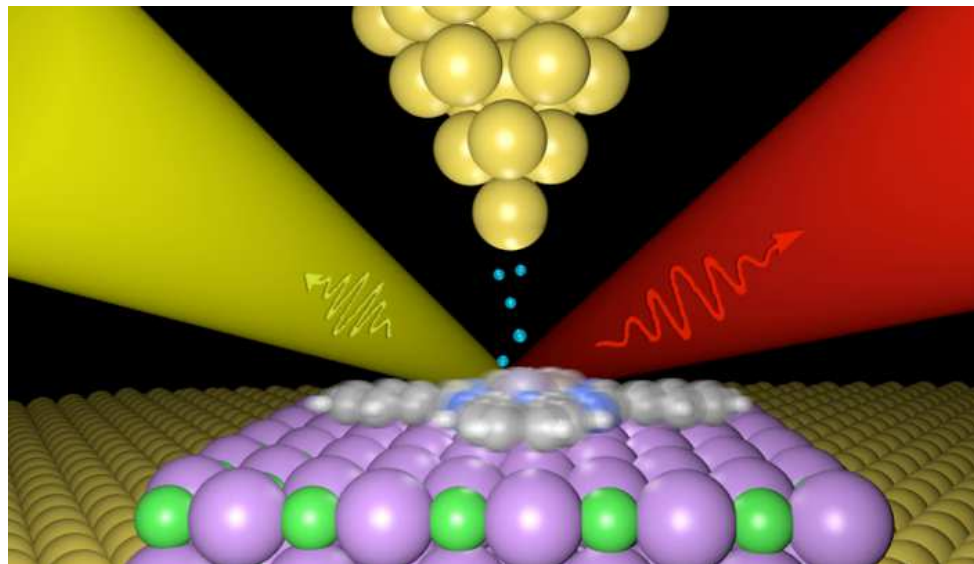


Fluorescence hyper-résolue de molécules uniques avec un STM.



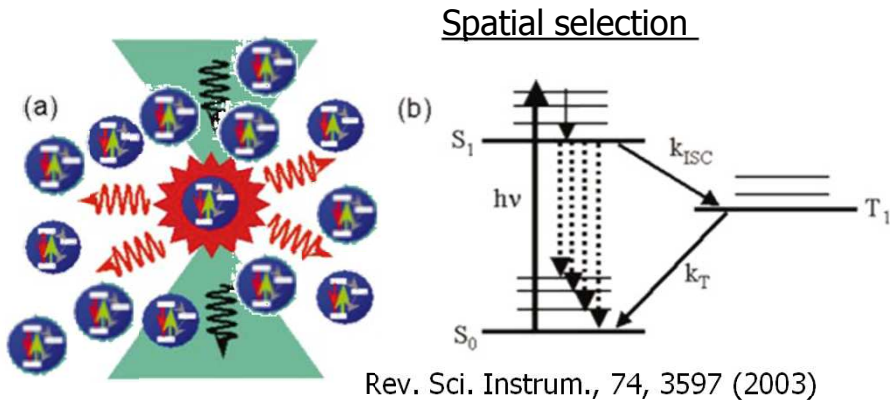
Guillaume Schull

Institut de Physique et de Chimie des Matériaux de Strasbourg (IPCMS)

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

Single-molecule fluorescence

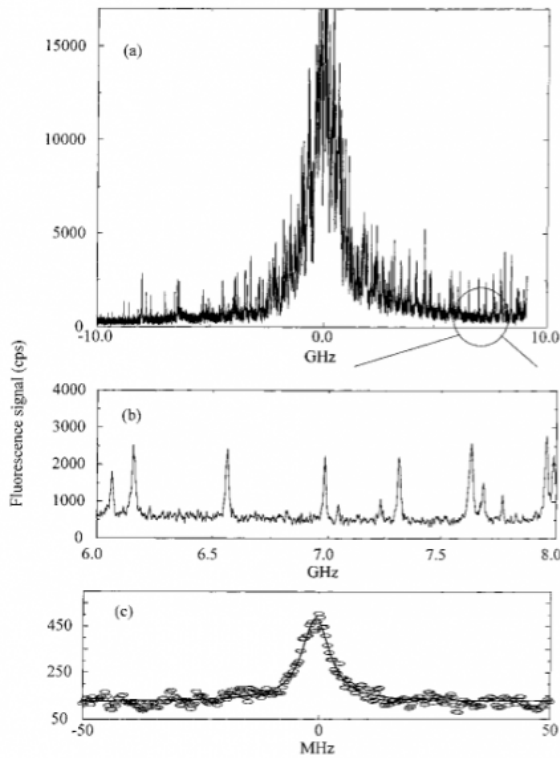
"Even with the best possible optics we can never even come close to a resolution corresponding to the dimensions of a single molecule (sub-nanometer scale)"



Web-page of Michel Orrit

<https://www.single-molecule.nl/notes/the-principles-of-single-molecule-detection/>

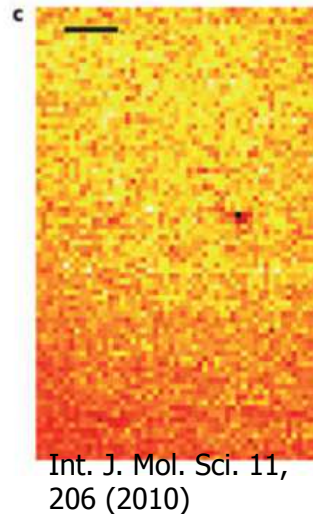
- Can we question this statement ?
- If yes, what could we learn ?



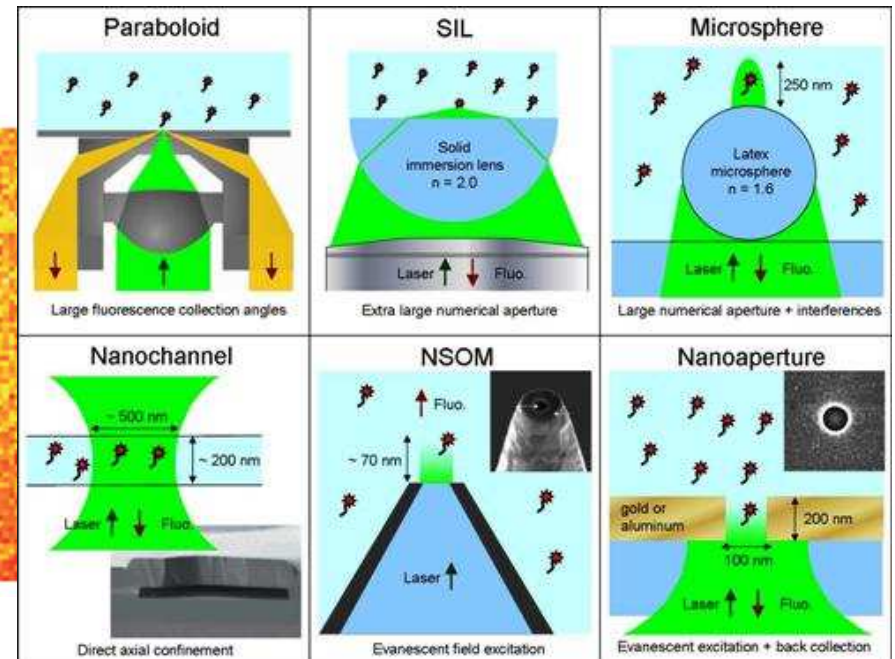
W.E. Morener and L. Kador
Phys. Rev. Lett. 62, 2535 (1989)

M. Orrit and J. Bernard
Phys. Rev. Lett. 65, 2716 (1990)

Spectral selection



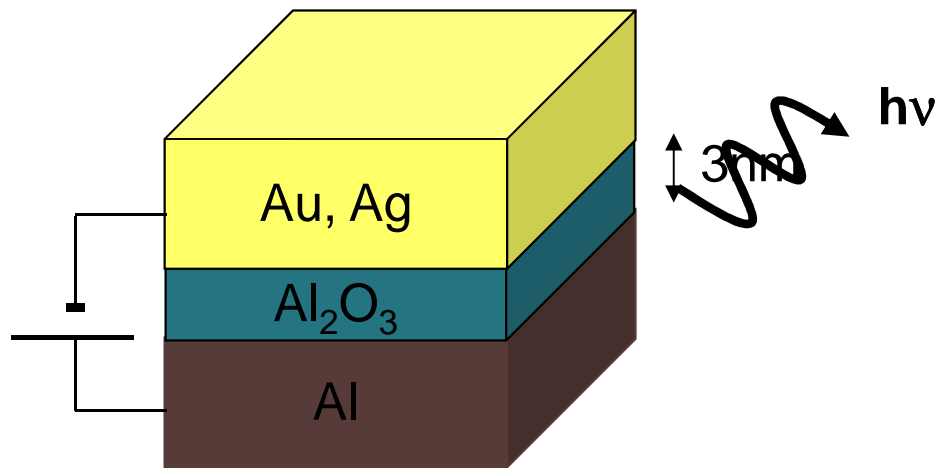
2014 Nobel Prize in Chemistry
E. Betzig, S.W. Hell, W.E. Moerner
"for the development of super-resolved fluorescence microscopy".



Light emission from STM junctions

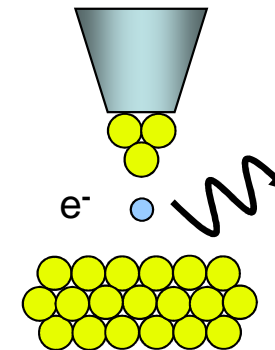
Metal-oxide-metal tunnel junction

J. Lambe and M.L. McCarthy
Phys. Rev. Lett. 37, 923 (1976)



Photons emitted are intimately linked to the tunnel electrons !!

Localized source of tunnel electrons: STM



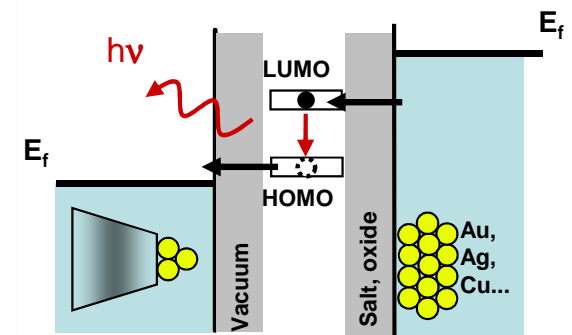
J. Gimzewski *et al.*
Z. Phys. B - Cond. Matt. 72, 497 (1988)

Si(111), metal (polycrystalline surfaces)

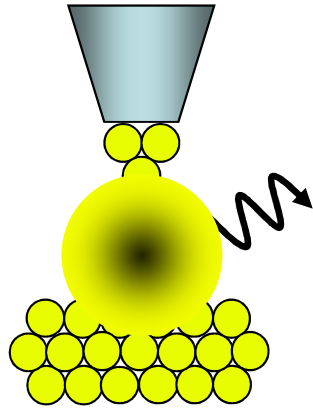
Light emission from STM junctions

Molecules

$$h\nu = \text{LUMO} - \text{HOMO}$$

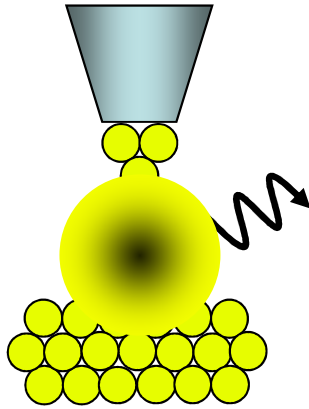


STM-induced light emission



Photon counting regime

STM-induced light emission



Photon counting regime

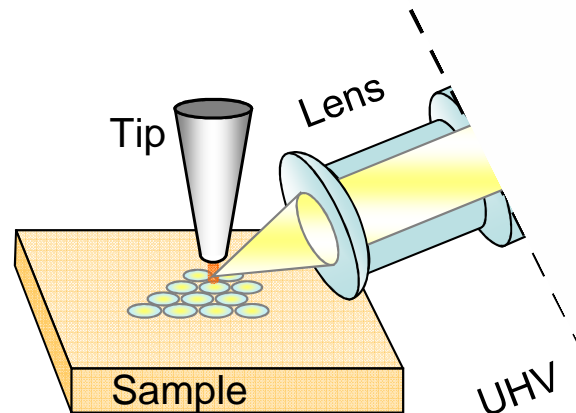
How much light ?

Best theoretical yields : 10^{-4} photon / electron

For 1nA => 10^5 emitted photons / second

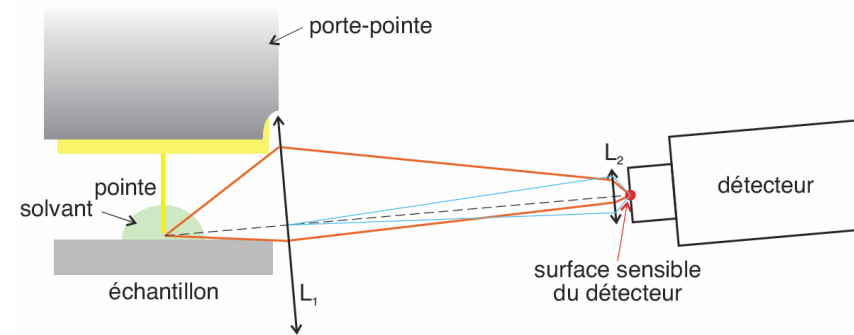
Photon counting regime

Collection of the light



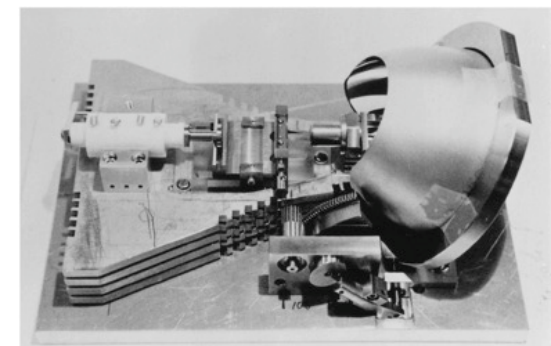
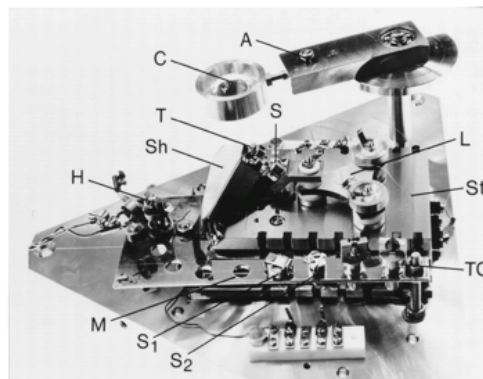
Collection of the light: Different experimental conditions

Air, and liquid-solid interfaces



K. Perronet, Phd thesis

UHV Room temperature

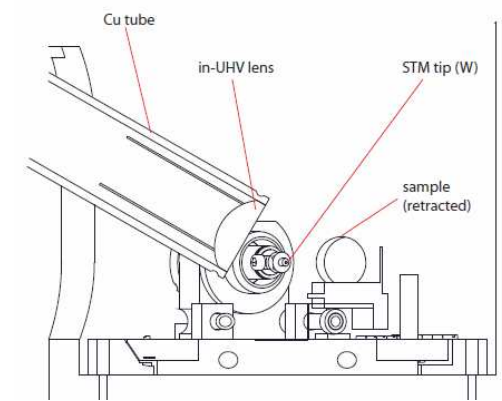
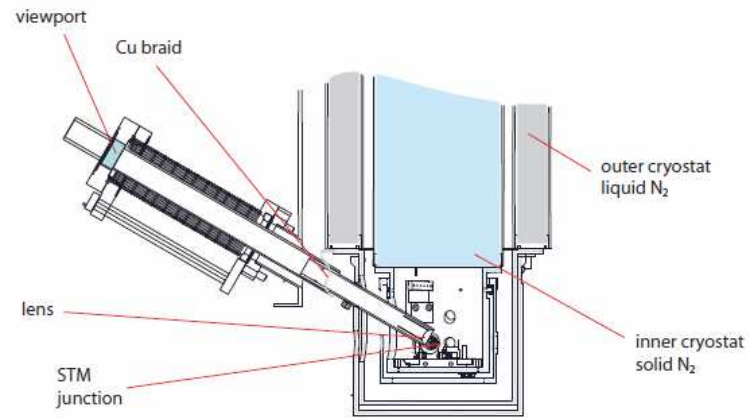


R. Berndt, Phd thesis

Collection of the light: Different experimental conditions

UHV - Low temperature

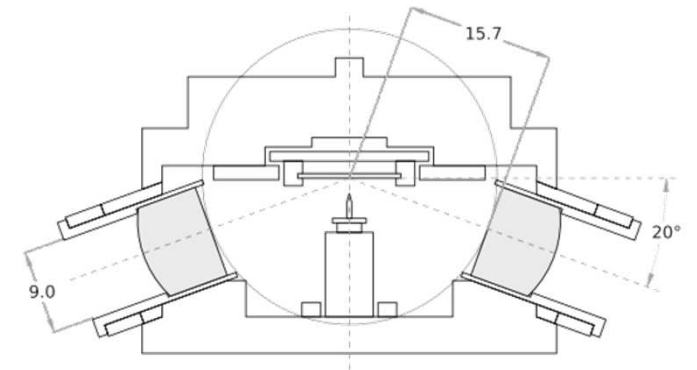
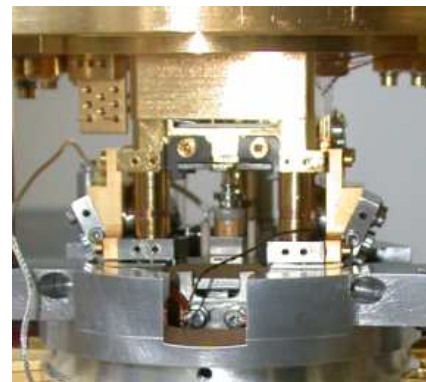
“Tube setup”



F. Rossel, Phd thesis

“Fixed lens setup”

Commercially available (Omicron)



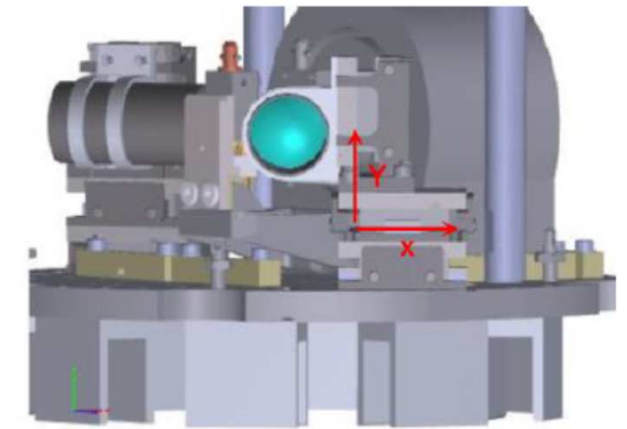
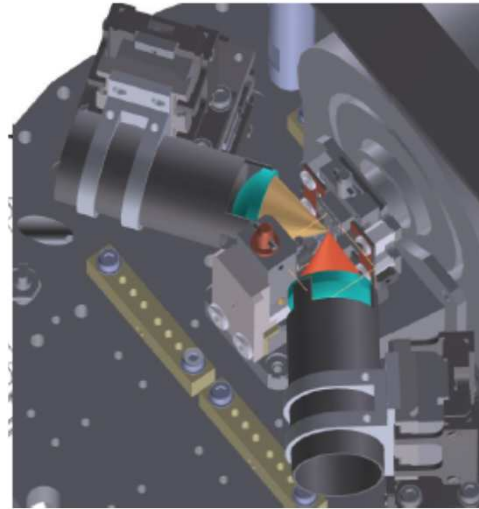
J. G. Keizer *et al.*, Rev. Sci. Instrum. 80, 123704, 2009

Collection of the light: Different experimental conditions

UHV - Low temperature

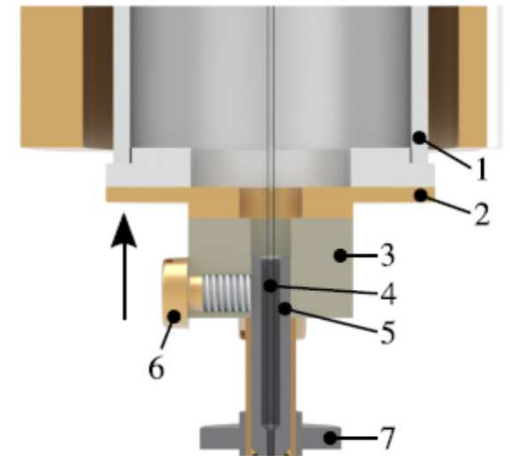
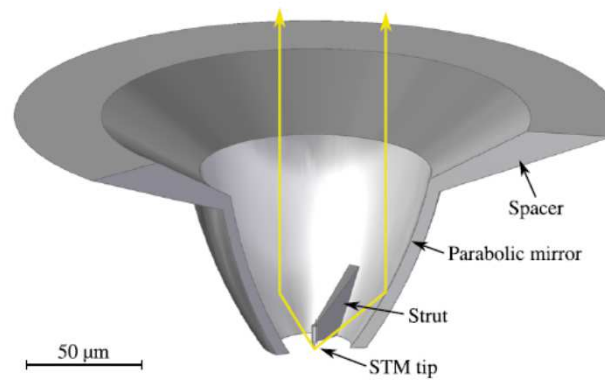
“Movable lens setup”

Commercially available (Unisoku)



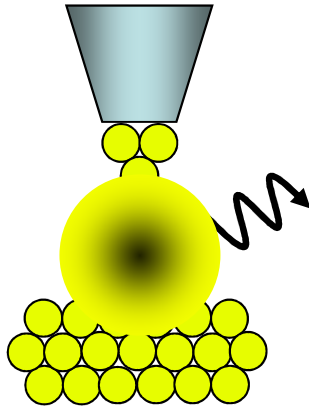
Y. Zhang *et al.*, Nature 531, 623 (2016)

“Integrated tip-mirror setup”



K. Edelmann *et al.*, Rev. Sci. Inst 89, 123107 (2018)

STM-induced light emission



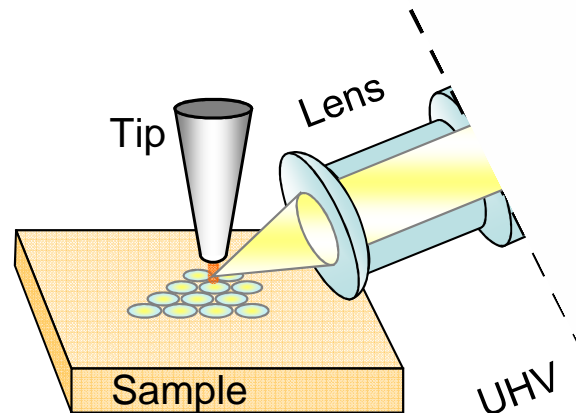
How much light ?

Best theoretical yields : 10^{-4} photon / electron

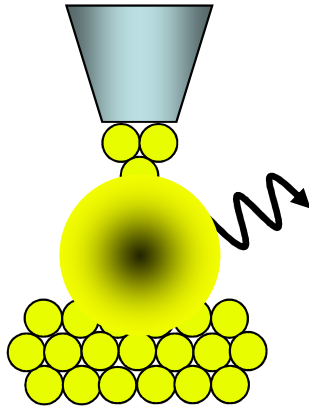
For 1nA => 10^5 emitted photons / second

Photon counting regime

Collection of the light



STM-induced light emission

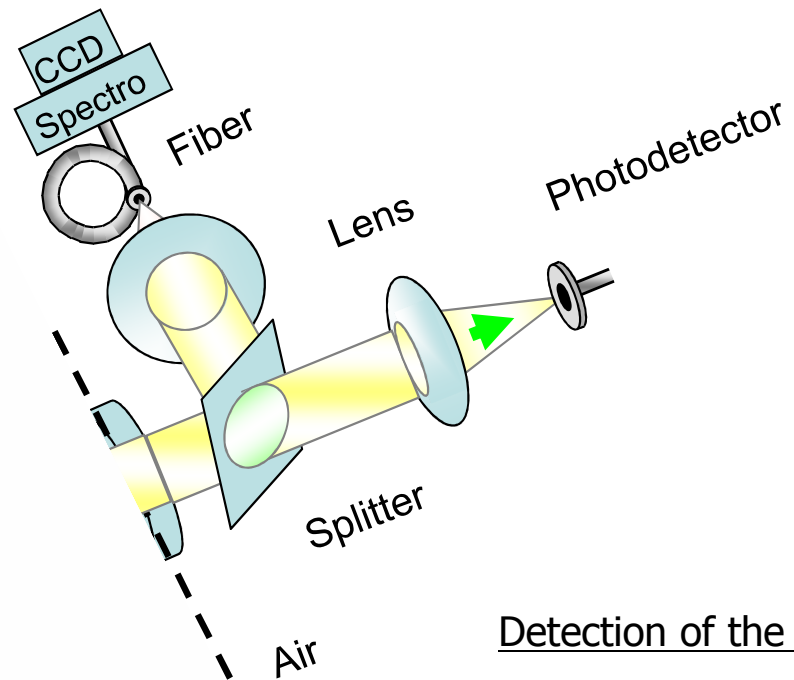


How much light ?

Best theoretical yields : 10^{-4} photon / electron

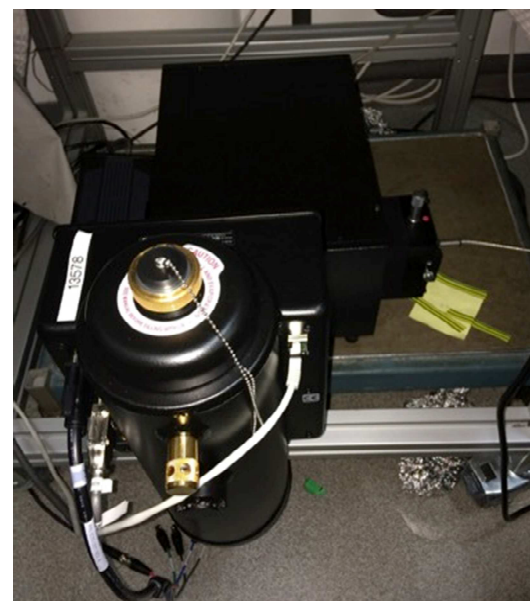
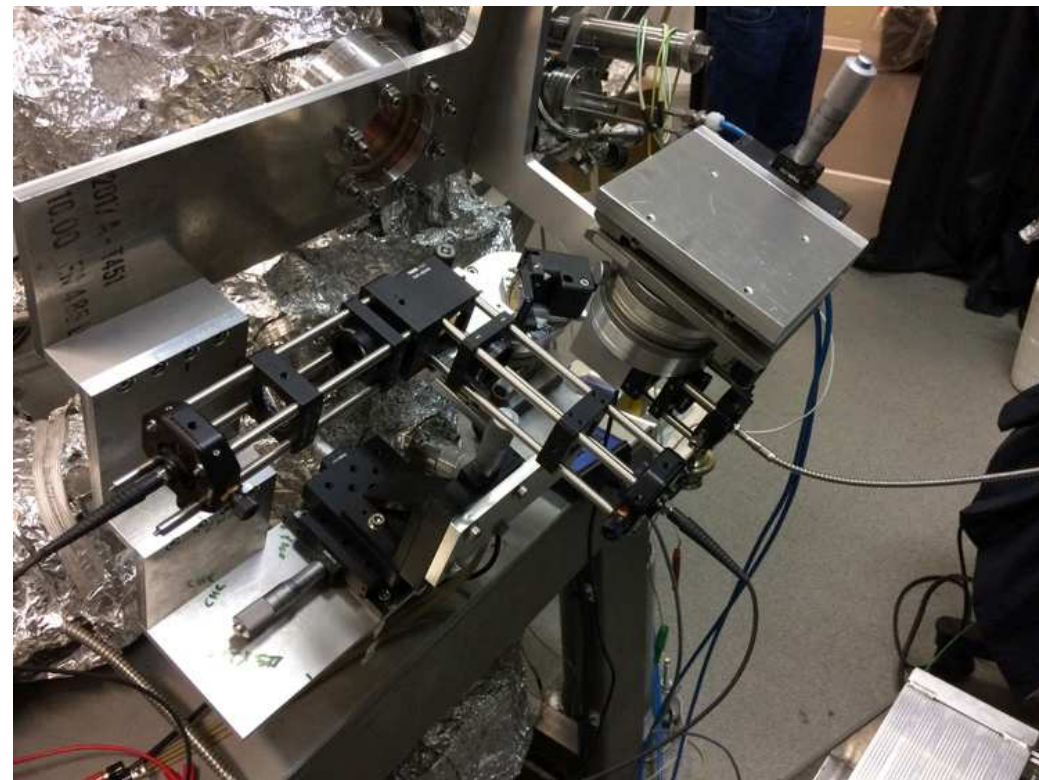
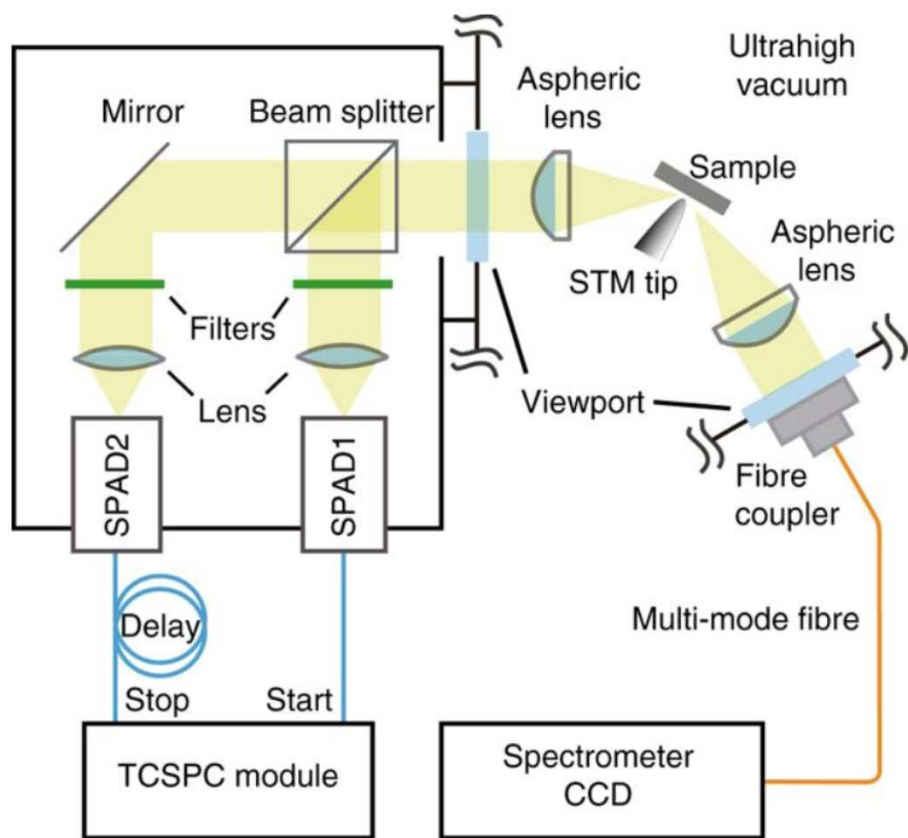
For 1nA => 10^5 emitted photons / second

