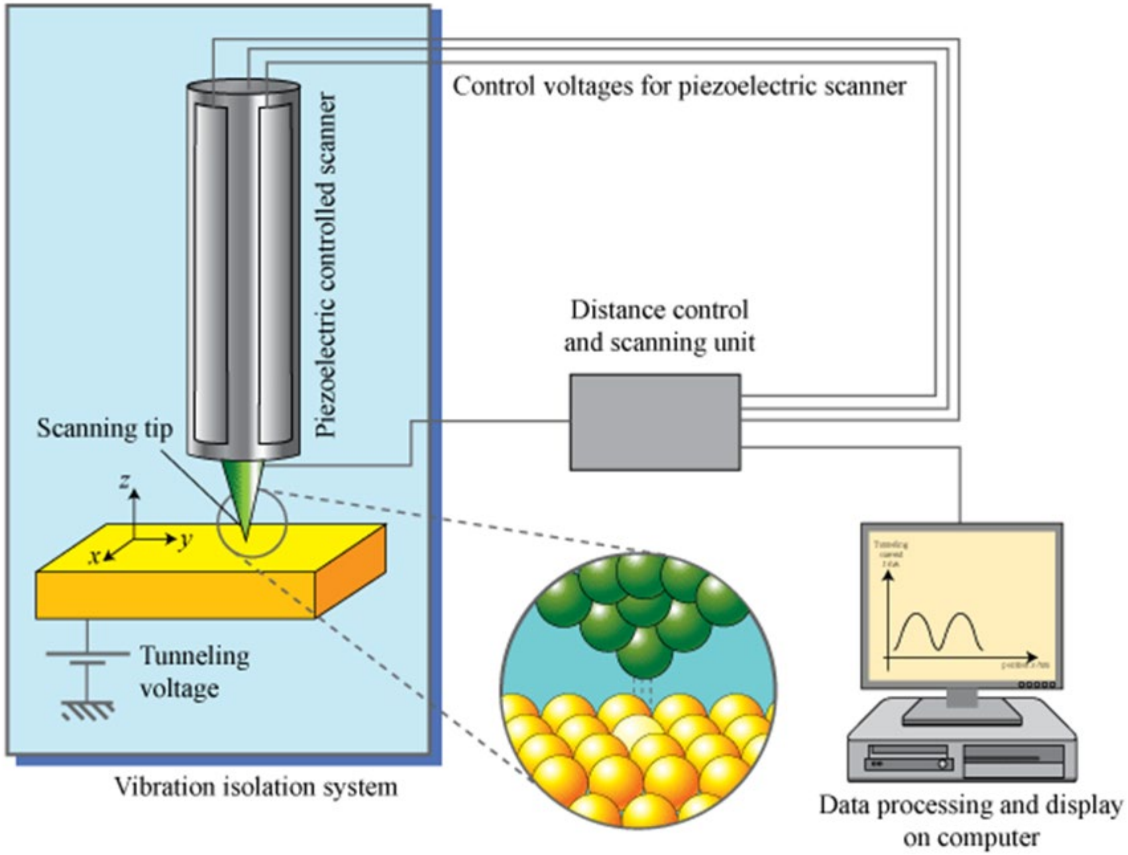
- Scale of the STM:
  - Optical diffraction **1µm**
  - Electronic Microscope **few nm**
  - **Scanning Tunneling Microscope sub-nm**

STM



STM – ElectroLuminescence (STM-EL)

STM working principle



Voltage V applied between the sample and the tip, tunneling current is amplified and then measured

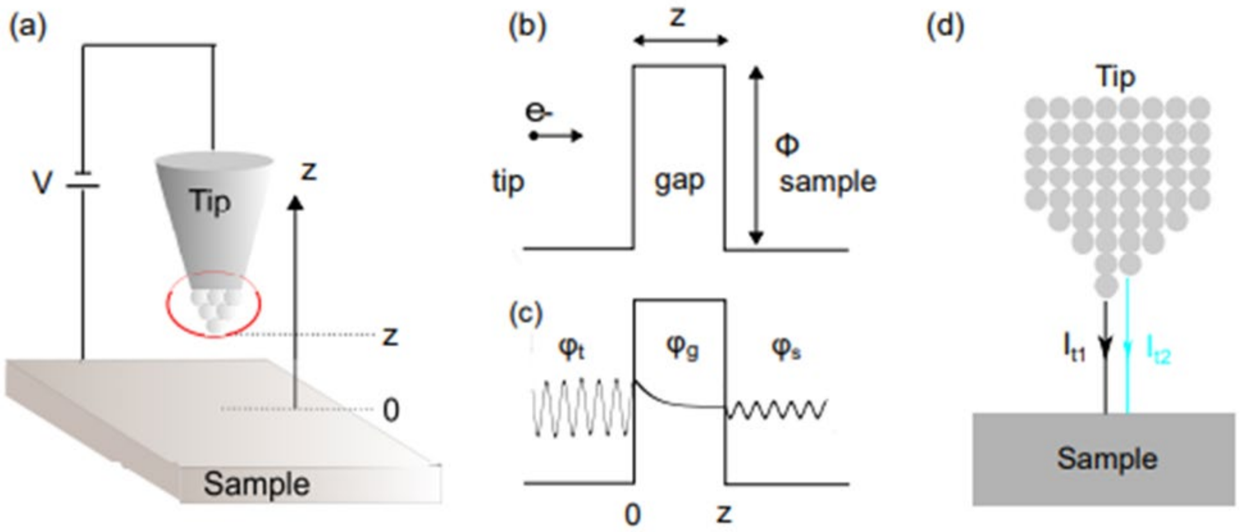
- The **STM head** (sample and tip) cooled at **4.7K**
  - **avoid thermal fluctuation on the sample**
- **Ultra High Vacuum (UHV)** with ionic pump ~ **10^{-11} mbar**
  - **avoid dirt**

STM – ElectroLuminescence (STM-EL)

Origin of the high special resolution of the STM

- Parameters:
  - Electrodes distance ~ **10 Å**
  - V ~ **1V ; Φ ~ 5 eV** (eV< Φ)

- Simple model for the **tunnel current BUT** gives the **High Resolution origin**



$$I_t = |\psi|^2 \propto e^{-2\rho z}$$

$$\frac{-\hbar^2}{2m}\frac{d^2\psi_{el}(z)}{dz^2} + V(z)\psi_{el}(z) = E\psi_{el}(z)$$

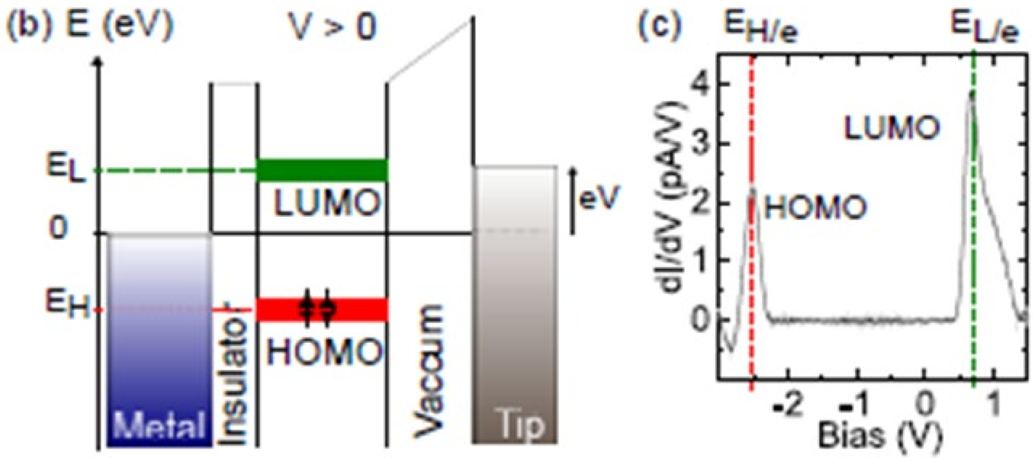
$$\psi_g(z) = Ae^{-\rho z} \qquad \rho = \sqrt{\frac{2m(\phi - E)}{\hbar^2}}$$

STM – ElectroLuminescence (STM-EL)

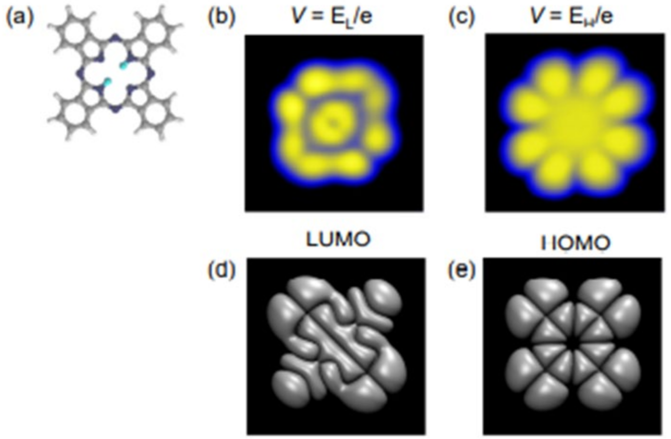
Origin of the strong electronic structure dependance of the STM

- **Differential conductance** measurement
  - **Strong dependance** of the **LDOS** of the **sample**
  - Existence of Sample states at E = eV

$$\frac{dI_t}{dV}(V) \propto \rho^S(\mathbf{r}_0, eV)$$



Tunneling through molecular orbitals - B. Doppagne Thesis IPCMS



***Current images** of the HOMO and LUMO **compared to the simulated orbitals** of H2PC molecule - B. Doppagne Thesis IPCMS*

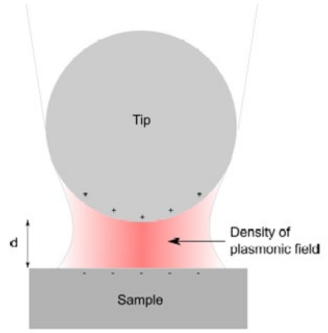
STM – ElectroLuminescence (STM-EL)

Light emission process in the STM junction

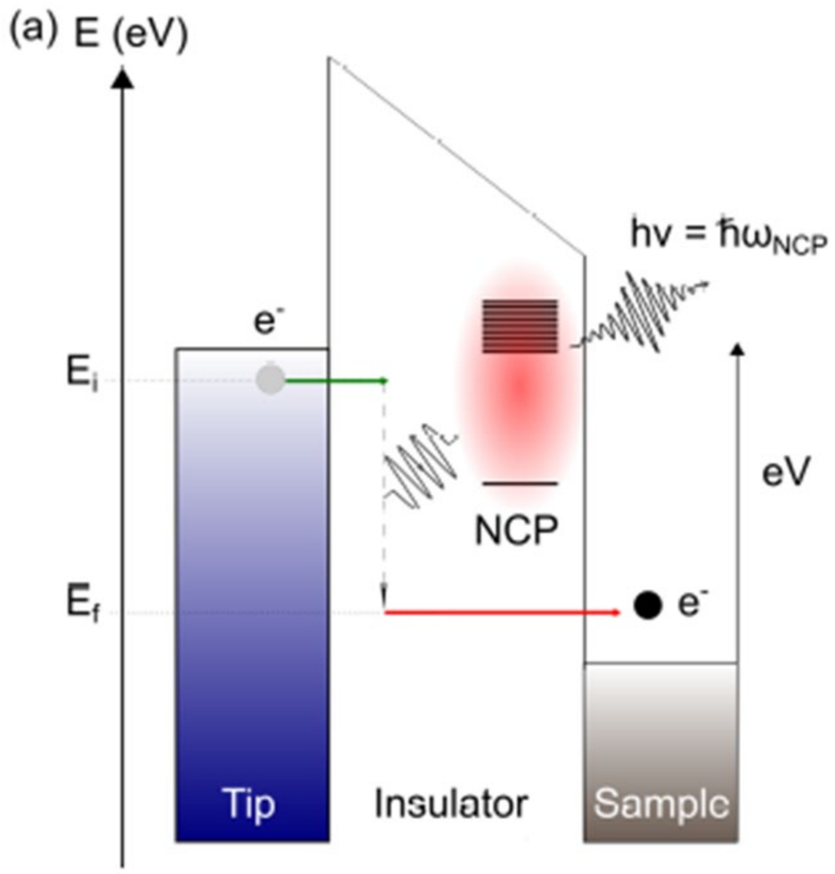
- **Inelastic tunneling** → **Excitation** of NCP mode → **Light emission**

$$\hbar\omega_{NCP} = E_i - E_f$$

- **Nano-Cavity Plasmon (NCP)** modes
  - Collective oscillation modes



Scheme of NCP modes in the STM junction



Light emission process in a STM junction - B. Doppagne Thesis IPCMS

Question

- Did the STM community succeed to measure Fluorescence from GNRs yet?

I. STM – induced Fluorescence on Graphene nanoribbons (GNRs)

a. Graphene nanoribbons (GNRs) for quantum electronics

b. STM – ElectroLuminescence (STM-EL)

c. **State of the art: 7-GNRs Fluorescence signal**

d. Our Experiment: 9-GNRs in STM junction

State of the art: 7-GNRs Fluorescence signal

IPCMS-STM team pre-publication article

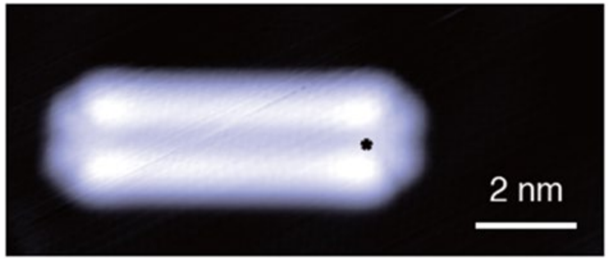
Topologically localized excitons in single graphene nanoribbons

Song Jiang[1*], Tomas Neuman[1], Alex Boeglin[1],

Fabrice Scheurer[1], Guillaume Schull[1*]

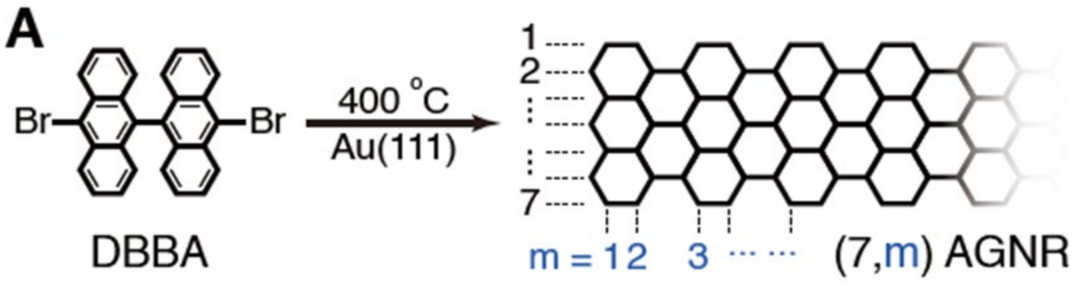
[1] Université de Strasbourg, CNRS, IPCMS, UMR 7504, F-67000 Strasbourg, France,

(Dated: April 4, 2022)



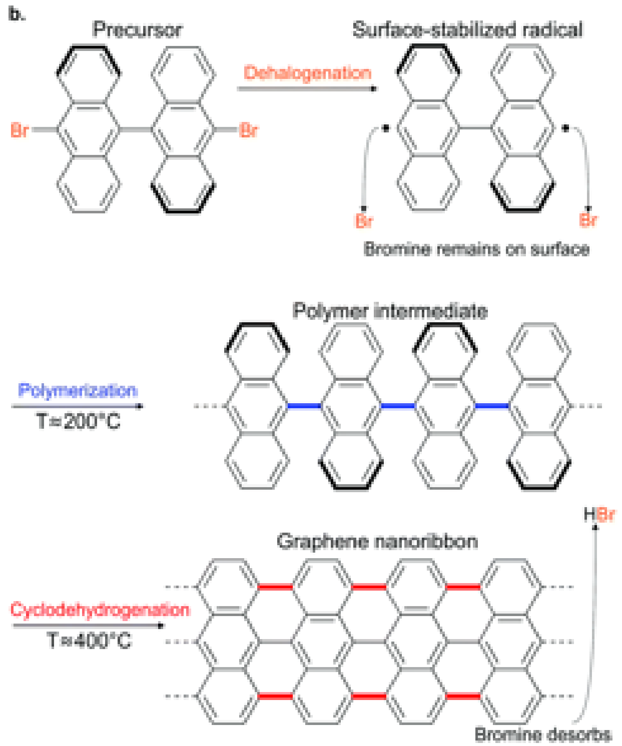
State of the art: 7-GNRs Fluorescence signal

