中国科学技术大学
University of Science and Technology of China

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Electrically driven single molecular fluorescence by STM

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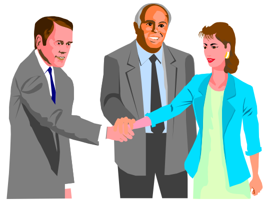
創寰宇學府
育天下英才
嚴濟慈 一九八八年五月 題

Acknowledgements



$$$: MOST, NSFC, CAS

USTC Hou Research Team

Profs. Jianguo Hou, Jinlong Yang, Yi Luo, Zhenyu Zhang, Bing Wang, Xiaoping Wang, Aidi Zhao, Yuan Liao

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Quantum control at the molecular scale

Single Molecular Electroluminescence (SMEL)

单分子电致发光

WHY?

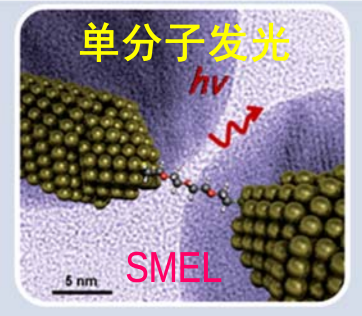
WHAT?

HOW?

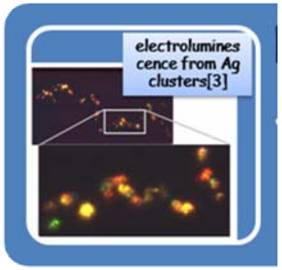
WHY Single Molecular Electroluminescence (SMEL)?

Energy Sciences
Interface optoelectronics
Solar energy,
Photocatalysis…

Technical Applications



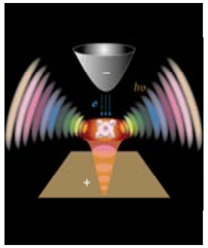
Nano-Optoelectronic Integration
Nanoplasmonics: Nano-LED,
Intrachip interconnect,
Switch, Coupler, Amplifier…



Nanoscale Point-Light Sources
Ultrahigh resolution imaging &
spectroscopy, Coherent control
in nano-devices, Spaser…

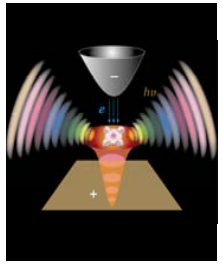
Quantum Light Sources
Single photon sources,
Entangled photon sources,
Quantum information processing

Fundamental Understanding



Electron → Photon: Optoelectronic Conversion at the nanoscale
Electron-hole pairs (Excitons): Formation, Transport, Decay
Quantum Control: Coupling and interconversion among electrons, excitons, plasmons, phonons, photons… Energy transfer…

Fundamental Understanding



Electron-Hole Pair (Exciton) ⇩ Formation, Transport, Decay

Optoelectronic Conversion at the nanoscale

Molecular Nanoplasmonics

电子→光子

声子

电子 → 等离激元 → 光子

激子

火

木 → 土 → 金

水

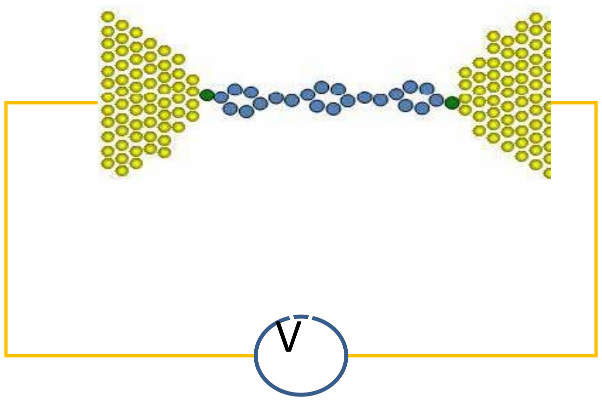
Coupling and Inter-conversion among quantum states

“五行“

Plasmon （“土“) mediated process!

SMEL Background

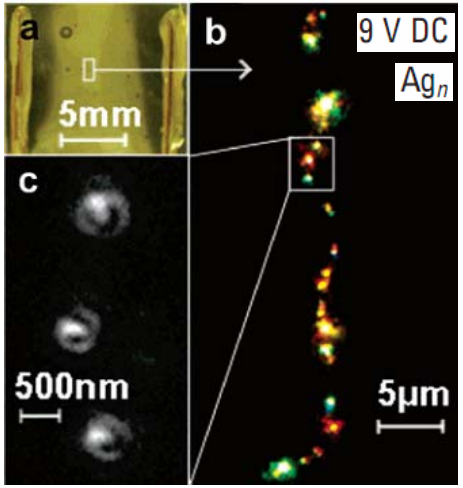
Approach 1:
Lateral device configuration



Route 1:
Ensemble Excitation

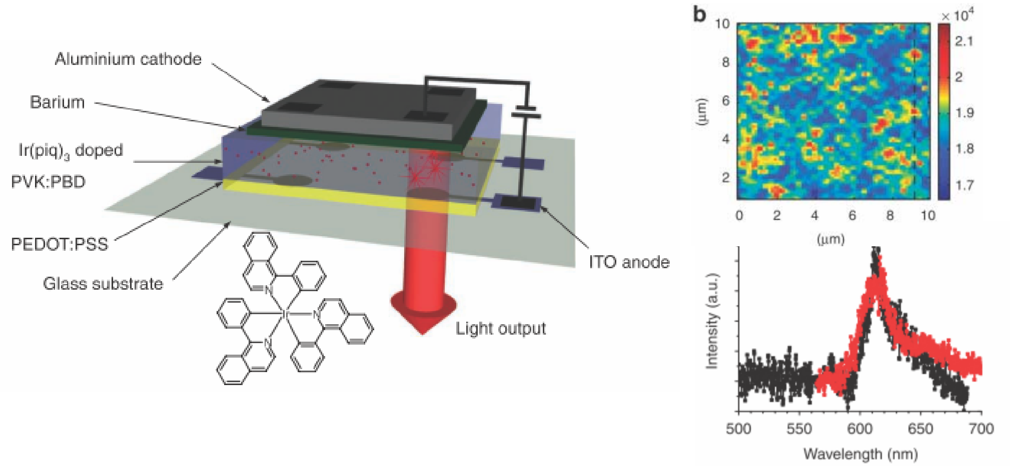
Instead of excitation on
a single molecule,
Ensemble excitation, but
selected emission detection
from individual spots

Single? Background Disturb?