Photon counting regime



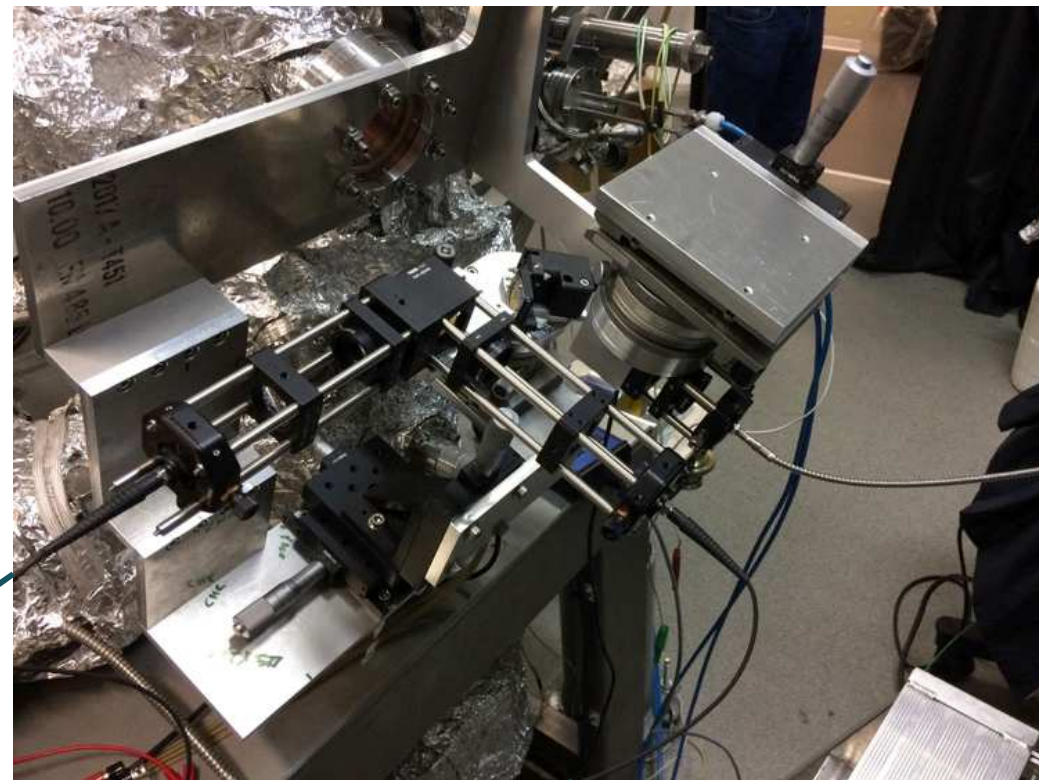
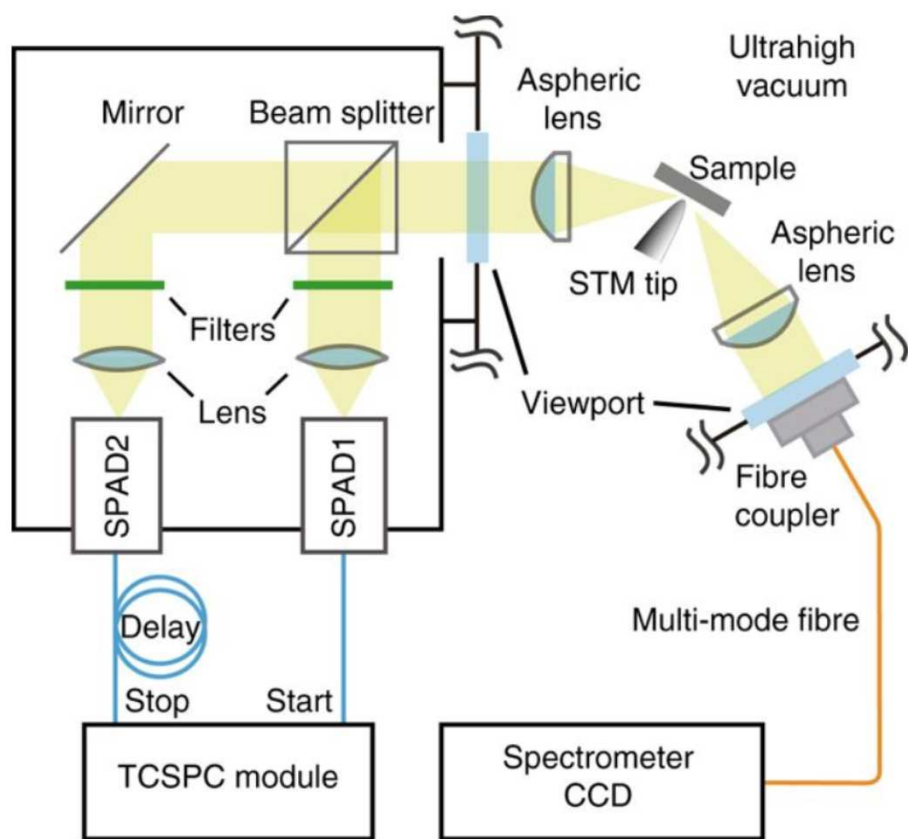
Detection of the light

Detection of the light:



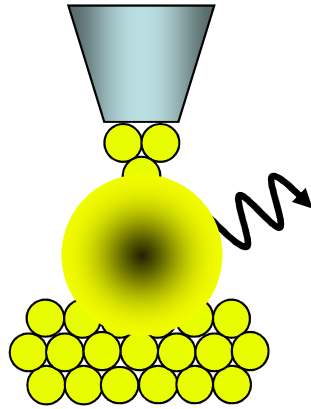
L. Zhang *et al.*, Nat. Comm. 8, 580 (2017)

Detection of the light:

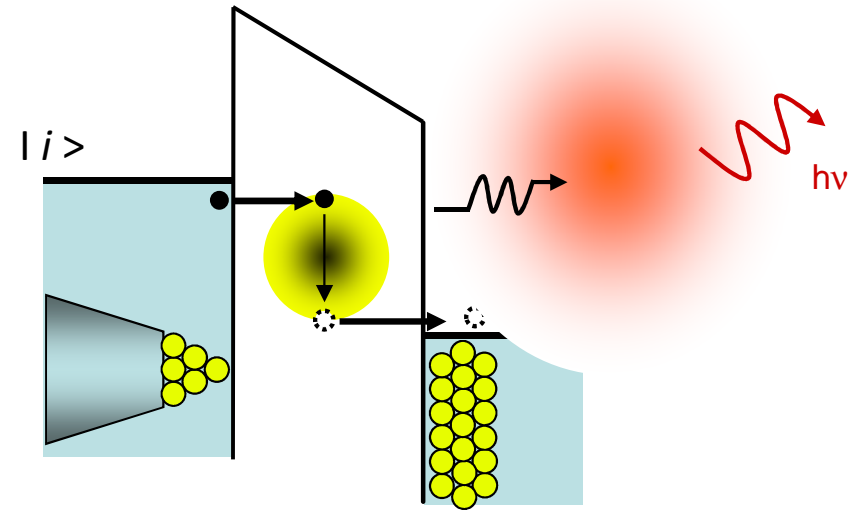


L. Zhang *et al.*, Nat. Comm. 8, 580 (2017)

Single-molecule fluorescence with STM:

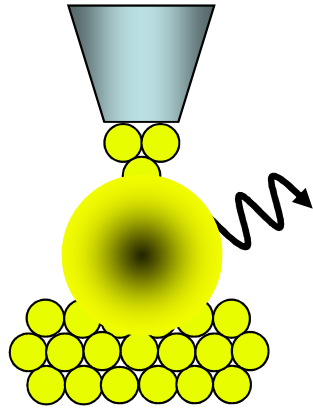


General idea

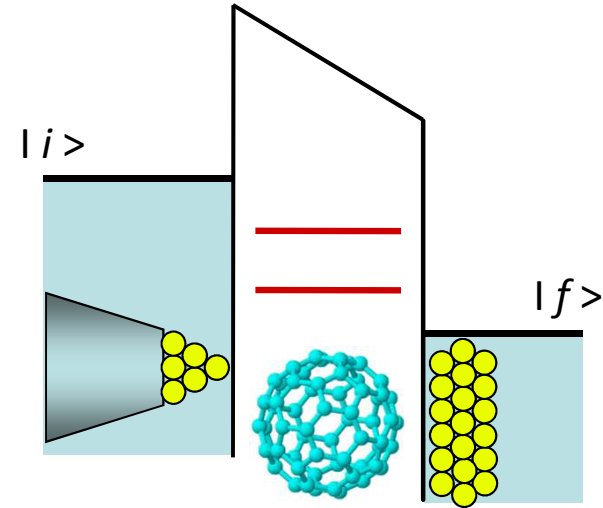


- **Photons are emitted by inelastic electrons**
- **Amplification by localized surface plasmons**

Single-molecule fluorescence with STM:



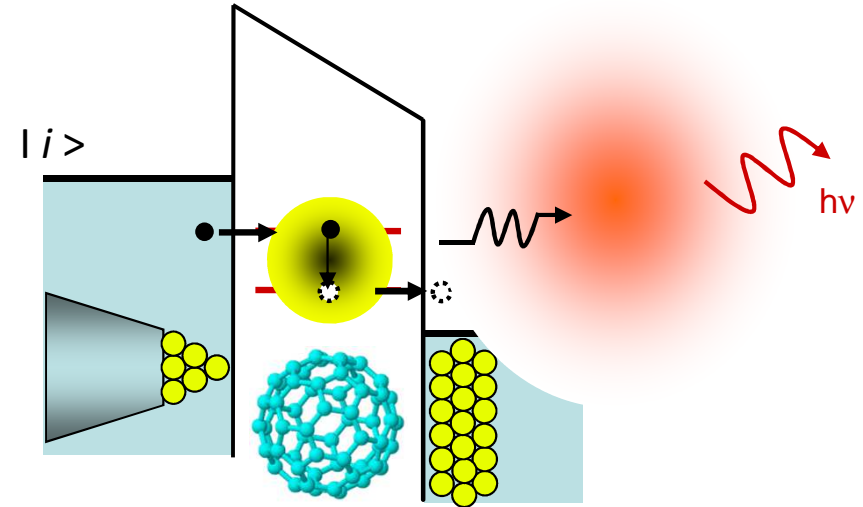
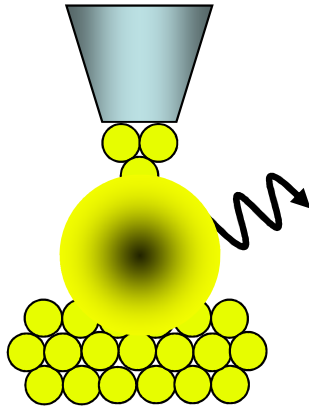
General idea



- **Photons are emitted by inelastic electrons**
- **Amplification by localized surface plasmons**

Single-molecule fluorescence with STM:

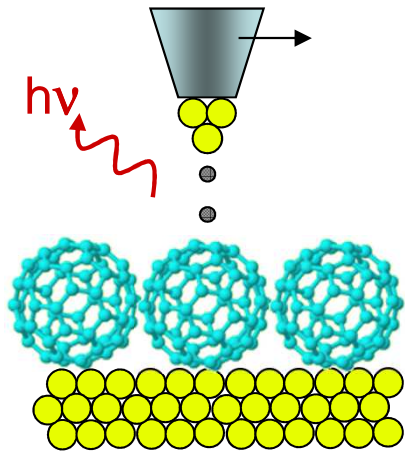
General idea



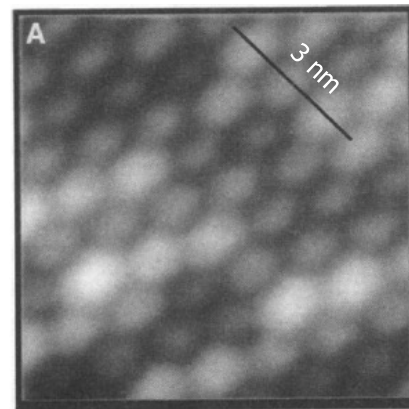
- Photons are emitted by inelastic electrons
- Amplification by localized surface plasmons

Single molecule fluorescence ?

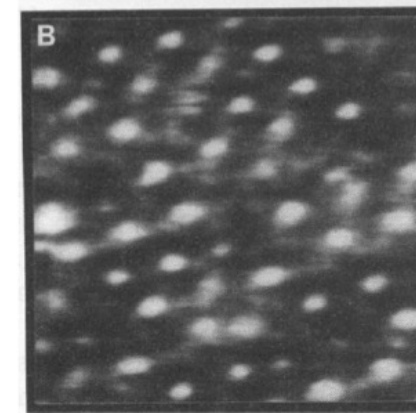
Single-molecule fluorescence with STM: General idea



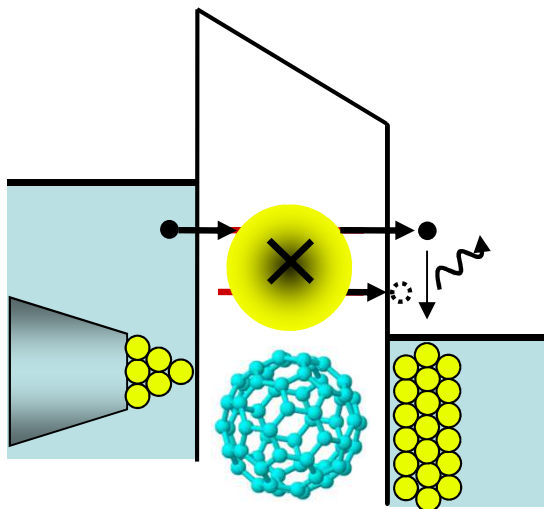
R. Berndt *et al. Science* 262, 1425 (1993)



STM topography

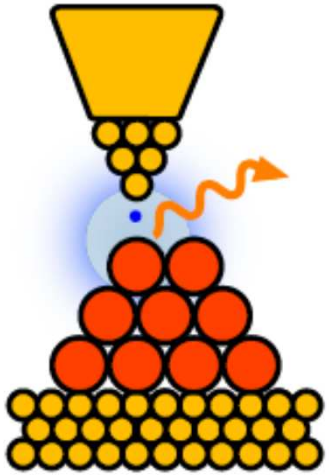


Photon map

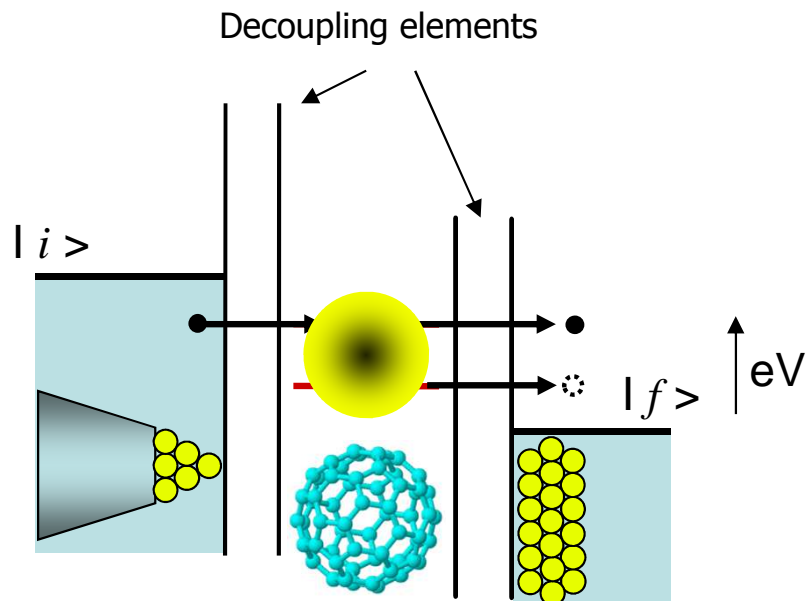


Quenching of the fluorescence !

Single-molecule fluorescence with STM: General idea

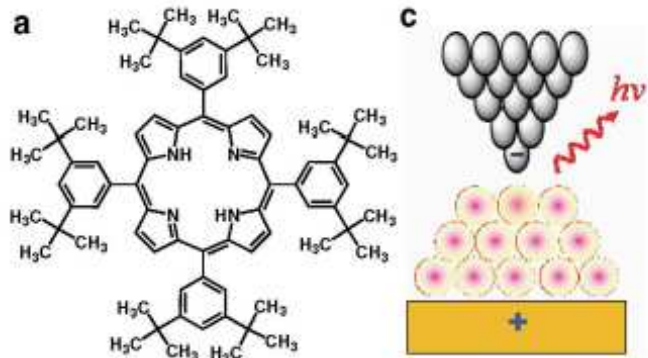


Multilayers of molecules

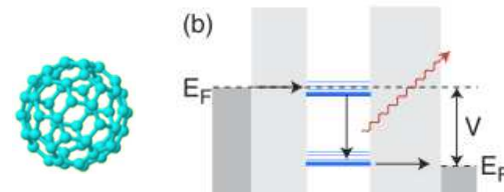
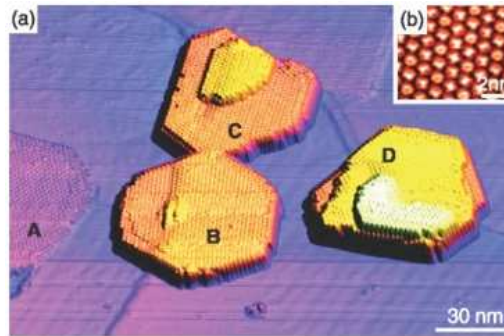


Single-molecule fluorescence with STM:

Multilayers of molecules



Z.-C. Dong *et al.*
Phys. Rev. Lett. 92, 086801 (2004)

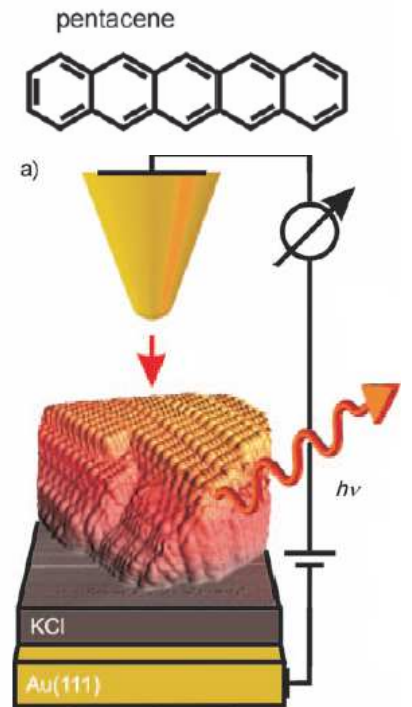
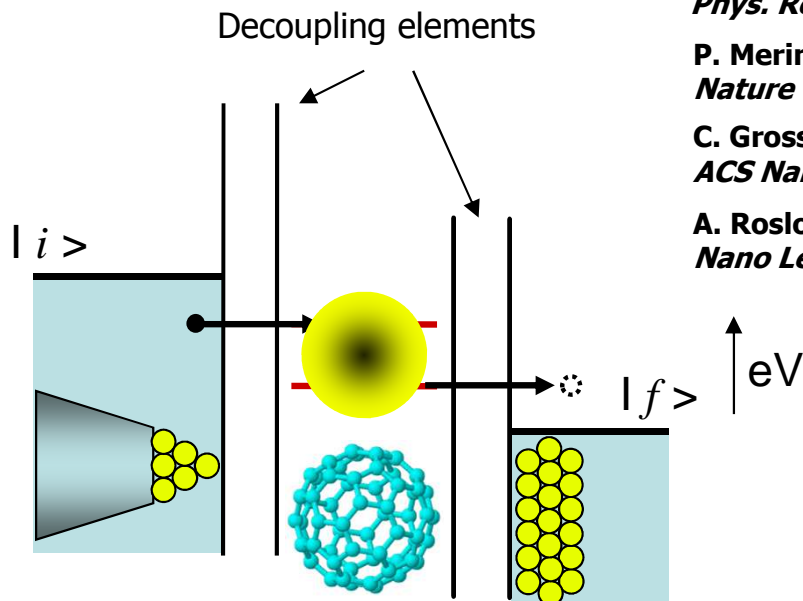


E. Cavar *et al.*
Phys. Rev. Lett. 95, 196102 (2005)

P. Merino *et al.*
Nature Commun. 6, 8461 (2015)

C. Grosse *et al.*
ACS Nano 11, 1230 (2017)

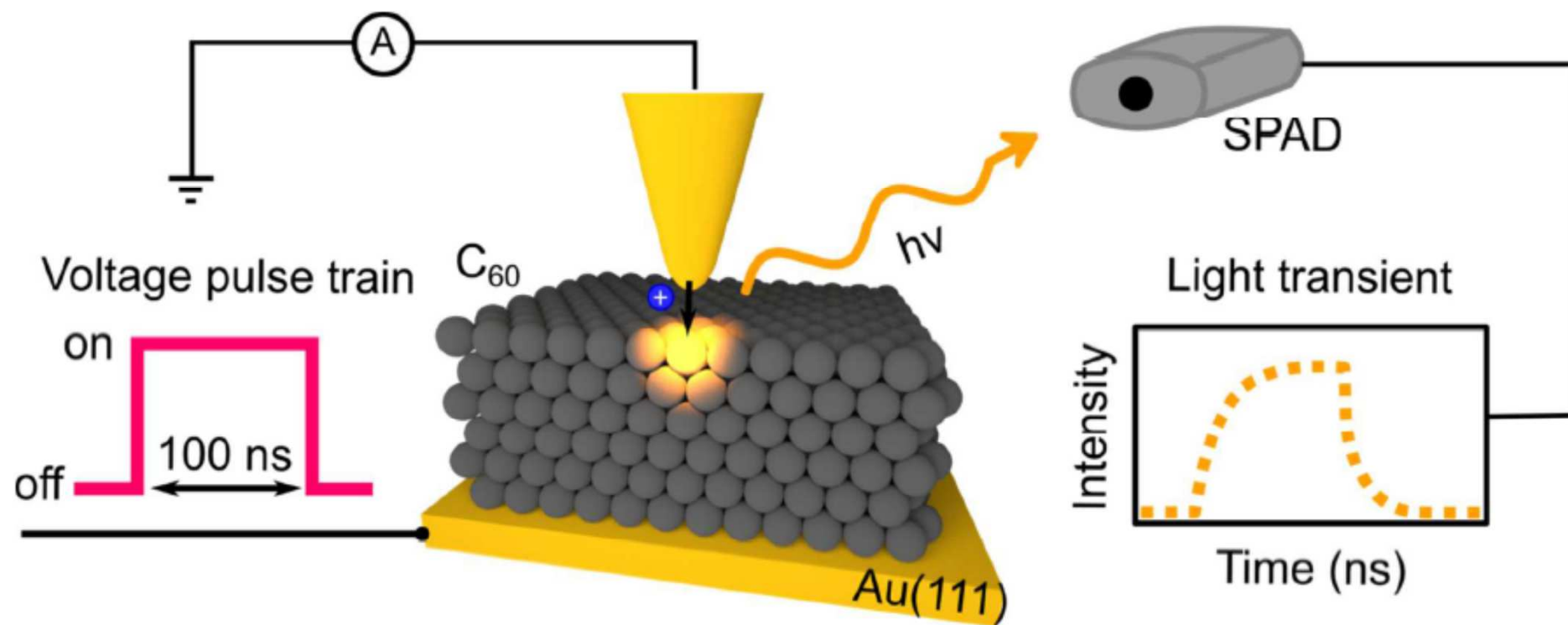
A. Rosłowska *et al.*
Nano Lett 18, 4001 (2018)



A. Kabakchiev *et al.*
ChemPhysChem 11, 3412 (2010)

Not single molecule !

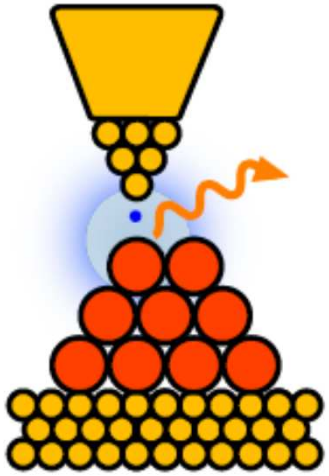
Single-molecule fluorescence with STM: Multilayers of molecules



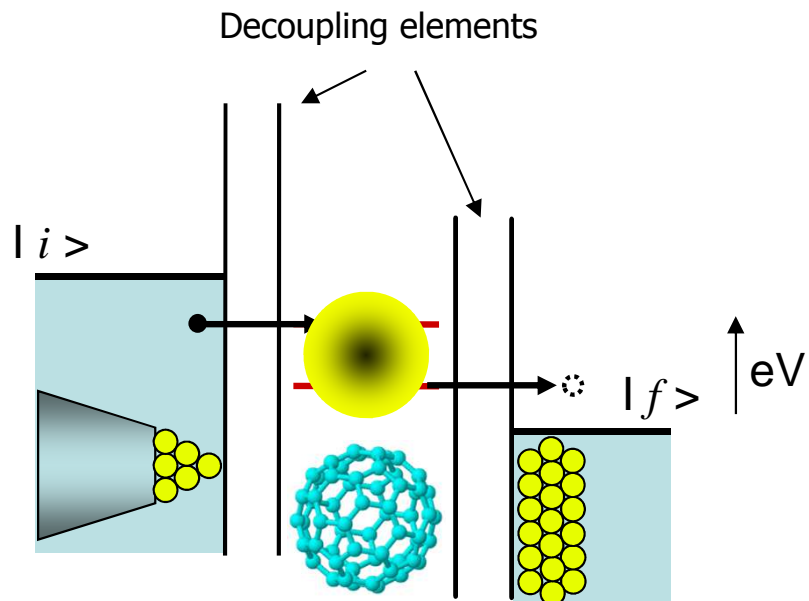
Probing single charge and exciton dynamics

A. Rosłowska *et al.* *Nano Lett* 18, 4001 (2018)

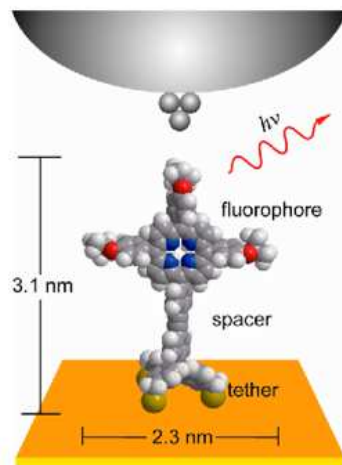
Single-molecule fluorescence with STM



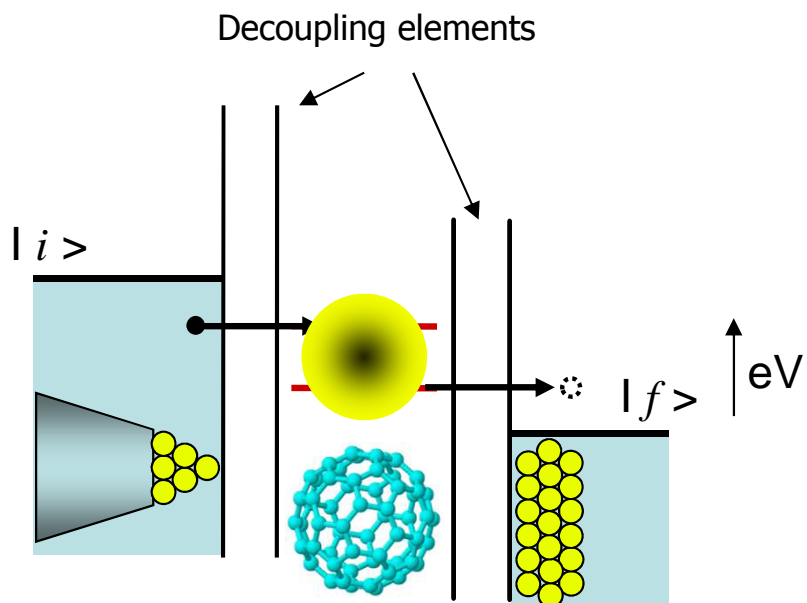
Multilayers of molecules



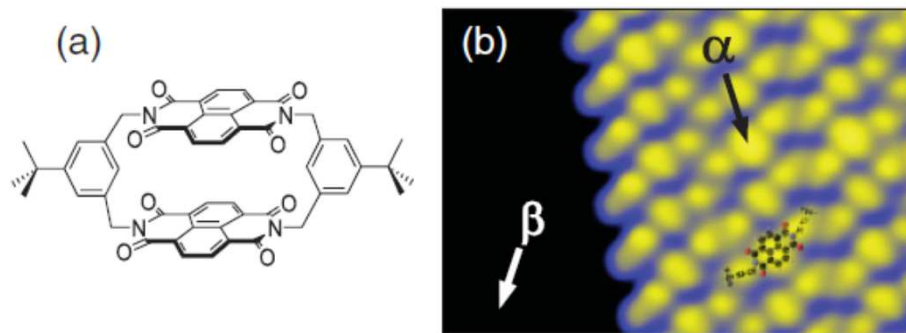
Single-molecule fluorescence with STM



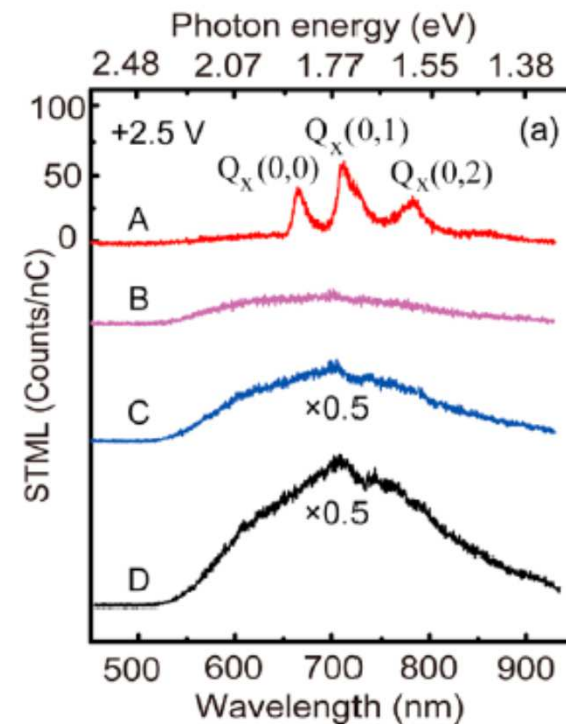
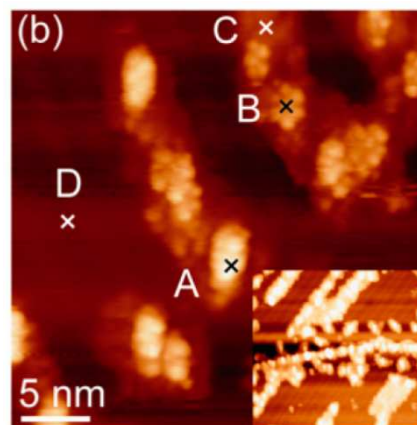
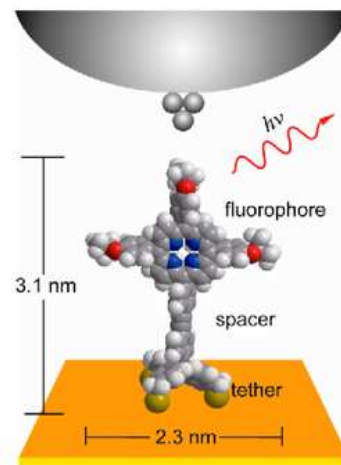
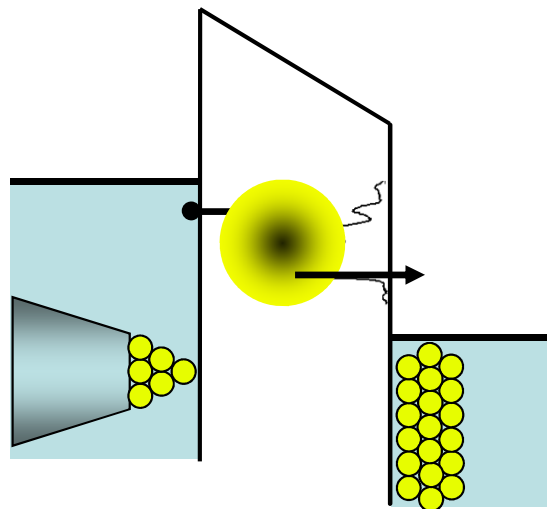
Self-decoupled molecules



Single-molecule fluorescence with STM: Self-decoupled molecules

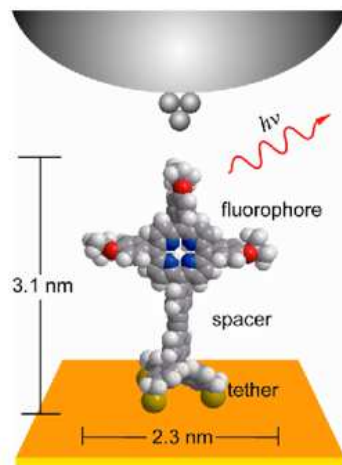


N. L. Schneider *et al.*
PRB 84, 153403 (2011)

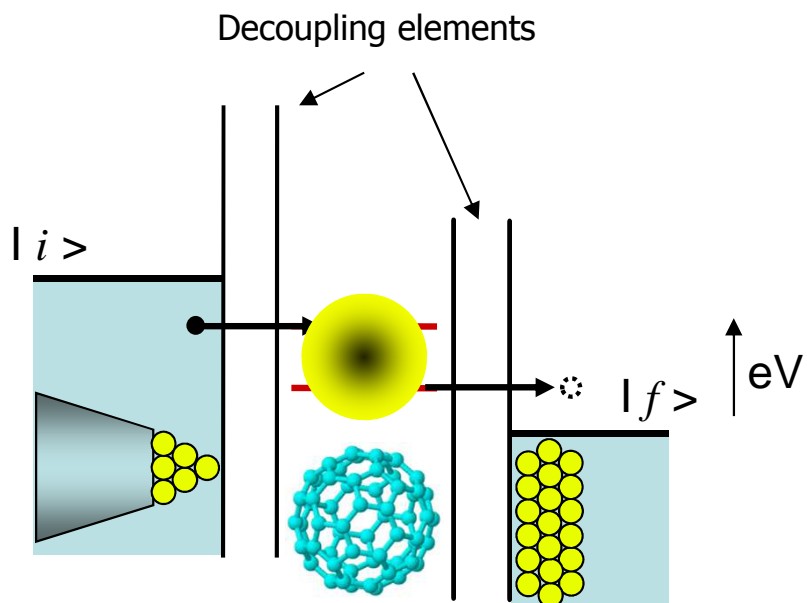


S.-E. Zhu *et al.*
JACS 135, 15794 (2013)