(7,m)GNRs structure: Armchair/ZigZag



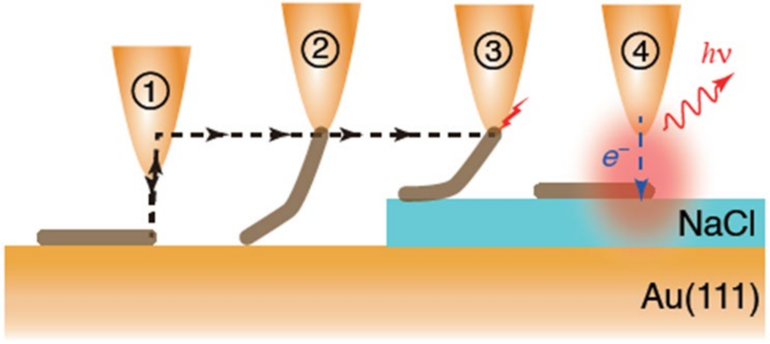
10,10'-dibromo-9,9'-bianthryl (DBBA) precursor (Left) - (7,m)GNR (right)

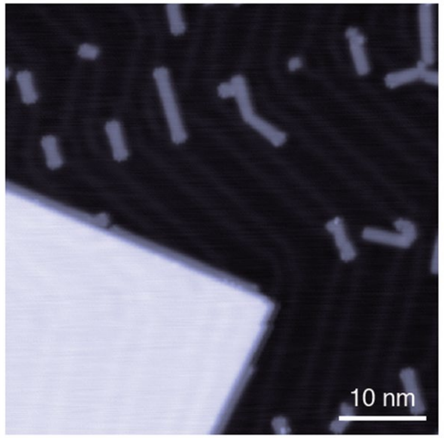
- (7,m) = **7 atom-wide ZigzZag** and **m atom-long Armchair**
  - 2 Simultaneous edges configurations : ZIgZag/Armchair



State of the art: 7-GNRs Fluorescence signal

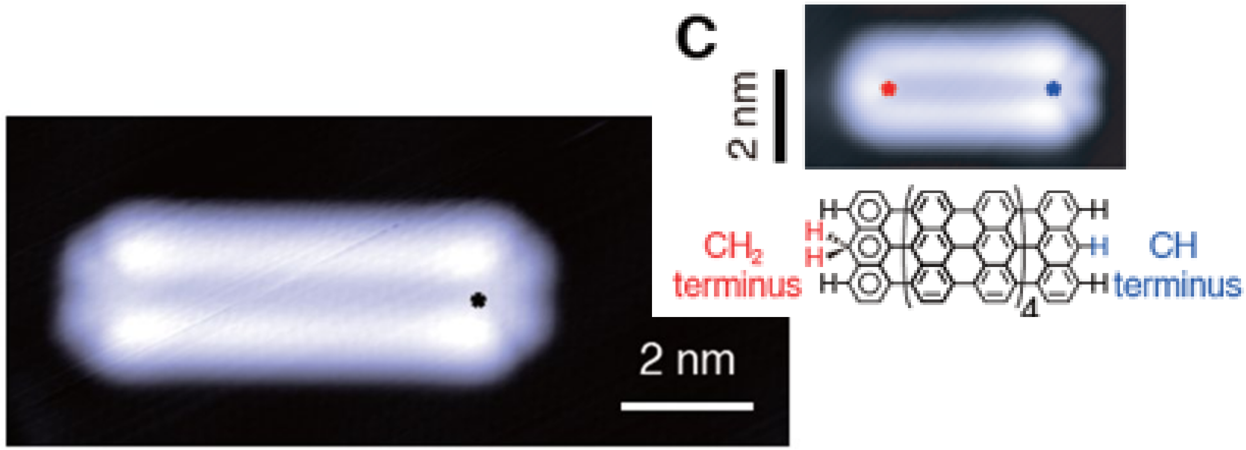
Experimental setup





(7,m)GNRs on Au(111) - salt on bottom left

- From Precursors to (7,m)GNRs on Au(111)surface (heating reactions)
- **Pull** the GNRs on the **salt**

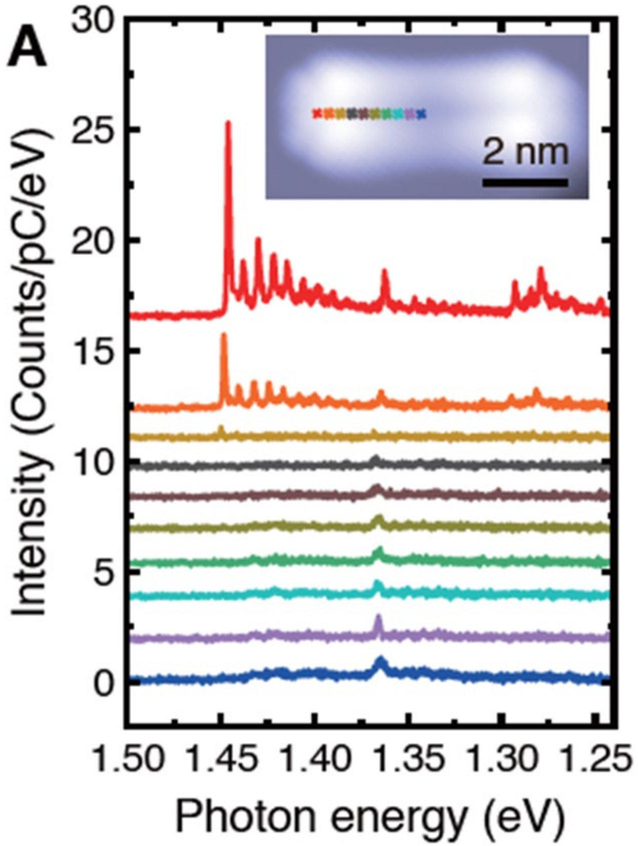


(7,28)GNR

State of the art: 7-GNRs Fluorescence signal

Results: Localized light emission states (topological states)

- topological states → **Localized light emission**
  - **Localized excitons**



Light emission with the tip at different positions

Our experiment

- By considering only Armchair-edges on the nanoribbons, could we obtain Fluorescence from delocalized excitons?

I. STM – induced Fluorescence on Graphene nanoribbons (GNRs)

a. Graphene nanoribbons (GNRs) for quantum electronics

b. STM – ElectroLuminescence (STM-EL)

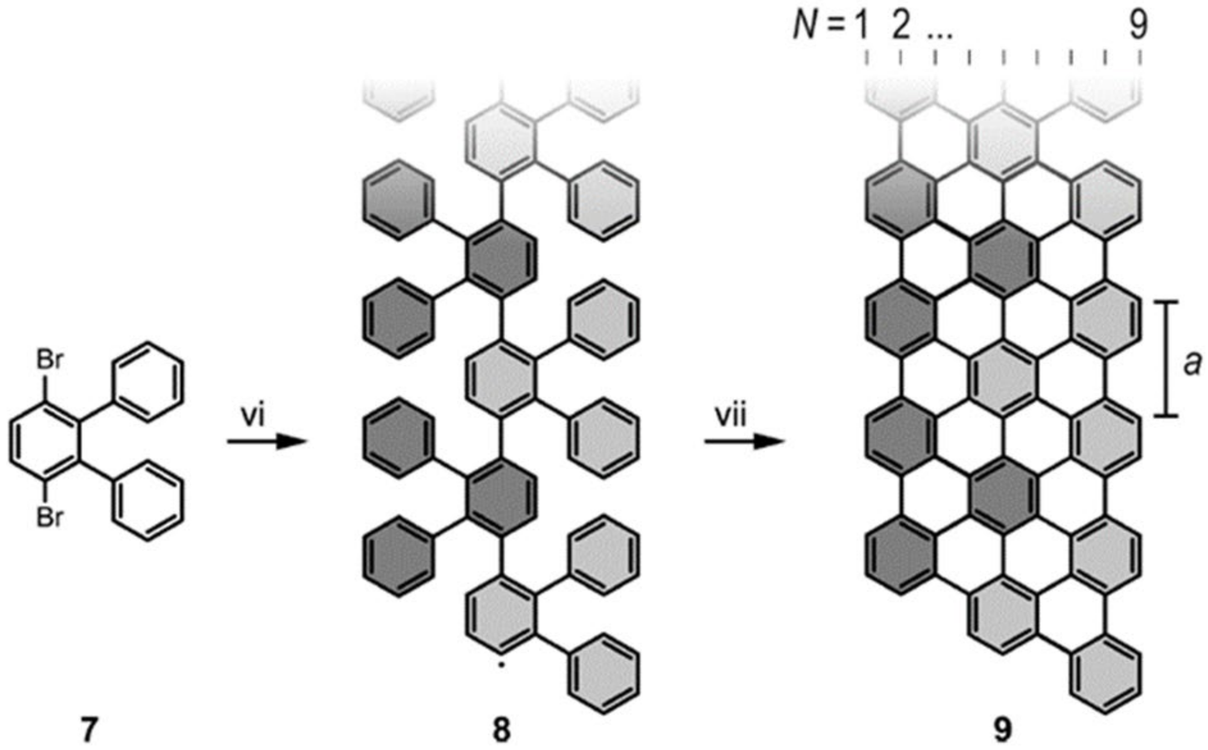
c. State of the art: 7-GNRs Fluorescence signal

d. Our Experiment: 9-GNRs in STM junction

Our Experiment: 9-GNRs in STM junction

Synthesis of 9 GNRs: chemical process

- **9-ArmChair GNR electronic** structure :
  - No **edges states**
  - **Optical bandgap**

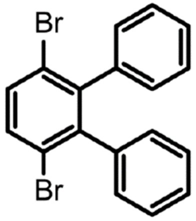


Synthesis of 9-atom wide Armchair GNR
- L.Talirz et al. ACS Nano 2017

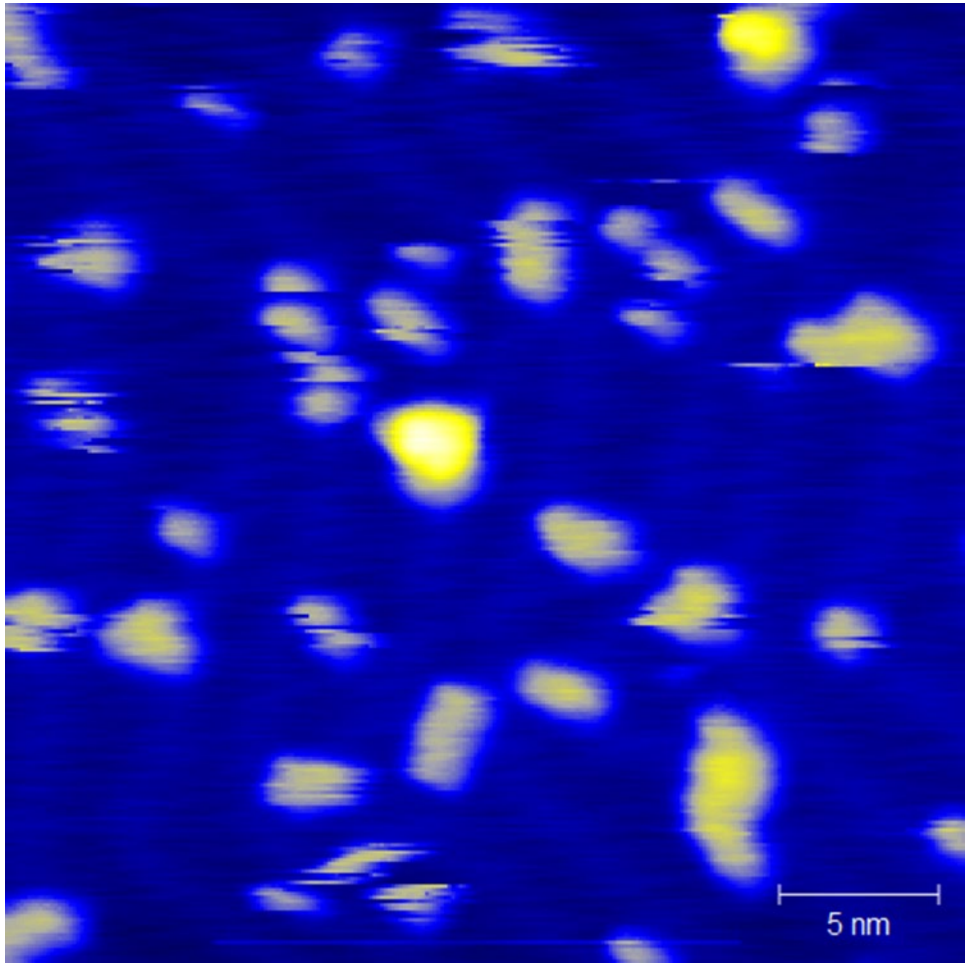
Our Experiment: 9-GNRs in STM junction

Deposition at low temperature – STM observations

- **Precursors evaporated** onto **Au(111) substrate (4 K)**



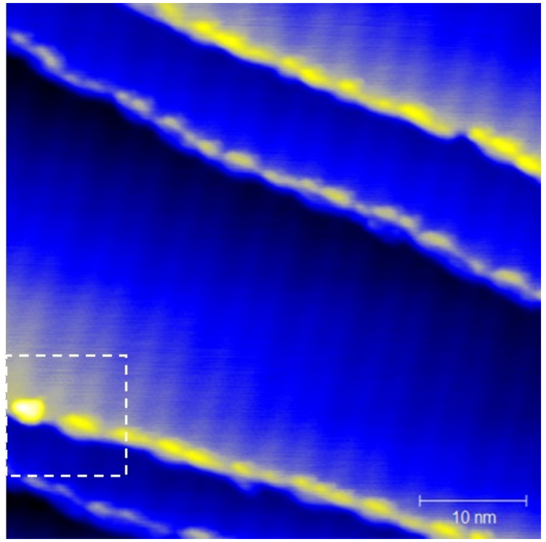
3′,6′-dibromo-1,1′:2′,1″-terphenyl (DBTP)