**Dickson et al: Au, Ag clusters.
PNAS 2002, PRL 2004**

Emission feature: Size-dependent, hard to control

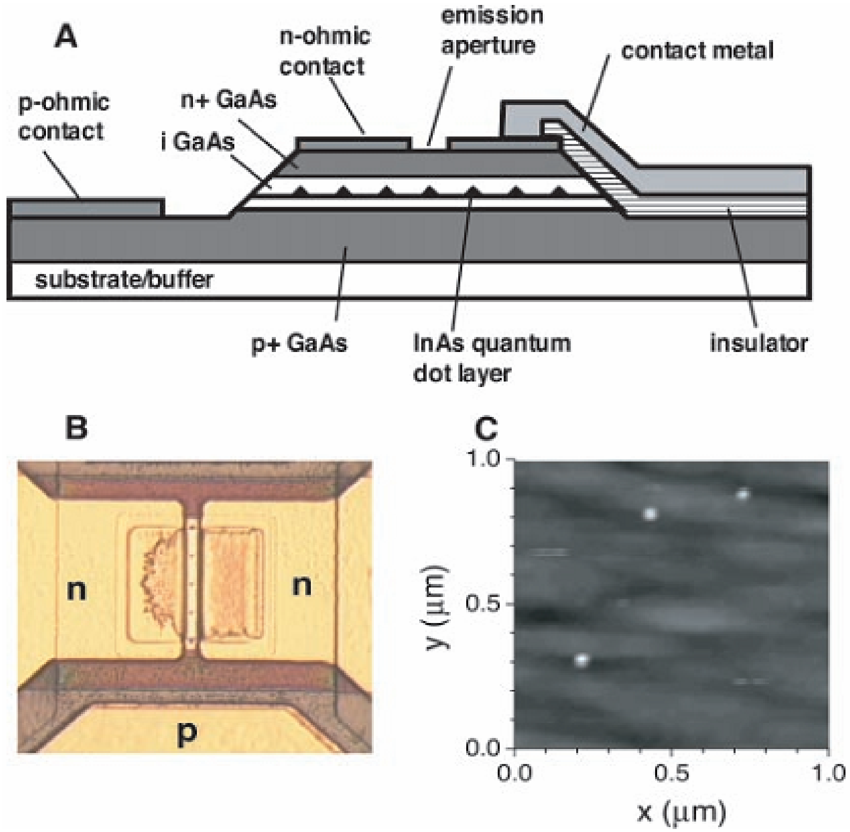


**Nothaft et al.: OLED of Ir(pig)3
Nature Commun.2012**

Single? Matrix Background?

Background

Single photon emission from a p-i-n diode containing a layer of InAs self-organized quantum dots



Single QD Electroluminescence

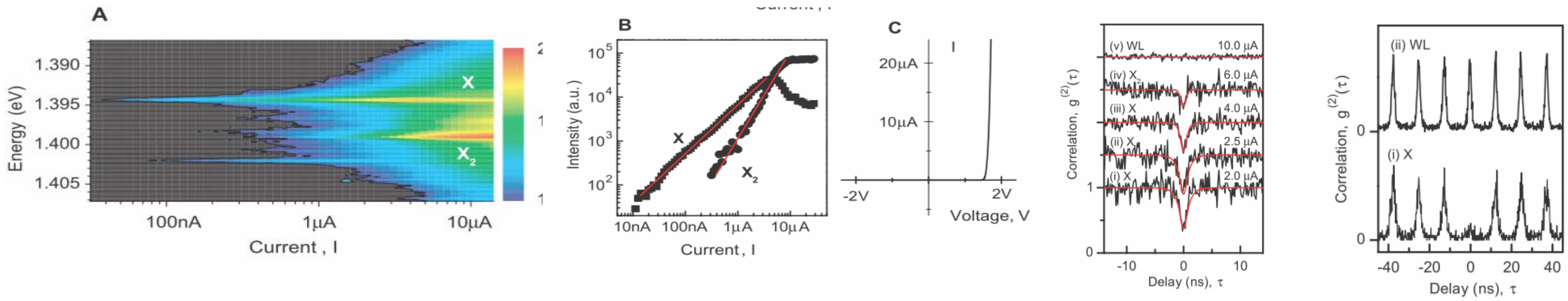
InAs QD: MBE

Sharp Emission!