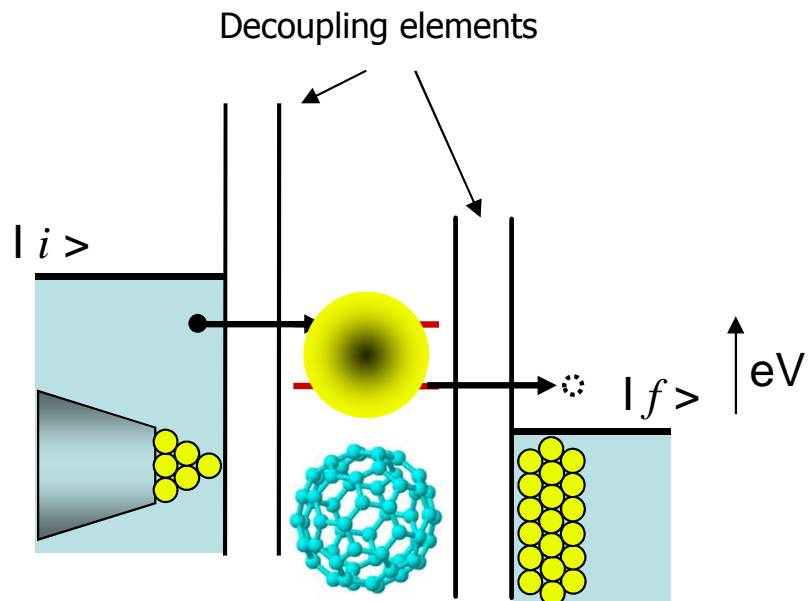
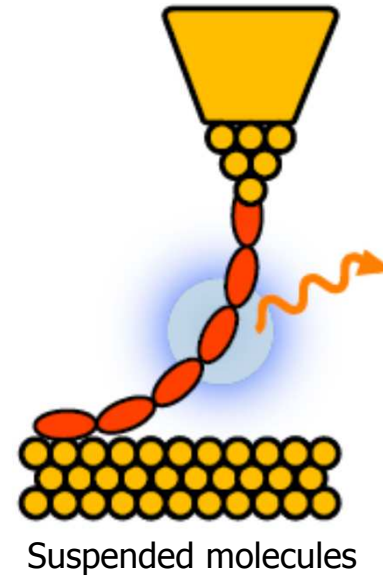
Single-molecule fluorescence with STM



Self-decoupled molecules

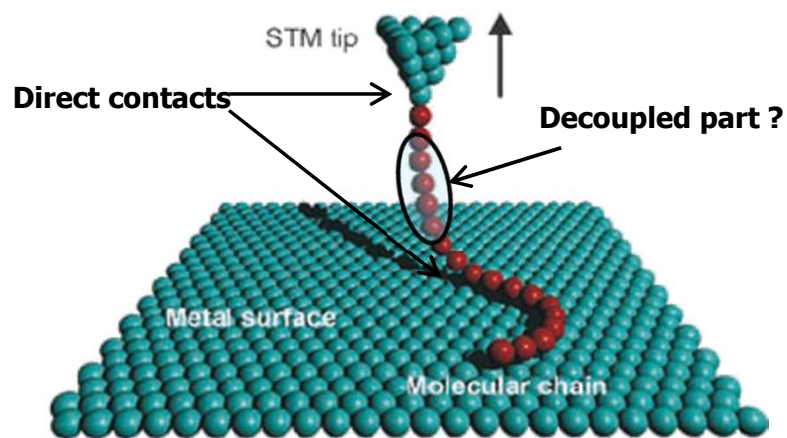


Single-molecule fluorescence with STM

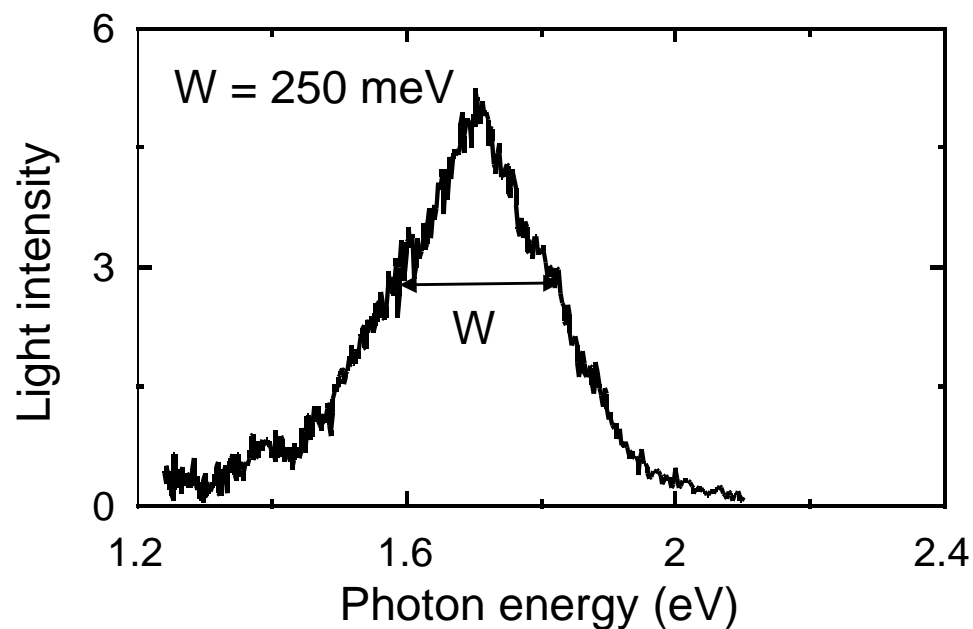
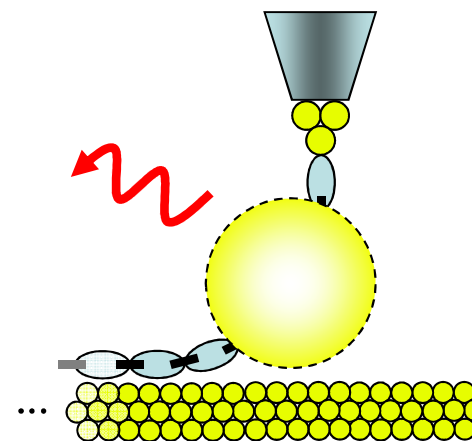
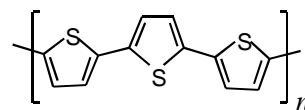


Single-molecule fluorescence with STM:

Suspended molecules



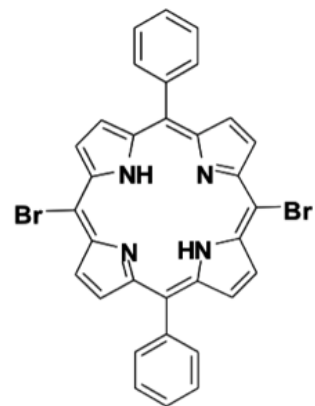
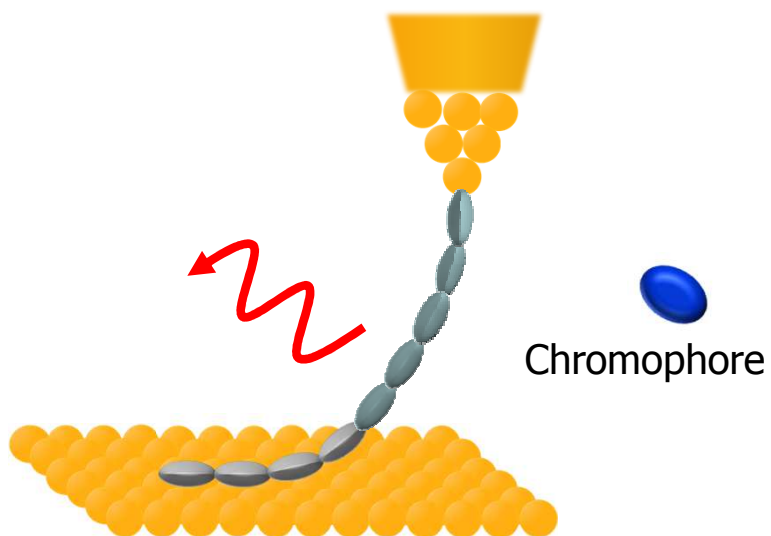
L. Lafferentz *et al.*, *Science* 323, 1193 (2009)



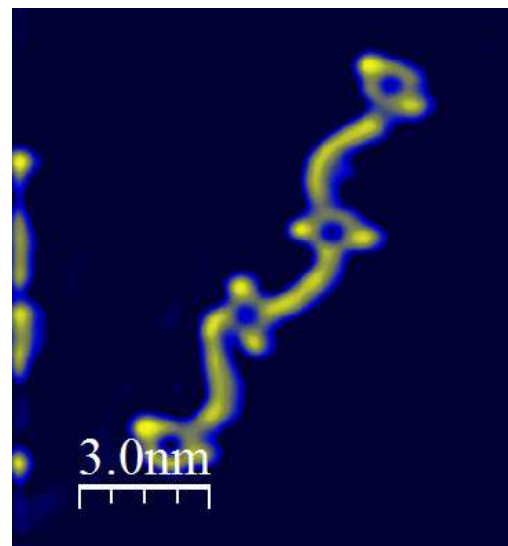
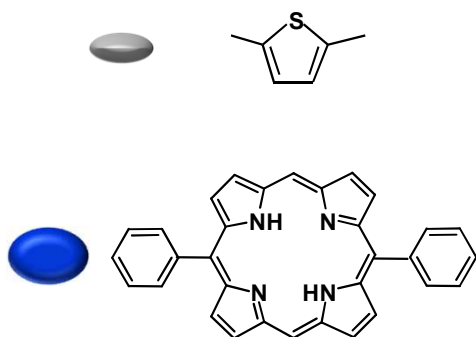
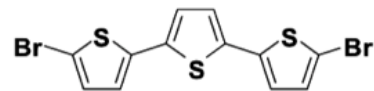
- Single-molecule fluorescence (?)
- Behaves like a LED

Reecht *et al.* *Phys. Rev. Lett.* 112, 047403 (2014)

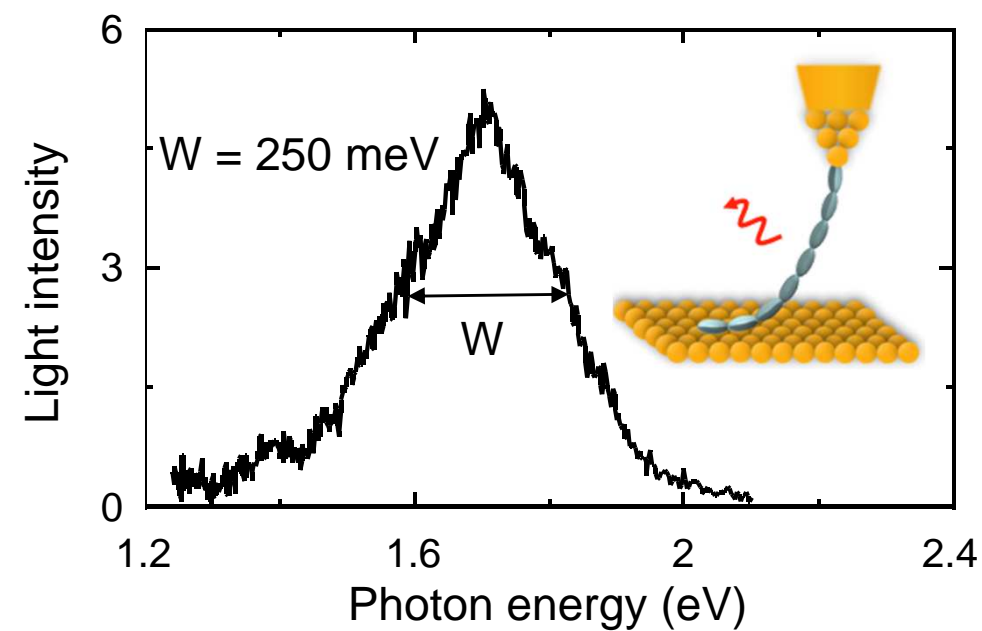
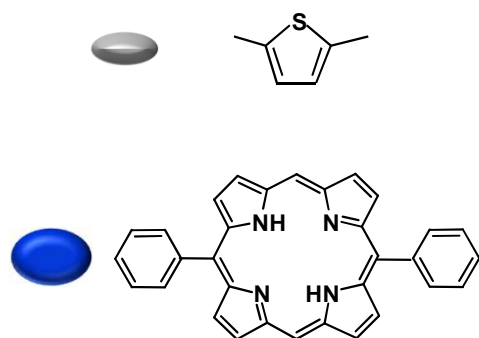
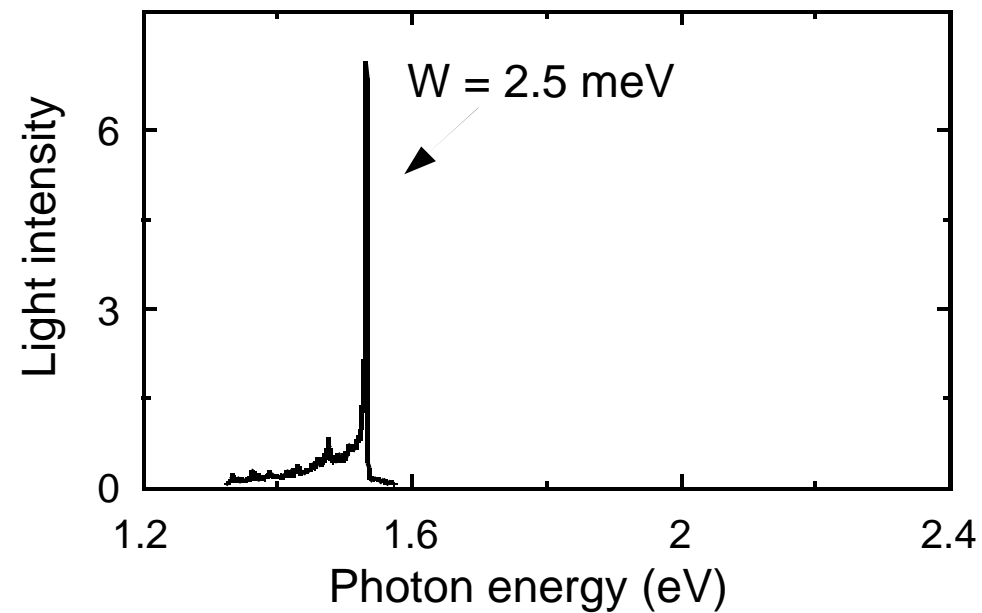
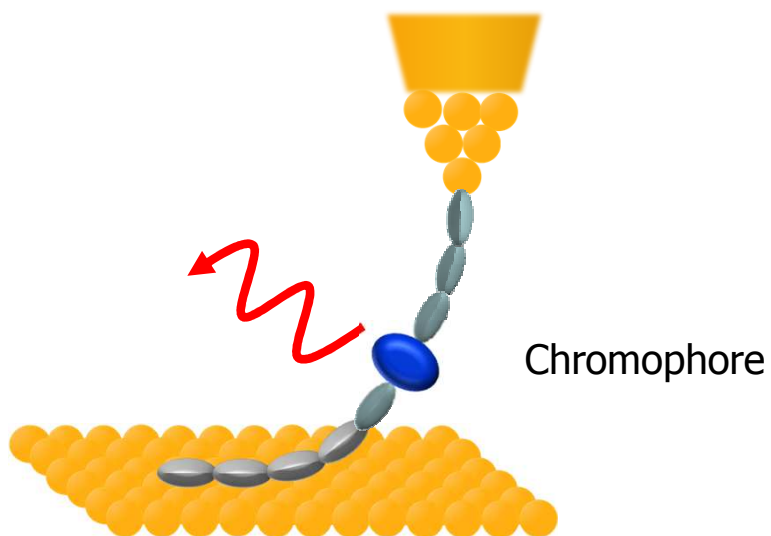
Single-molecule fluorescence with STM: Suspended molecules



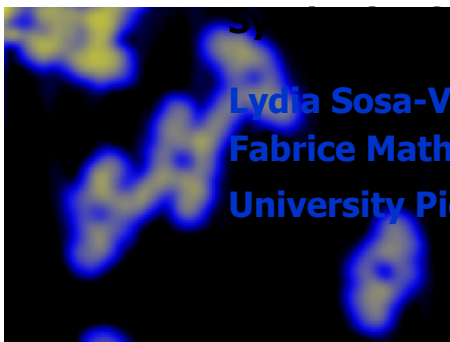
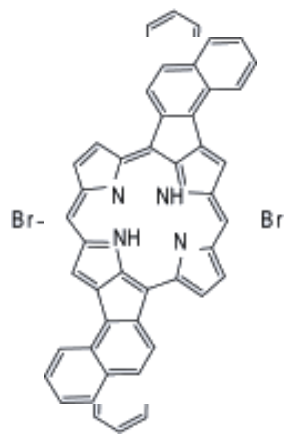
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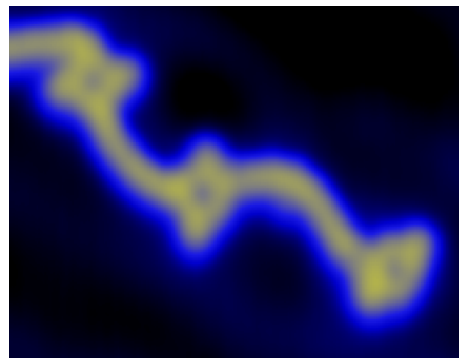
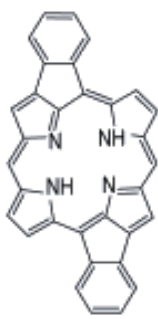
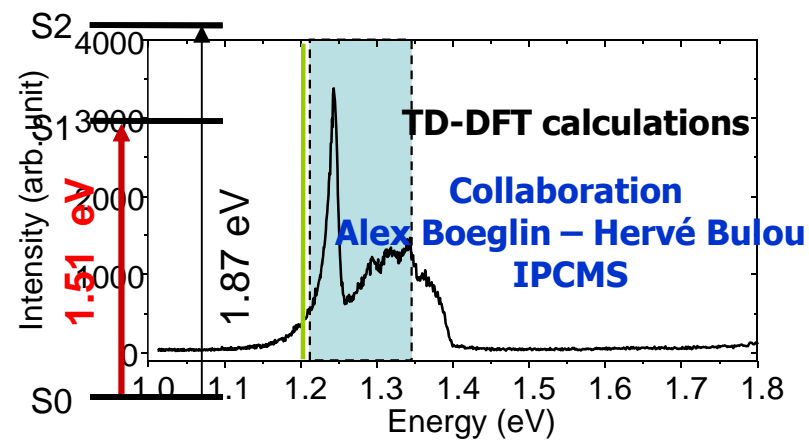
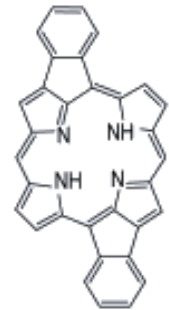
Single-molecule fluorescence with STM: Suspended molecules



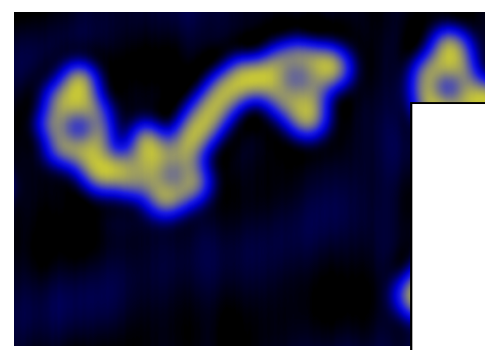
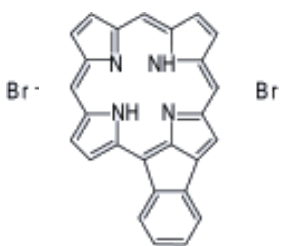
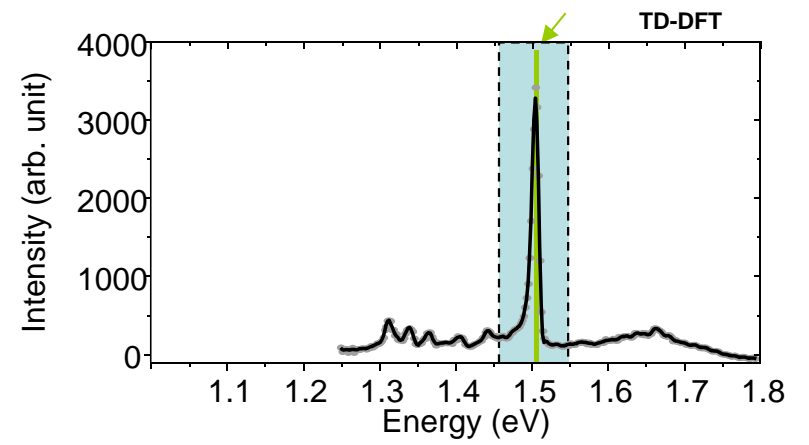
Single-molecule fluorescence with STM: Suspended molecules



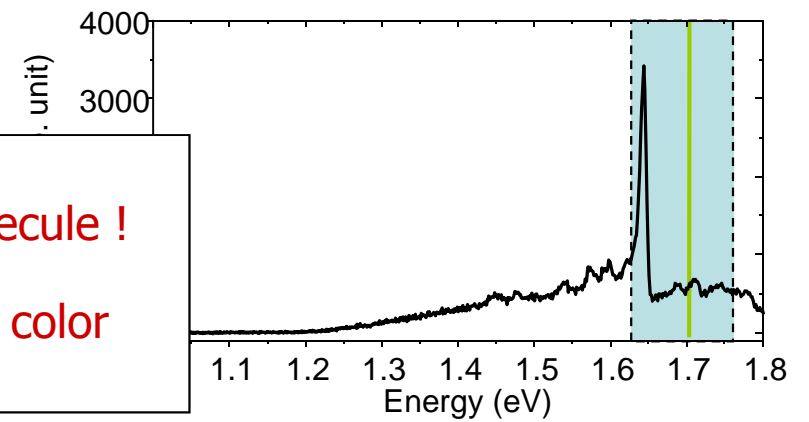
the porphyrin p
 Lydia Sosa-Vargas
 Fabrice Mathevet
 University Pierre et Marie Curie
 $h\nu_{\text{exp}} = 1.28$ eV



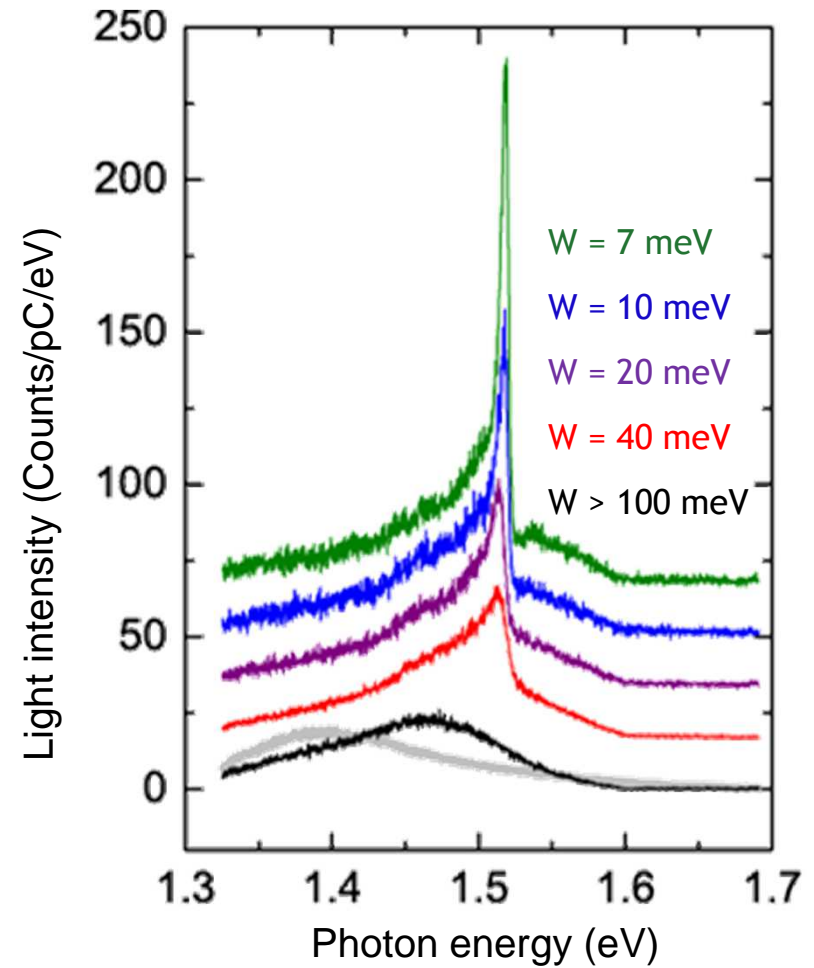
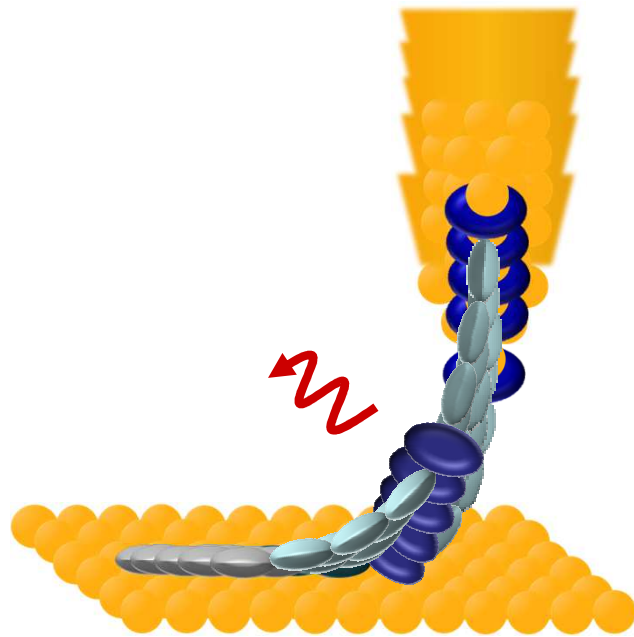
$h\nu_{\text{exp}} = 1.50 \pm 0.04$ eV



Fluorescence of the molecule !
 Controlling the emission color



Single-molecule fluorescence with STM: Suspended molecules

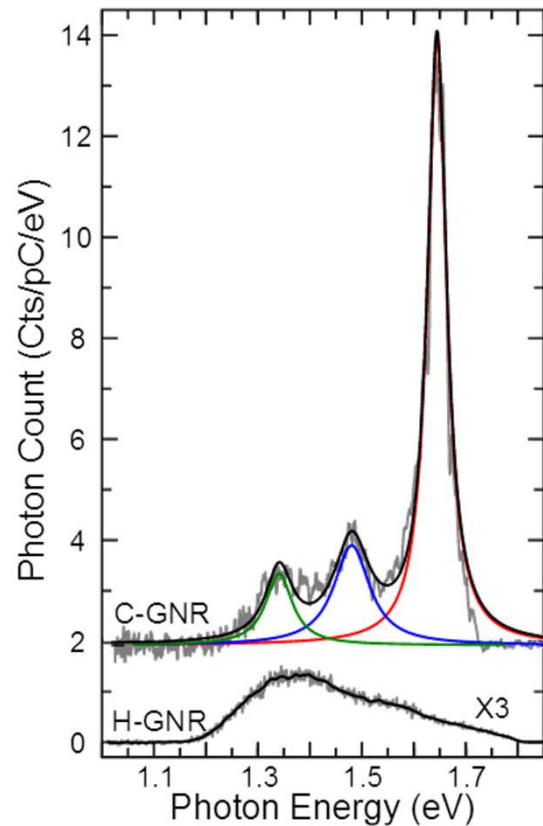
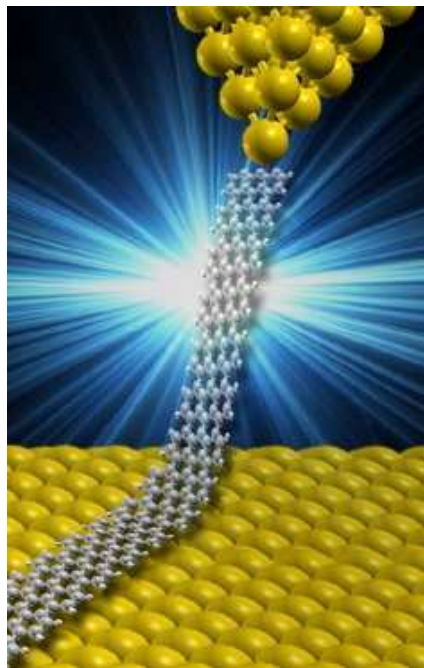
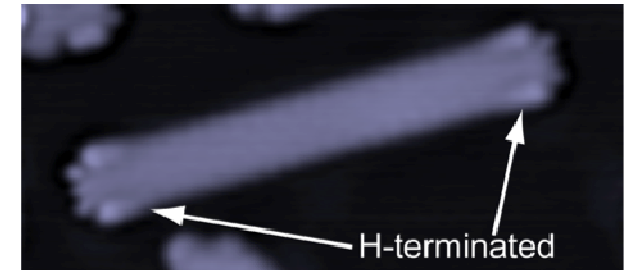
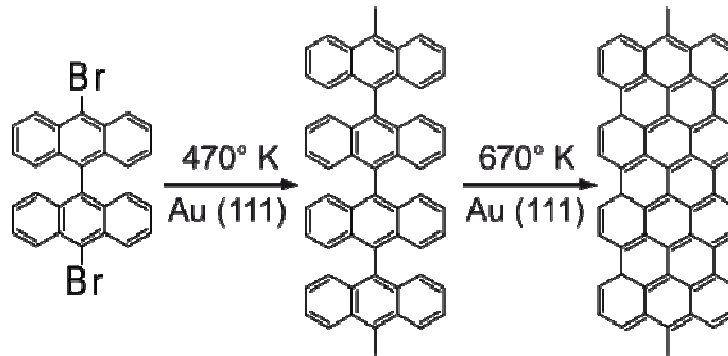