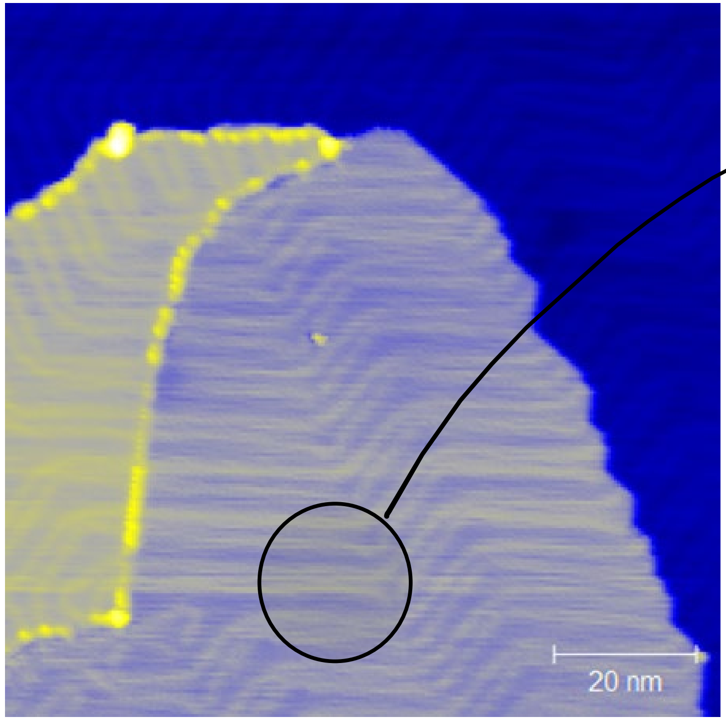


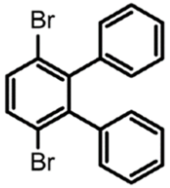
Our Experiment: 9-GNRs in STM junction

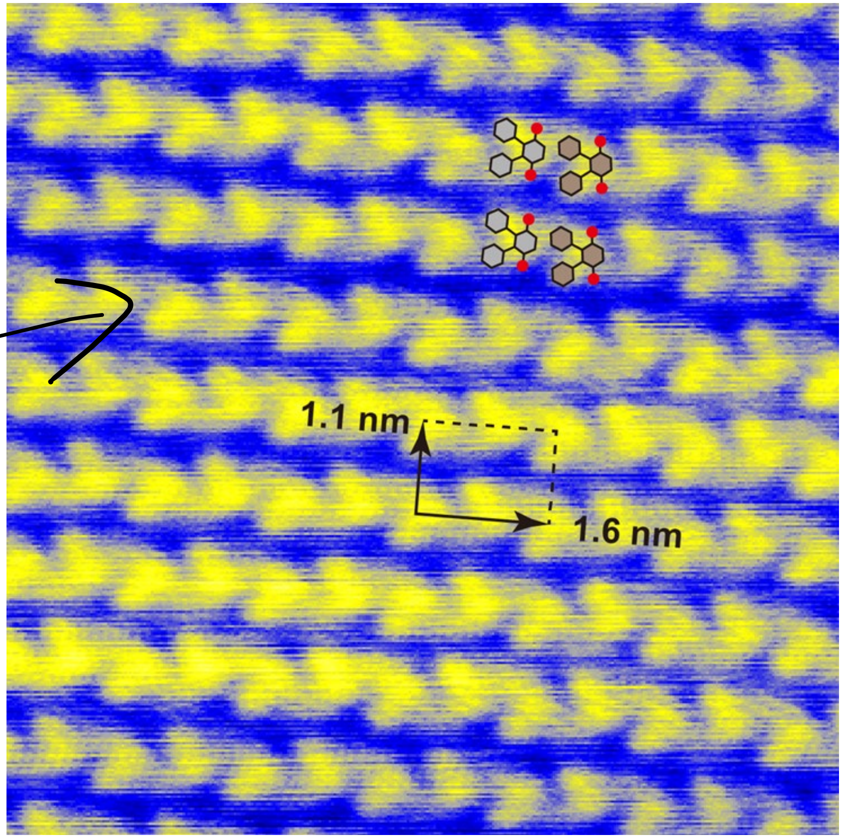
Sample at room temperature – STM observations

- Sample at **room temperature** for **20mins : Molecule drift**
  - Au(111) **step edges**
  - **Islands** formation





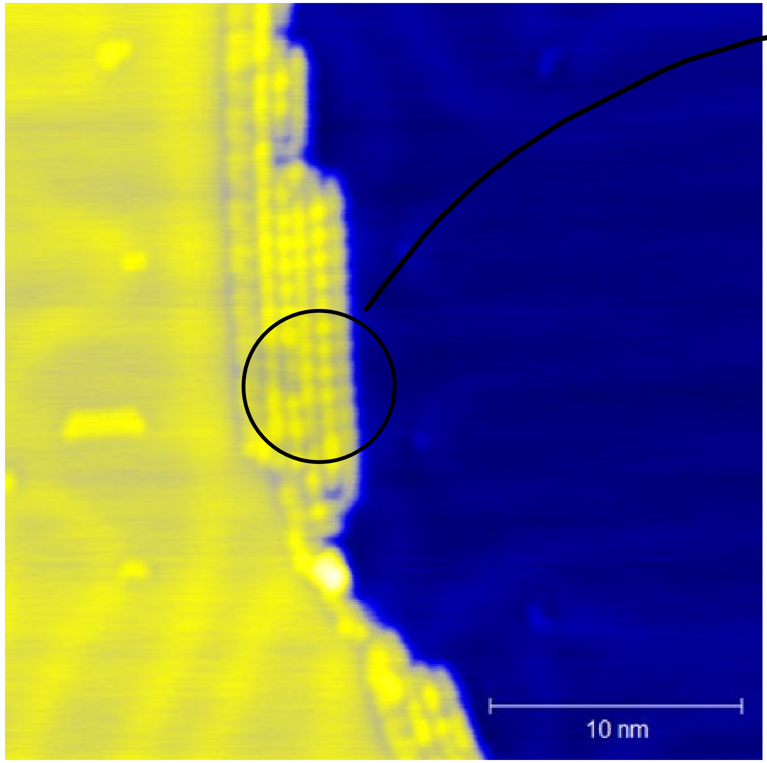


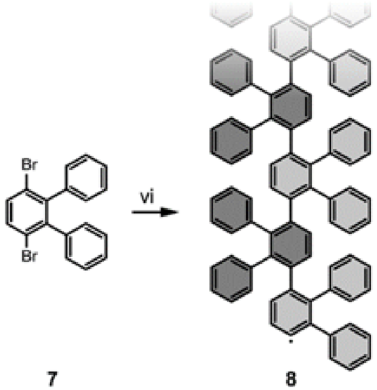


Our Experiment: 9-GNRs in STM junction

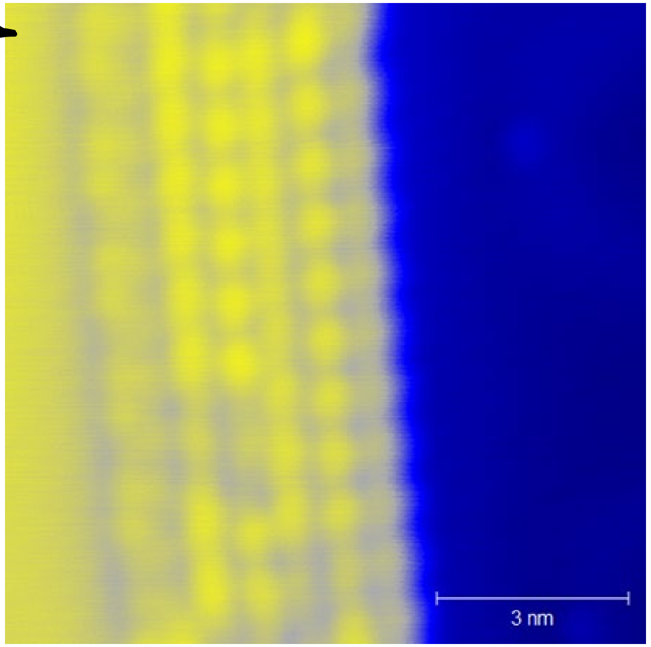
1st annealing: Polymerization process – STM observations

- **Dehalogenation and Polymerization** at 140 °C





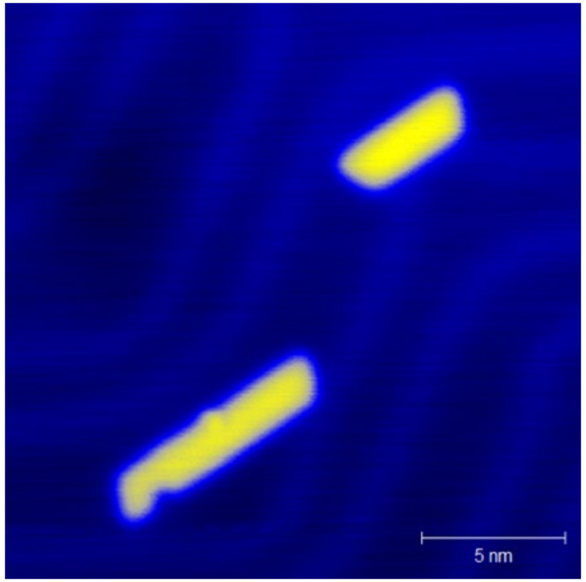
7 8

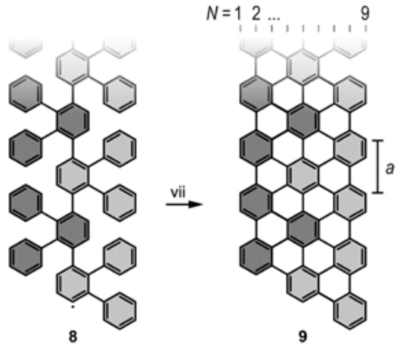


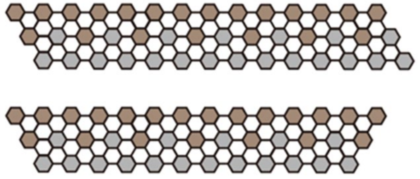
Our Experiment: 9-GNRs in STM junction

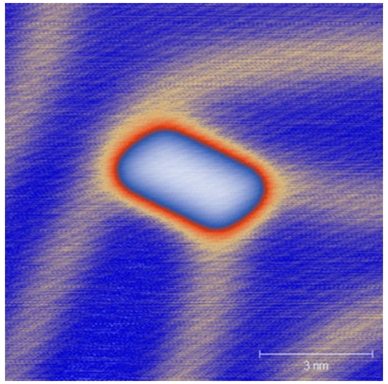
2^{nd} annealing: Cyclodehydrogenation – STM observations

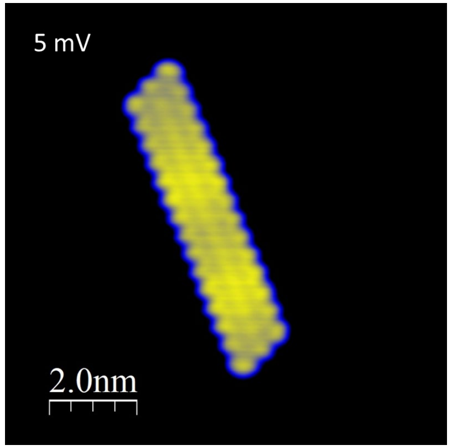
- **Cyclodehydrogenation** at 250 ℃

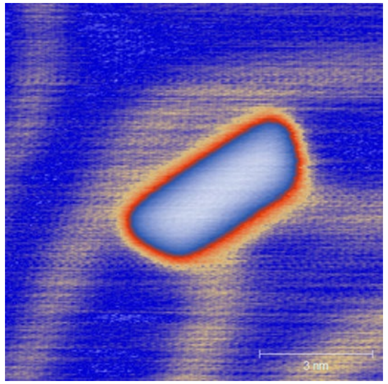






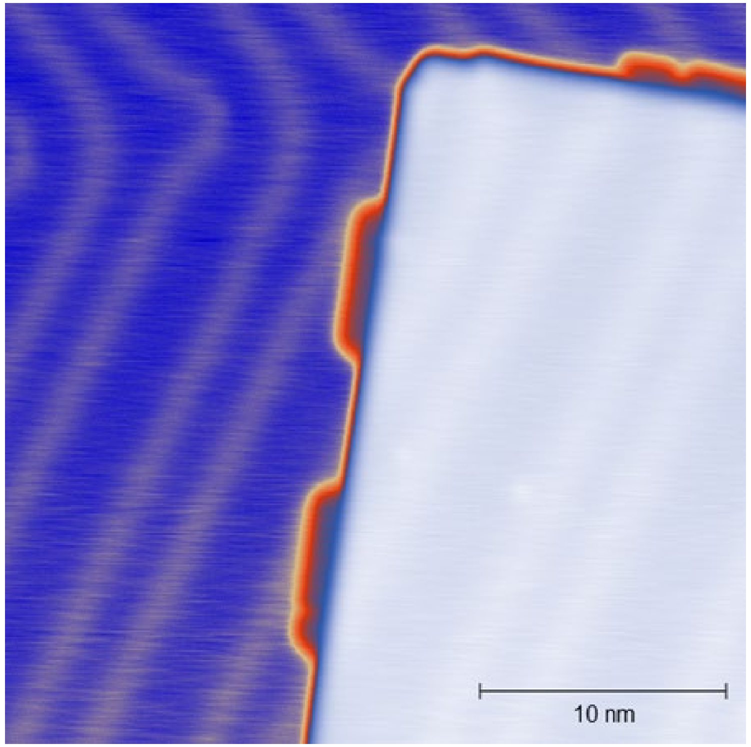


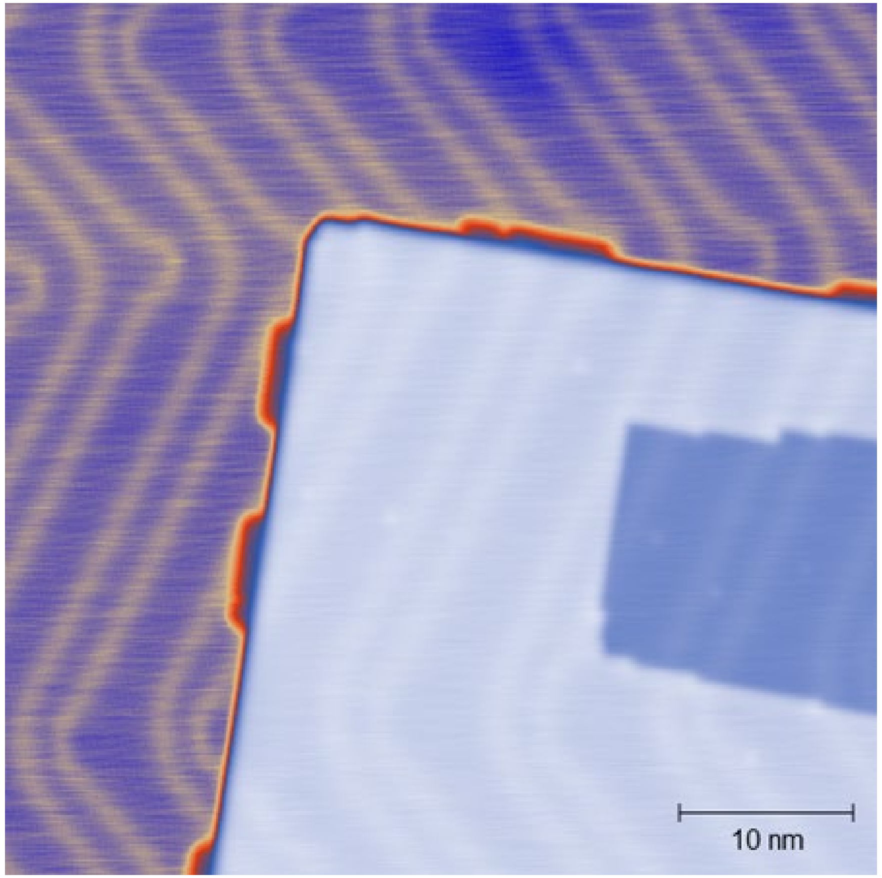




Our Experiment: 9-GNRs in STM junction
Deposition of Salt layers

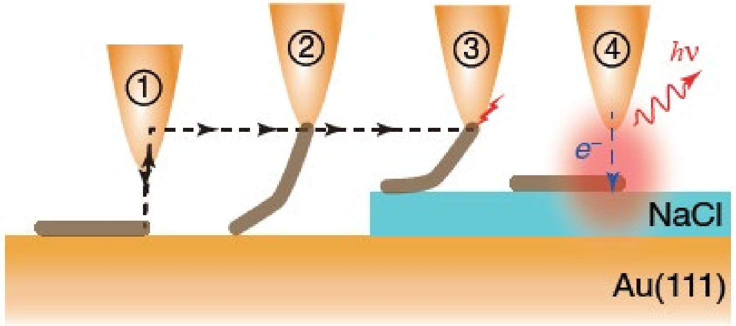
- NaCl deposition
  - GNRs drift - **edges of NaCl island**

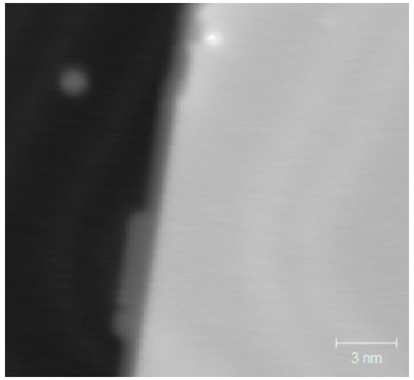


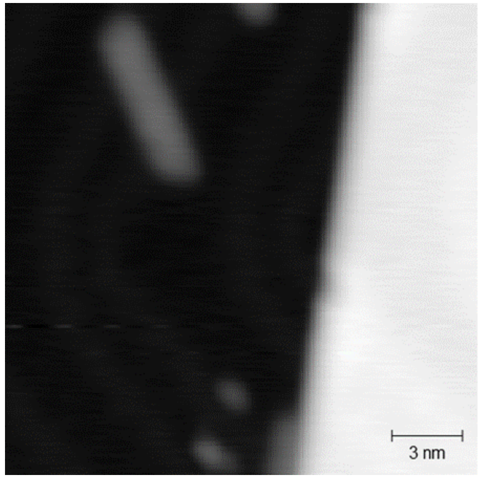


Our Experiment: 9-GNRs in STM junction
GNR manipulation

- Pull GNR on Salt
  - **Displacement only**
  - **Fluorescence signal impossible**







Question

- In what extend could we improve the experimental setup of the STM junction to get a single molecule Fluorescence ?