Yuan, Z. L.; et al.
Science 2002, 295, 102–105

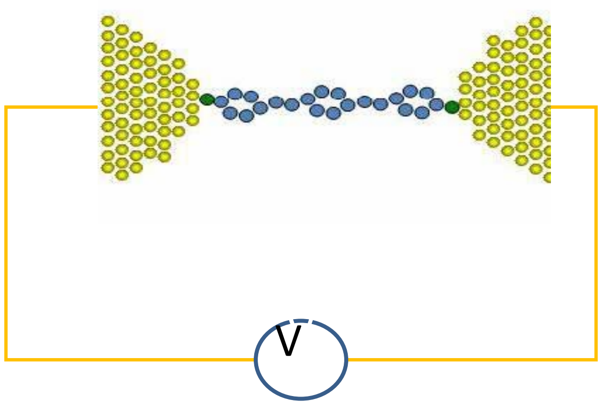
Emission: Size-dependent

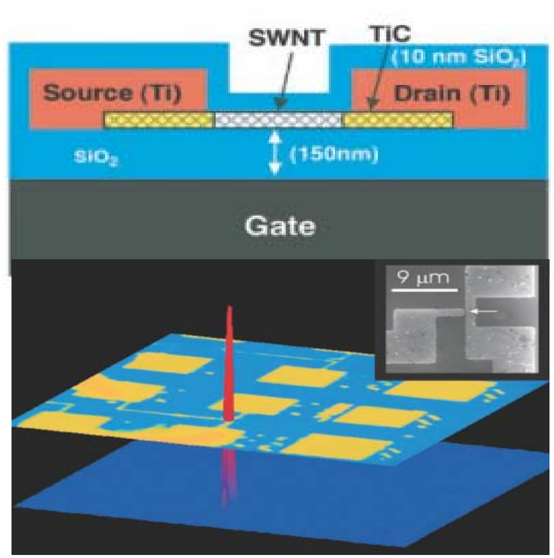
Hard to locate the individual spot



SMEL Background

Approach 1:
Lateral device configuration





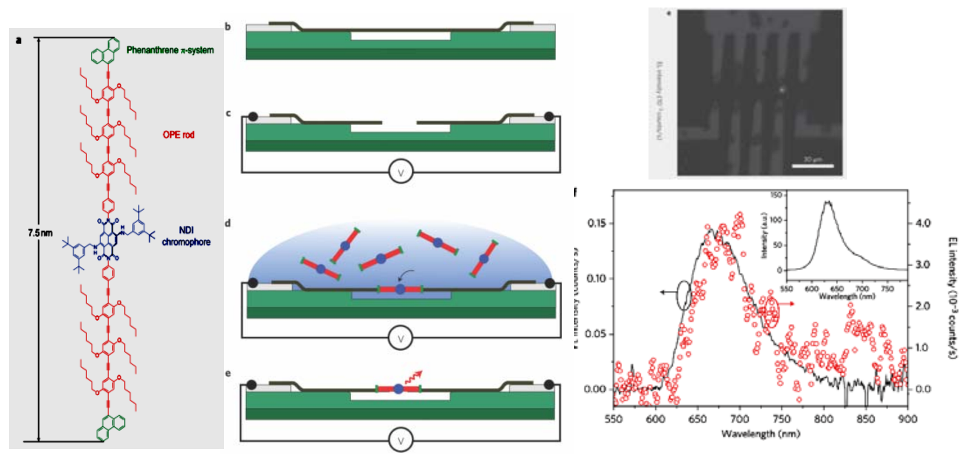
IBM: Avouris et al: Single CNT.
Science 2003, 2005

CNT-dependent? Nanoscale? Emission (HOMO-LUMO)?

Route 2:
Single-molecule excitation

Intensive effort
but
limited well-defined reports

HOMO-LUMO of Neutral Molecules?

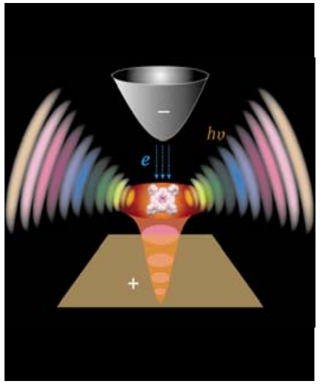


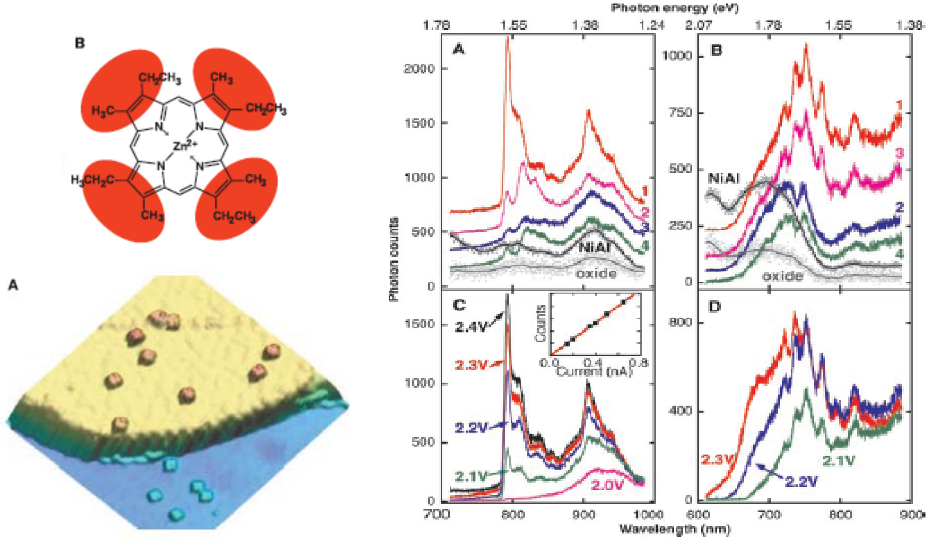
Marquardt et al.: Single Perylene?
Nature Nanotech. 2010

Single? EL: 1 hour: SNR? Red-shift (HOMO-LUMO)?