Progressive decoupling of the molecular emitter

Controlling the emission linewidth

Single-molecule fluorescence with STM: Suspended molecules

J. Cai *et al.*
Nature, 466, 470-473 (2010)



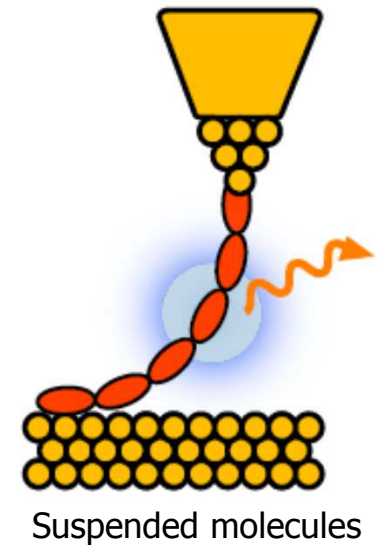
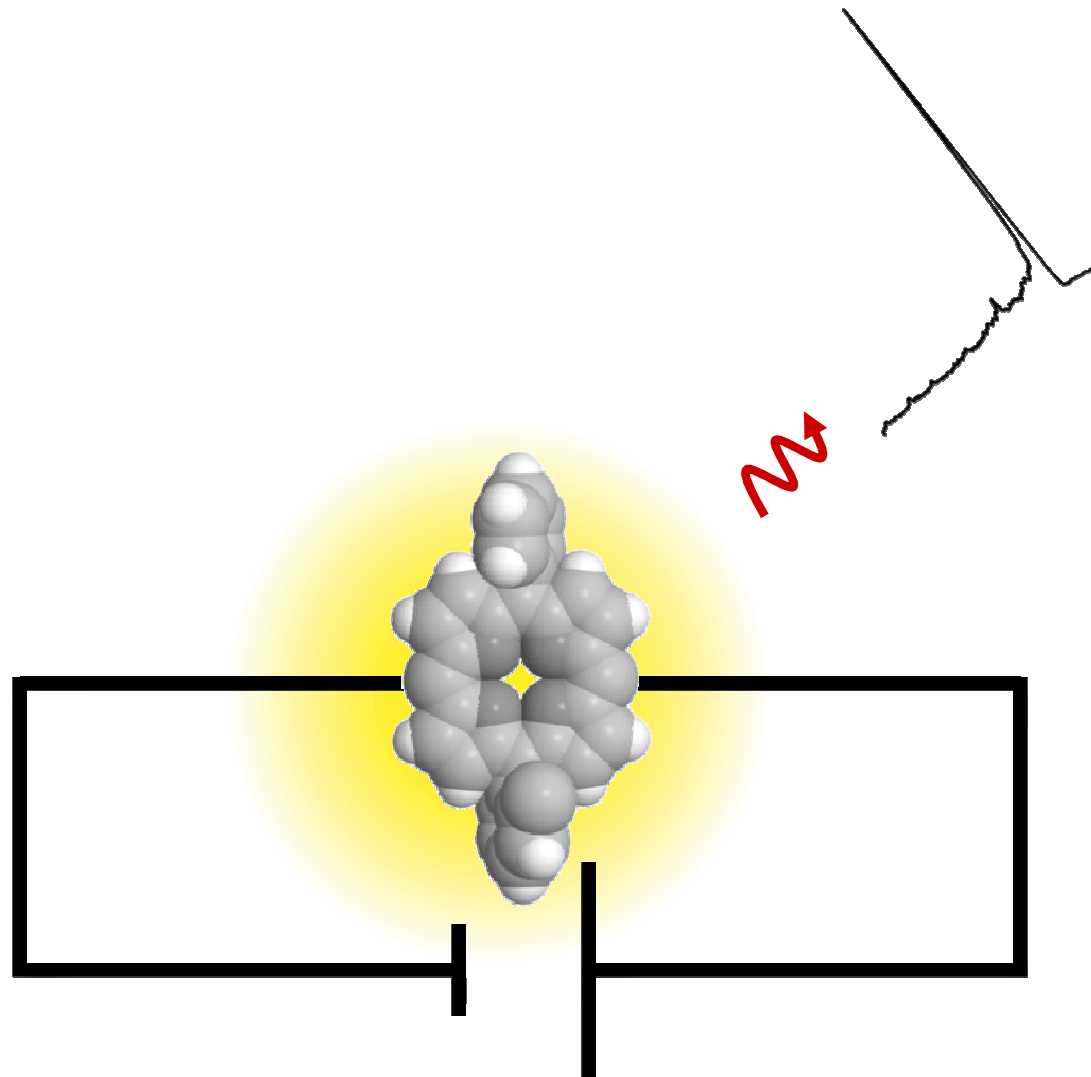
Intense light emission (x 100),
stand high currents (tens of nA)

Brilliant and robust single-molecule
optoelectronic device

M.C. Chong *et al.* *Nanoletters* 18, 175 (2018)

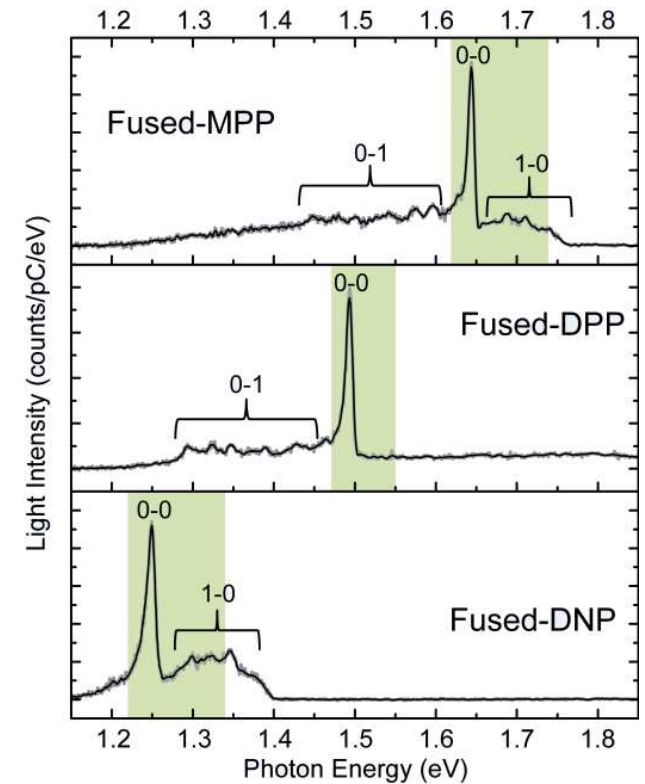
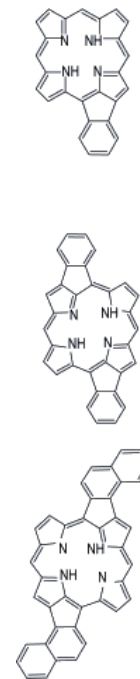
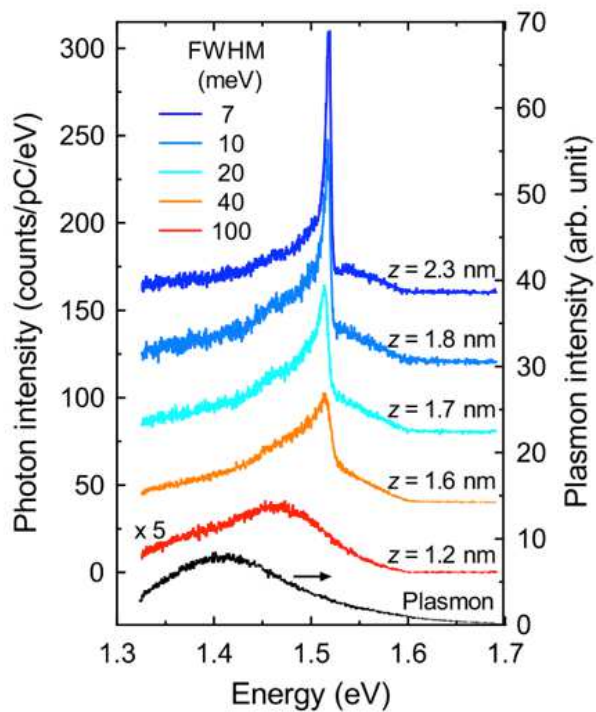
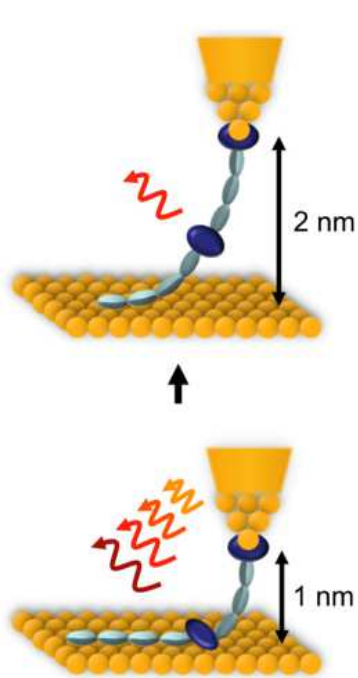
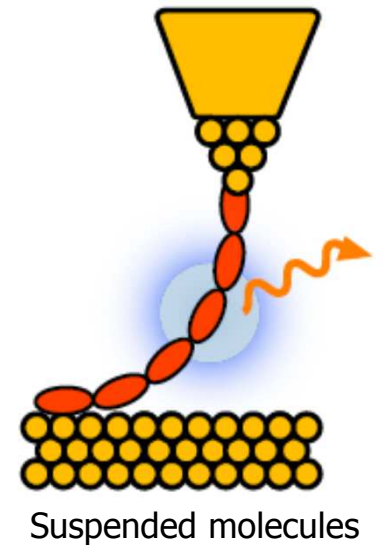
Single-molecule fluorescence with STM: Suspended molecules

- Narrow-line emission in contact with electrodes



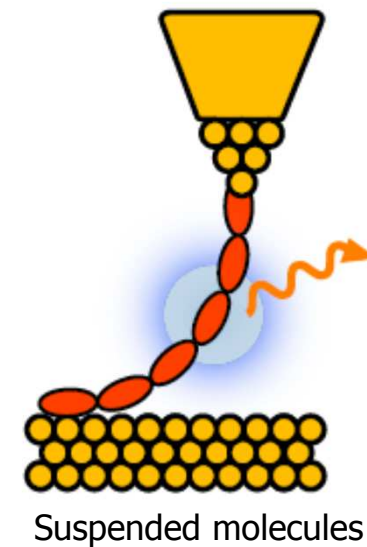
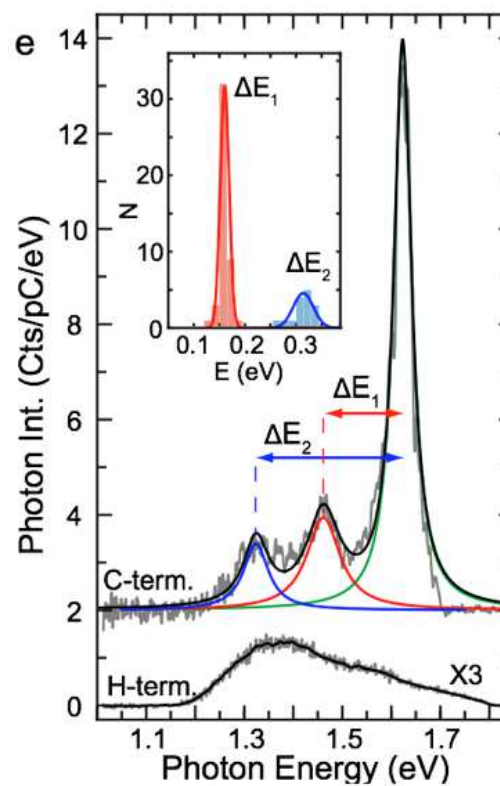
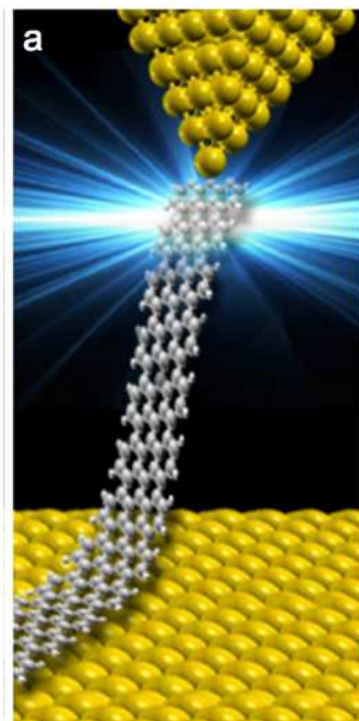
Single-molecule fluorescence with STM: Suspended molecules

- Narrow-line emission in contact with electrodes
- Control of the linewidth and the color of the emission



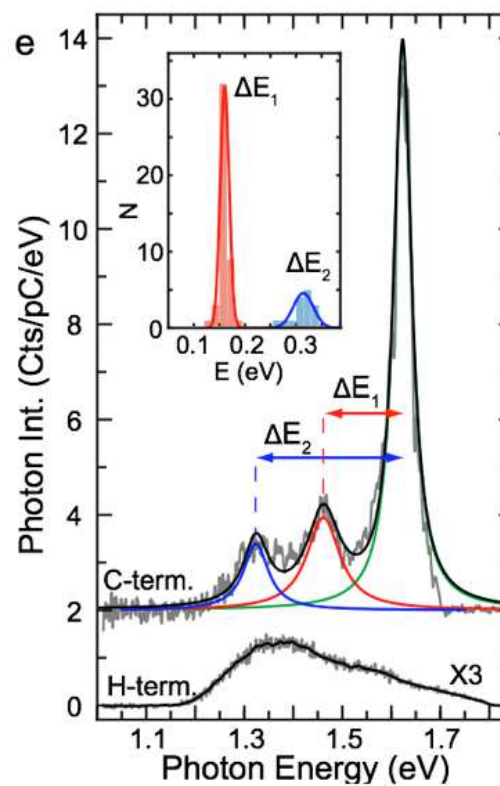
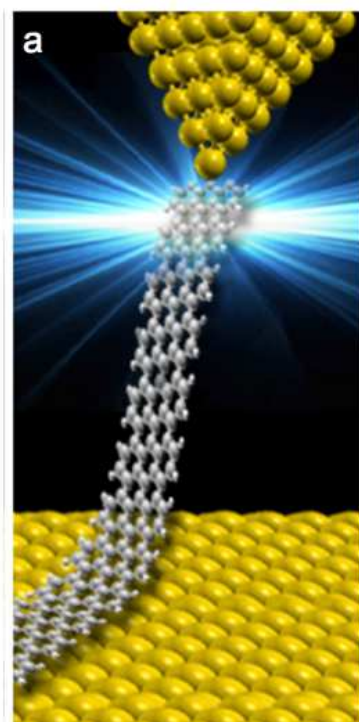
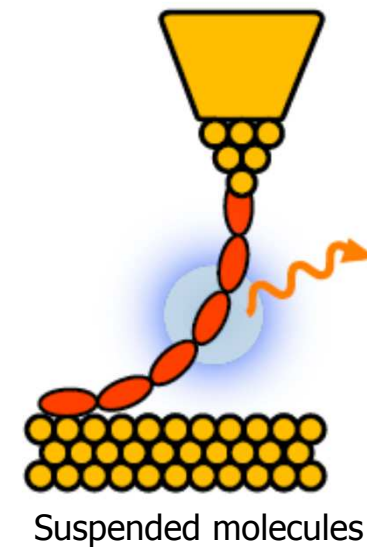
Single-molecule fluorescence with STM: Suspended molecules

- Narrow-line emission in contact with electrodes
- Control of the linewidth and the color of the emission.
- Brilliant GNR optoelectronic devices



Single-molecule fluorescence with STM: Suspended molecules

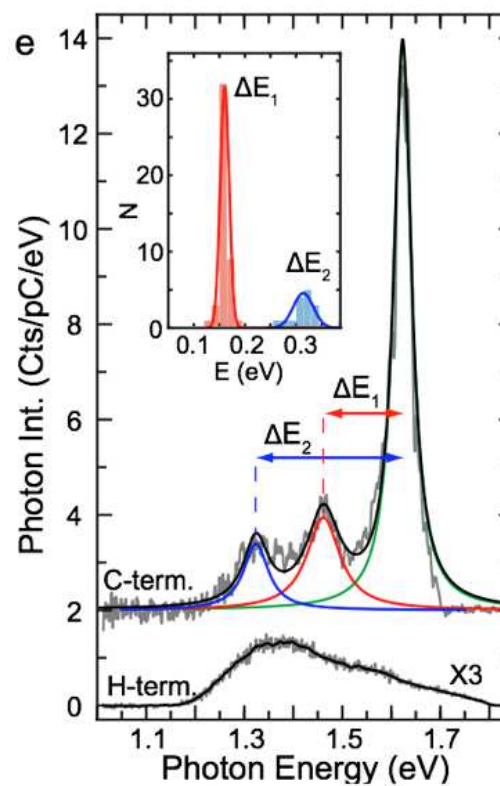
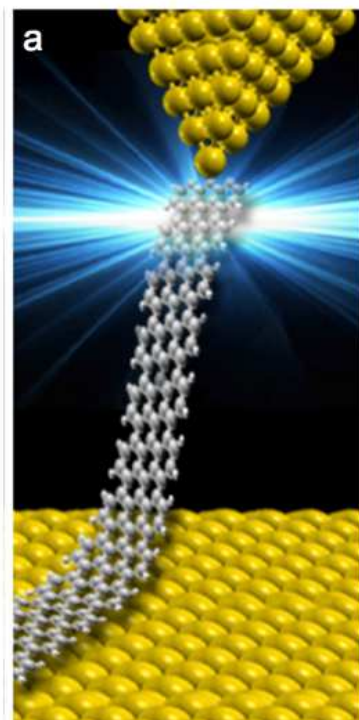
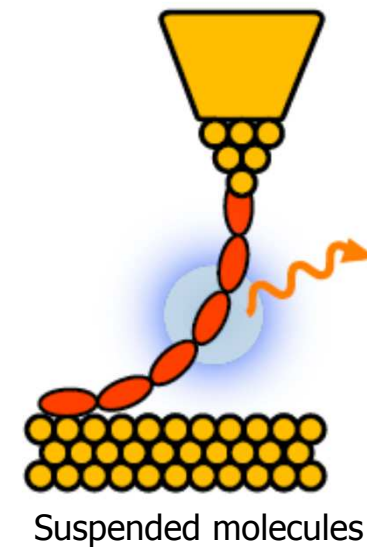
- Narrow-line emission in contact with electrodes
- Control of the linewidth and the color of the emission.
- Brilliant GNR optoelectronic devices



Single-molecule fluorescence ...

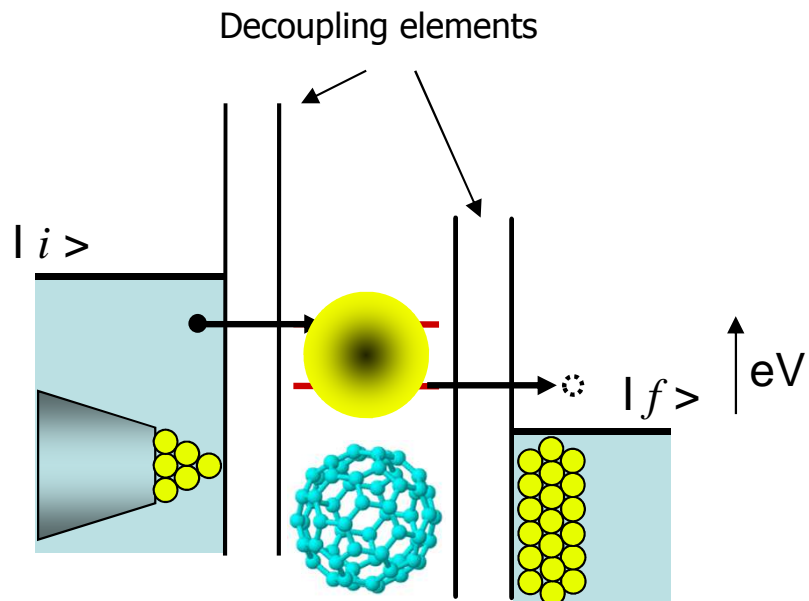
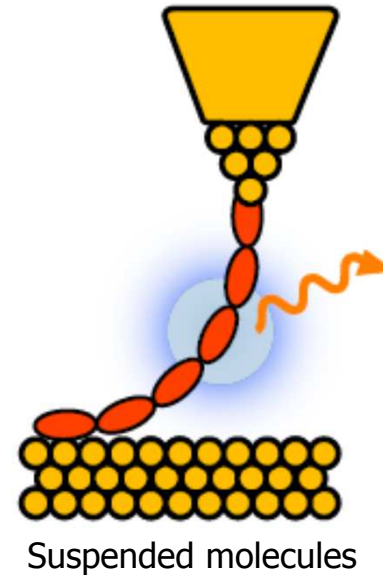
Single-molecule fluorescence with STM: Suspended molecules

- Narrow-line emission in contact with electrodes
- Control of the linewidth and the color of the emission.
- Brilliant GNR optoelectronic devices

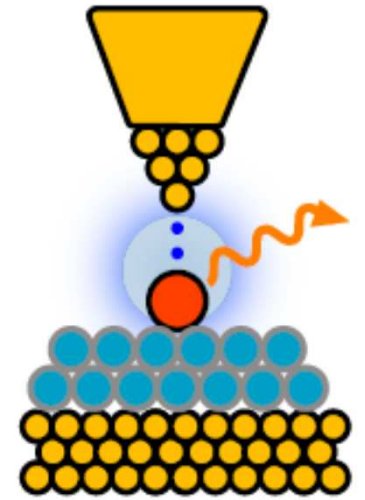


Single-molecule fluorescence no spatial resolution !

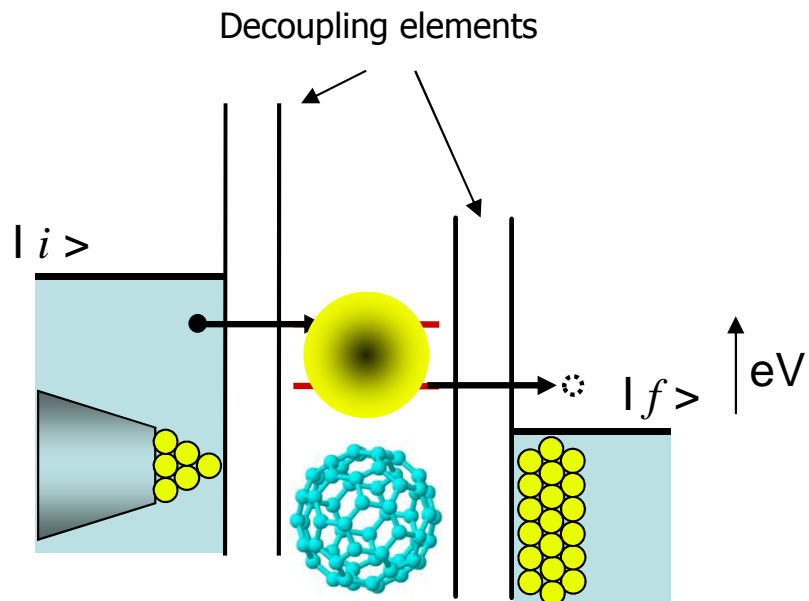
Single-molecule fluorescence with STM



Single-molecule fluorescence with STM



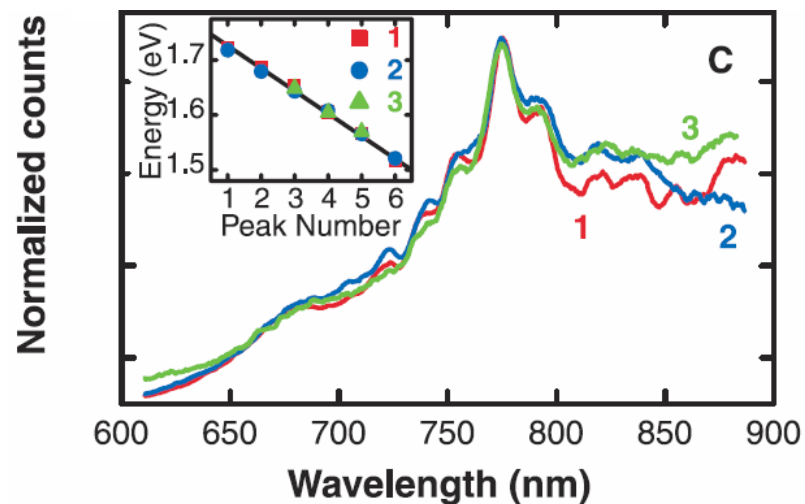
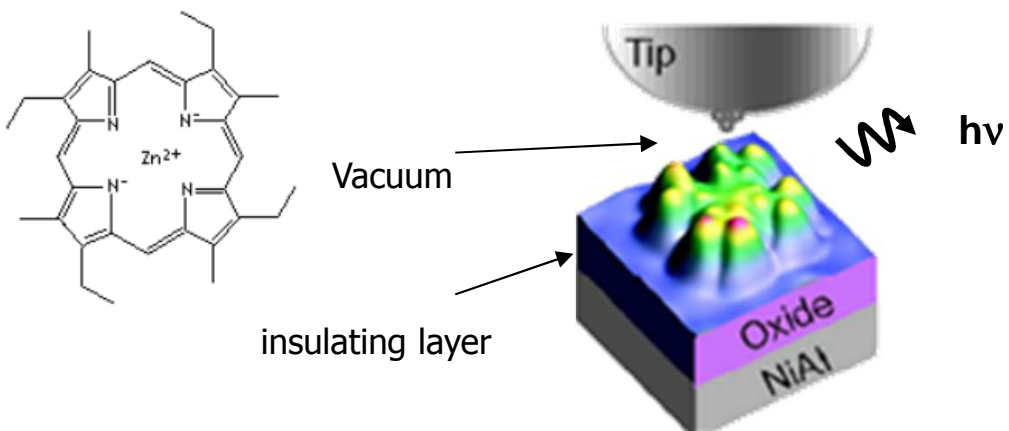
Molecules on insulating layer



Single-molecule fluorescence with STM:

Molecules on insulating layer

Double tunneling junction



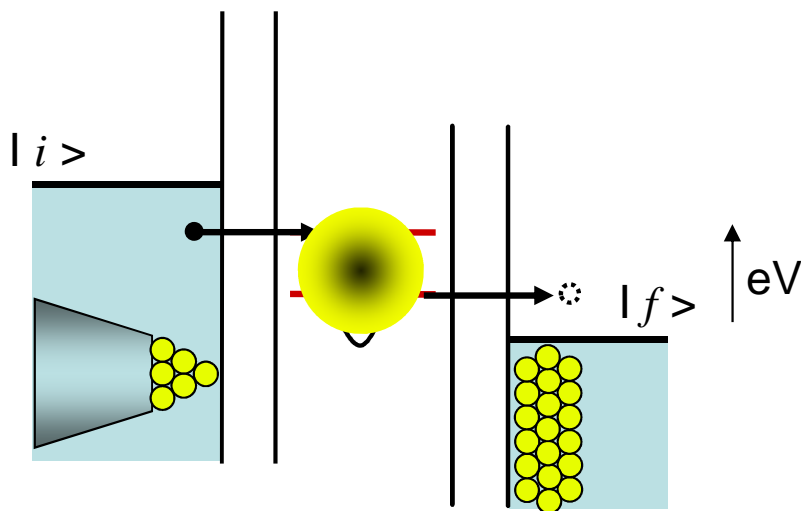
X. H. Qiu, G. V. Nazin, W. Ho, *Science*, 299, 542 (2003)

Intrinsic radiative transition

Lumo+1 -> Lumo transition (?)

Vibronic features

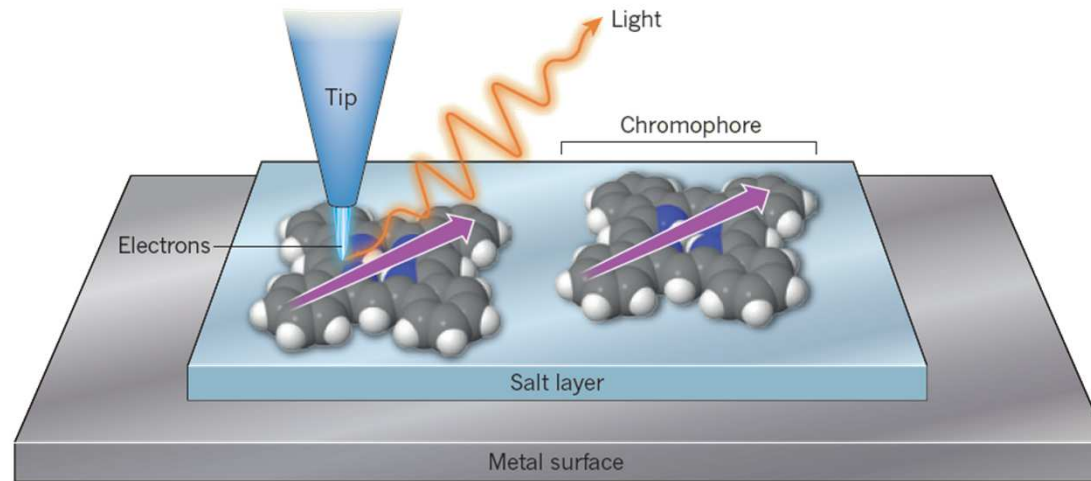
→ Chemical information ?



Preserves the imaging capability of the STM

Single-molecule fluorescence with STM: Molecules on insulating layer

Fluorescence microscopy with atomic-scale resolution ?