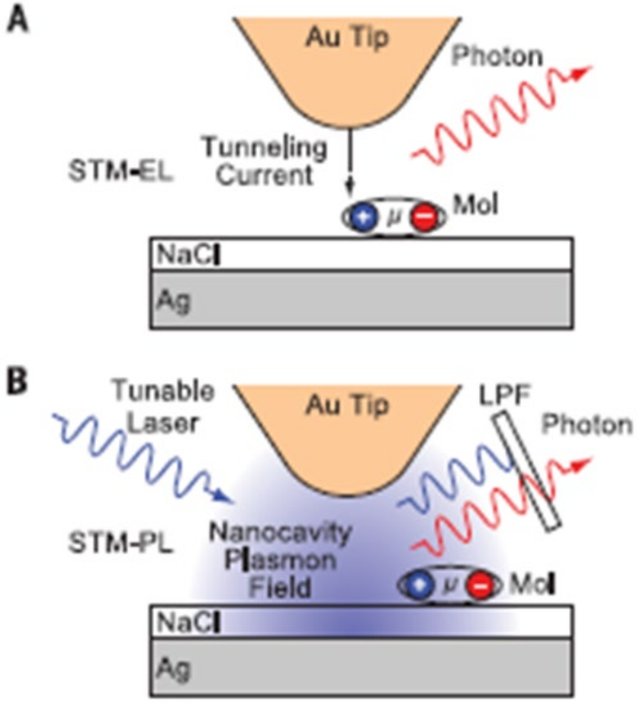
II. STM – PhotoLuminescence enhancement

a. Fluorescence emission enhancement

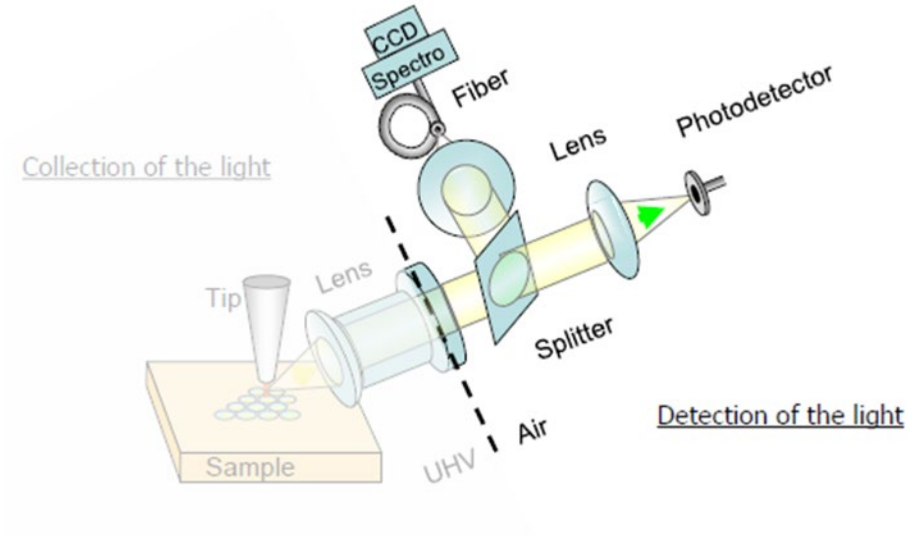
b. Our experiment: Tip preparation

Fluorescence emission enhancement

STM-PhotoLuminescence principle (≠ STM –ElectroLuminescence)



Scheme of STM-EL and STM-PL experiment – Imada el al. Science 2021



Sketch of the detection optical setup - G.Schull presentation

Fluorescence emission enhancement

Important recent paper: parameters of the Fluorescence enhancement (Yang et al. – Nature Photonics 14, 693-699) published in 2020

nature photonics

ARTICLES

https://doi.org/10.1038/s41566-020-0677-y

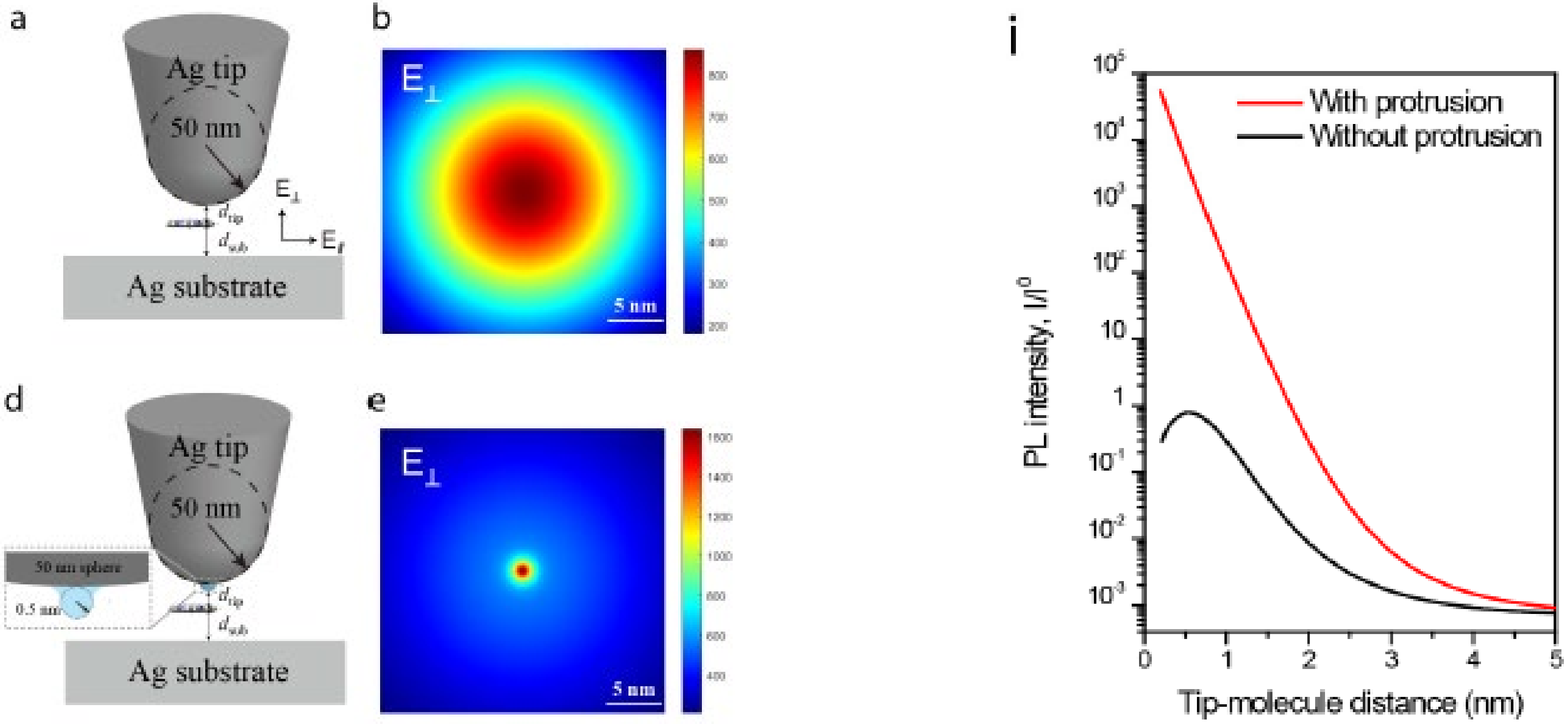
Check for updates

Sub-nanometre resolution in single-molecule photoluminescence imaging

Ben Yang[1,4], Gong Chen[1,4], Atif Ghafoor[1], Yufan Zhang[1], Yao Zhang[1], Yang Zhang[1]✉, Yi Luo[1], Jinlong Yang[1], Vahid Sandoghdar[2], Javier Aizpurua[3], Zhenchao Dong[1]✉ and J. G. Hou[1]✉

Fluorescence emission enhancement

Tip with atomic-protrusion – Strong and confined Nano-Cavity Plasmons (NCP)



Simulations for the electric fields in the junction *and* ***PL emission*** *properties for a* ***tip with or without protrusion structures*** *– Suppl. article Yang & al 2020*

Our experiment

- What would be the etching process to get an atomic-protrusion on the tip?

II. STM – PhotoLuminescence enhancement

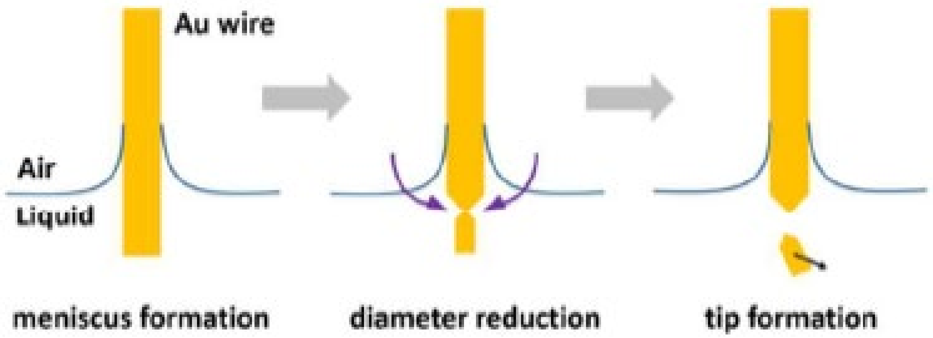
a. Fluorescence emission enhancement

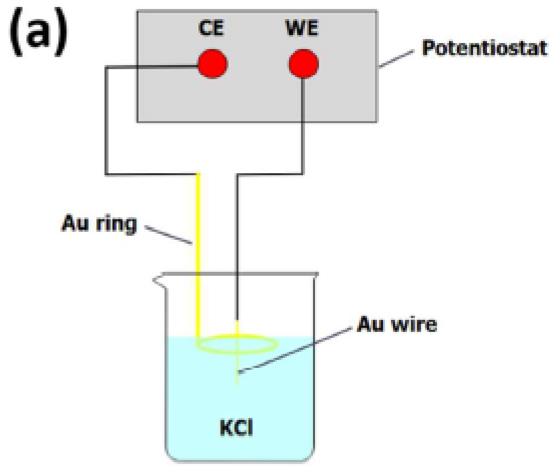
b. Our experiment: Tip preparation

Our experiment: Tip preparation

Electrochemical-etching process

- **Silver** or **Gold tip** - depending on experiment
- Sharp tips :
  - **electrochemical etching**