SMEL Background

Approach 2:
Vertical STM configuration



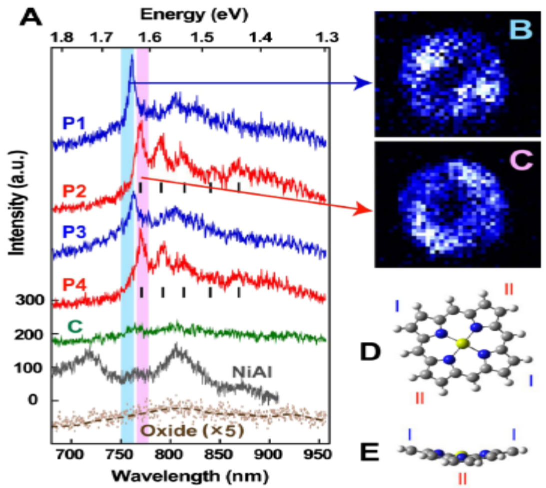


Wilson Ho et al (UC Irvine):
Zntiol/Al2O3/NiAl, Science 2003

Two Claims by Wilson Ho (UC Irvine)
Single-molecule electroluminescence

Science: Anionic, LUMO+1 → LUMO?
PRL: Neutral, HOMO-LUMO?

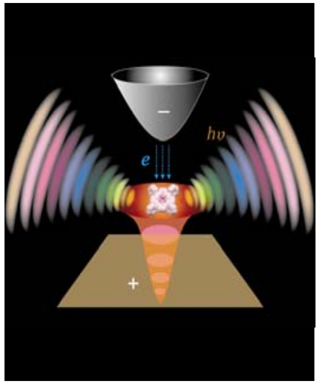
Problems: Site-dependent emission;
Don't agree with neutral PL data (HOMO-LUMO);
Bias-dependent energy cutoff.



Wilson Ho et al (UC Irvine):
MgP/Al2O3/NiAl, PRL 2010

SMEL Background

Approach 2:
Vertical STM configuration

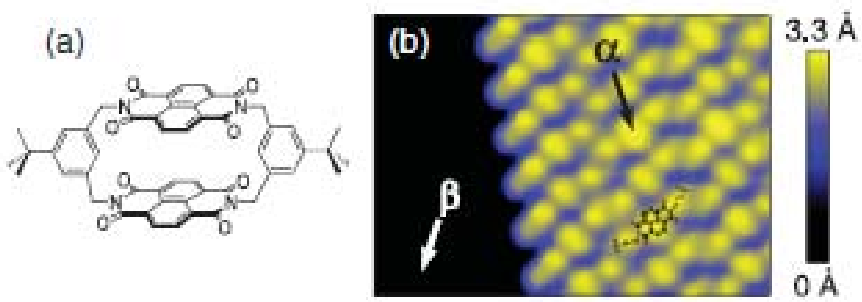


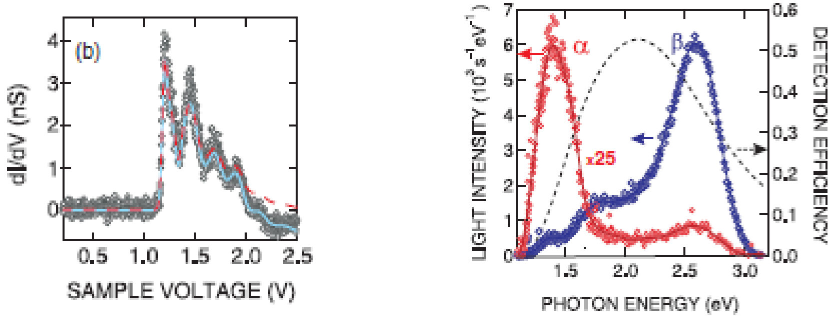
Richard Berndt et al (Kiel U): NDIC/Ag(111). PRB 2011.

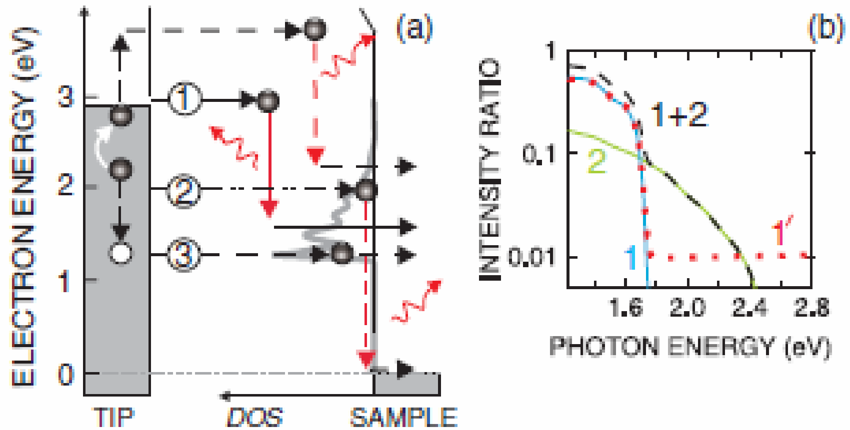
Plasmonic Emission!

with LDOS modulated by molecule electronic states,

Not intramolecular transition!







Single Molecular Electroluminescence (SMEL)

Status Summary

Intensive efforts, but still lack of
well-defined SMEL with clear molecular origin
that is consistent with standard PL data,

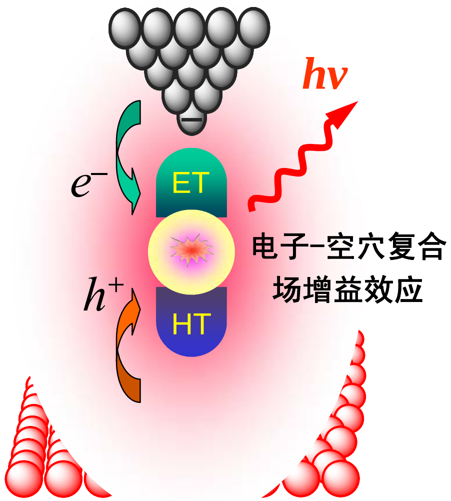
namely, fluorescence originating from
the intramolecular HOMO-LUMO transition
of neutral organic molecules.