Zhenchao Dong's Group - Hefei National Laboratory, China

Y. Zhang *et al.*, Nature 531, 623 (2016)

Y. Zhang *et al.*, Nature Com. 8, 15225 (2017)

L. Zhang *et al.*, Nature Comm. 8, 580 (2017)

Youso kim's Group - Riken Laboratory, Japan

H. Imada *et al.*, Nature 538, 364 (2016)

H. Imada *et al.*, Phys. Rev. Lett. 119 013901 (2017)

K. Miwa *et al.*, Nano Lett. asap (2019)

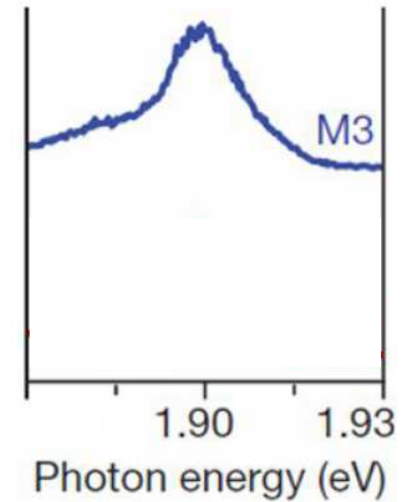
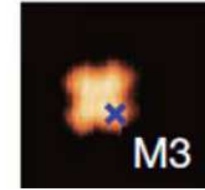
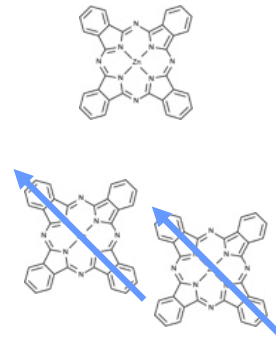
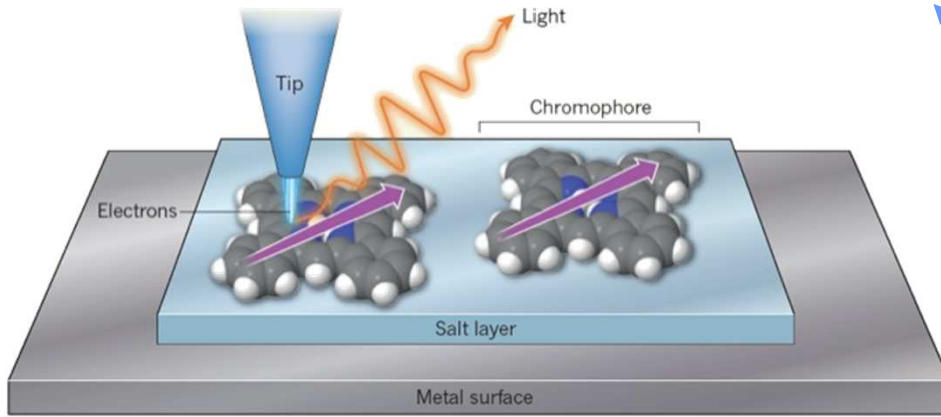
IPCMS

B. Doppagne *et al.*, Phys. Rev. Lett. 118, 127401 (2017)

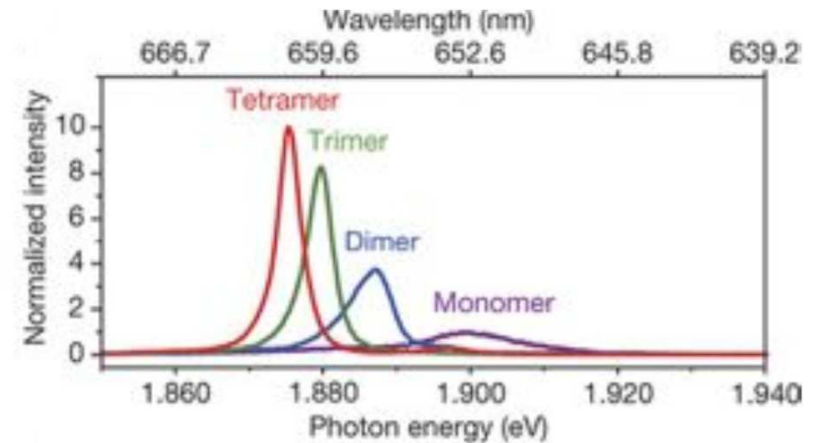
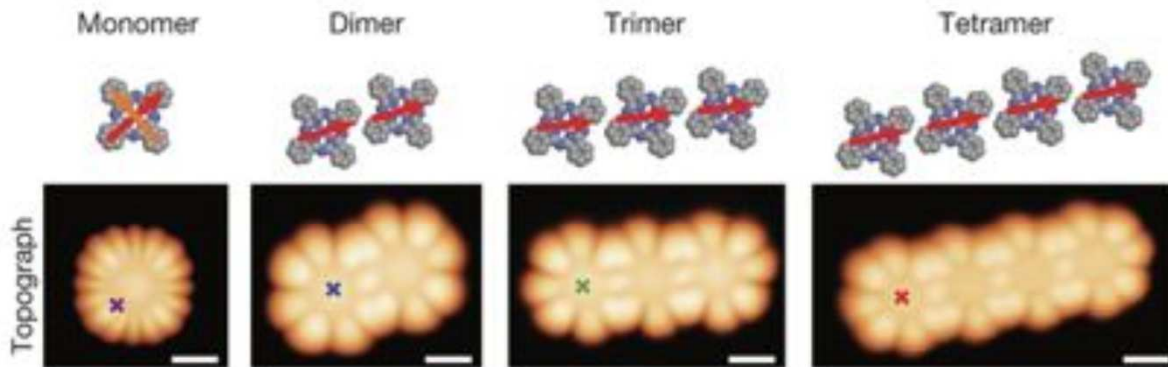
J. Kroeger *et al.*, Nanoletters 18, 3407 (2018)

B. Doppagne *et al.* Science, 361, 251 (2018)

fluorescence of single-molecule



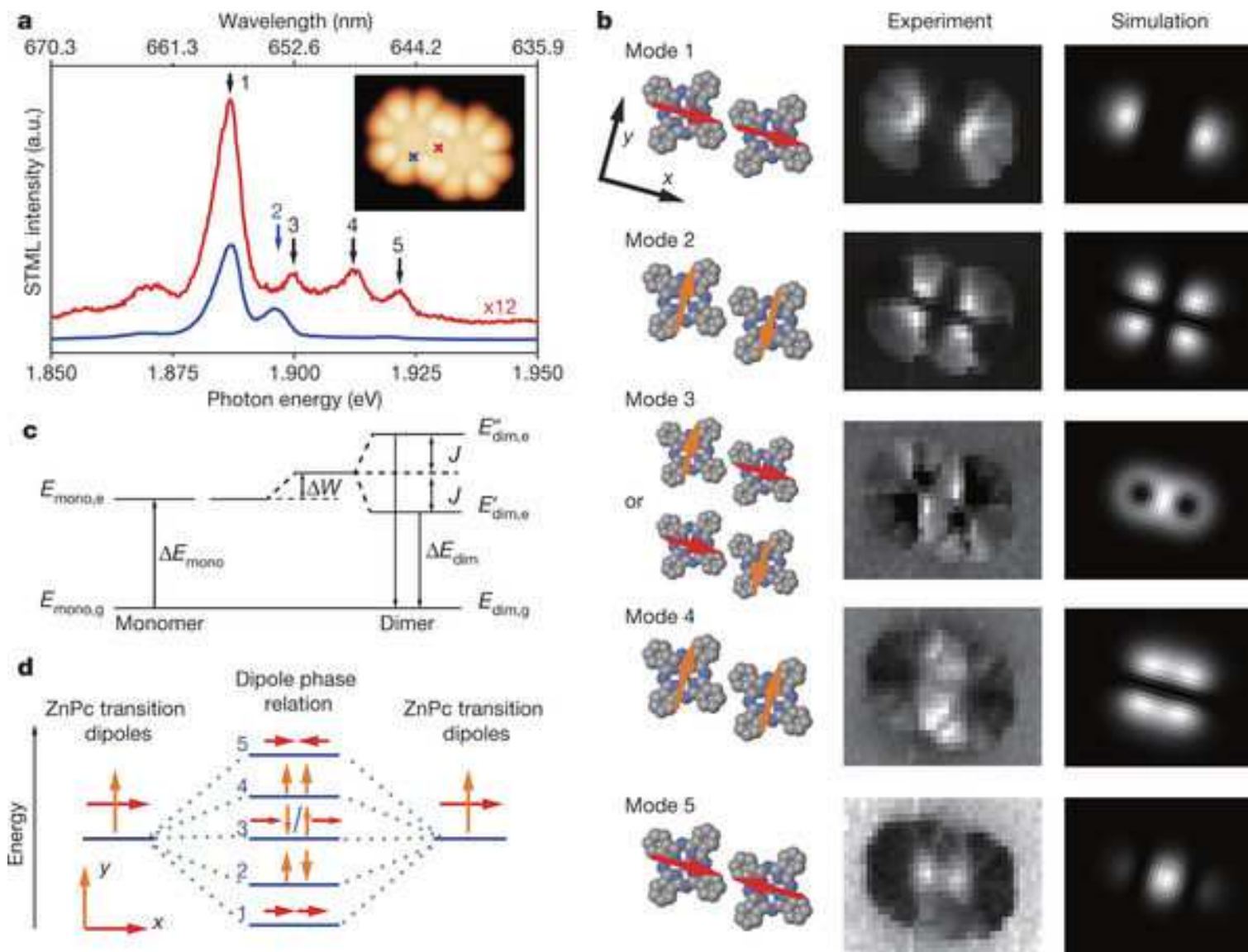
Coherent coupling between molecular dipoles



Building a J-aggregate molecule per molecule

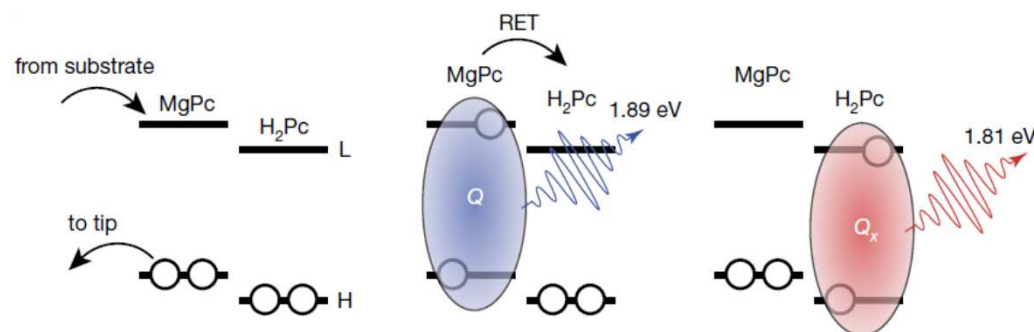
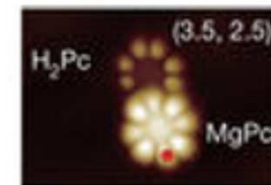
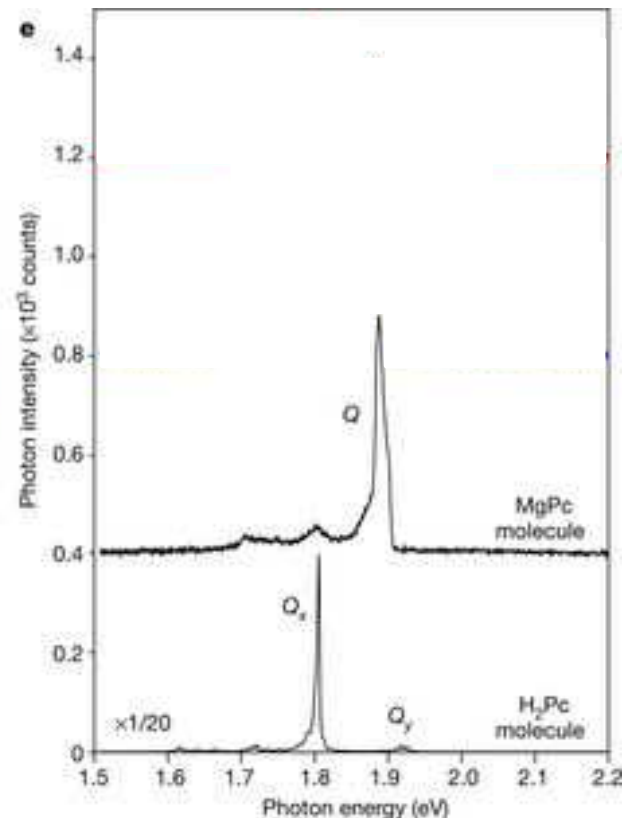
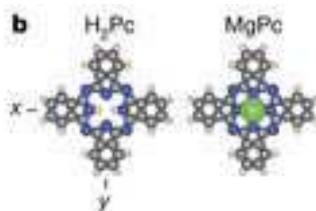
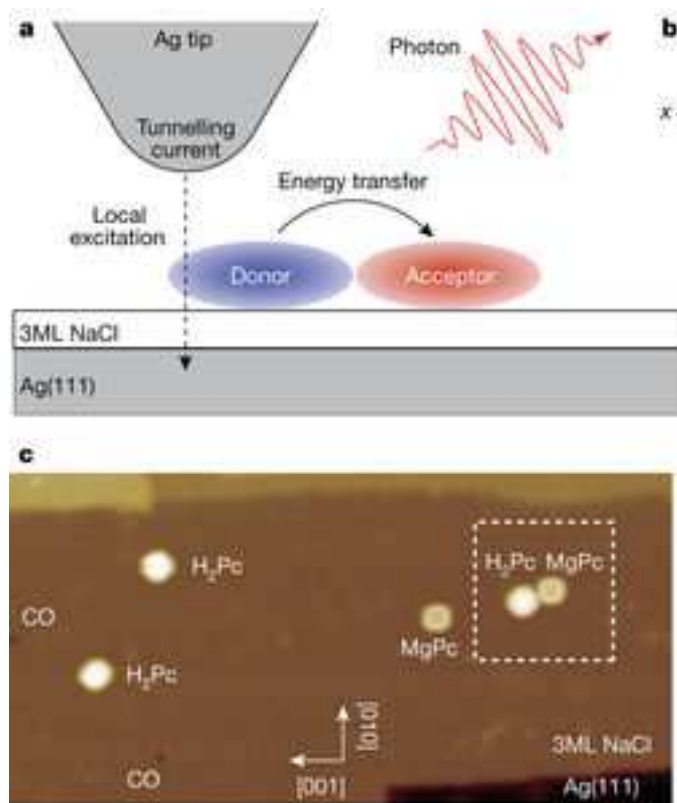
Single-molecule fluorescence with STM: Molecules on insulating layer

Y. Zhang *et al.*
Nature 531, 623 (2016).



Fluorescence imaging with sub-molecular resolution

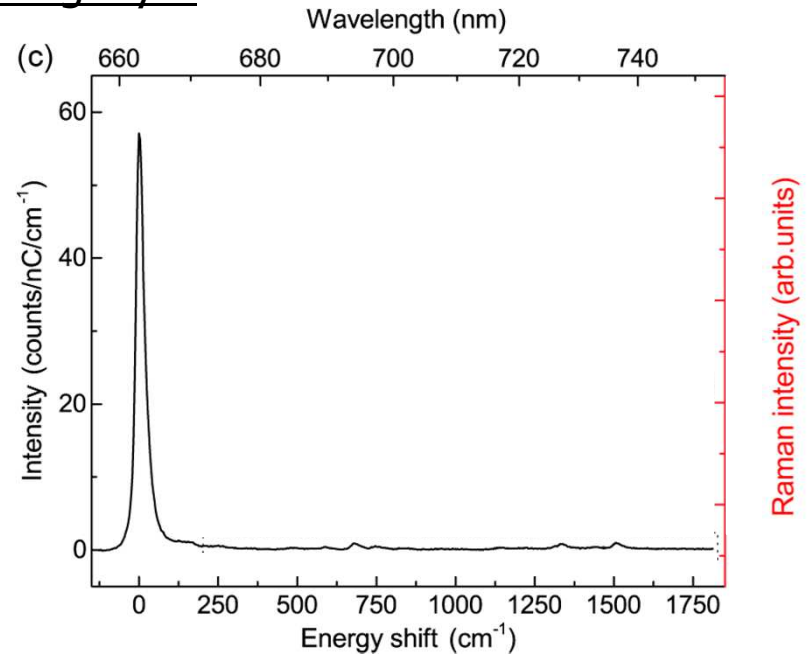
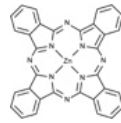
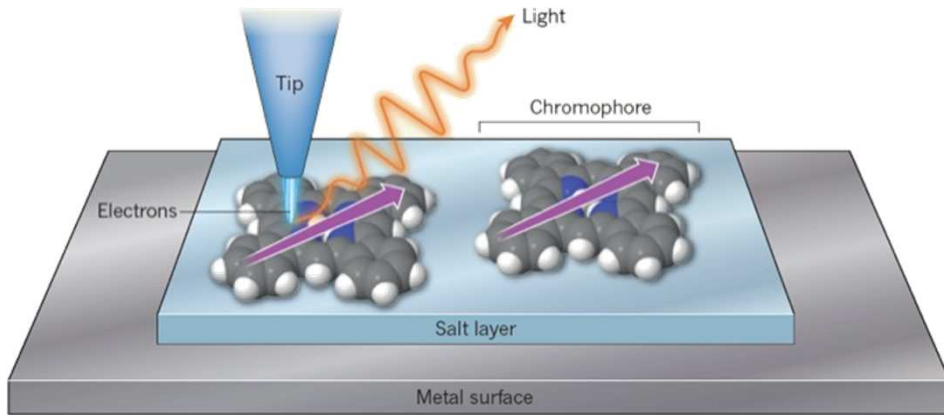
Single-molecule fluorescence with STM: Molecules on insulating layer



H. Imada *et al.*,
Nature 538, 364 (2016)

Energy transfer between two molecules

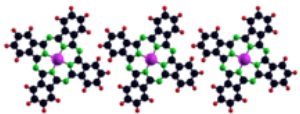
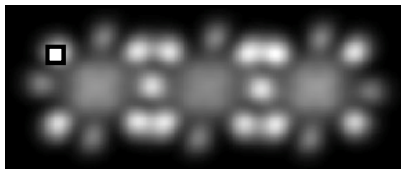
fluorescence of single-molecule



Raman spectroscopy

Etienne Lorchat - Stéphane Berciaud
IPCMS

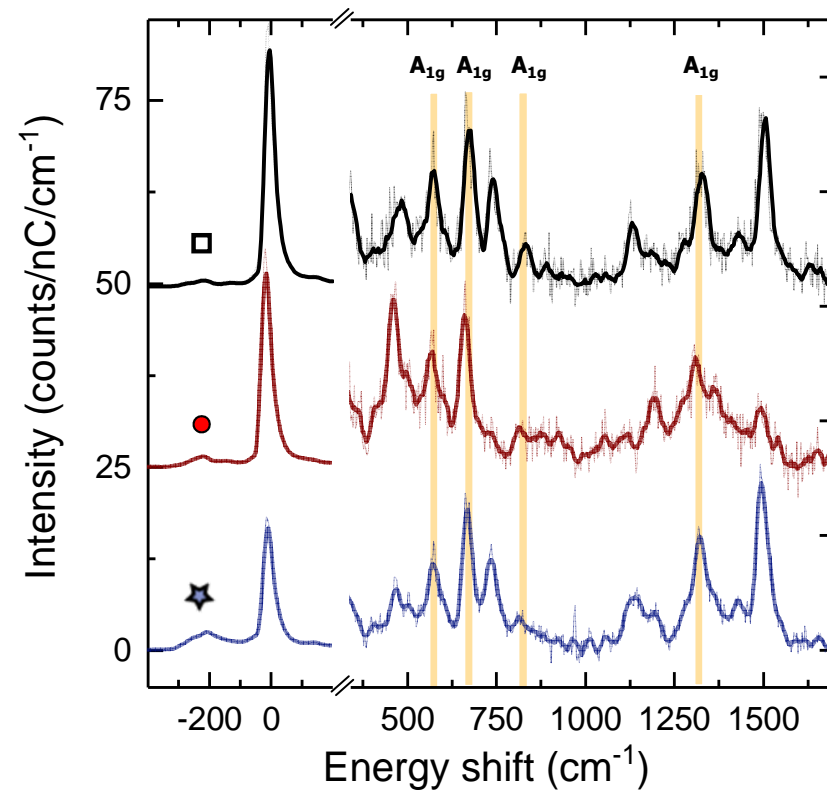
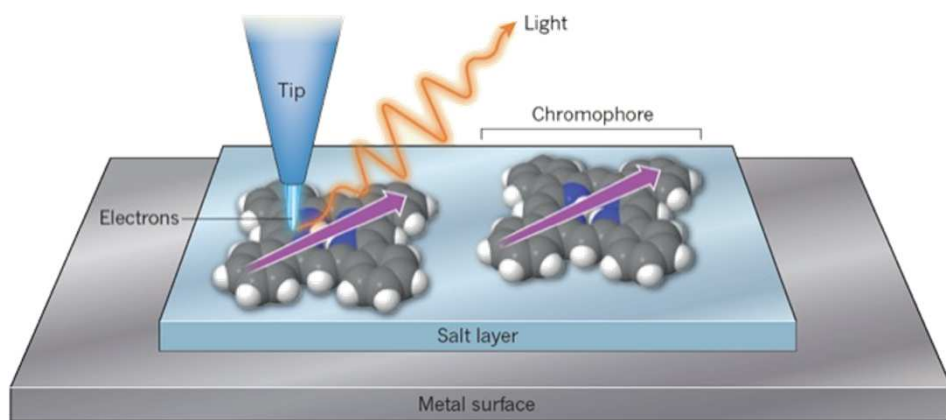
STM image



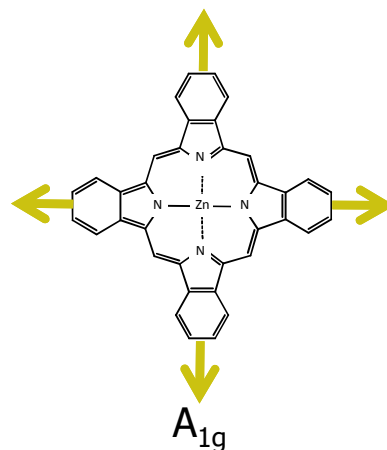
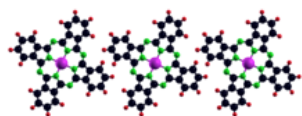
- Same informations as that obtained in Raman spectroscopy on a **single-molecule**.
- **Vibronic fingerprint of the molecule**

Single-molecule fluorescence with STM: Molecules on insulating layer

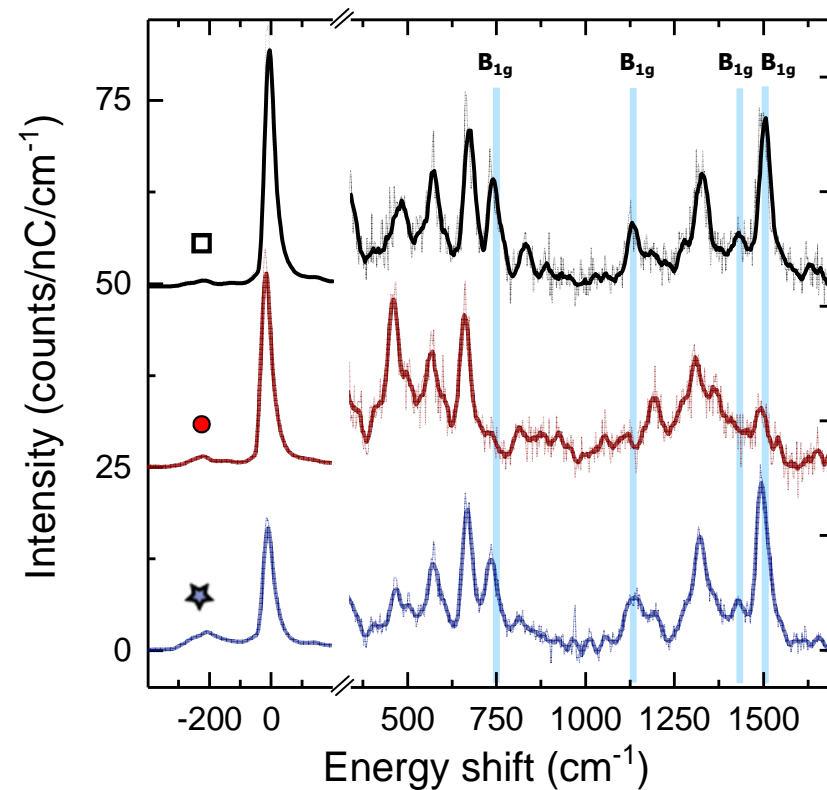
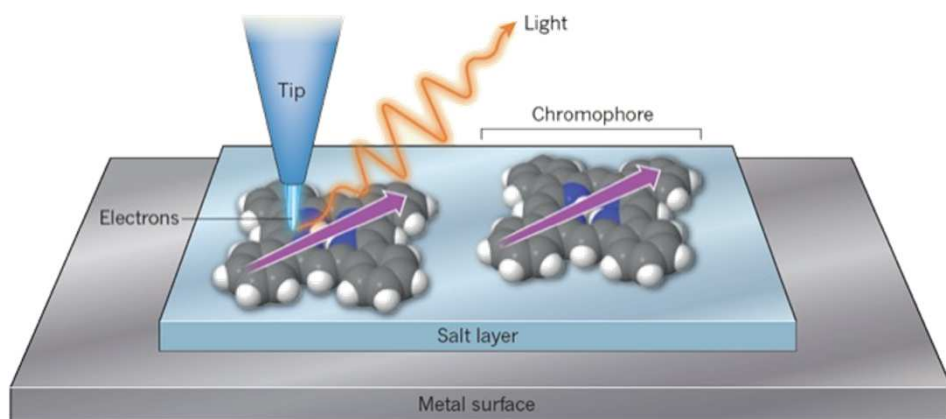
fluorescence of single-molecule



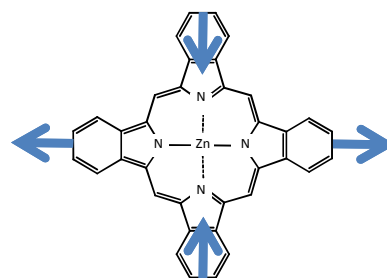
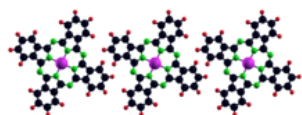
STM image



fluorescence of single-molecule

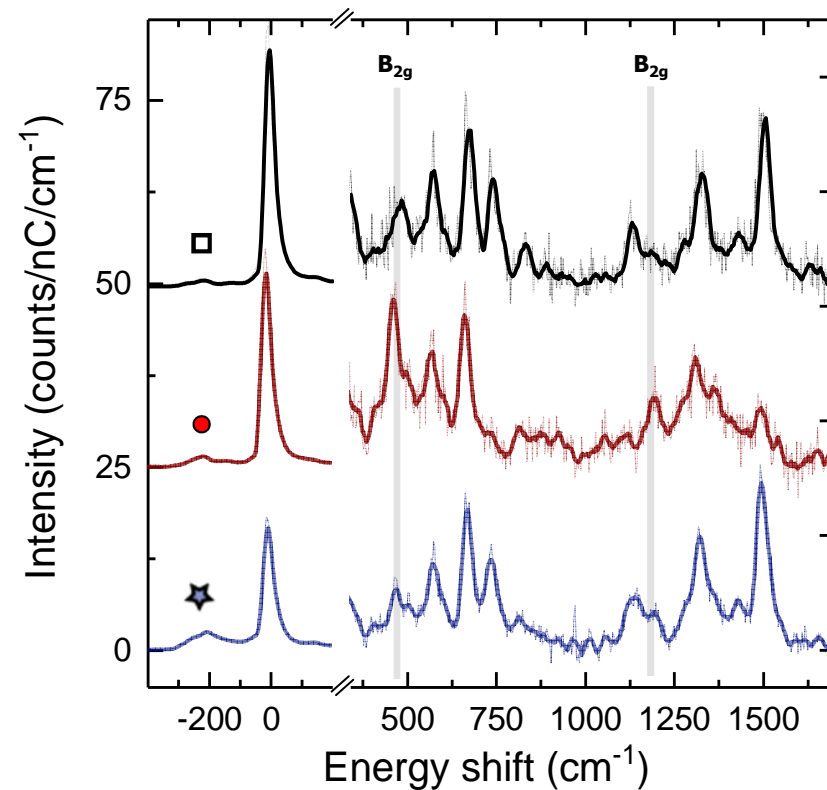
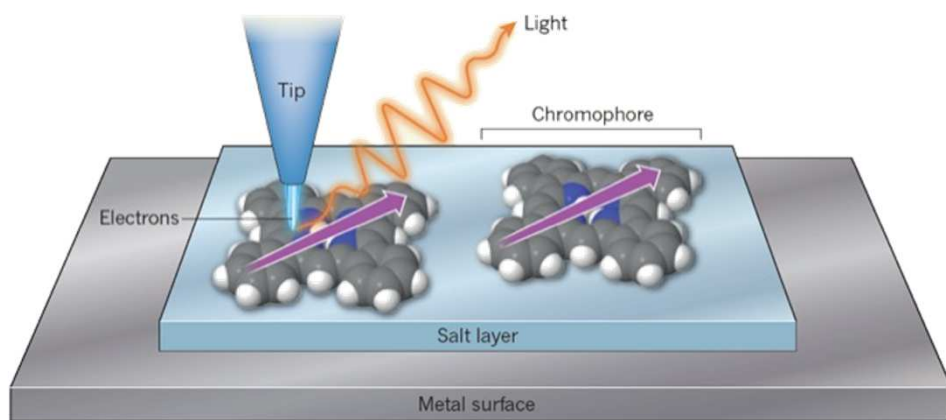


STM image

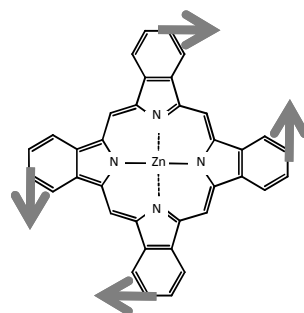
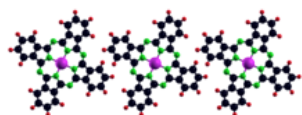


B_{1g}

fluorescence of single-molecule



STM image



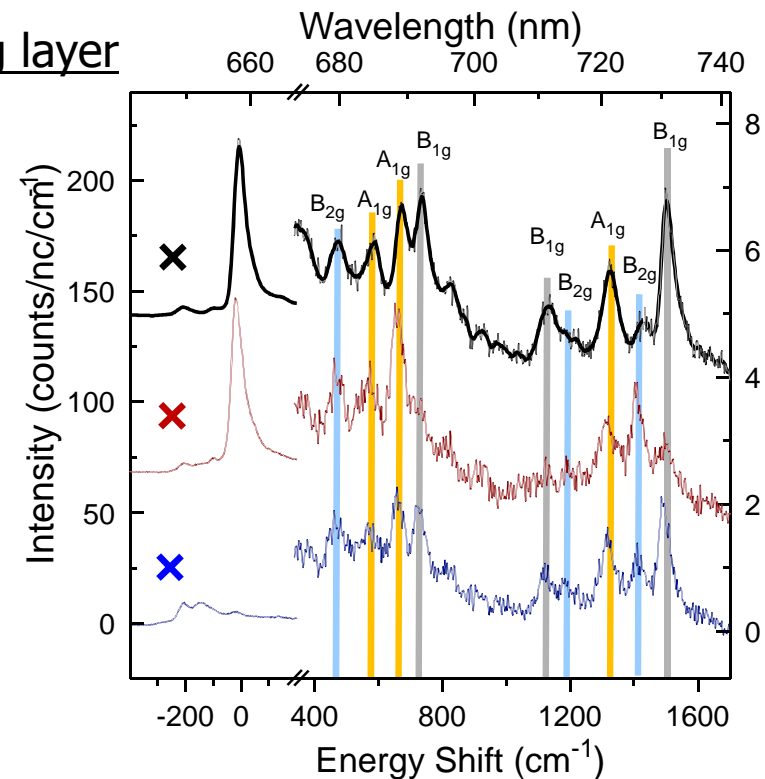
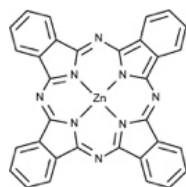
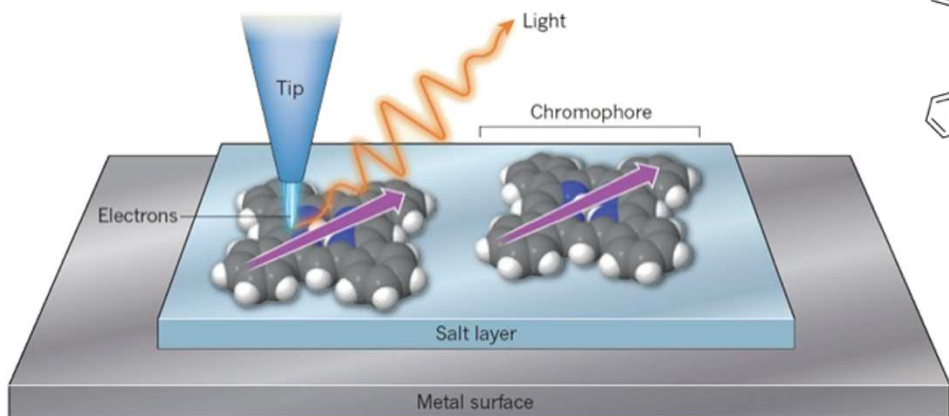
B_{2g}

Peaks associated to modes having the same symmetry have similar spatial distribution ?