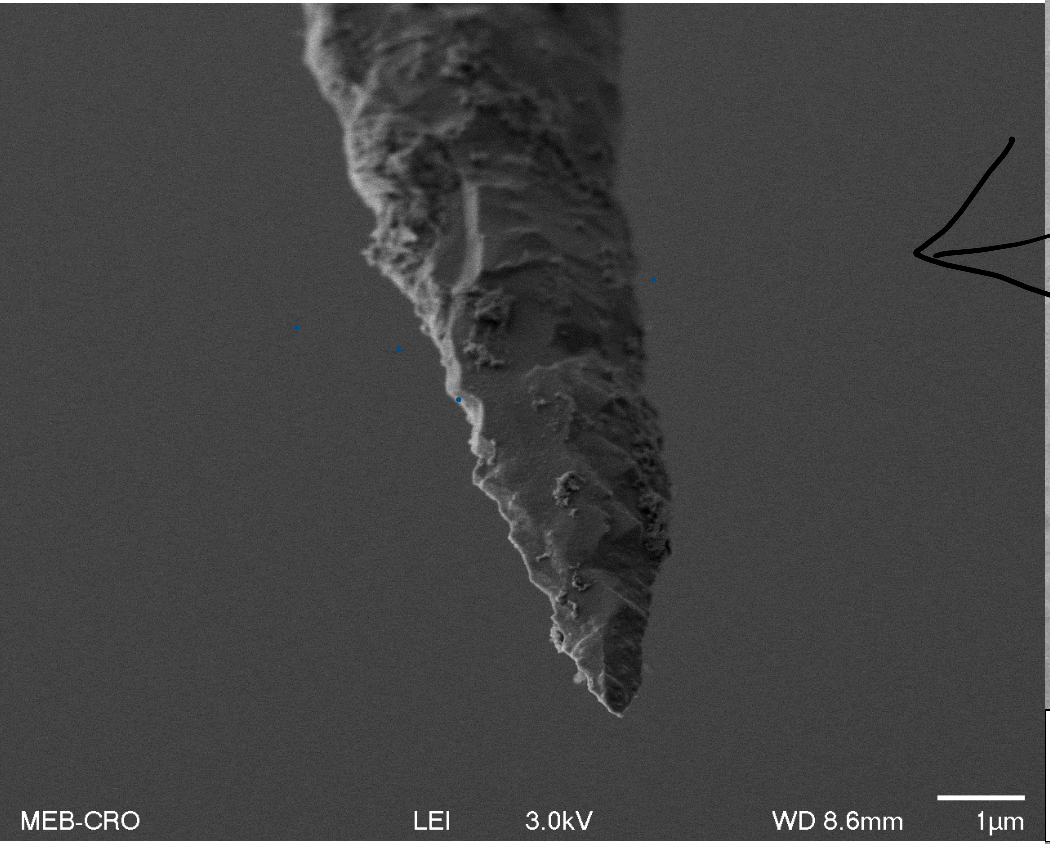


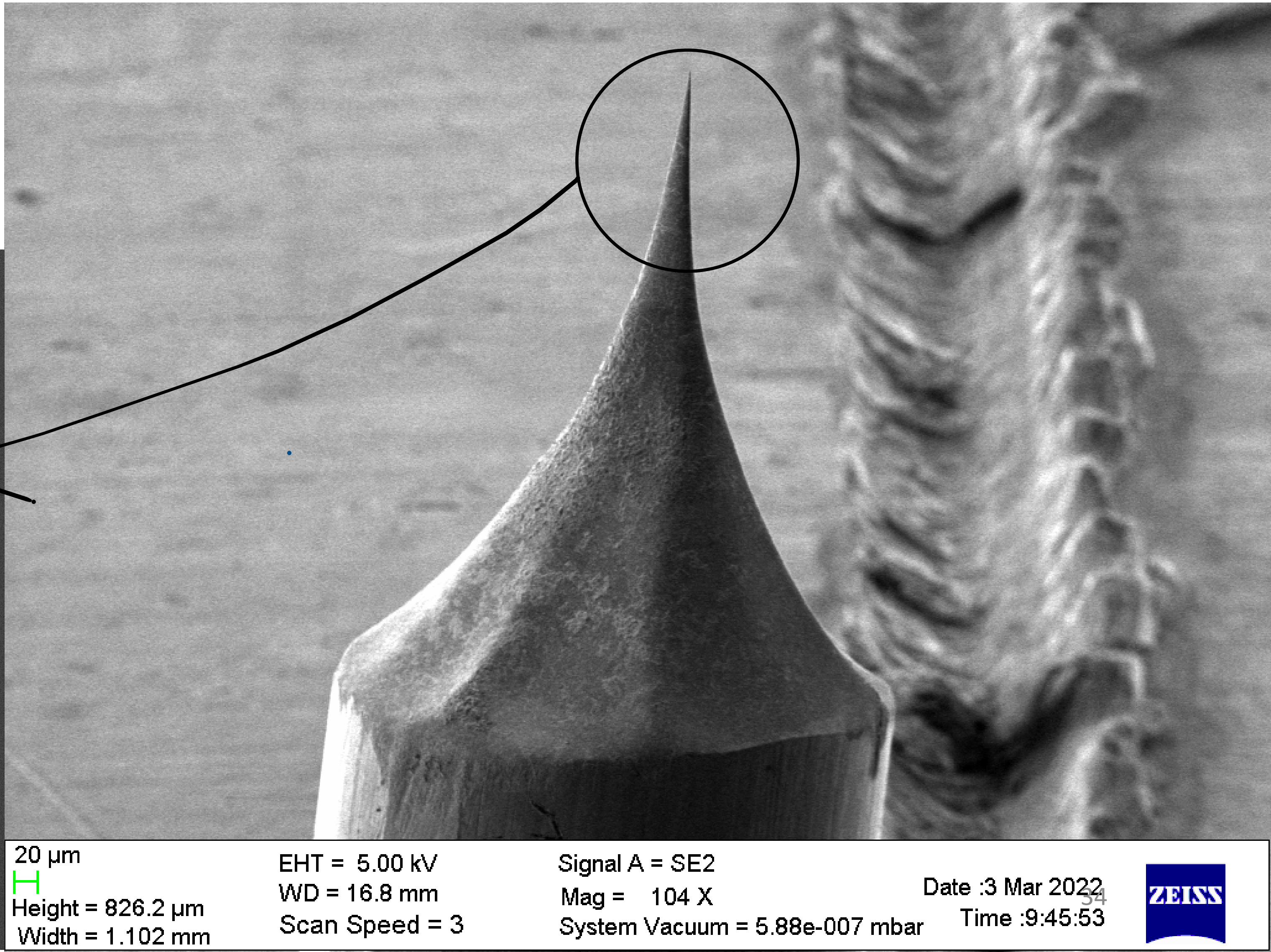
Schematic experimental setup for the electrochemical etching of Au tip

Our experiment: Tip preparation

Microscope (SEM) observations

- SEM observation

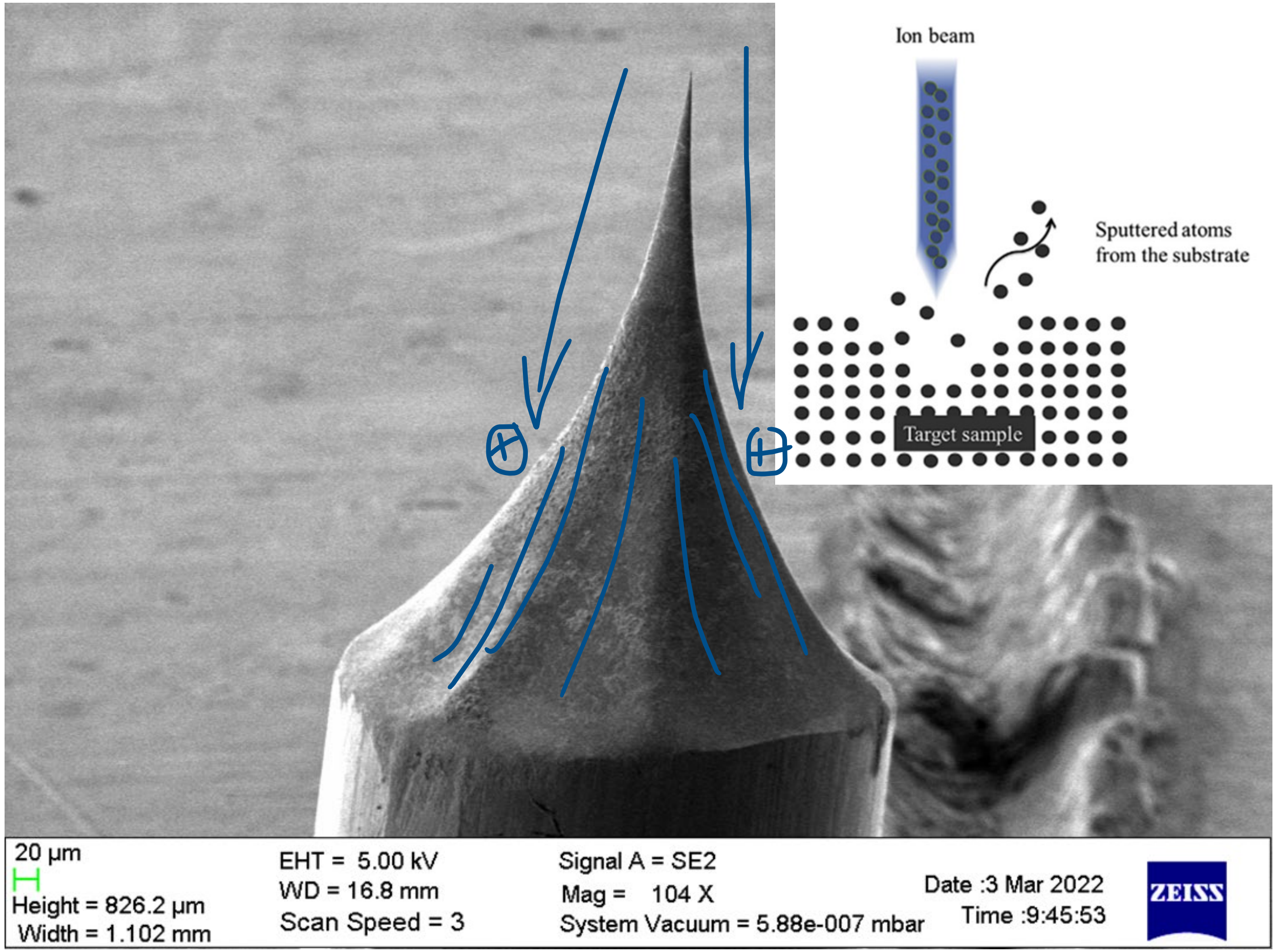




Our experiment: Tip preparation

Focus Ion Beam (FIB) etching

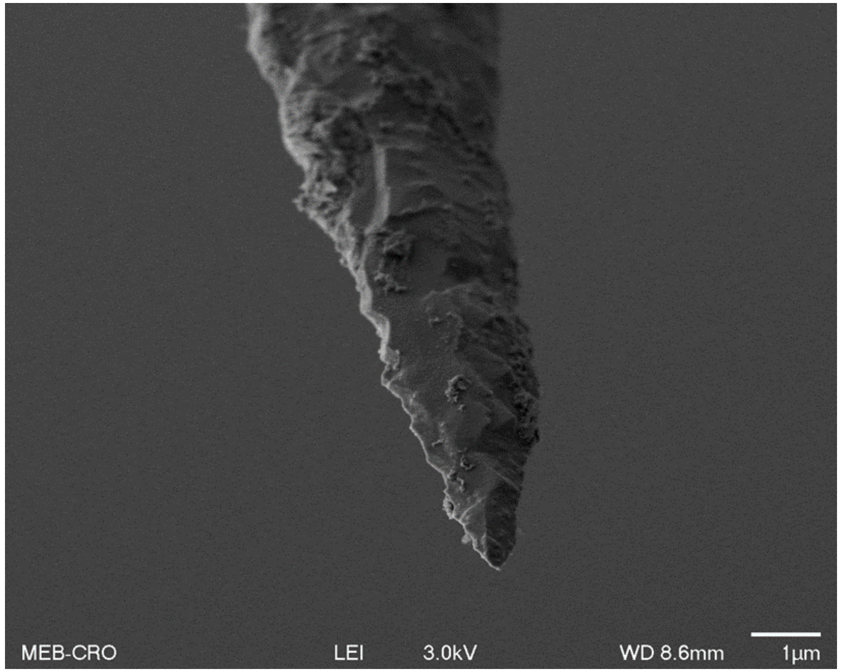
- Sharper tips :
  - **Focus Ion beam etching**
- FIB at ISIS lab
  - Sputtering of the tip - Ga+ ions
  - Time of FIB for one tip : few hours



Our experiment: Tip preparation

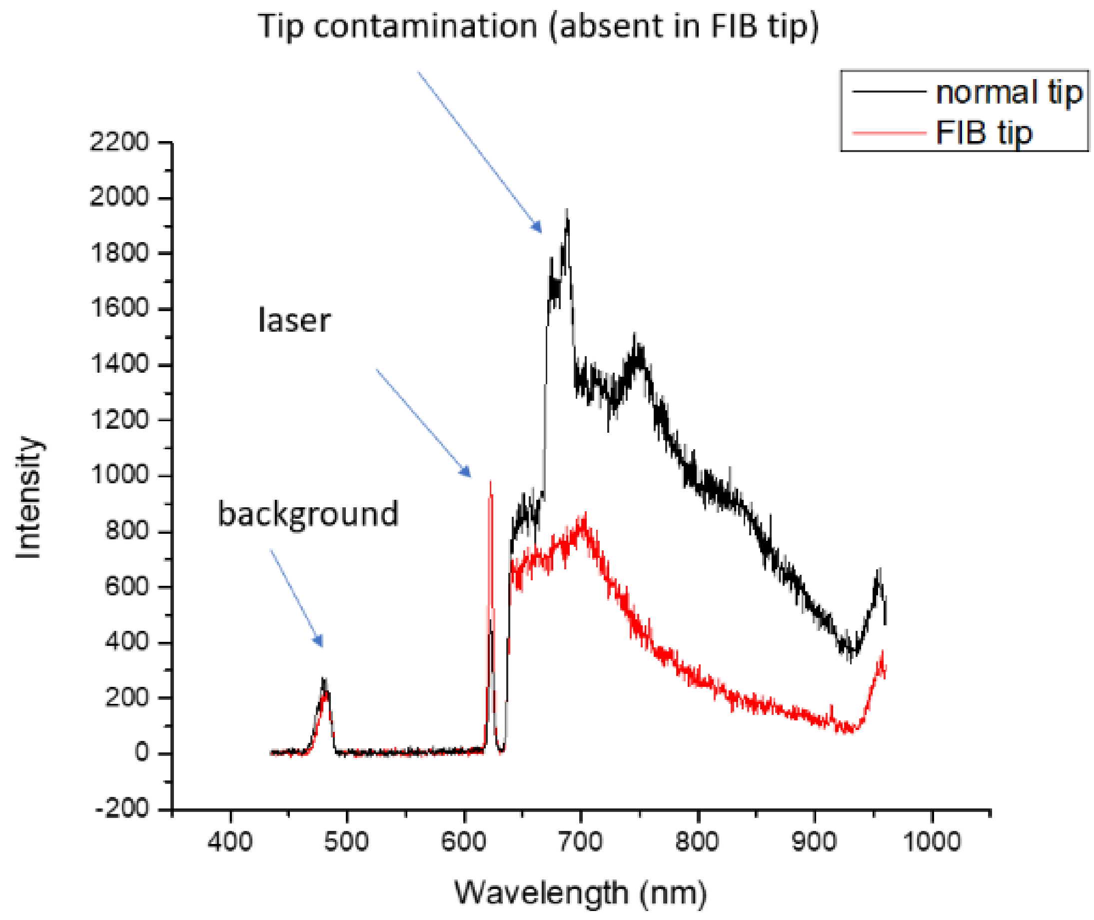
Focus Ion Beam (FIB) etching

- SEM observation **after FIB Bombarding** :
  - **Very sharp**
  - **Protrusion**
  - **Smooth**



Our experiment: Tip preparation

Results: Spectrum without and with FIB tip etching



*STM-PL spectrum from **TIP before and after FIB** with incident laser at 620nm*

- **Huge attenuation** of 650-950 signal → **much less contamination** on **FIB tip**

Conclusion

Conclusion

- Brief answer to the problematic
  - **STM appears as a major experimental system to probe fluorescence**
  - **Experimental failure to get delocalized light emission from single graphene nanoribbon**
  - **Identification of significant parameters to get an enhancement of the fluorescence**

- Do we have access to the intrinsic behaviour of the molecule ?

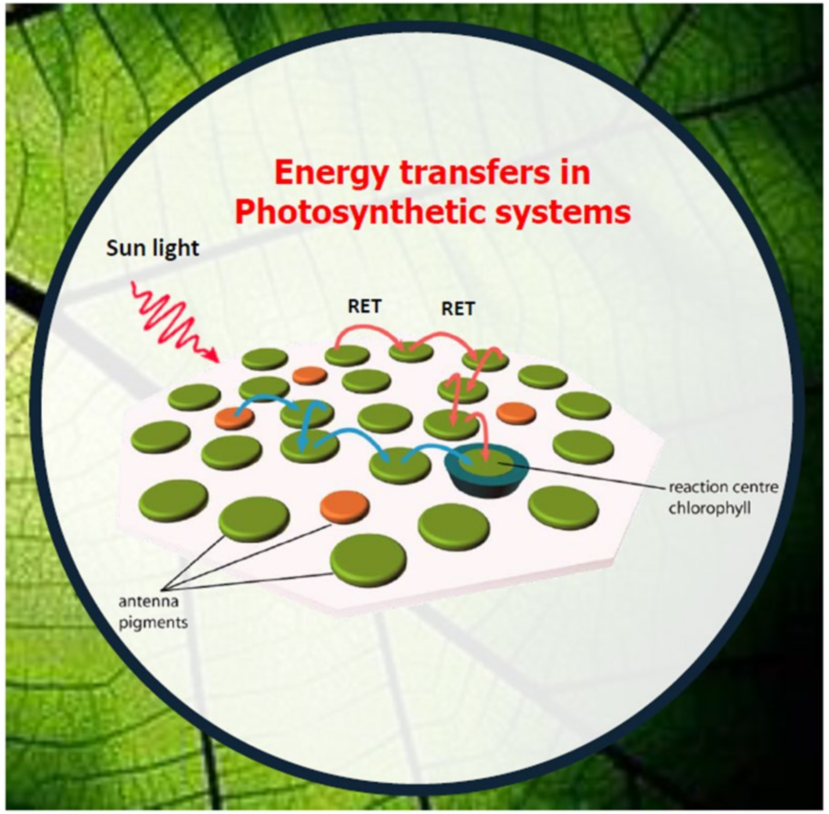
Thank You For Your Attention !