Reasons:

Fluorescence quenching
&
Lack of in-depth understanding on the mechanism

Single Molecular Electroluminescence by STM

STM-induced luminescence: *Beyond imaging and manipulation*



原子分辨
STM
空间、能量

单光子计数
Optical Detectors
光谱、寿命

空间、能量、时间
高分辨

Tunneling electrons!

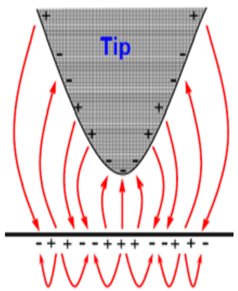
Highly localized excitation source!

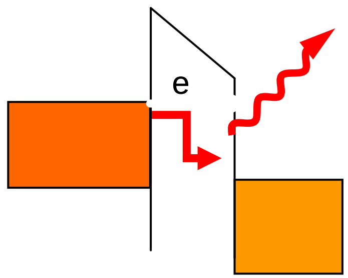
+

Nanotip!

Nanoantenna effect & Controlled nanoscale gap spacing!

Strong plasmonic confinement !
Intense field enhancement (10^4–10^6)!





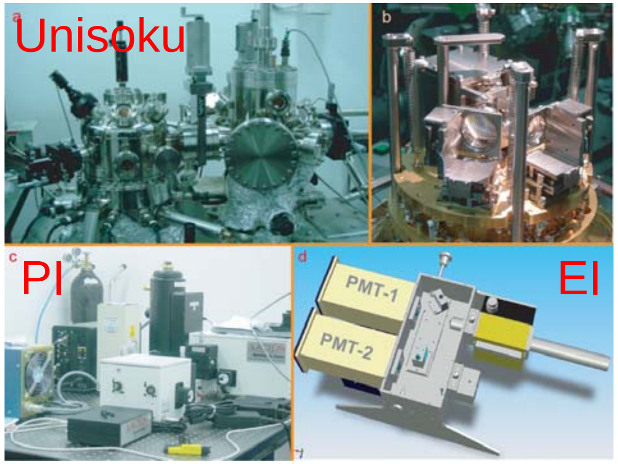
Electrodynamic, G | **Quant. Mech., j**

New optoelectronic effect?
New mechanism and understanding?

Inelastic tunneling (IET)

$$\frac{d^2P}{d\Omega d(\hbar\omega)} = \frac{\omega^2}{8\pi^2\varepsilon_0 c^3}\sum_{i,f}\left|\int d^3r' G(\theta,\vec{r}',\omega)\,\vec{j}_{if}(\vec{r}',\omega)\right|^2 \delta(E_i - E_f - \hbar\omega)$$

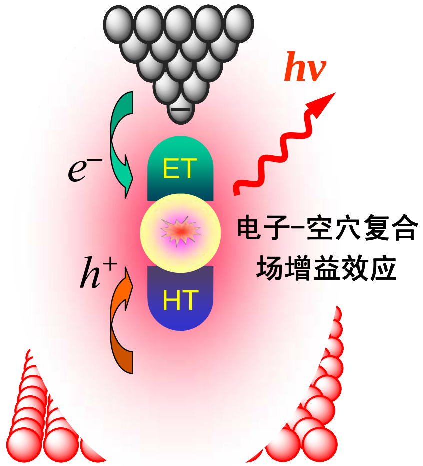
设备研制：低温、超高真空STM和光学检测相结合的联用系统



STM 分辨率:
X ,Y 方向 ~0.1 nm
Z 方向 ~0.01 nm
能量分辨率: 5 meV

光谱分辨率: 0.2 nm
寿命分辨率: 8 ps
光子图分辨率: <1 nm

光子收集效率: 11%
光子检测灵敏度: 单光子



原子分辨
STM
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单光子计数
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光谱、寿命

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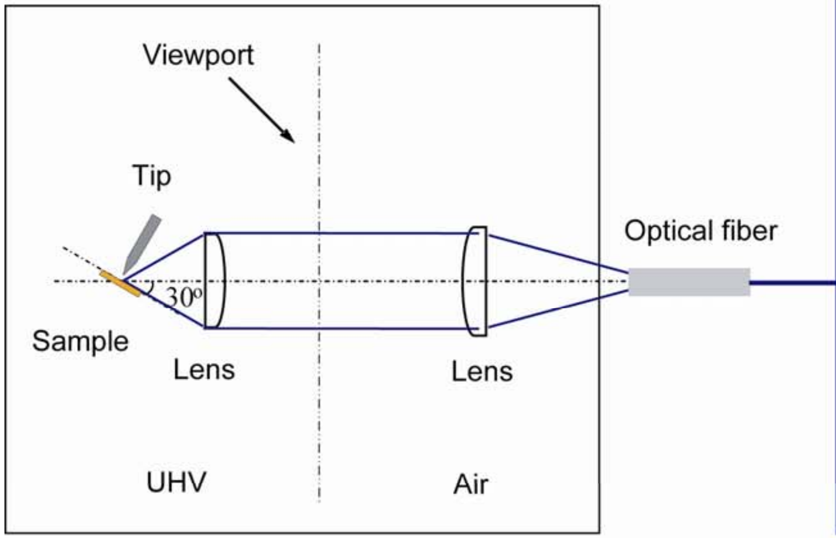
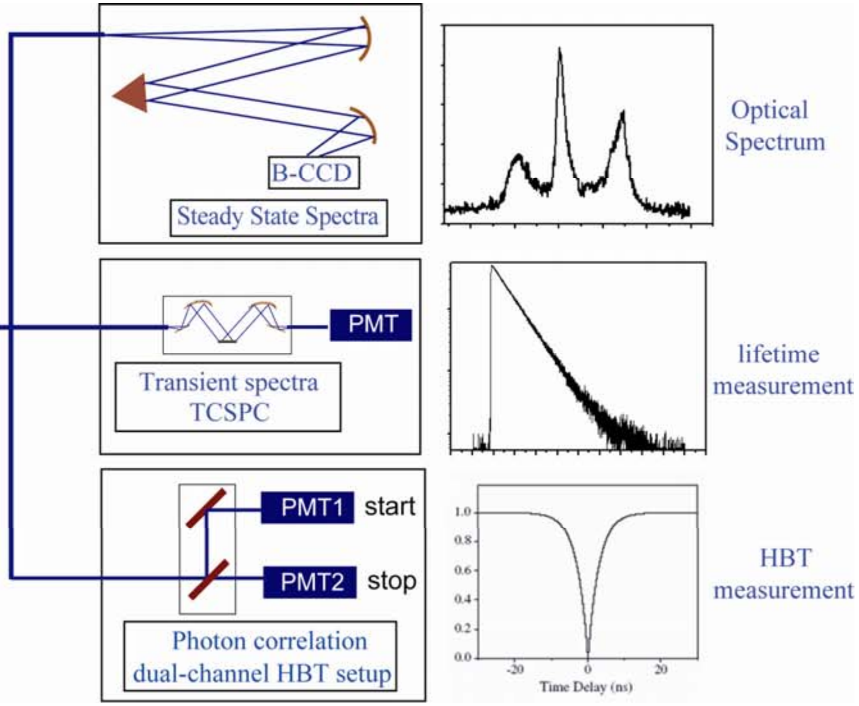
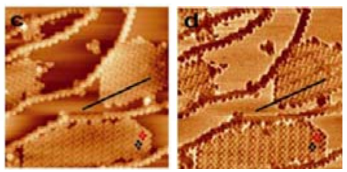