Single-molecule fluorescence with STM:

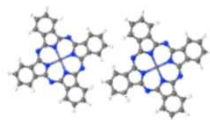
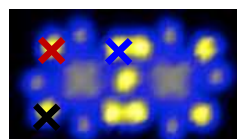
Molecules on insulating layer

fluorescence of single-molecule

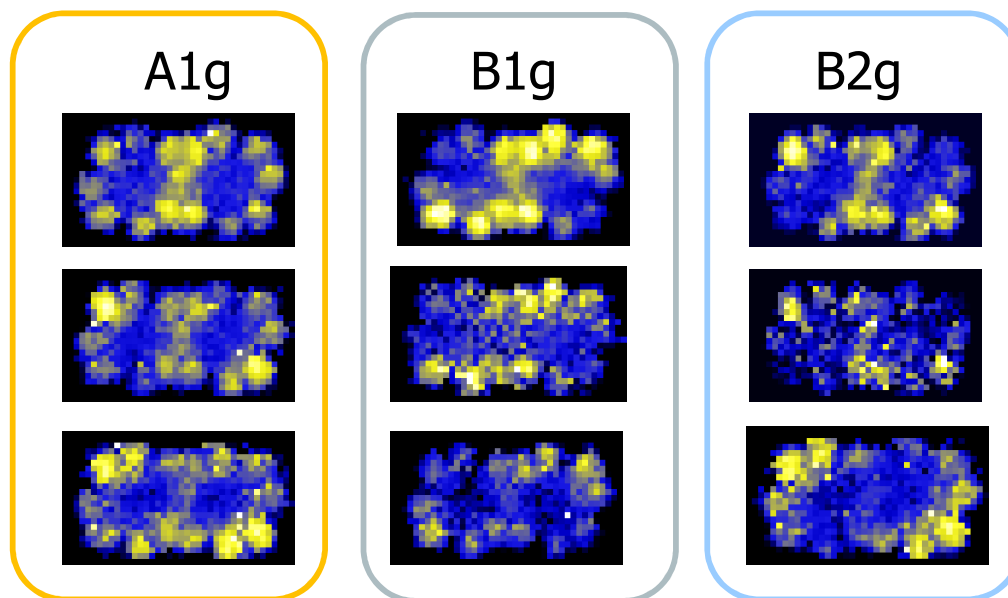


Poster: Benjamin Doppagne

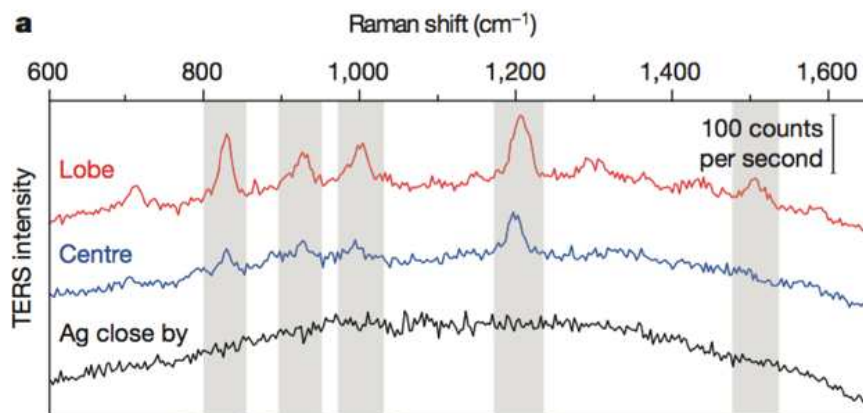
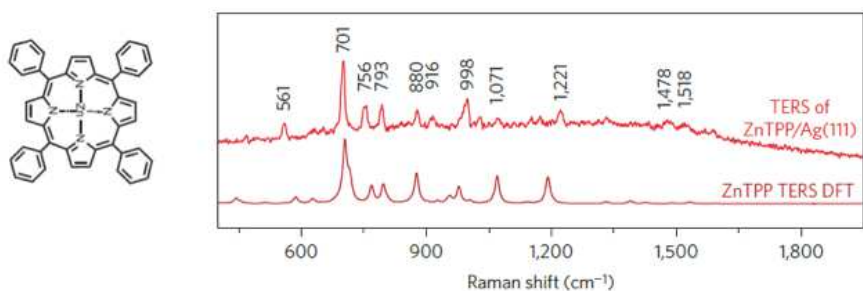
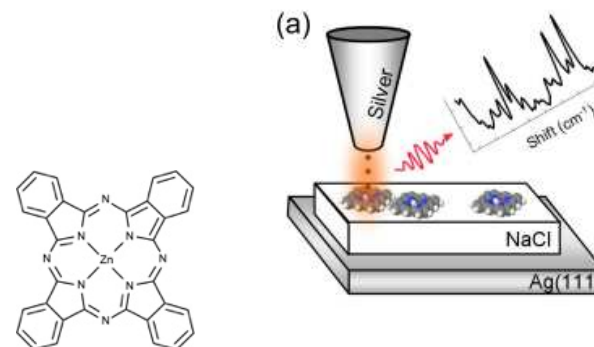
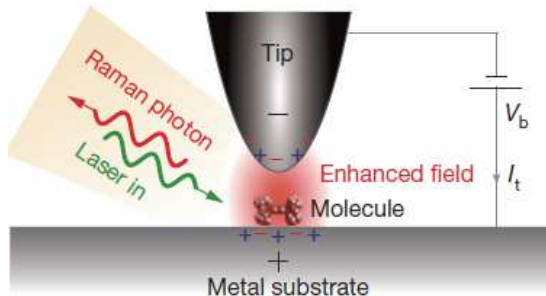
STM image



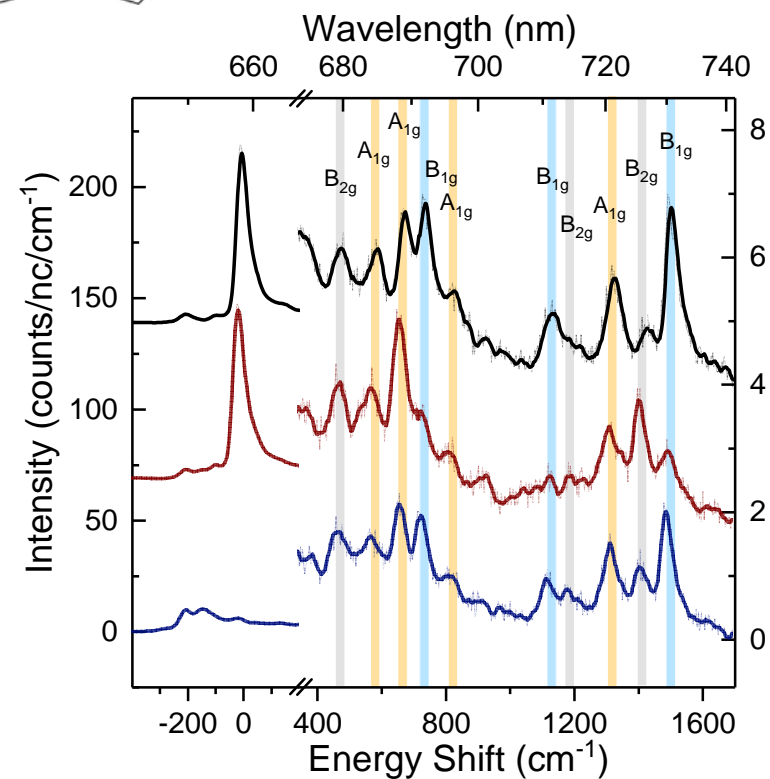
Energy resolved photon maps (acq. time 19H)



Vibratic spectroscopy with
submolecular resolution



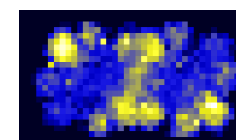
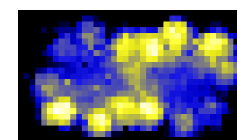
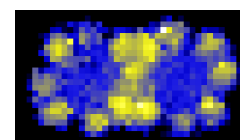
R. Zhang *et al.* **Chemical mapping of a single molecule by plasmon-enhanced Raman scattering**
Nature 498, 82 (2013)



A1g

B1g

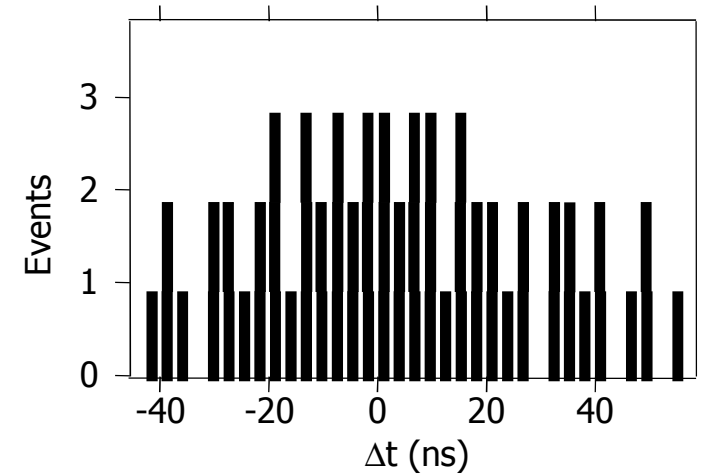
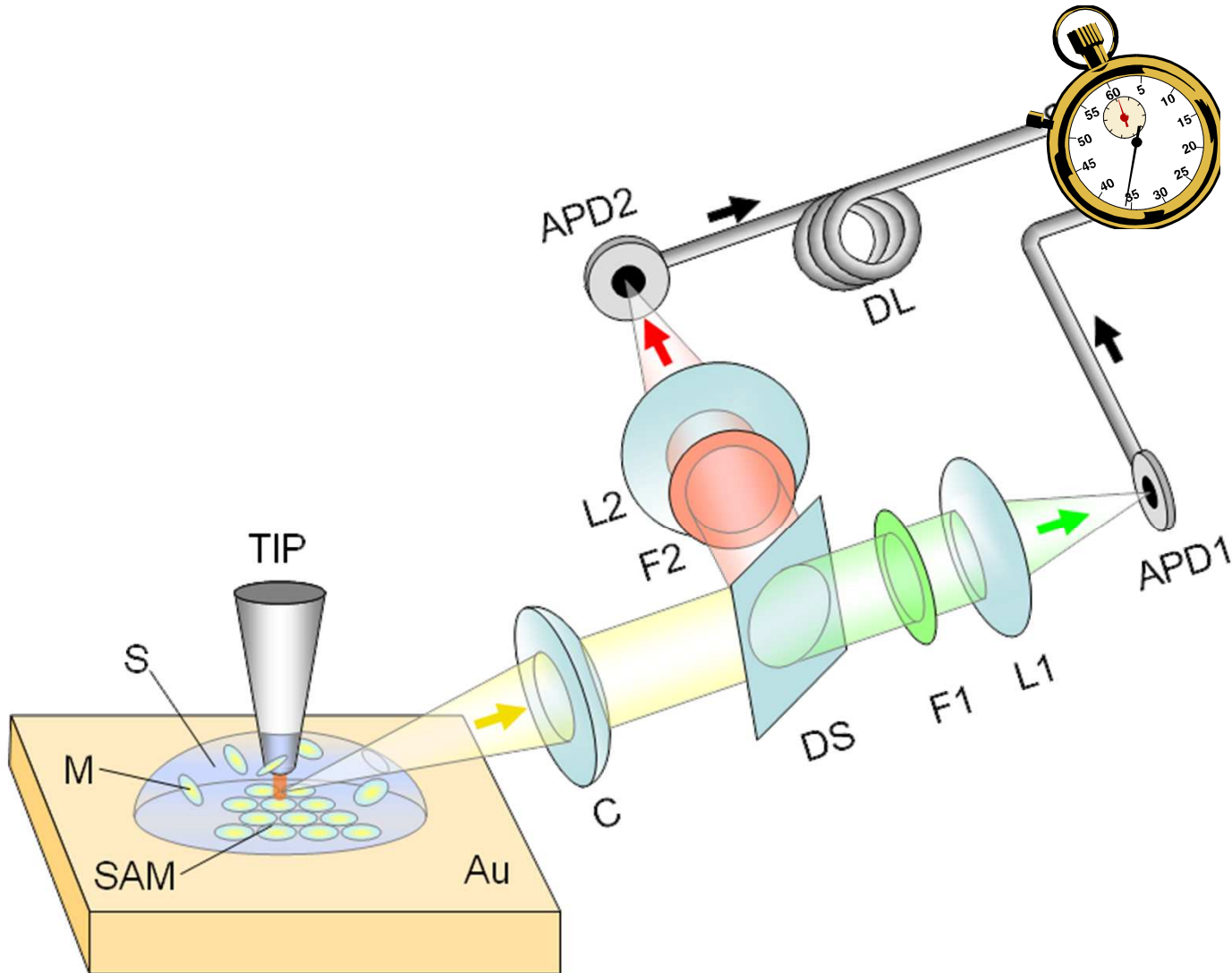
B2g



B. Doppagne *et al.* *Phys. Rev. Lett.* 118, 127401 (2017)

Combining spatial- and time-resolved fluorescence microscopy

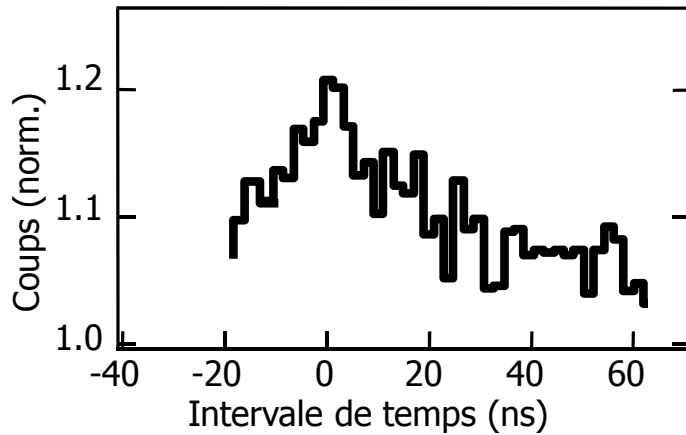
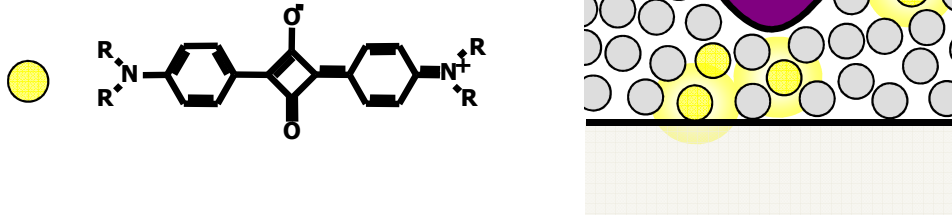
Courtesy of Fabrice Charra
CEA Saclay



Probabilité de détecter
un photon au temps Δt
si un photon est
détecté au temps 0

Combining spatial- and time-resolved fluorescence microscopy

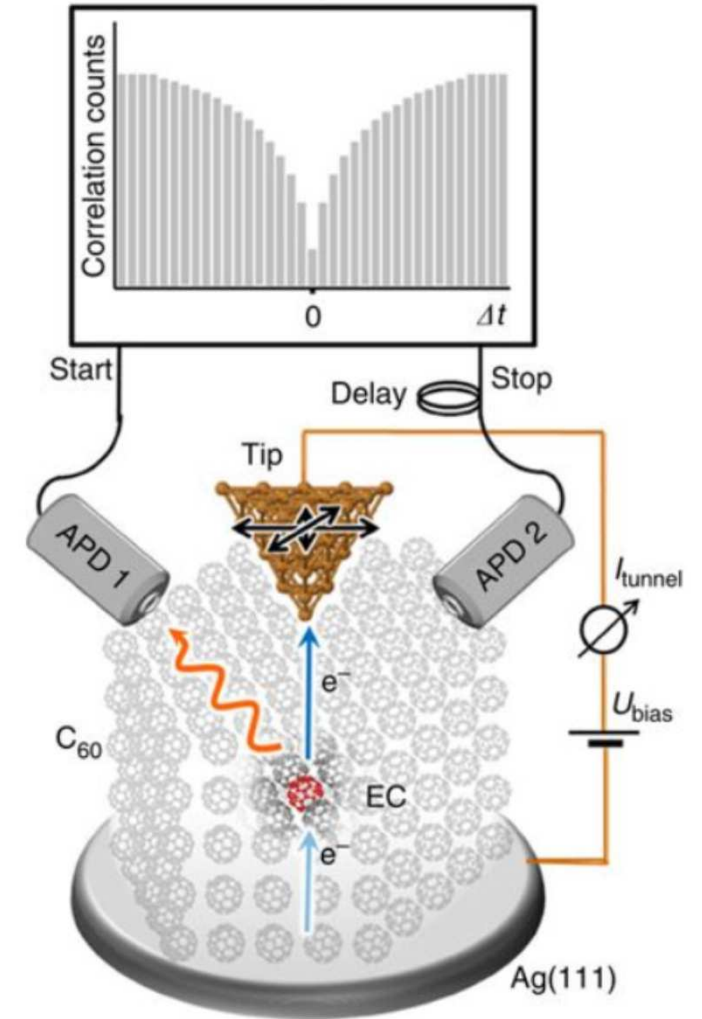
fluorophore



F. Silly *et al.* *Appl. Phys. Lett.* 77, 3648 (2000).

K. Perronet *et al.*, *Europhys Lett.* 74, 313 (2006).

**Measuring fluctuations
with nanosecond
accuracy**

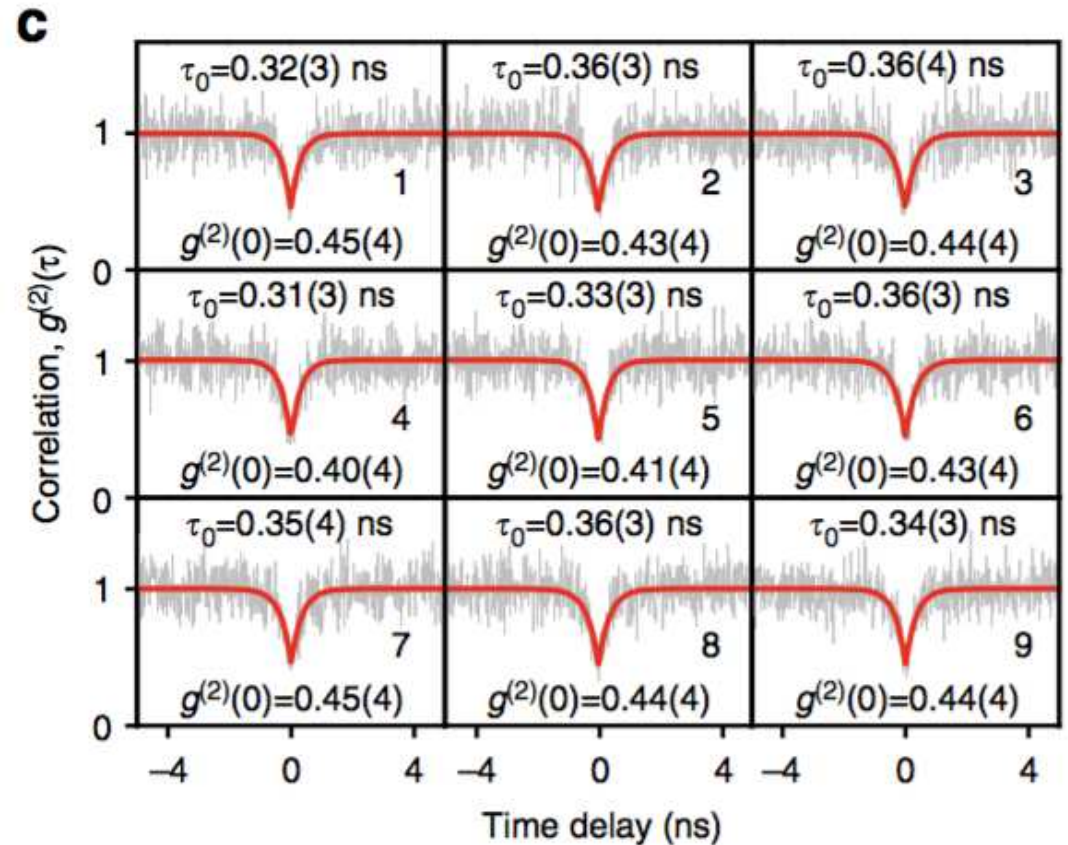
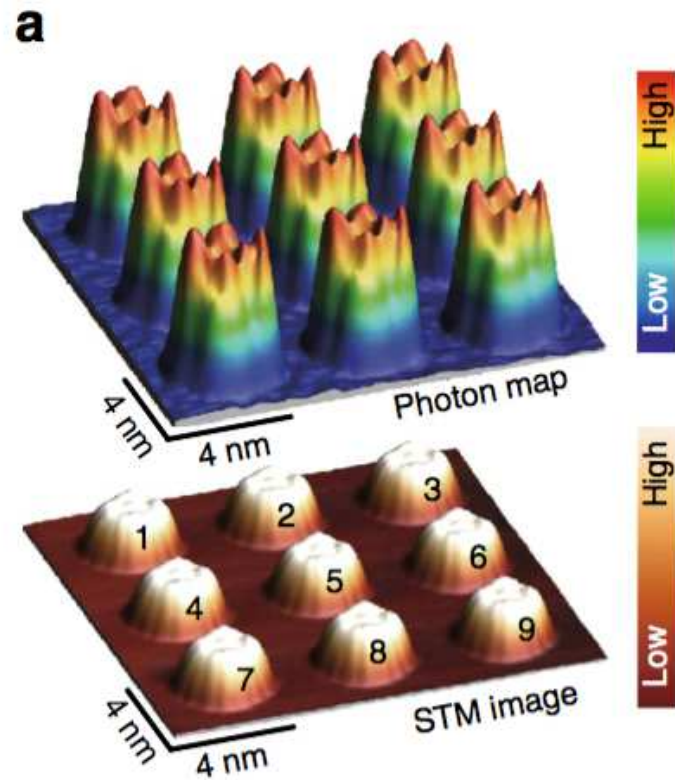


P. Merino *et al.* *Nature Comm.* 6, 8461 (2015).

**Single photon sources
from defects in C60
multilayers**

Combining spatial- and time-resolved fluorescence microscopy

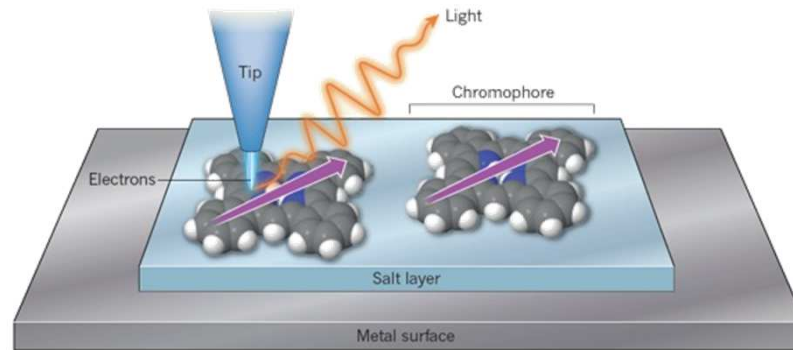
Single - photon sources from single molecule excited by STM



Time resolution

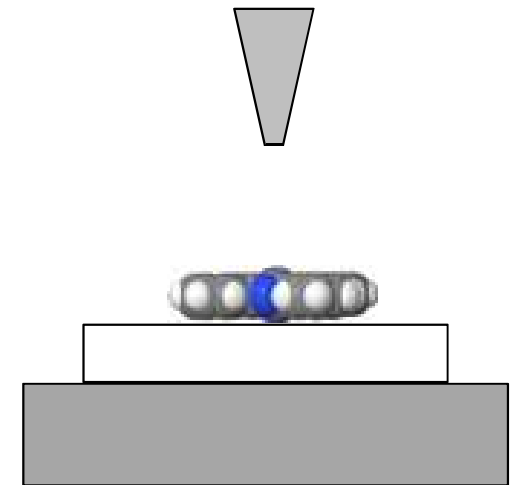
Spatial resolution

Spectral resolution



Combining spatial and time-resolved fluorescence microscopy

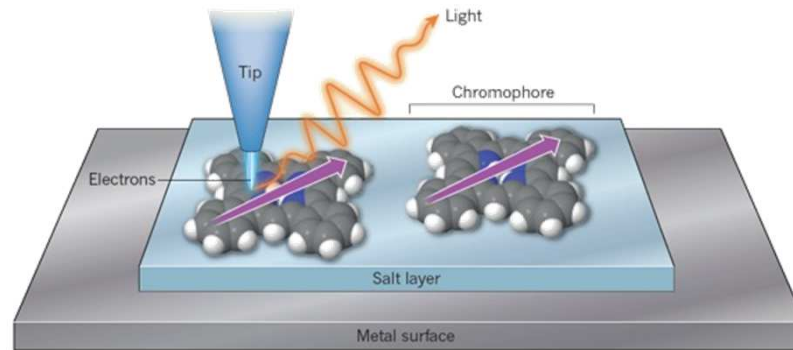
Can we also control the **redox state** of the probed molecule ?



Time resolution

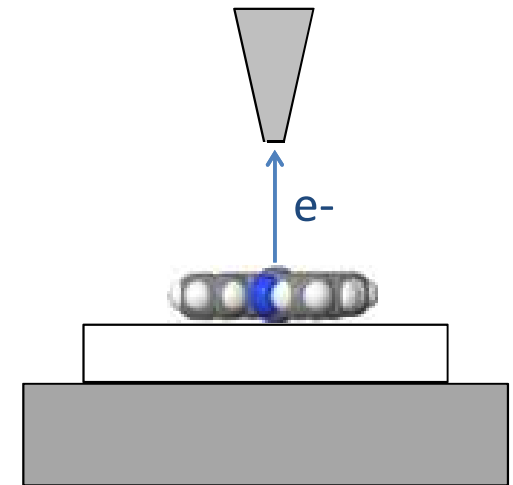
Spatial resolution

Spectral resolution



Combining spatial and time-resolved fluorescence microscopy

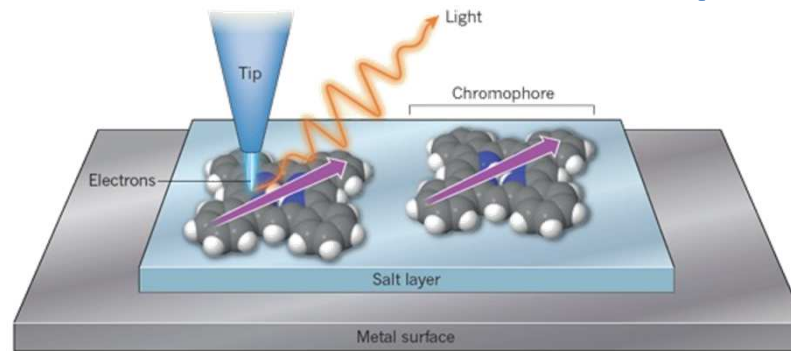
Can we also control the **redox state** of the probed molecule ?



Time resolution

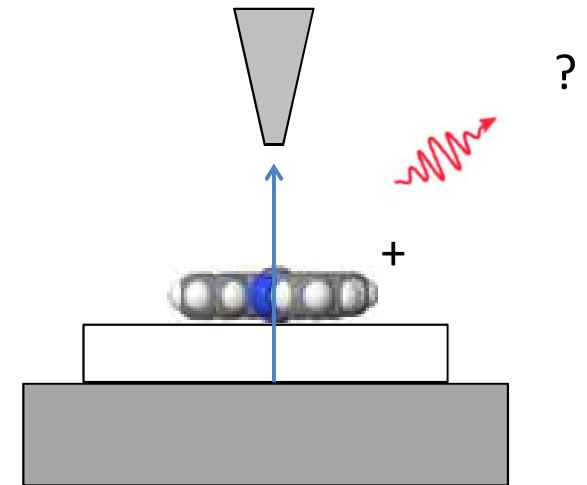
Spatial resolution

Spectral resolution

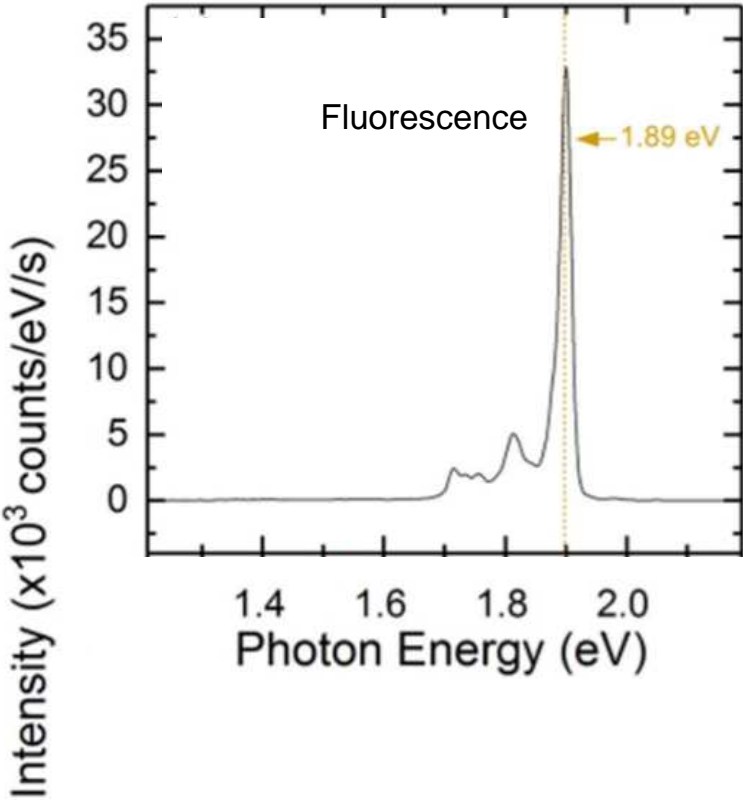
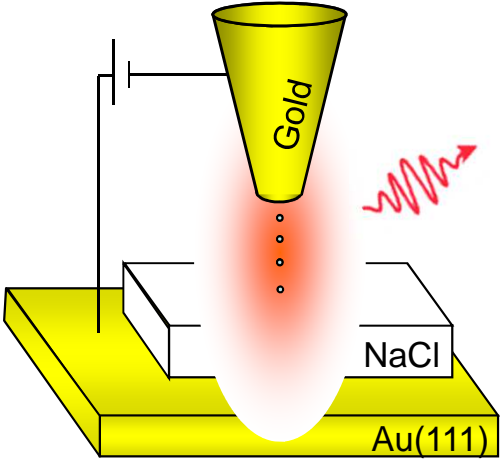
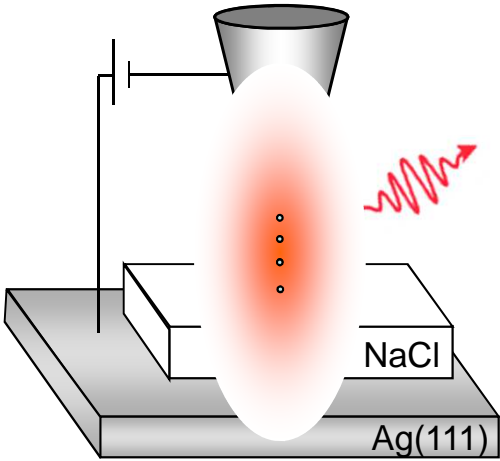


Combining spatial and time-resolved fluorescence microscopy

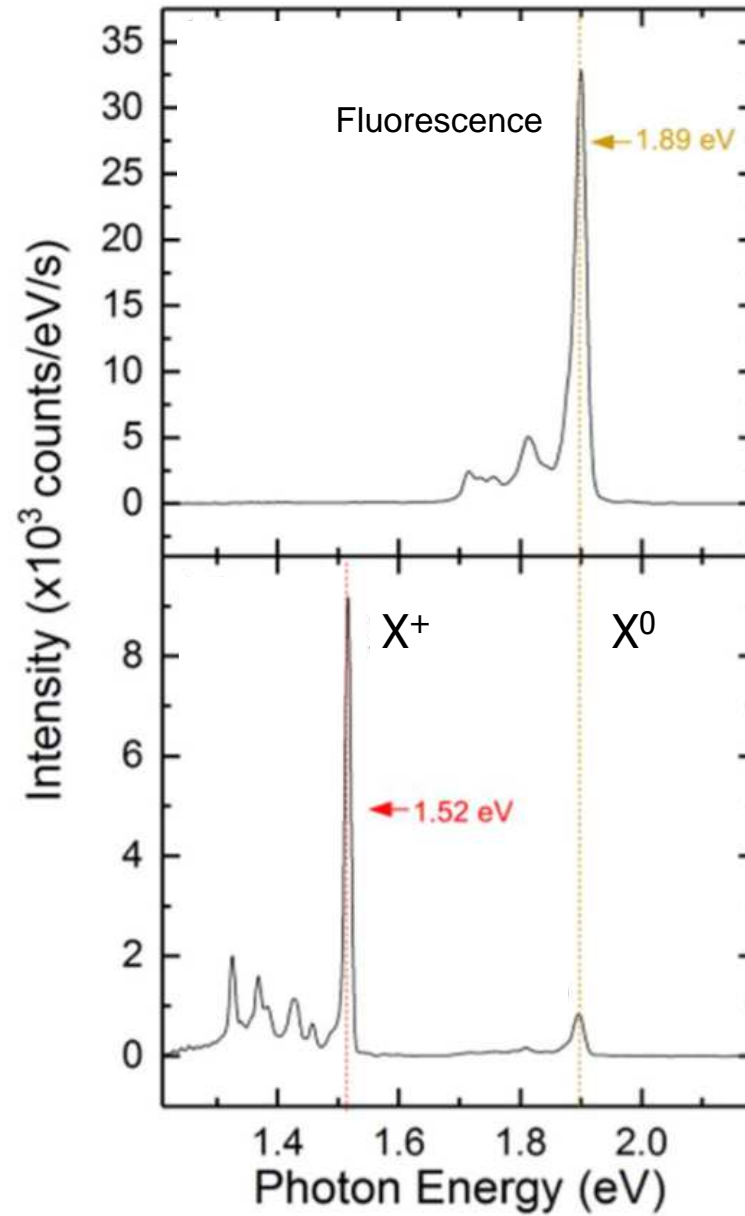
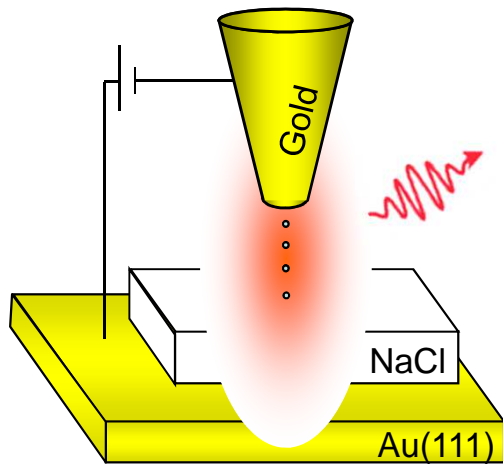
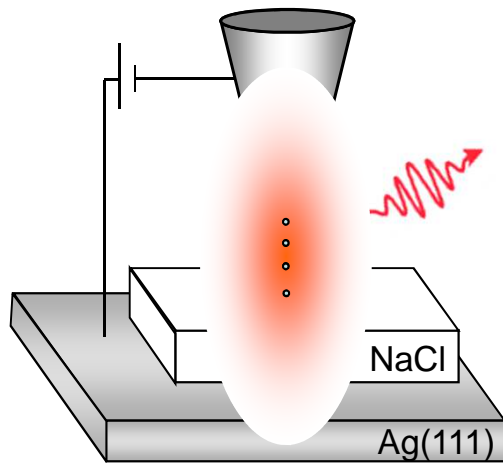
Can we also control the **redox state** of the probed molecule ?