Appendix

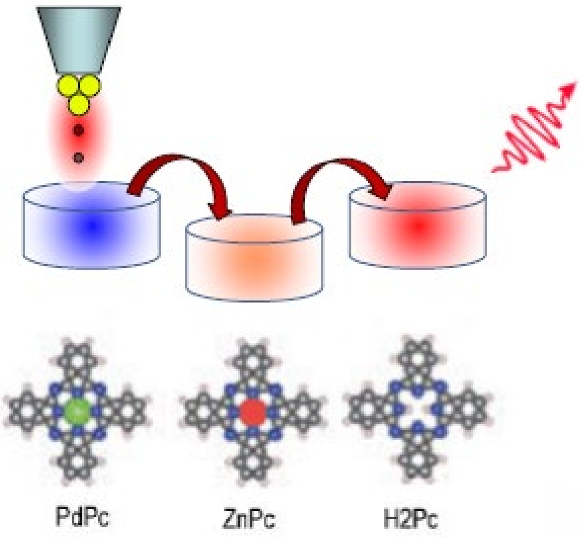
Opening

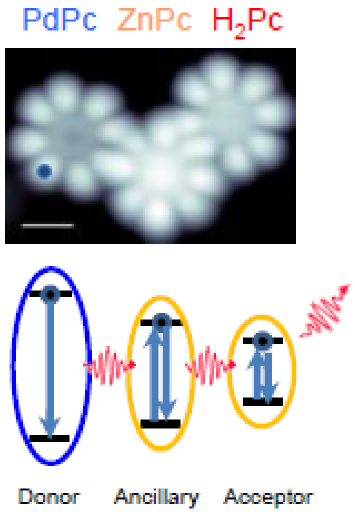
Opening

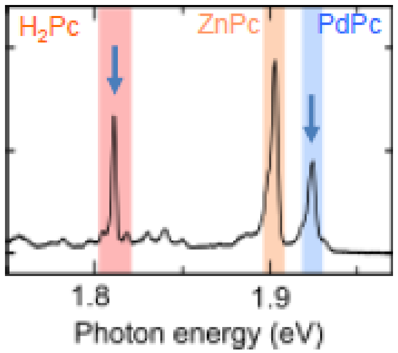
Mimic photosynthesis



Sun light absorption then light
Propagation of emitting cells





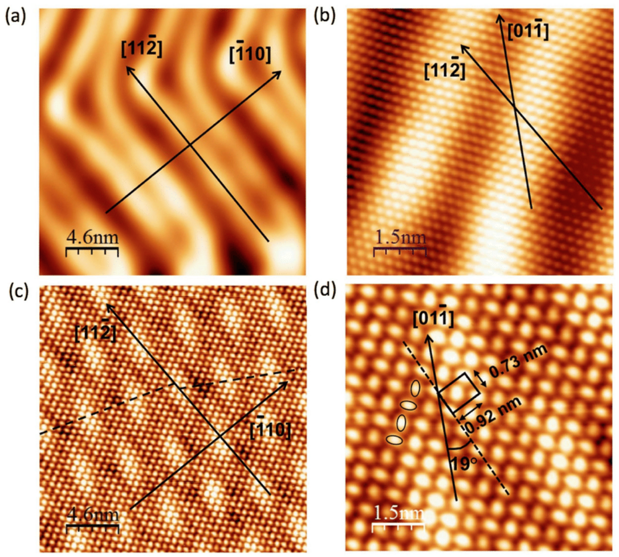


Sequential energy
transfer events

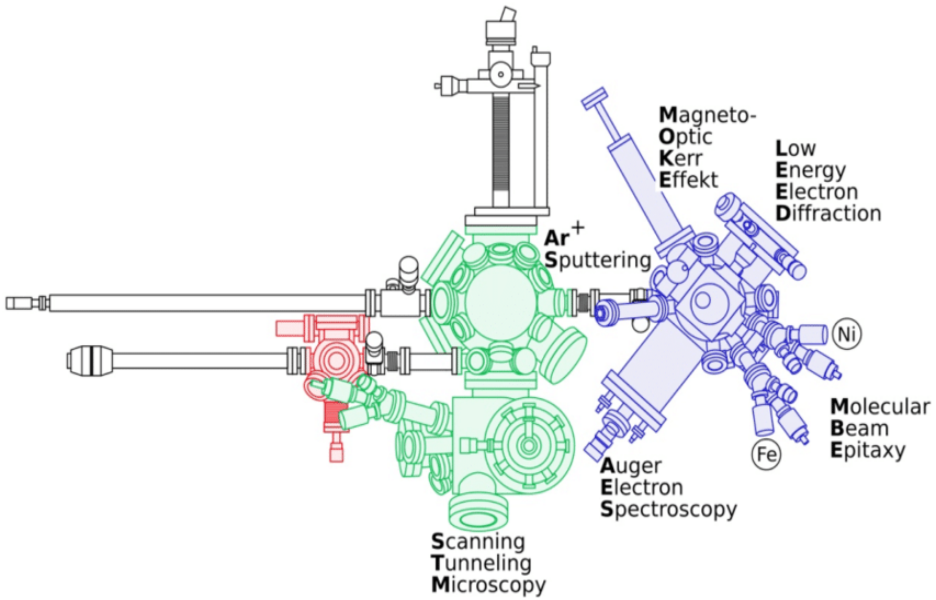
Experimental Setup

Sample Preparation

- **Preparation chamber** at **UHV**
- **Molecular evaporator :** evaporate **organic compound** and **salt**
- Evaporate on the **cooled (4.7 K) sample : avoid molecular diffusion**



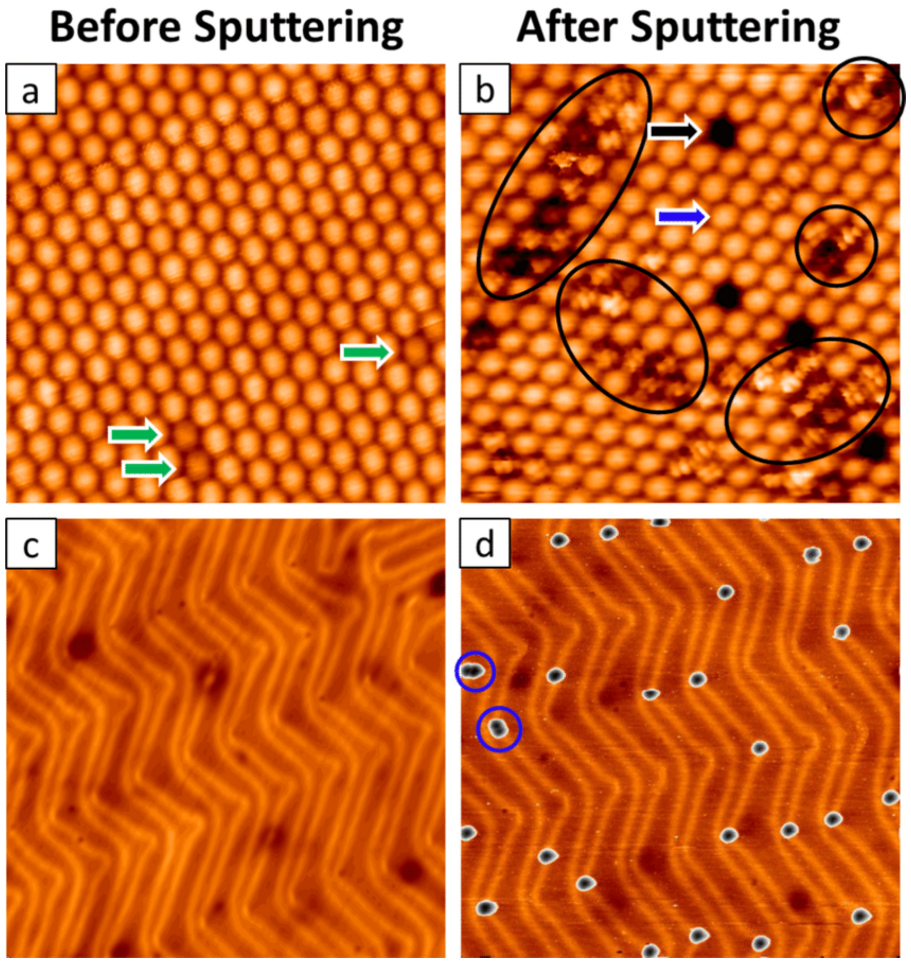
Au(111) observed by STM current imaging



Scheme example of STM chamber preparation

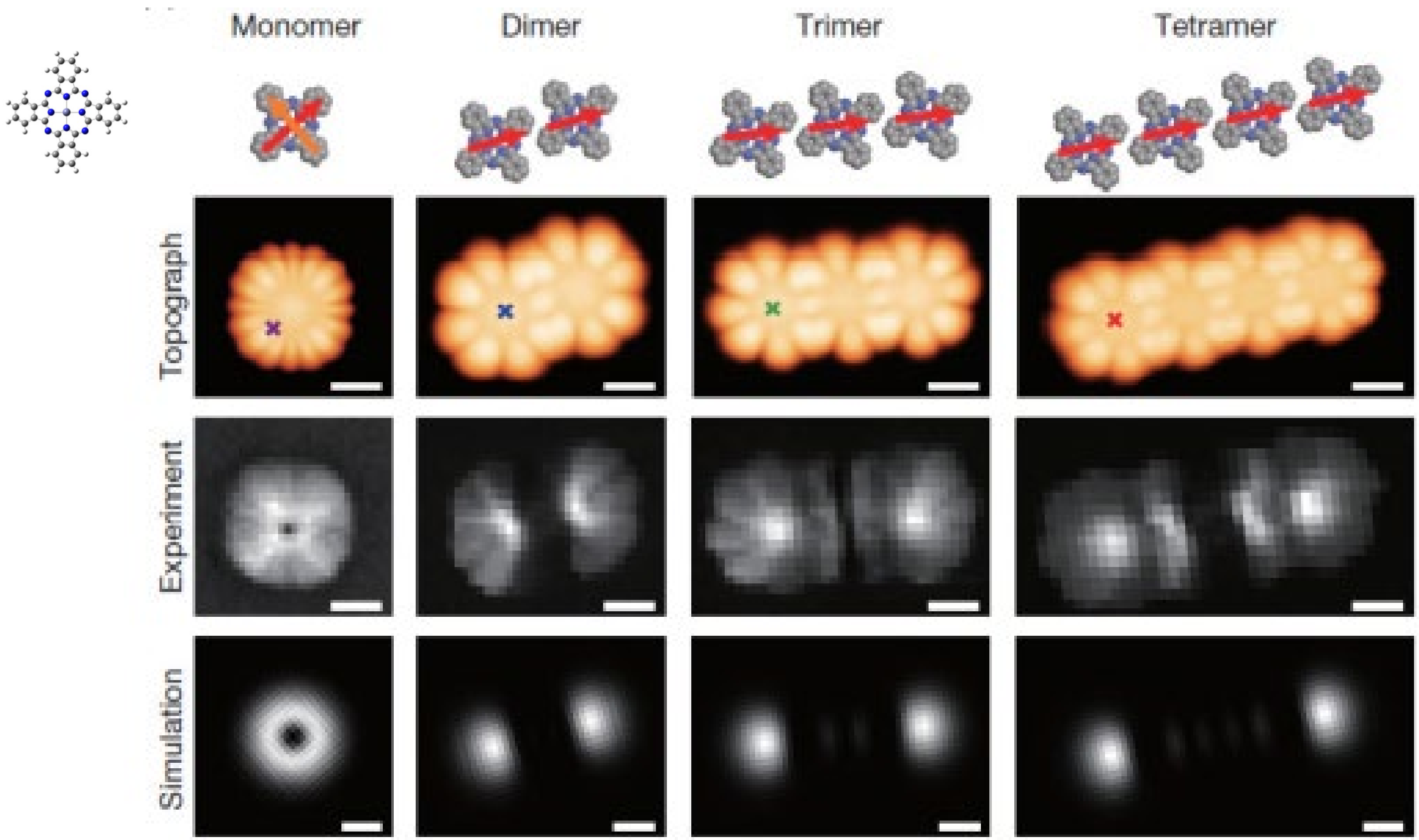
Experimental Setup
Sample Preparation

- **Sample preparation** : cycles of **sputtering** and **annealing**.
- Argon ion **bombarding**



Sputtering process on Au(111) surface

Practical S.T.M current and photon images recording on molecules



Corresponding current images and experimental photon maps compared to the simulated maps of ZnPc molecules - B. Doppagne Thesis IPCMS

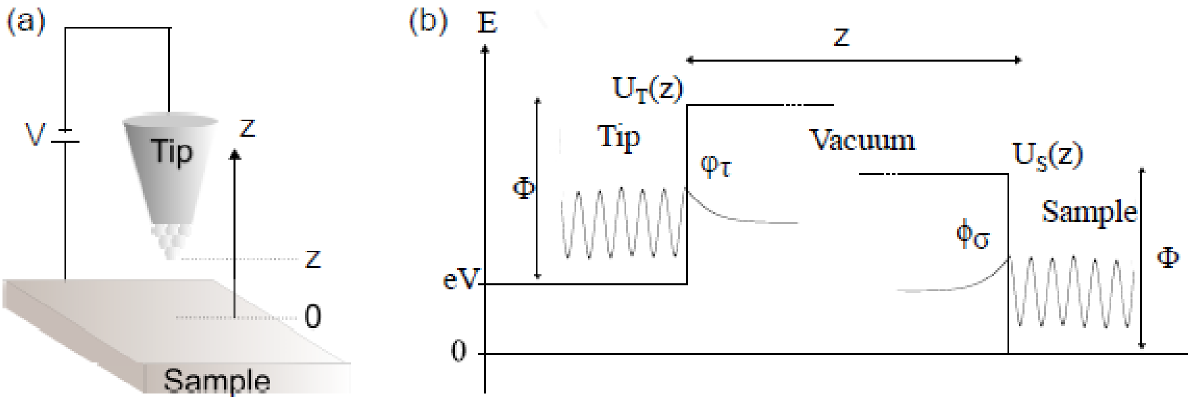
Expression of the tunnel current

Bardeen's model

- **Probability of crossing**:
  - from state tip φ_τ to state sample ϕ_σ after time t

$$P_{\tau\sigma}(t) = \frac{2\pi}{\hbar}|M_{\sigma\tau}|^2\delta(E_\tau - E_\sigma)t$$

- Bardeen's model :
  - Tunneling only from **occupied states tip** to **unoccupied states sample**



Description of a STM junction and model of Bardeen - B. Doppagne Thesis IPCMS

$$I_t = \frac{4\pi e}{\hbar}\sum_{\tau\sigma}|M_{\tau\sigma}|^2\delta(E_\tau - E_\sigma)\{f_{E_F+eV}(E_\tau) - f_{E_F}(E_\sigma)\}$$

Expression of the tunnel current
Tersoff and Hamann model (WKB approximation)

- Tip states φ_τ are **spherical waves**

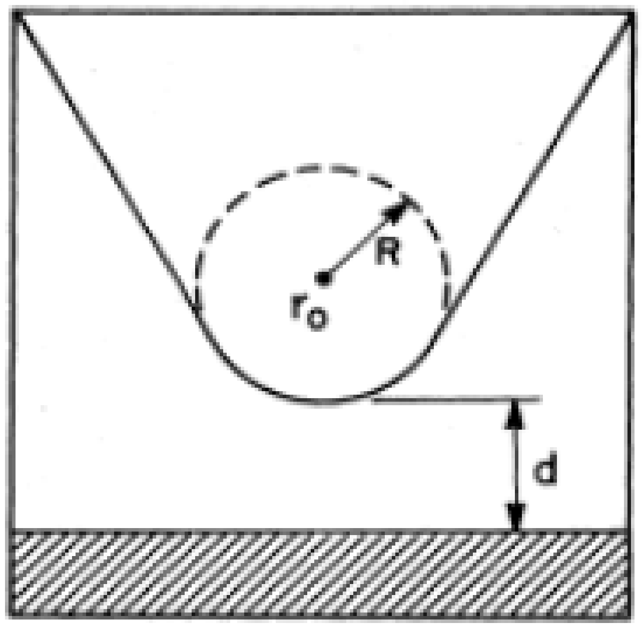
$$\psi_\tau(\mathbf{r}) = C_\tau \frac{e^{-\rho_\tau|\mathbf{r}-\mathbf{r}_0|}}{|\mathbf{r}-\mathbf{r}_0|}$$

- **Integrated form** with LDOS (sample and tip)

$$I_t \propto \int_{-\infty}^{+\infty} dE\rho^T(E-eV)\rho^S(\mathbf{r}_0,E)\{f(E-eV)-f(E)\}$$