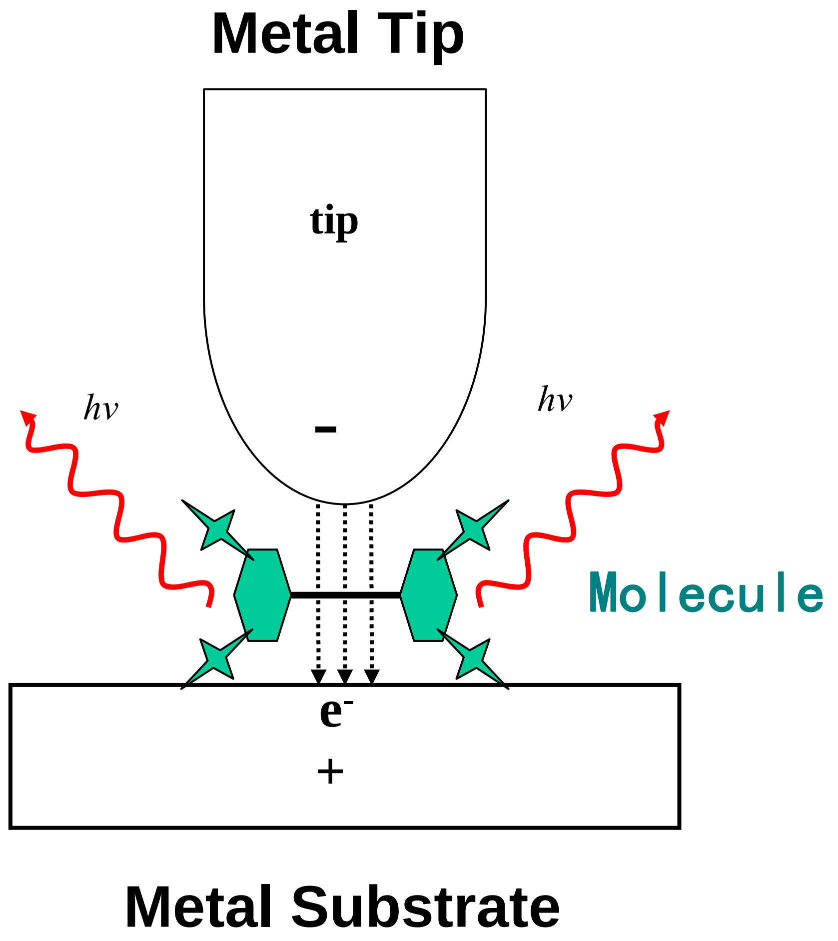


形貌图



光子图

突破
衍射极限！



For a single molecule directly adsorbed on the metal surface，

Any emission？ What kind of emission？

Photon mapping with sub-molecular resolution

Beyond the diffraction limit

STM Topograph

Photon Map

Resolution: ~1 nm

Beating diffraction limit?

Raleigh criteria:
R~ λ/2NA

Edge-Enhanced Optical Response

Chen *et al.*, PRL under review.

Photon mapping with sub-molecular resolution

Beyond the diffraction limit

Edge-Enhanced
Optical Response

Plasmonic emission
Molecular fluorescence quenched

Edge-Enhanced Optical Response of Molecular Islands

Probed by Nanoscale Photon Mapping of Tip Induced Plasmonic Emission

发光功率

$$RP \propto \left| \vec{j} \cdot \vec{P}^{tot} \right|^2$$

总偶极矩

非弹性隧穿电流
(IET)

分子对等离激元发光
的调制作用：
改变LDOS → IET 速率

Role of molecules:
Indirect,
LDOS modification!

Chen *et al.*, PRL under review.