Fluorescence of a charged molecule ?

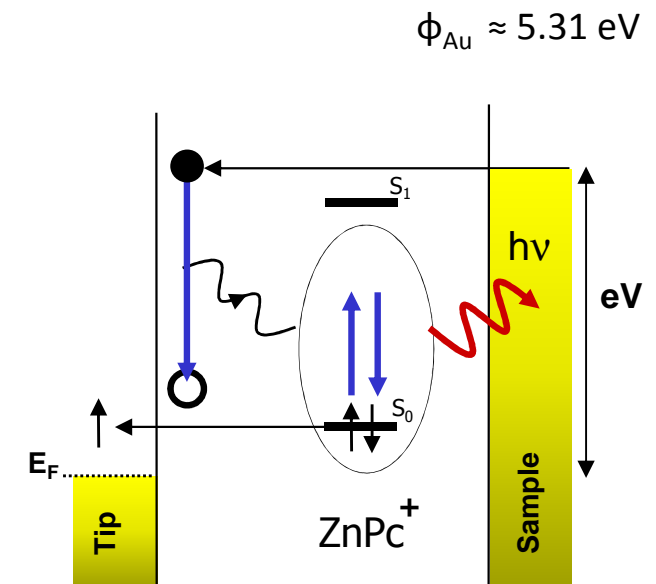


Fluorescence of a charged molecule ?



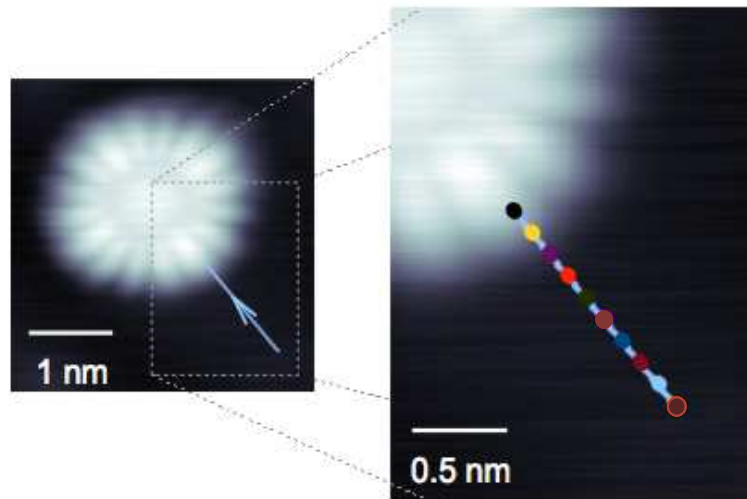
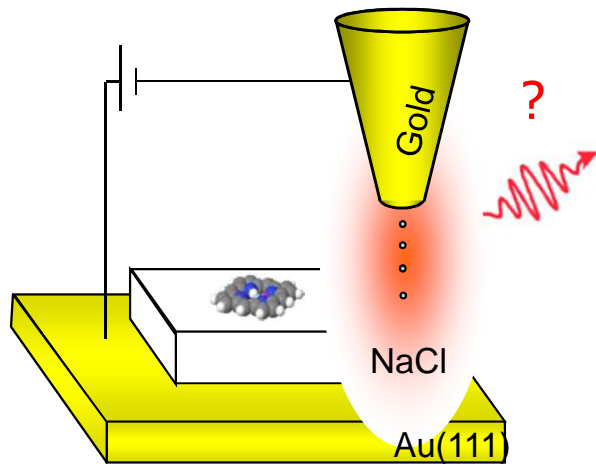
X^+ = radical cation of ZnPc

X^0 = ZnPc

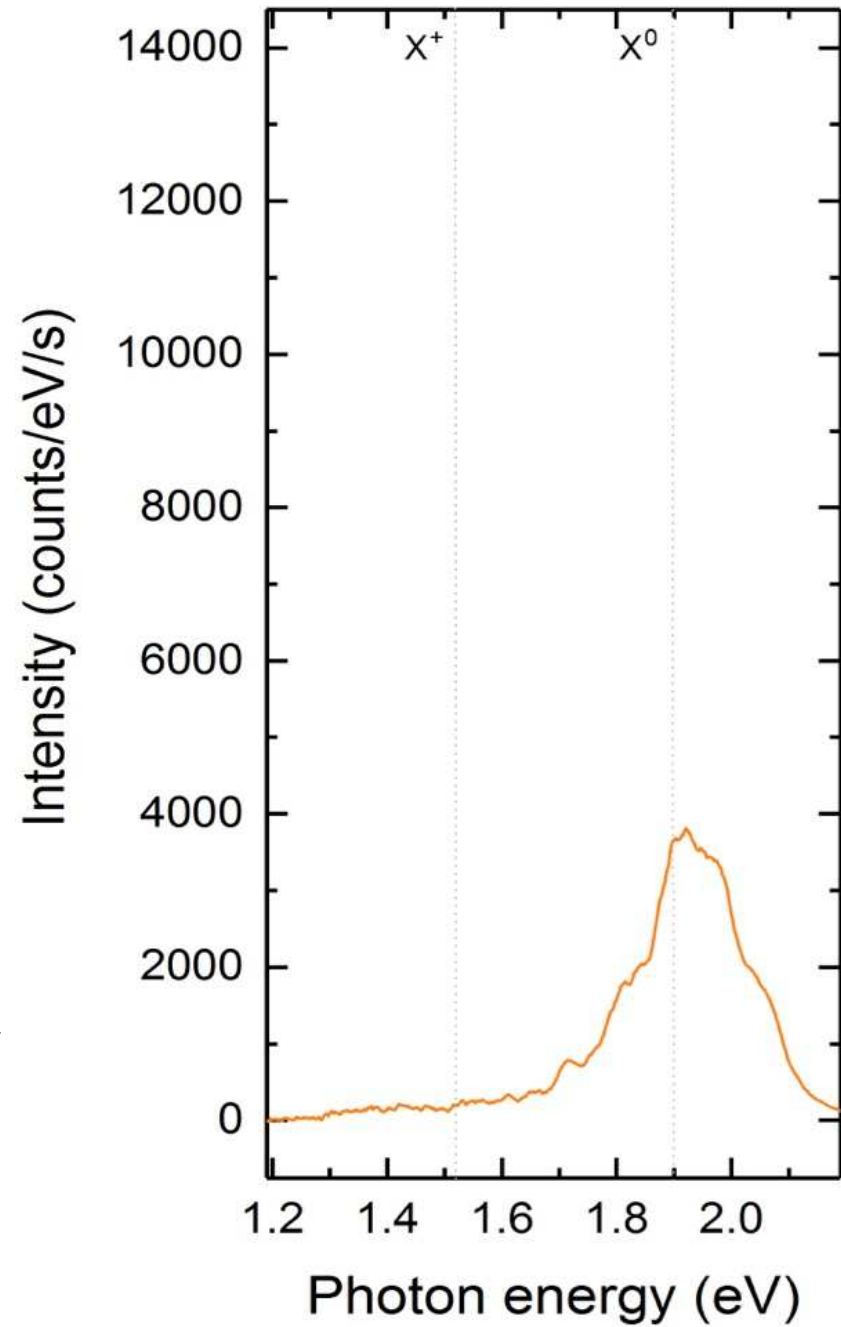
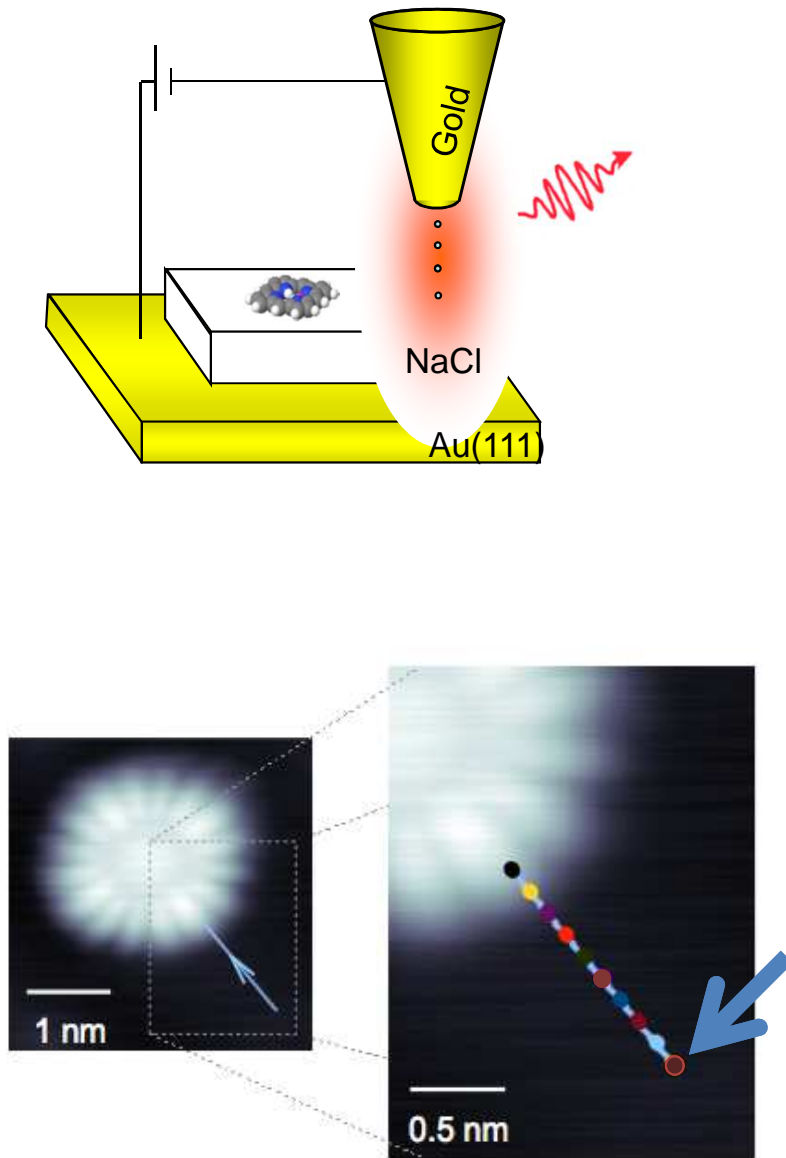


Fluorescence of a ZnPc radical cation

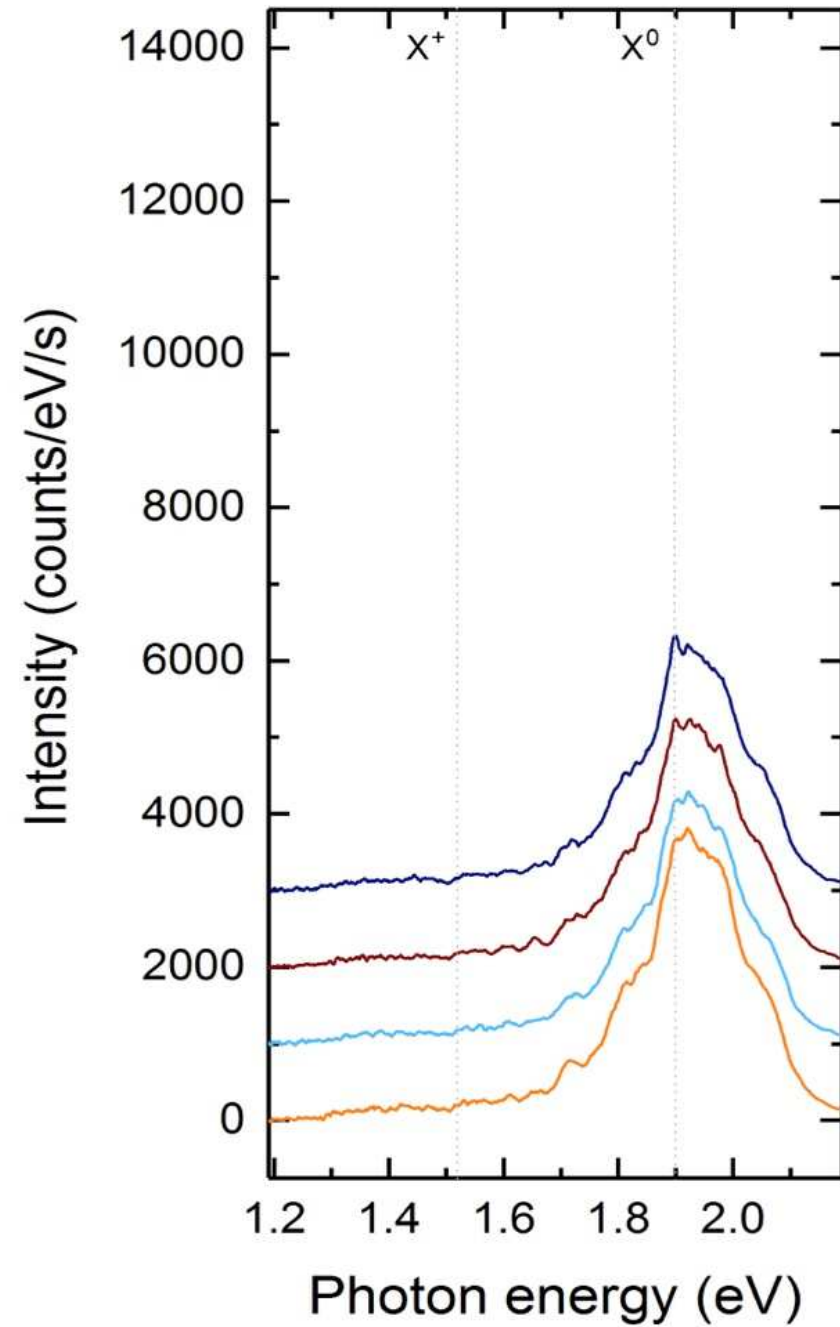
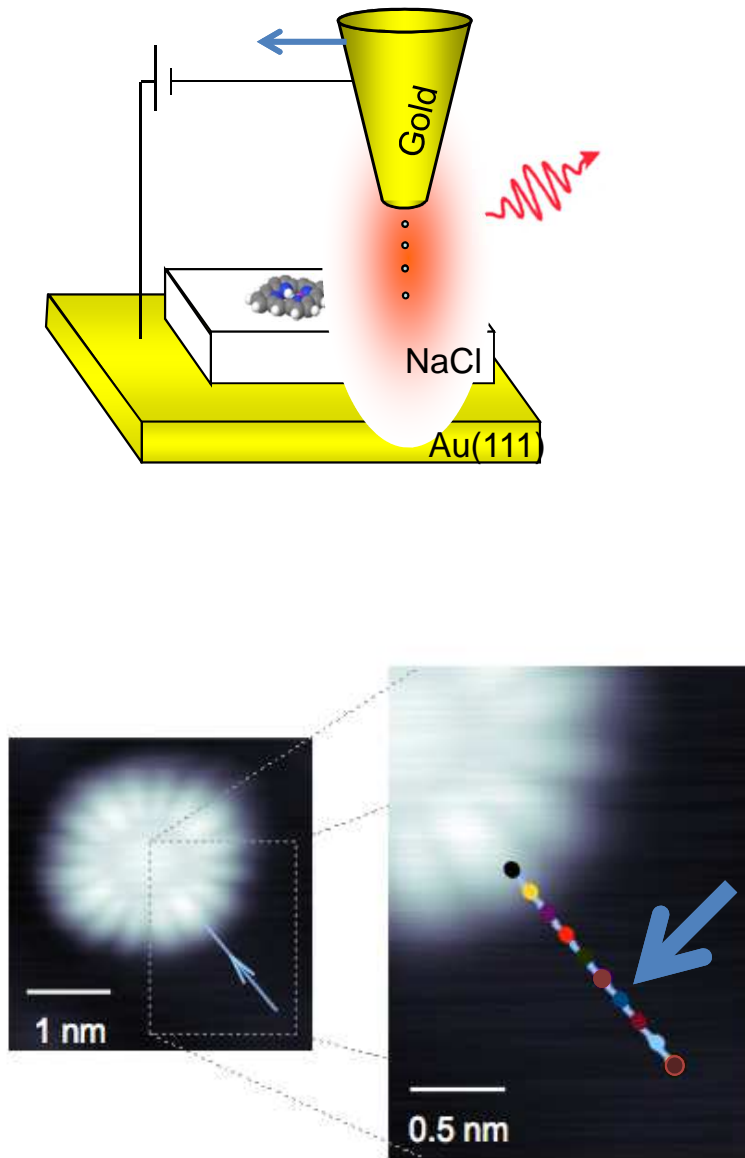
Fluorescence of a charged molecule ?



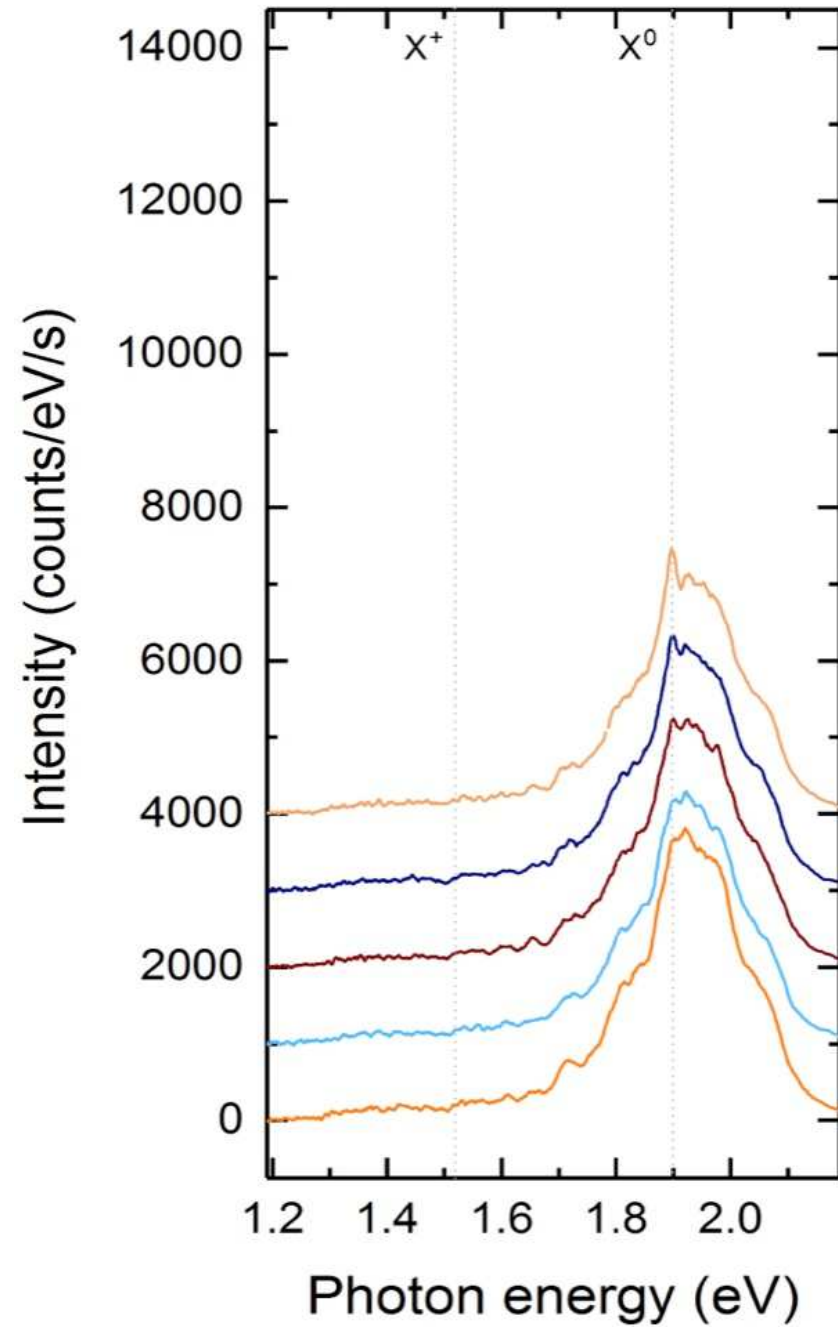
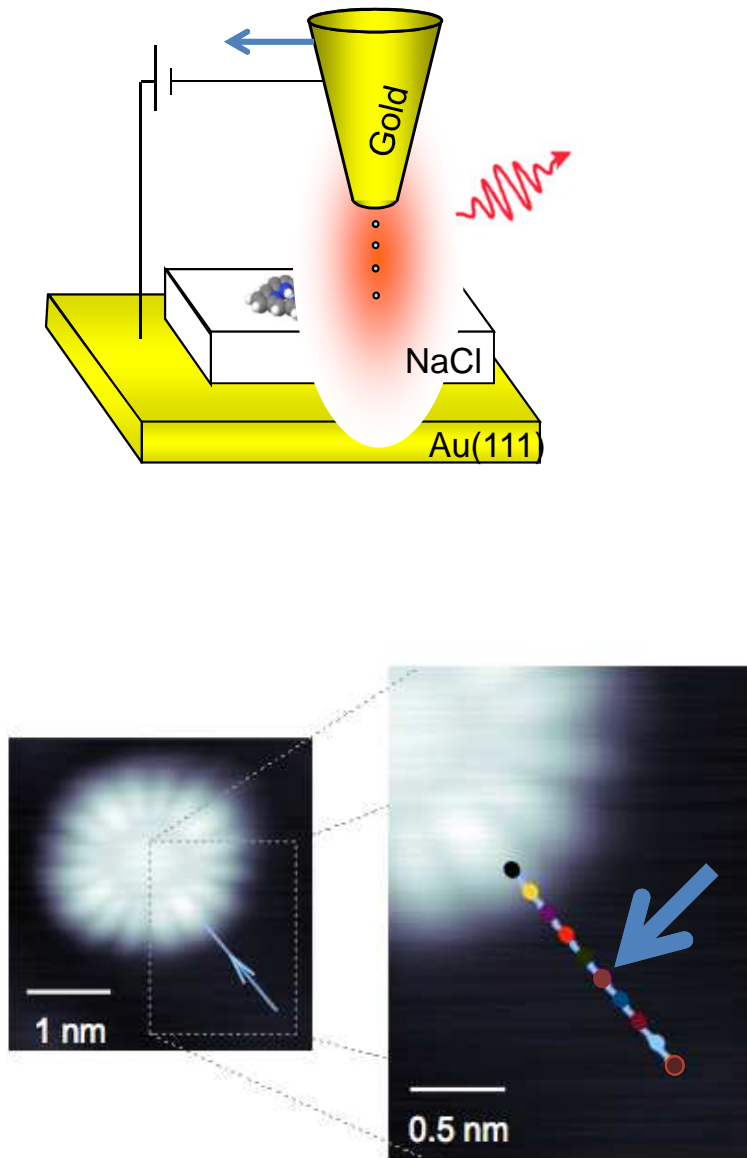
Fluorescence of a charged molecule ?



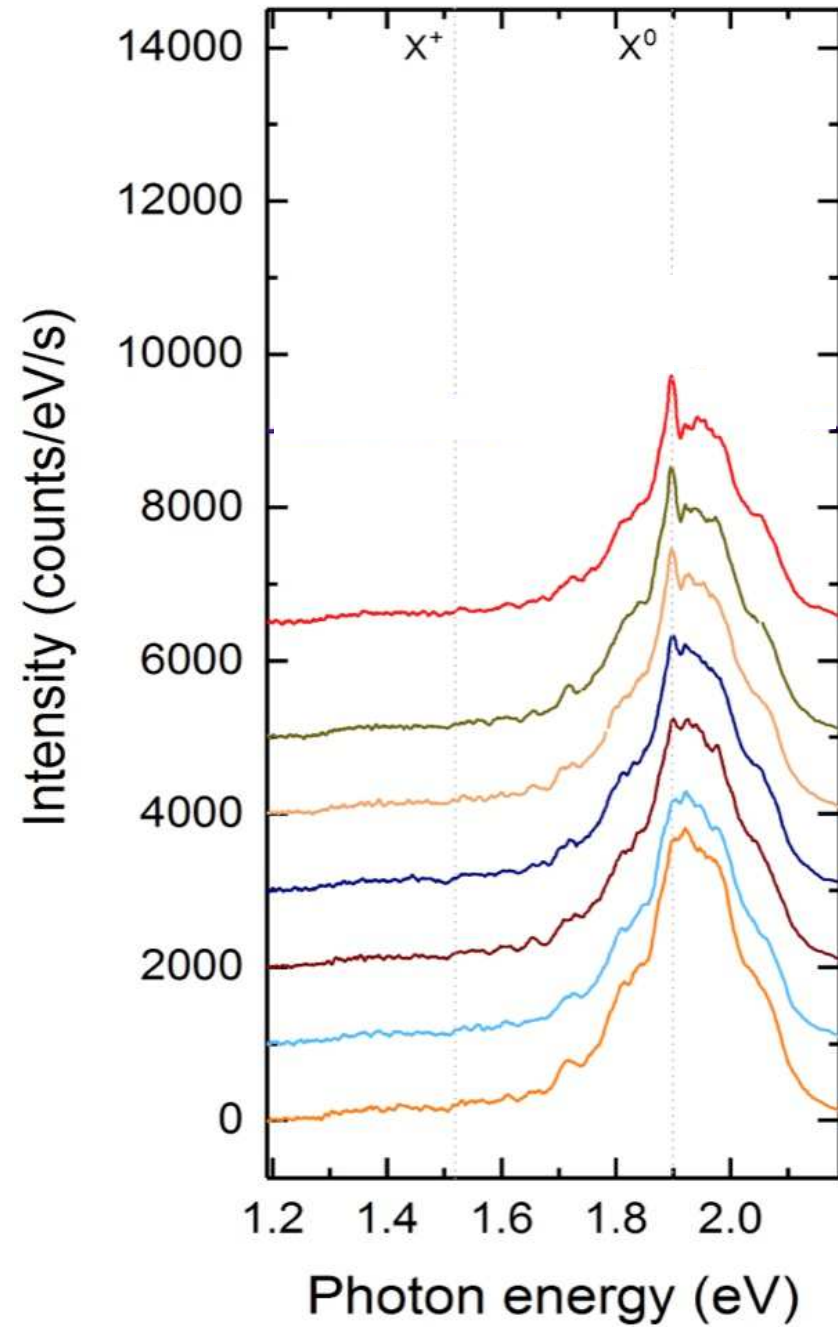
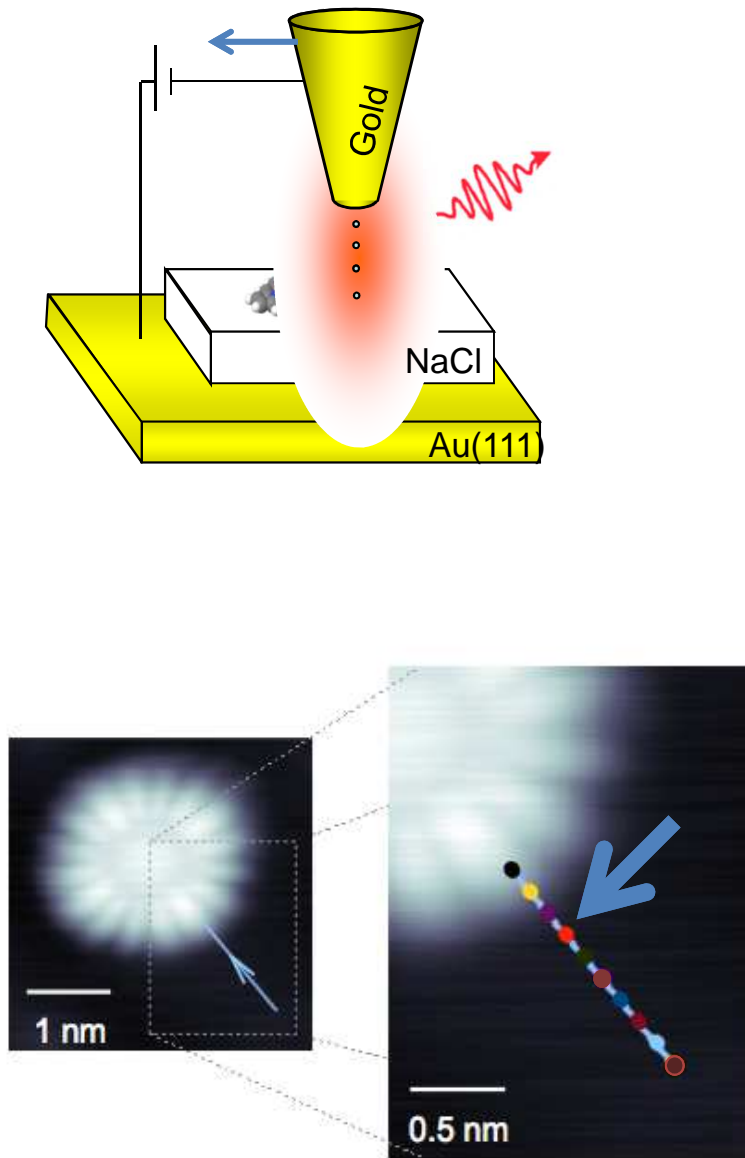
Fluorescence of a charged molecule ?



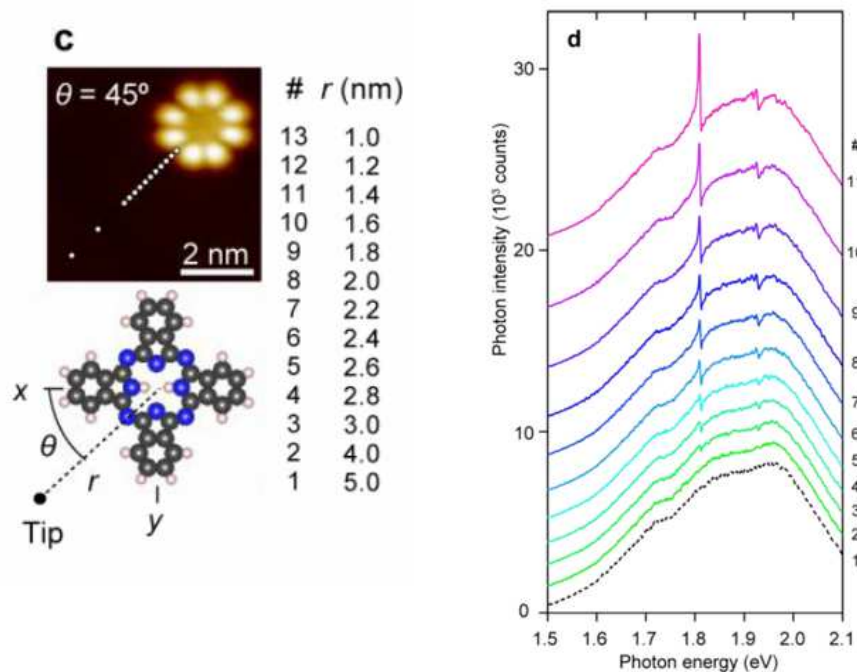
Fluorescence of a charged molecule ?



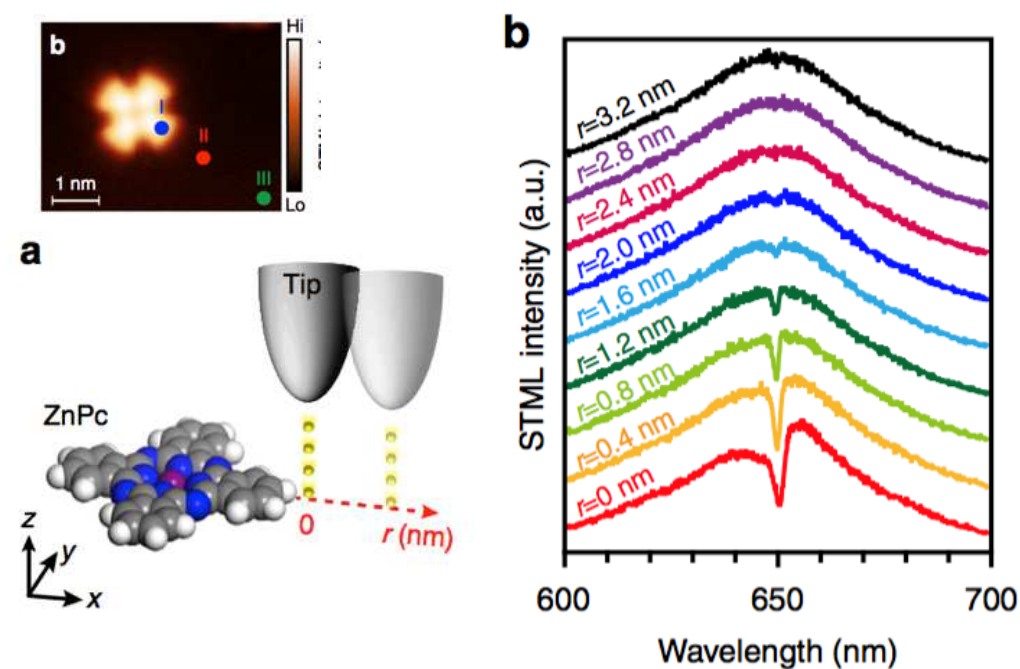
Fluorescence of a charged molecule ?