- Semi-classical WKB theory :
  - Approximation a 4K (Heavyside function)
  - **Transmission coefficient**
  - **Tip apex : single atom**

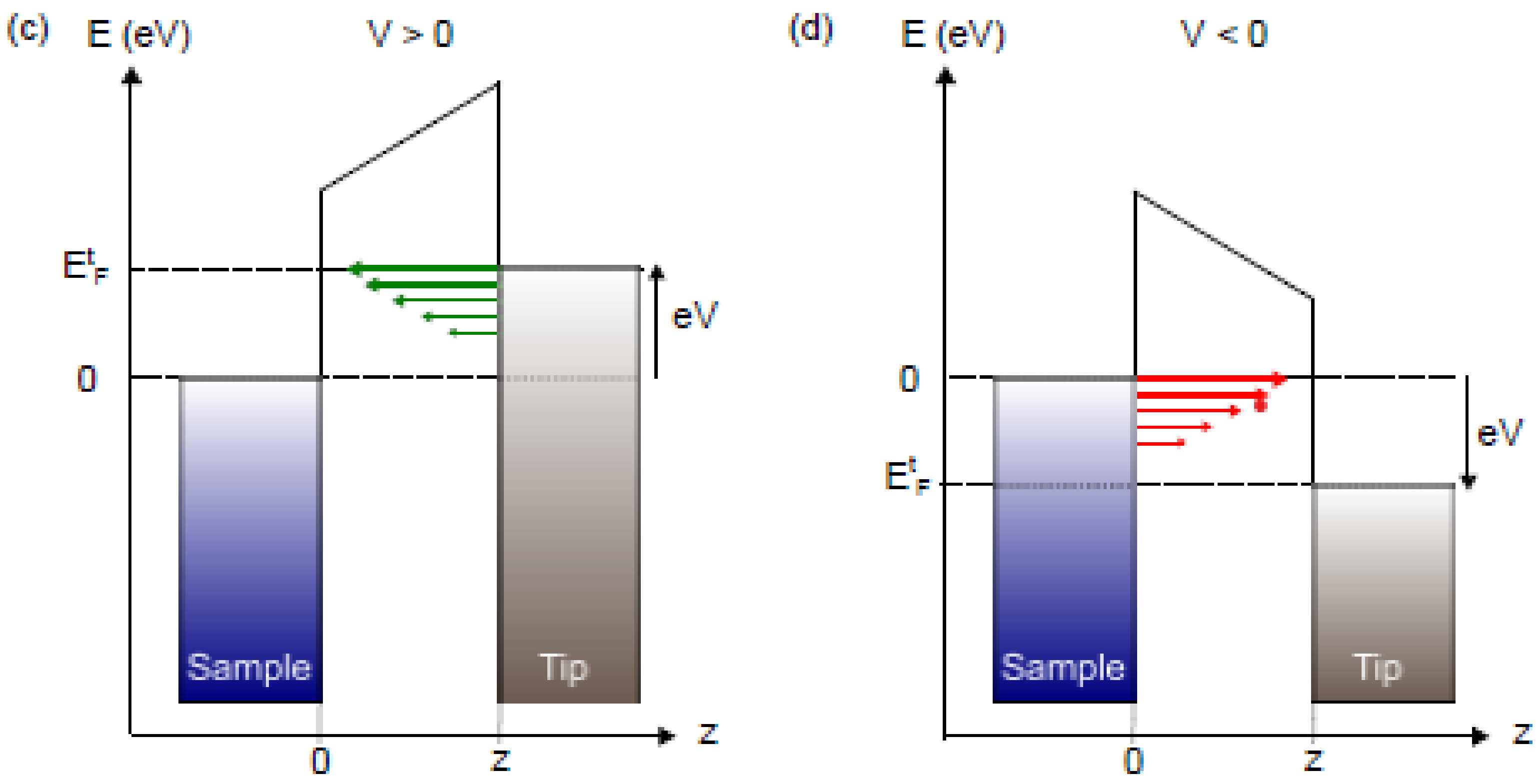
$$I_t \propto \int_0^{eV} dE\rho^S(E)T(z,E,V)$$



Sketch of the tip geometry assumed by Tersoff and Hamann- B. Doppagne Thesis IPCMS

Expression of the tunnel current

Tersoff and Hamann model (WKB approximation)



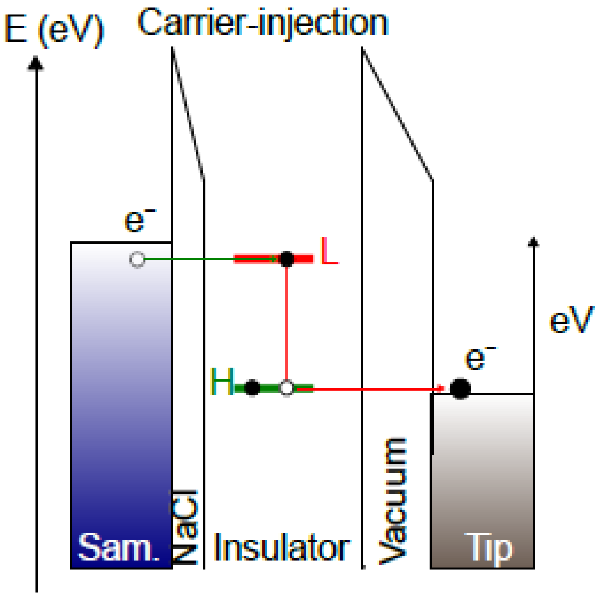
Description of a metal-metal tunnel junction -
B. Doppagne Thesis IPCMS

$$I_t \propto \int_0^{eV} dE \rho^S(E) T(z,E,V)$$

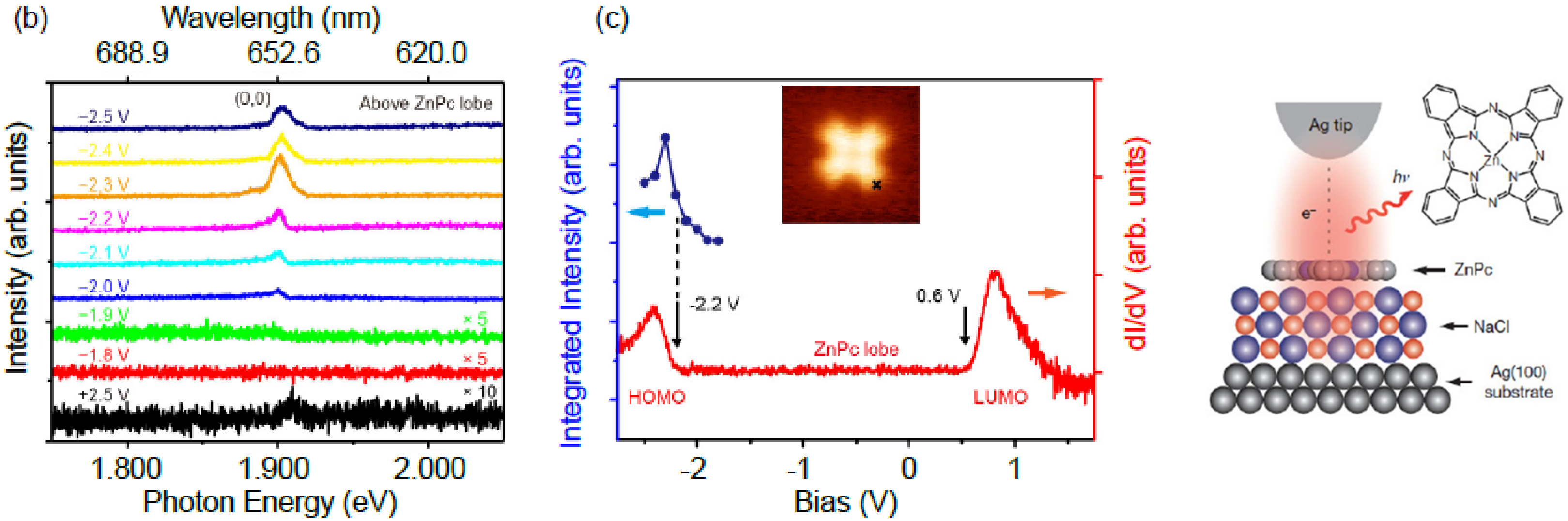
STM – ElectroLuminescence (STM-EL)

Light emission process in the STM junction

- **Charge Carrier injection**
  - Hole (HOMO)-electron (LUMO) pair creation → **Reconbination**
  - **Threshold : Alignment** : Orbitals – Fermi levels



Charge Carrier injection mechanism - B. Doppagne Thesis IPCMS

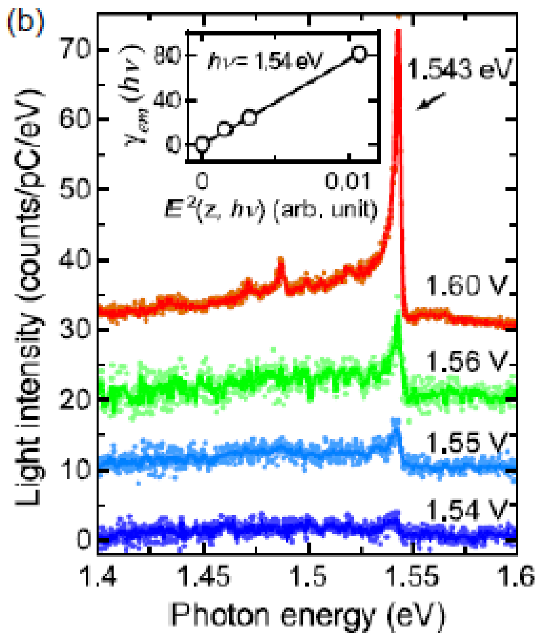


Voltage dependency of the intensity of a single ZnPc molecule - B. Doppagne Thesis IPCMS

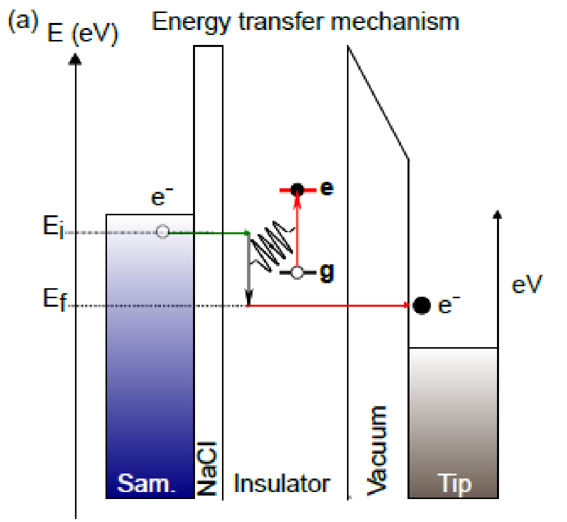
STM-Fluorescence of single molecules

Excitation mechanism

- **Energy Transfer mechanism**
  - Similar to **NCP luminescence : inelastic tunneling**
  - Fluorescence onset voltage : **(eV = hν)**



STM-LE intensity of a suspended porphyrin molecule - B. Doppagne Thesis IPCMS

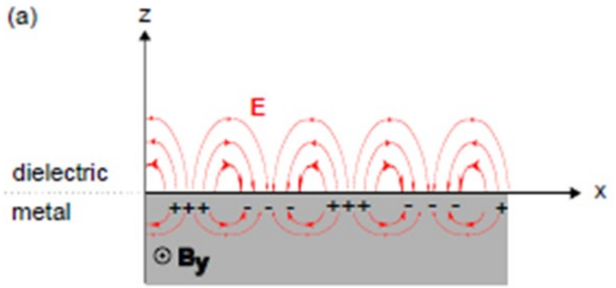


Energy Transfer mechanism mechanism at negative bias voltage - B. Doppagne Thesis IPCMS

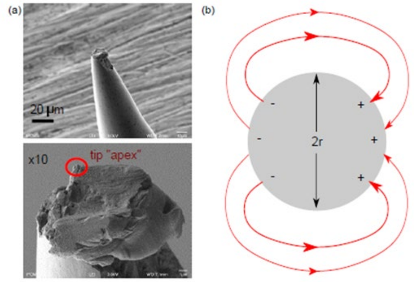
STM – ElectroLuminescence (STM-EL)

Light emission process in the STM junction

- Collective oscillations **sample** :
  - Coexistence with induced EM field - **Surface Plasmon Polariton (SPP)**
- Collective oscillations **tip** :
  - **Confinement – Localized Surface Plasmon (LSP)**

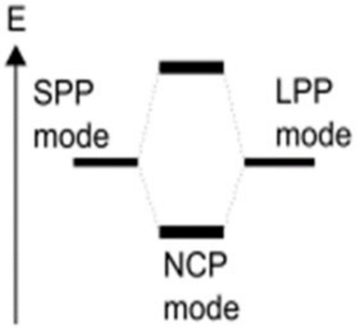


Scheme of the SPP on the sample

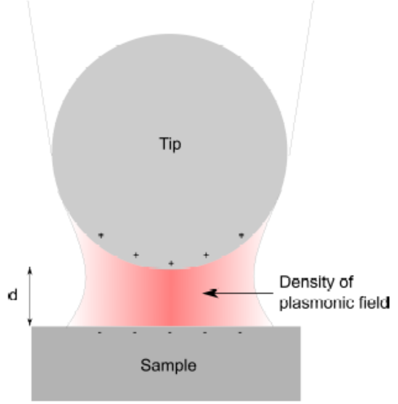


Scheme of LSP confined in the tip apex.

- **Hybridization** of the SPP and LSP
  - **Nano-Cavity Plasmon (NCP)** modes



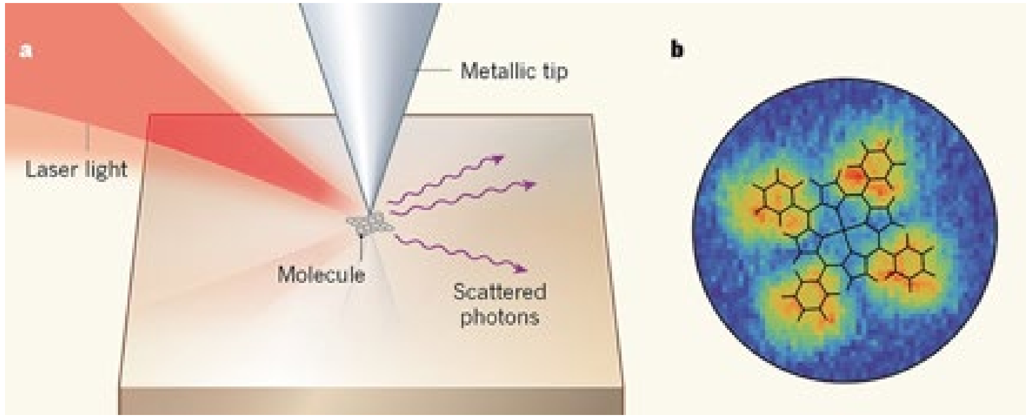
Scheme of the hybridization

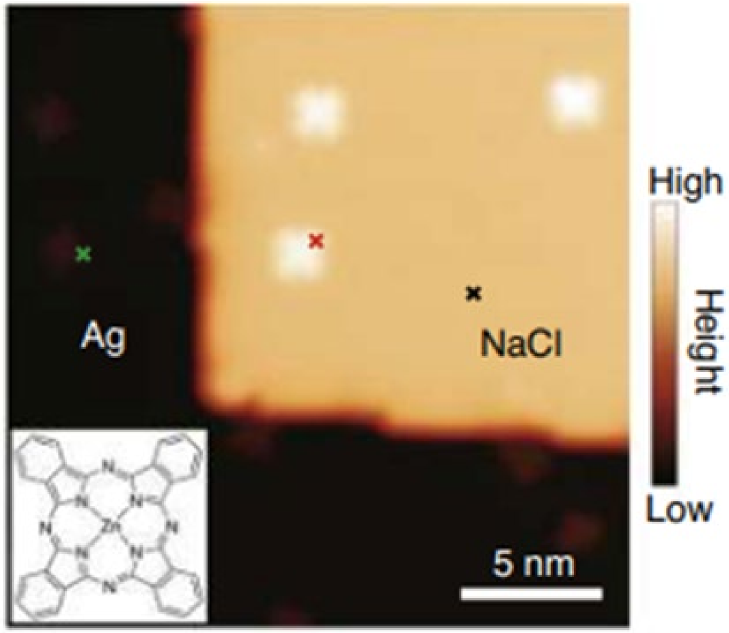


Scheme of NCP modes in the STM junction

Fluorescence emission enhancement

Single-molecule decoupling from substrate – avoid hybridization



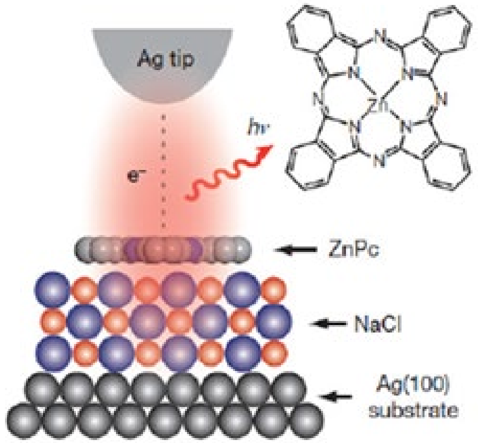


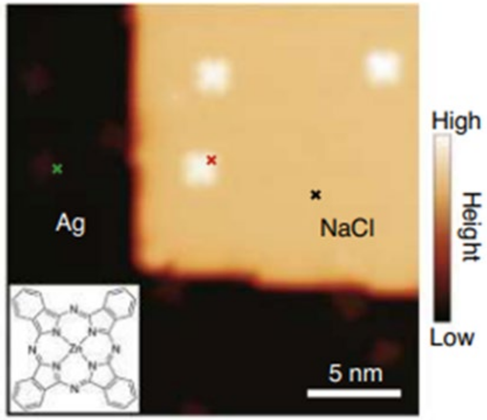
*STM image of **ZnPc molecules on a 3-layer NaCl island** OR **on Ag surface** - article Yang & al 2020*

Fluorescence emission enhancement

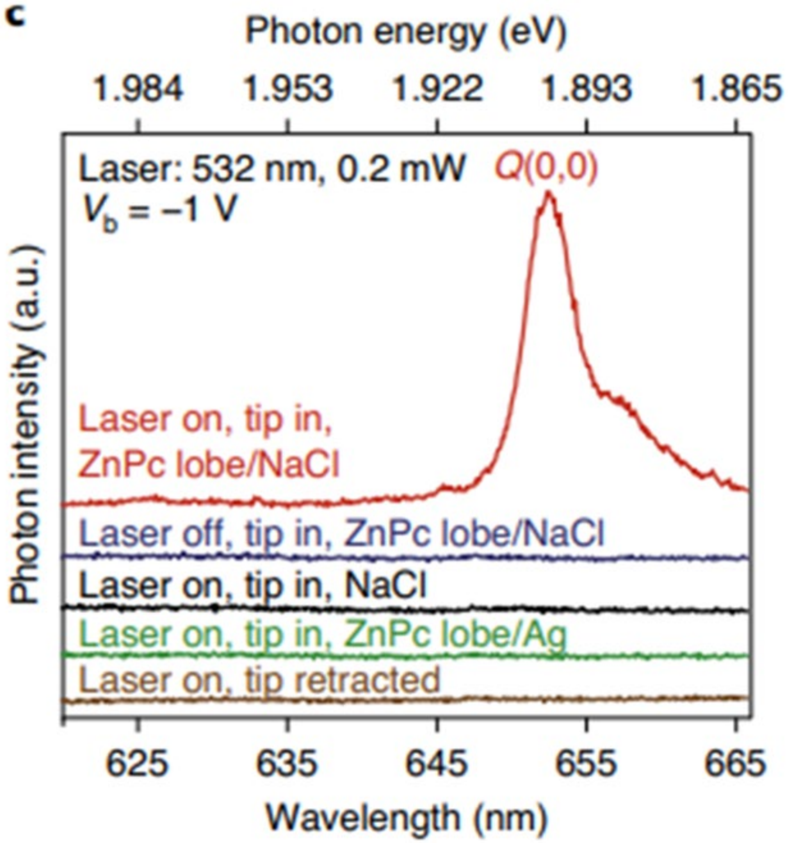
Single-molecule decoupling from substrate – avoid hybridization

- Molecule **direct contact to** metal
  - **Faster channel decay** – electron-hole pair in the metal
  - **No Fluorescence**
- Molecule **Decoupled** – NaCl 3 layers
  - **Fluorescence signal**





*STM image of **ZnPc** molecules **on a 3-layer NaCl island** OR **on Ag surface** - article Yang & al 2020*

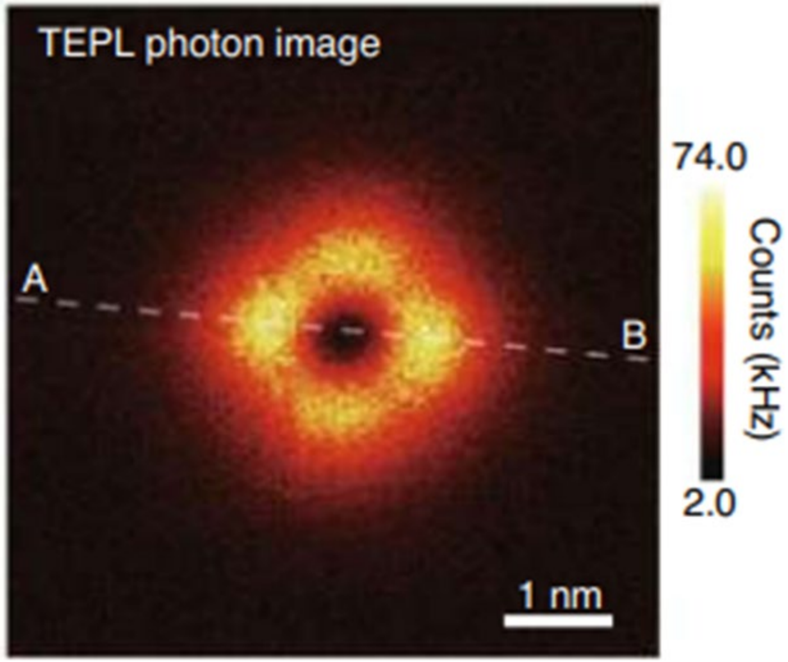


STM-PL spectra at different tip positions - article Yang & al 2020

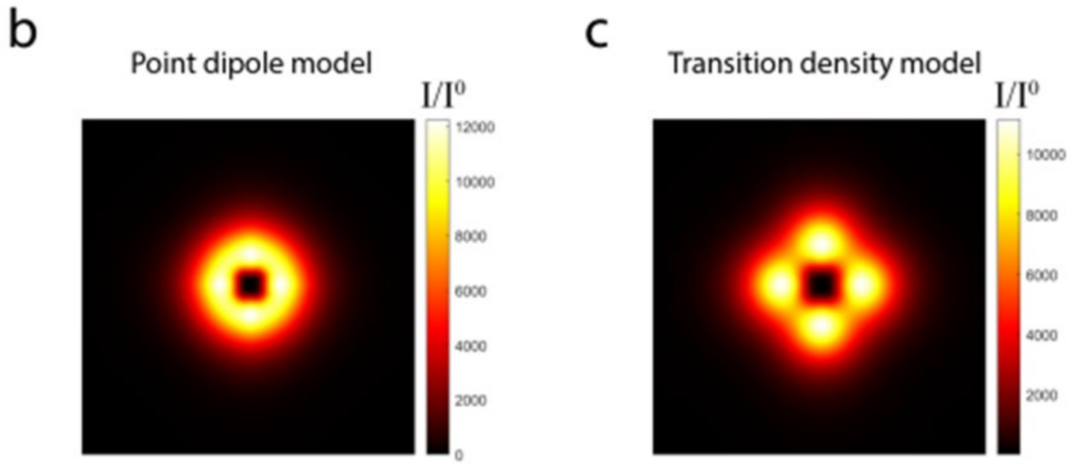
Fluorescence emission enhancement with STM-PhotoLuminescence

Tip with atomic-protrusion – Sub-nanometer resolution

- 2 transition dipoles oriented both **horizontally** and **orthogonally**
- **4-bright-maxima pattern** instead of **ring pattern**
  - **Sub-nanometer scale experimental confirmation**



*STM-PL **photon image** of a single ZnPc molecule - article Yang & al 2020*



Simulated photon images for a single ZnPc molecule – Suppl. article Yang & al 2020

STM-PhotoLuminescence vs STM-ElectroLuminescence

Important recent paper: STM-PL compared to STM-EL
(Imada et al. – Science 373,95-98) published in 2021

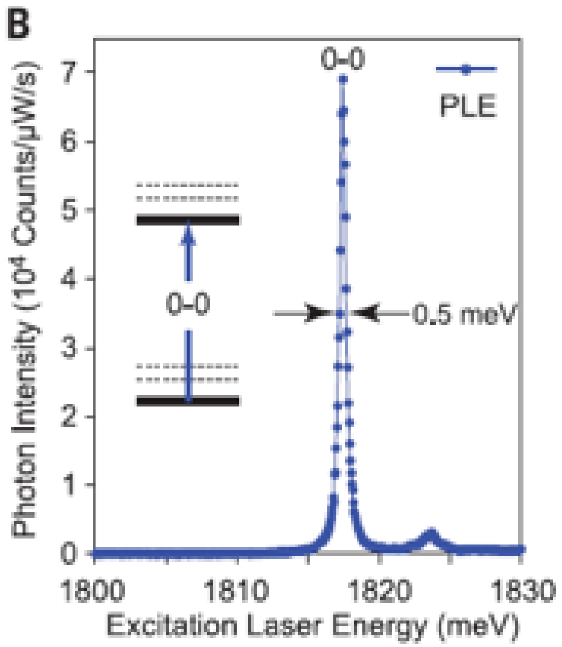
SPECTROSCOPY

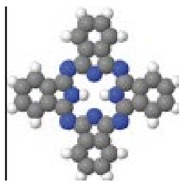
Single-molecule laser nanospectroscopy with micro–electron volt energy resolution

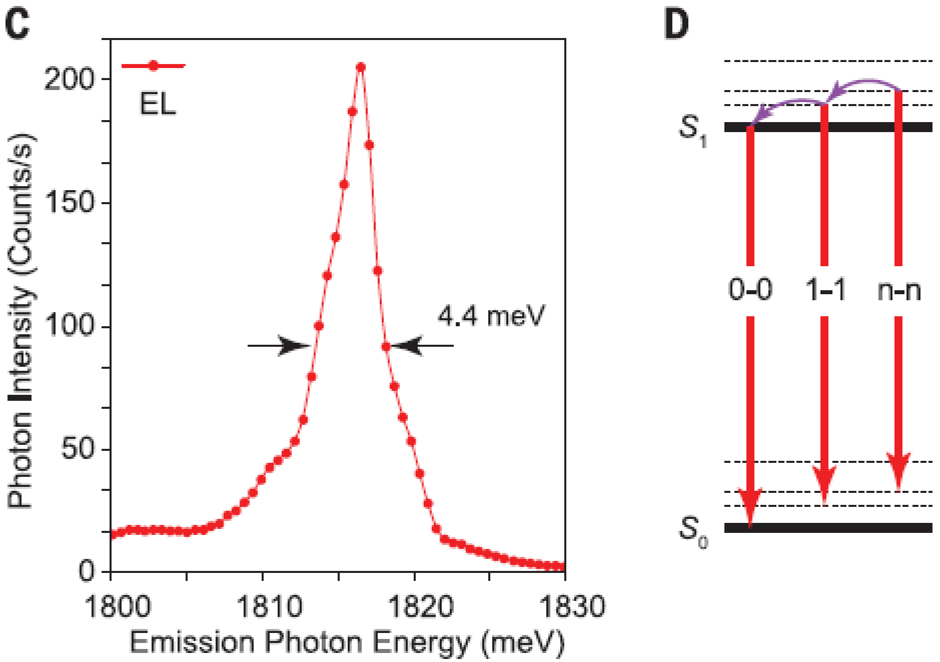
Hiroshi Imada[1,2]*, Miyabi Imai-Imada[1], Kuniyuki Miwa[1,3], Hidemasa Yamane[4], Takeshi Iwasa[2,5,6], Yusuke Tanaka[7,8], Naoyuki Toriumi[8]†, Kensuke Kimura[1], Nobuhiko Yokoshi[4], Atsuya Muranaka[7,8], Masanobu Uchiyama[7,8], Tetsuya Taketsugu[5,6], Yuichiro K. Kato[9,10], Hajime Ishihara[4,11,12], Yousoo Kim[1]*

STM-PhotoLuminescence vs STM-ElectroLuminescence

Principal interest - Selectivity in the excitation







*(B) Scheme Energy diagram for **STM-PL measurement**.*
*(B) A **STM-PhotoLuminescence** spectrum of H2Pc.*

*(C) A **STM-ElectroLuminescence** spectrum of H2Pc.*
*(D) Scheme Energy diagram for **STM-EL measurement**.*

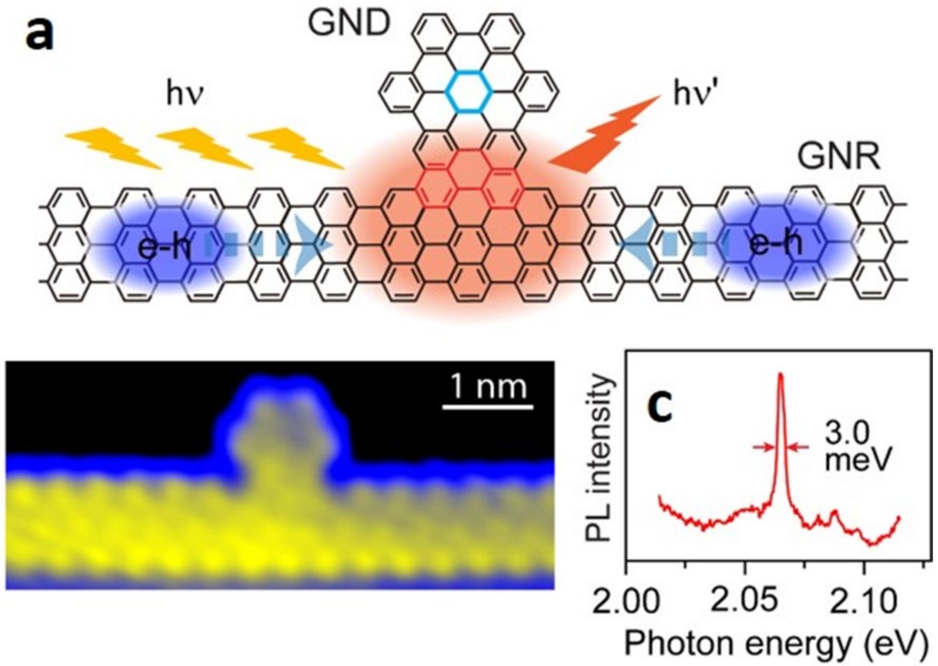
- **Only 0-0 transition - selectivity**
  - **Narrow and symmetrical peak**

- **Radiative transitions from vibrationally excited states**
  - **broad and asymmetric peak**

Graphene nanoribbons (GNRs) for quantum electronics

Fluorescence from a single molecule

- **GNR nanodot (GND)** :
  - **heterojunction** - between Armchair-edges
  - Act as **quantum emitters** with light excitation



Example of quantum emitter GNR, STM-PhotoLuminescence