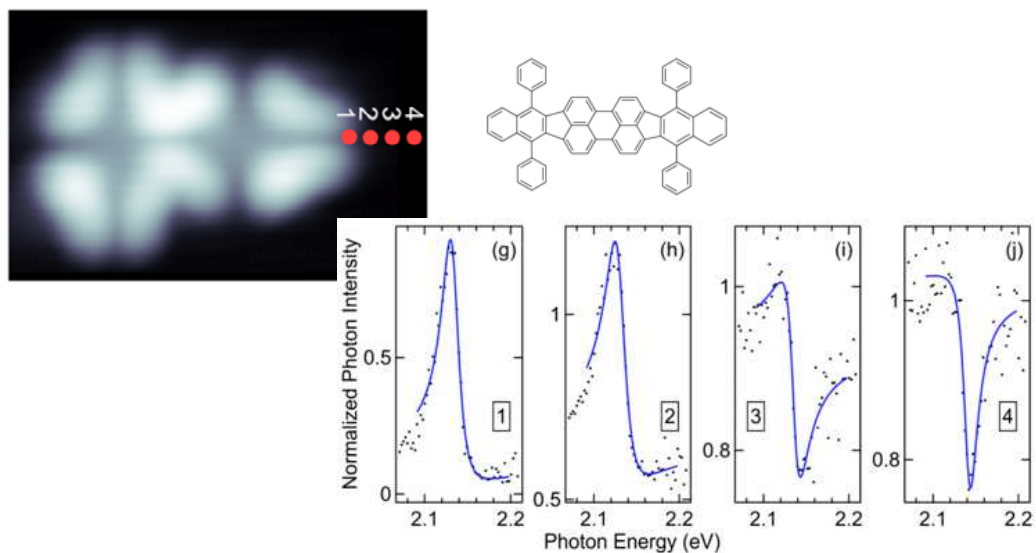
Control of the Exciton – Plasmon coupling at the atomic-scale



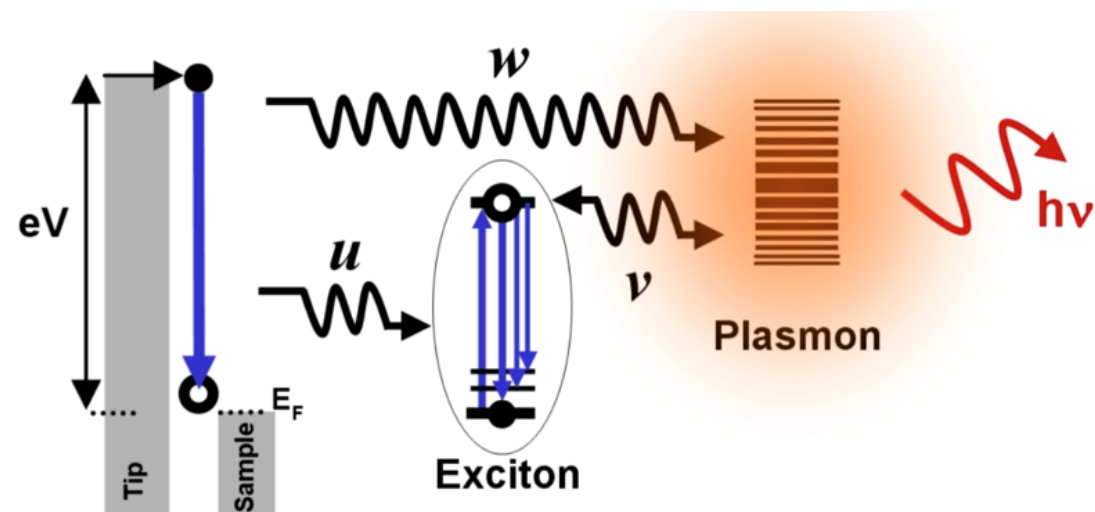
H. Imada *et al.* Phys. Rev. Lett. 119, 013901 (2017)



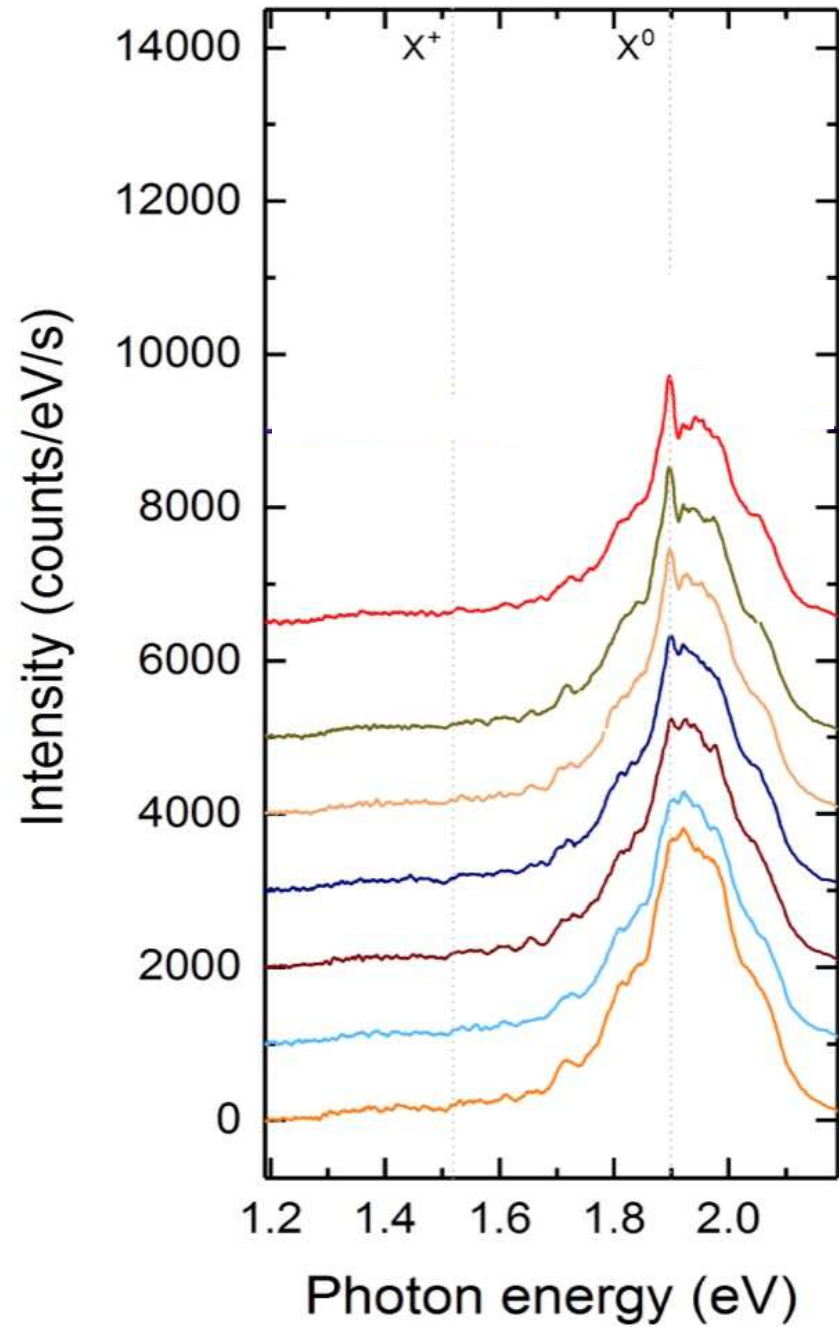
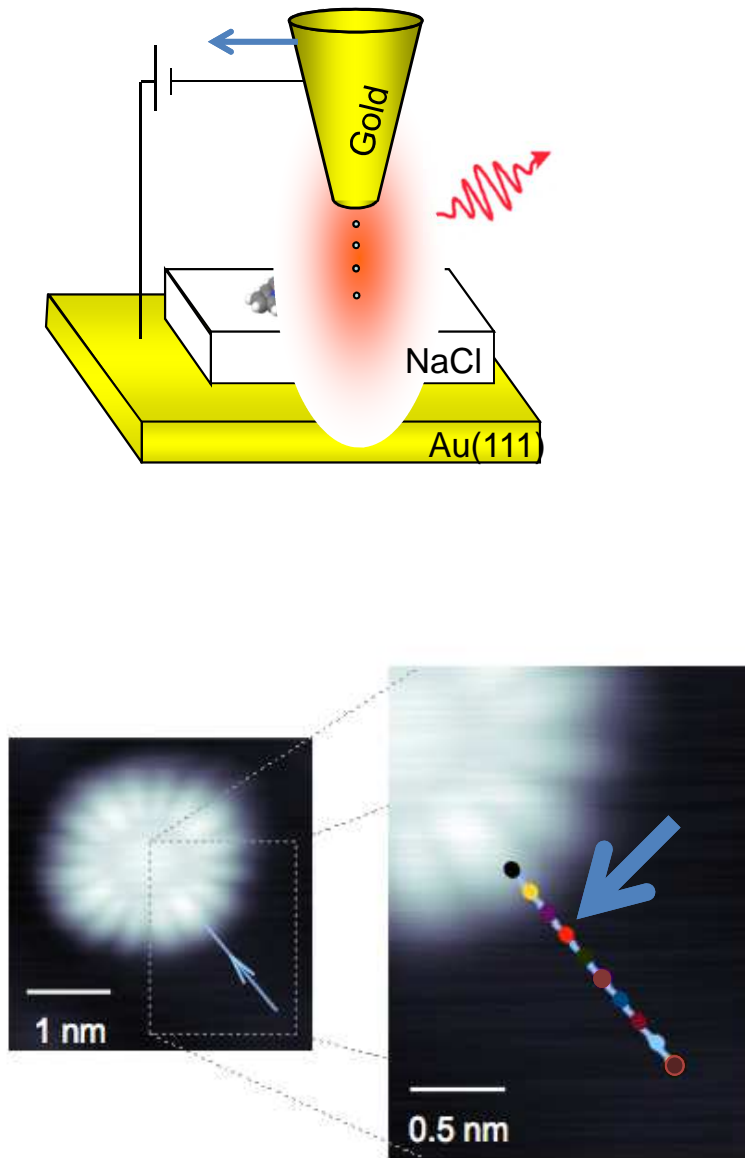
Y. Zhang *et al.* Nature Comm. 8, 15225 (2017)



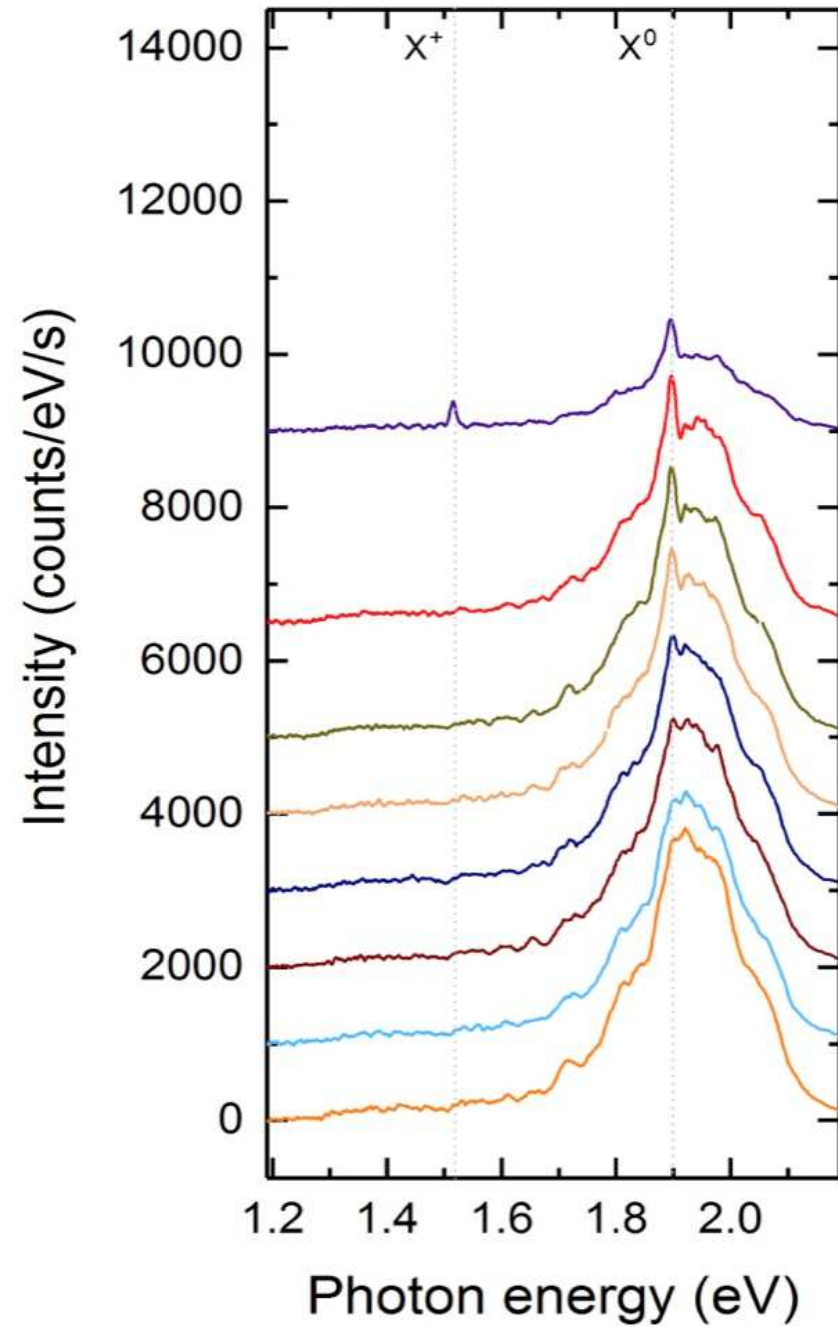
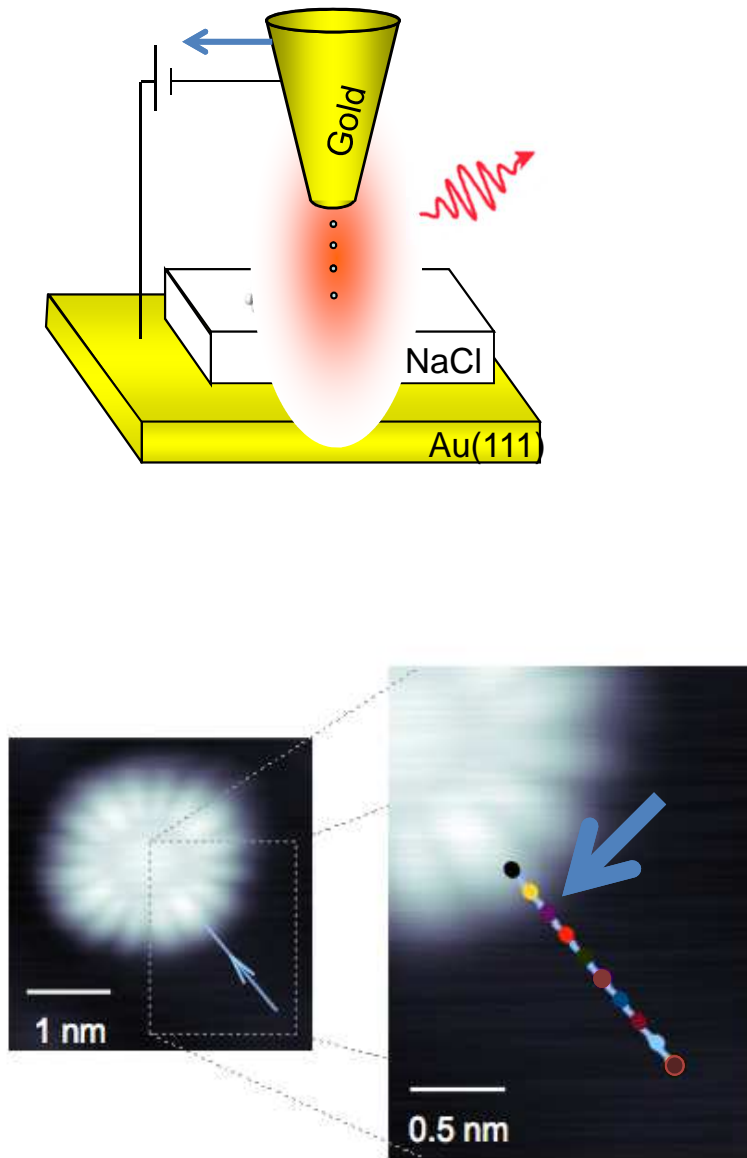
J. Kroeger *et al.* Nanoletters 18, 3407 (2018)



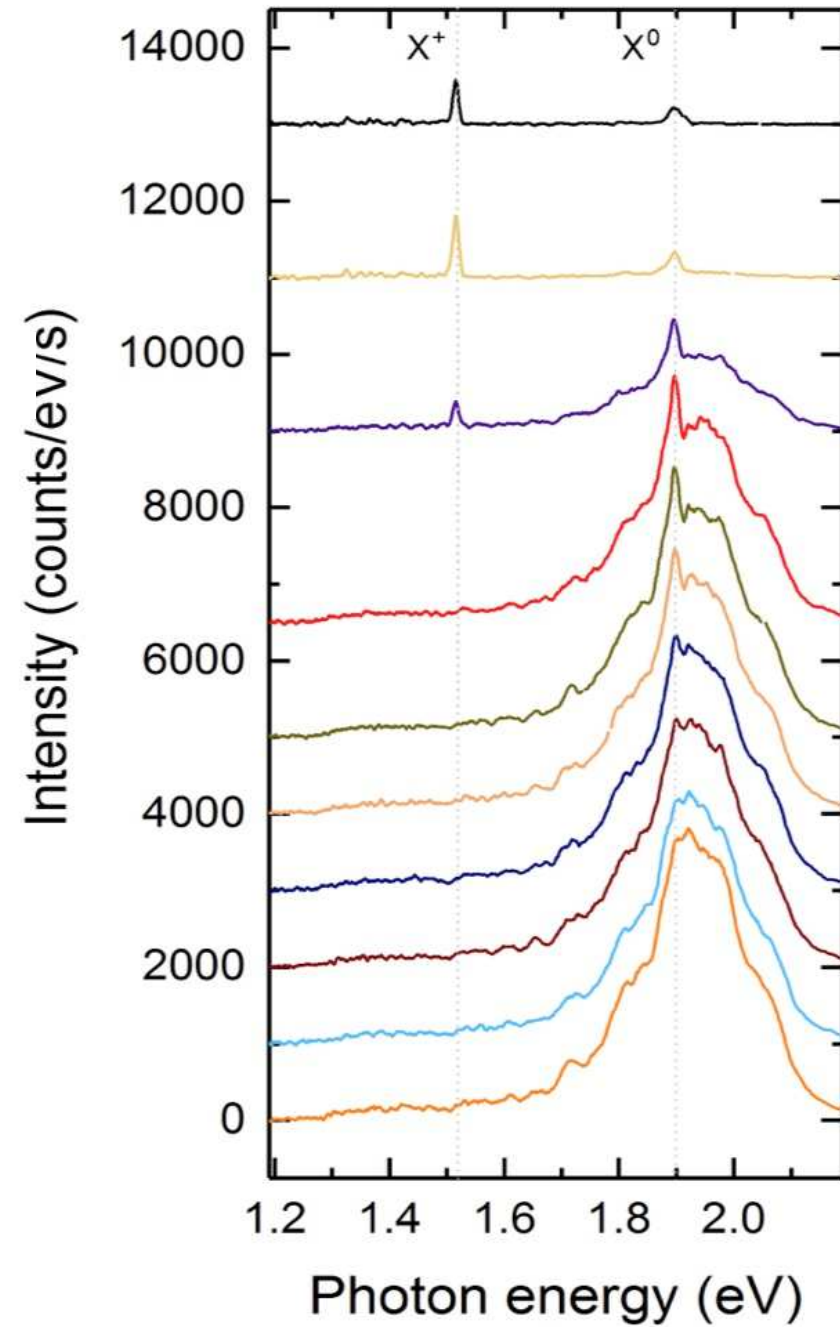
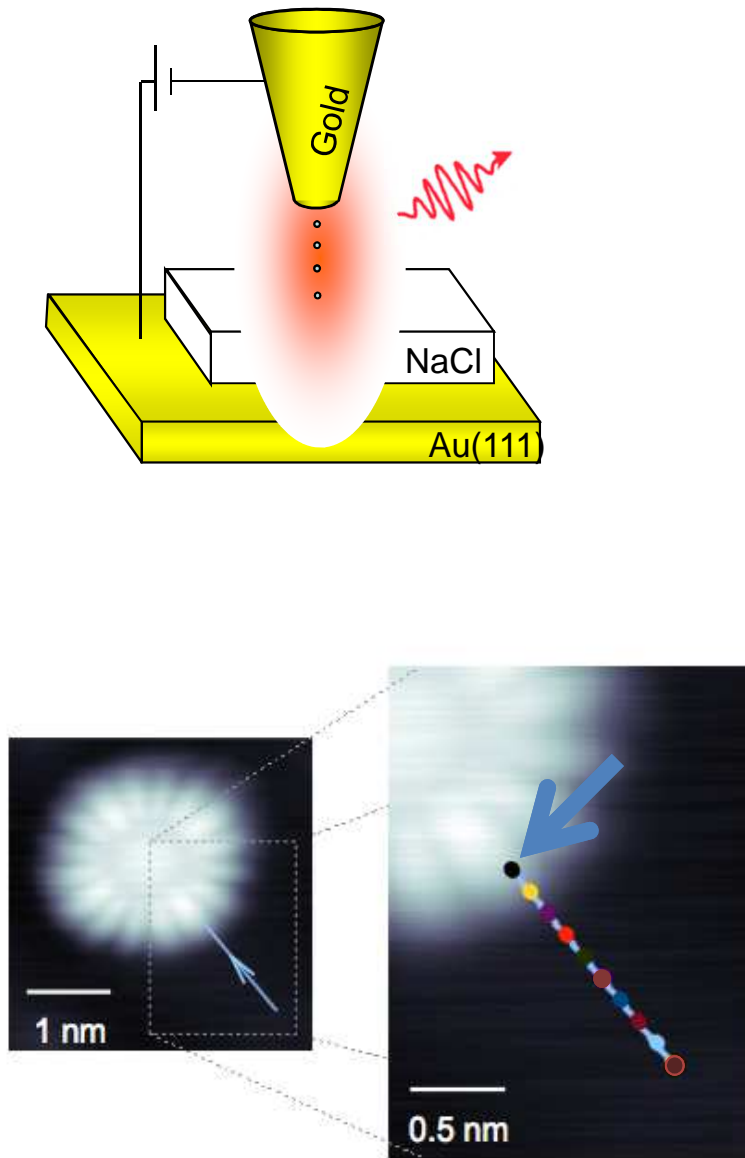
Fluorescence of a charged molecule ?

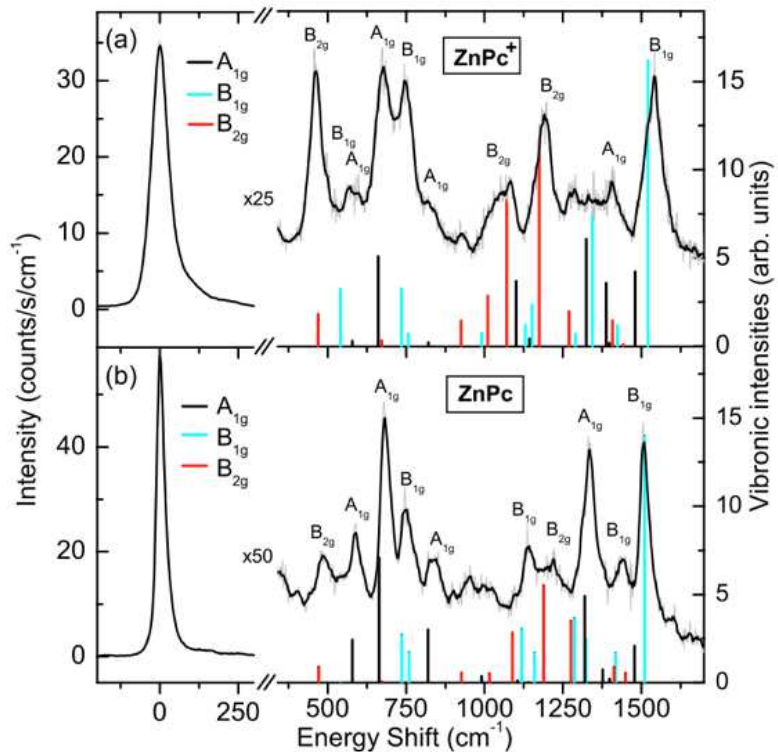


Fluorescence of a charged molecule ?

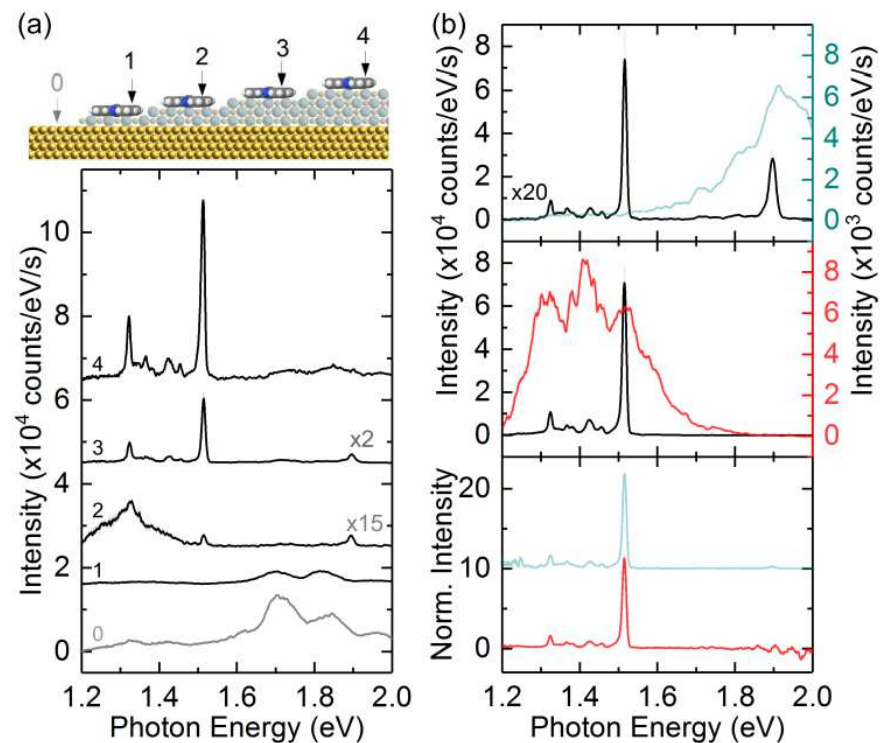


Fluorescence of a charged molecule ?

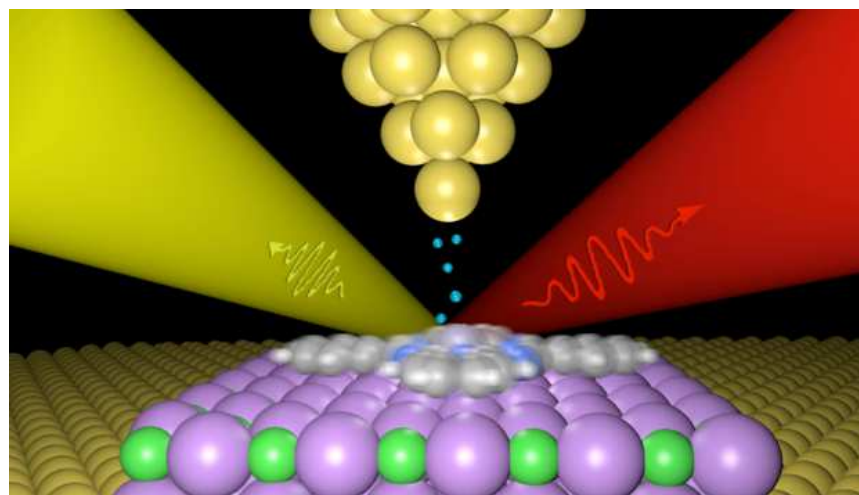




Vibronic fingerprint of the two redox states

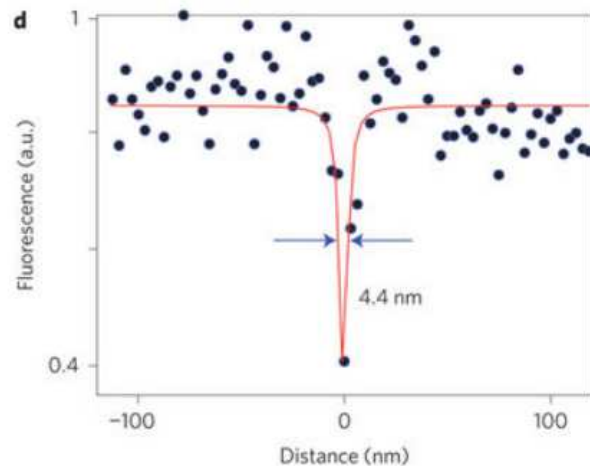
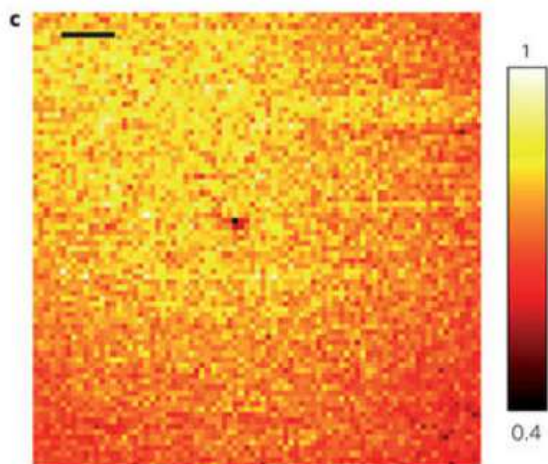


Controlling the respective emission intensity of the two redox states



Electrofluorochromism at the single-molecule level

Single molecule spectroscopy with atomic-scale resolution ?

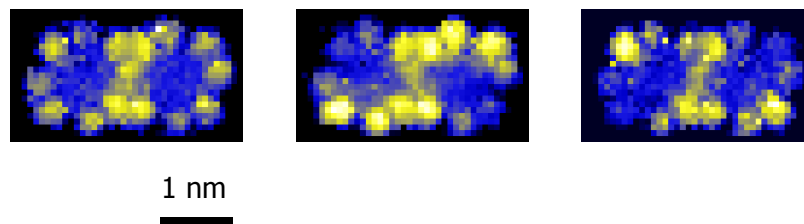
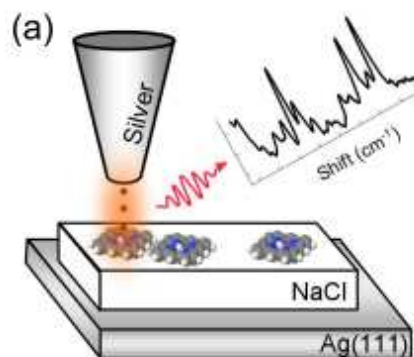


Nature Photonics 9, 658–662 (2015)

Super-resolved fluorescence microscopy:

best spatial resolution ~ 10 nm

Going beyond this limit
with STM-LE



What do we learn ?

- Optical spectroscopy with sub-molecular resolution
- Single-molecule electrofluorochromism
- Dipole-dipole interactions
- Atomic-scale physics of quantum sources

Supported by :



Thank You !!