Challenge:

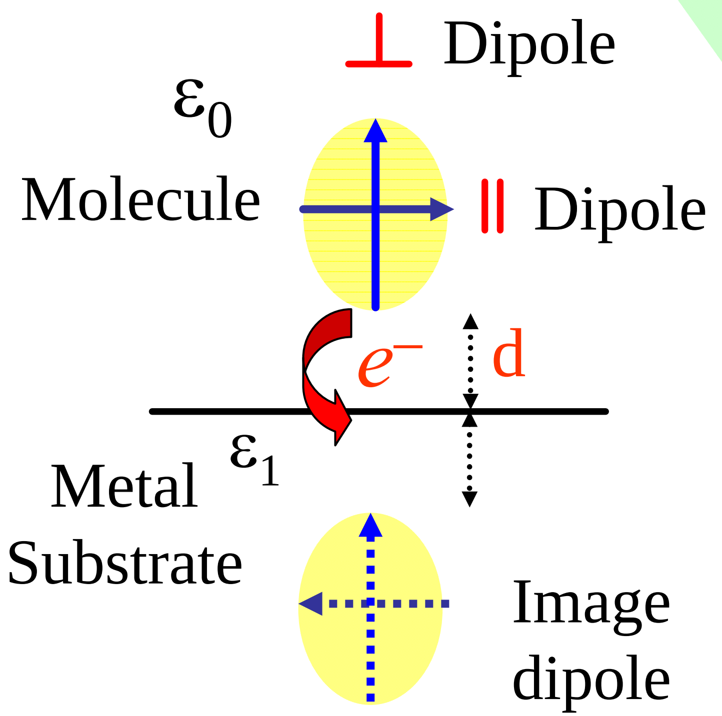
Energy Transfer near Metal Surfaces

Fluorescence Quenching

Route 1: charge transfer

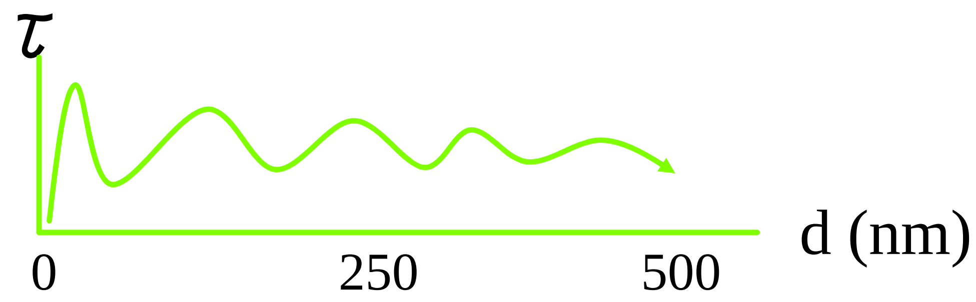
Route 2: dipole quenching

Nonradiative damping



Classical electromagnetic theory:

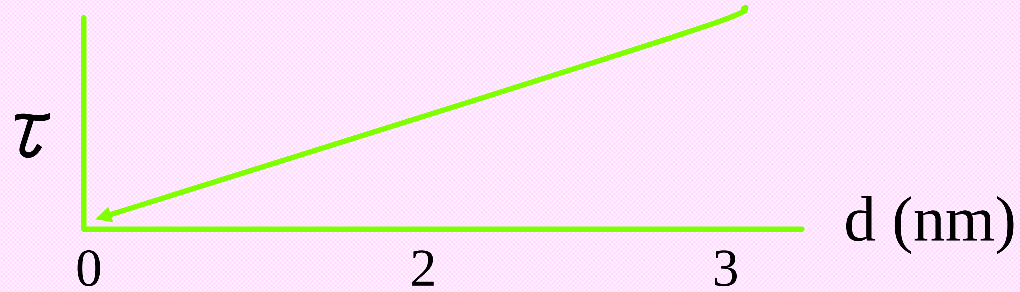
For large distances, the surface acting as a mirror to cause electric field interference, the luminescent lifetime **oscillates** as a function of d.



For small distances (<5 nm), via ***dipole field coupling***, the lifetime goes monotonically towards zero.

damping rate = $1/\tau \propto 1/d^3$, bulk transfer

$1/\tau \propto 1/d^4$, surface transfer



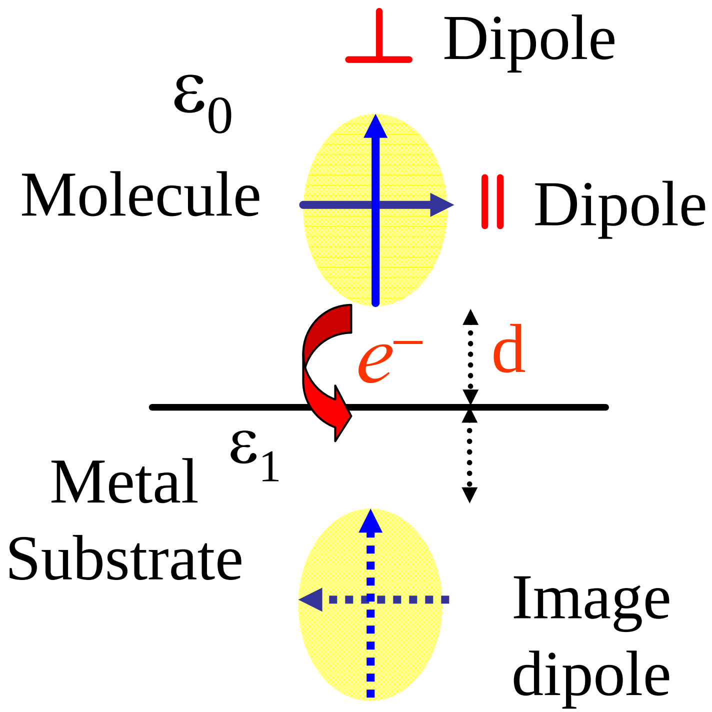
Challenge:

Fluorescence Quenching

Route 1: charge transfer

Route 2: dipole quenching

Nonradiative damping



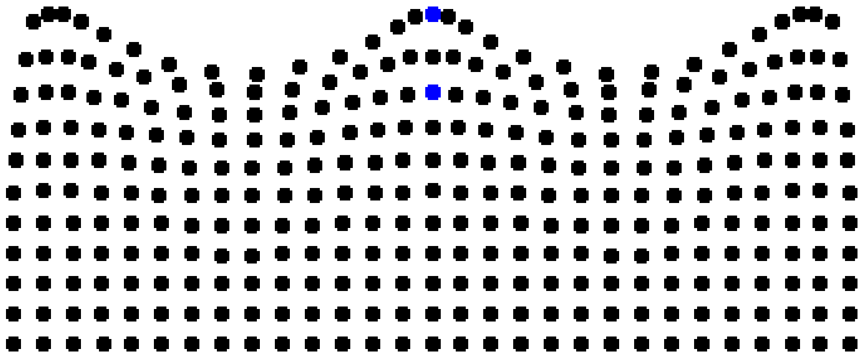
Single Molecular Electroluminescence:

Feasible?

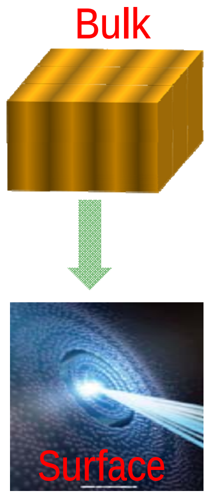
Surface Plasmon (SP): Plasmon Confined to the Surface

表面等离激元

Water Wave:

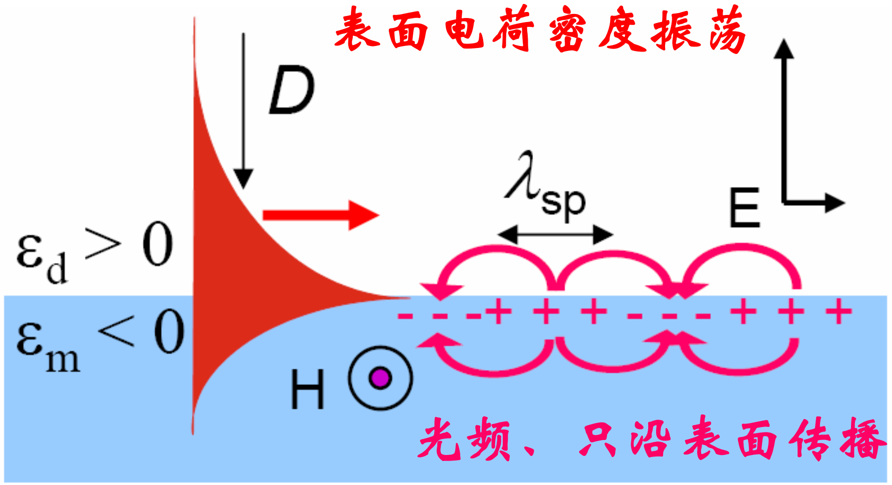


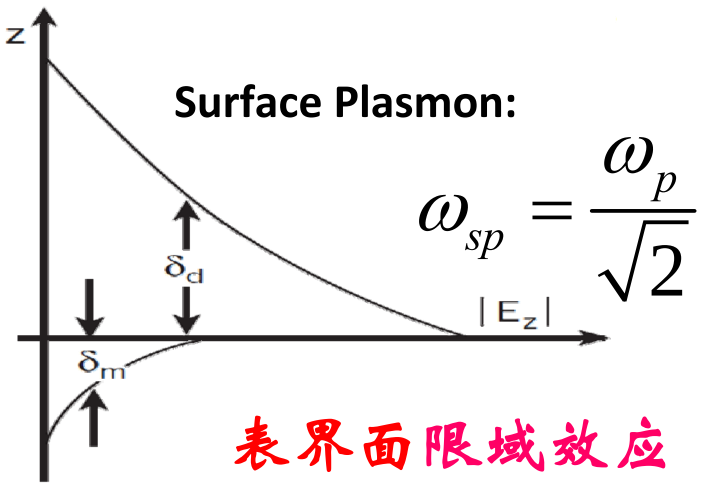
Surface wave of water



R. H. Ritchie, "*Plasma Losses by Fast Electrons in Thin Films*", Phys. Rev. 106, 874 (1957)

Surface Plasmon Wave:





Nanoscale Confinement → Strong Field Enhancement!

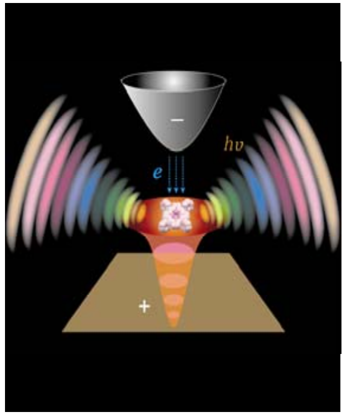
Tuning of Photonic States (PMD) by Resonant Plasmonic Fields

Toward single molecular electroluminescence (SMEL)

S_F: Fluorescence Signal

$$S_F = CKQ$$

C: Collection Efficiency



Nanogap effect

$K \sim 10^{4-6}$

K: Excitation enhancement

$$K = \frac{|E_{loc}|^2}{|E_{inc}|^2} = \frac{|E_{ind} + E_{inc}|^2}{|E_{inc}|^2}$$

Q: Quantum efficiency

$$Q = \frac{\Gamma}{\Gamma + k_{nr}}$$

Fermi golden rule:

$$\Gamma_{ij} \propto |M_{ij}|^2 \rho(\nu_{ij})$$

结构 外场

$\rho(\nu_{ij})$: **Photonic mode density (PMD), E_{loc}-dependent!**

One possible approach to SMEL:

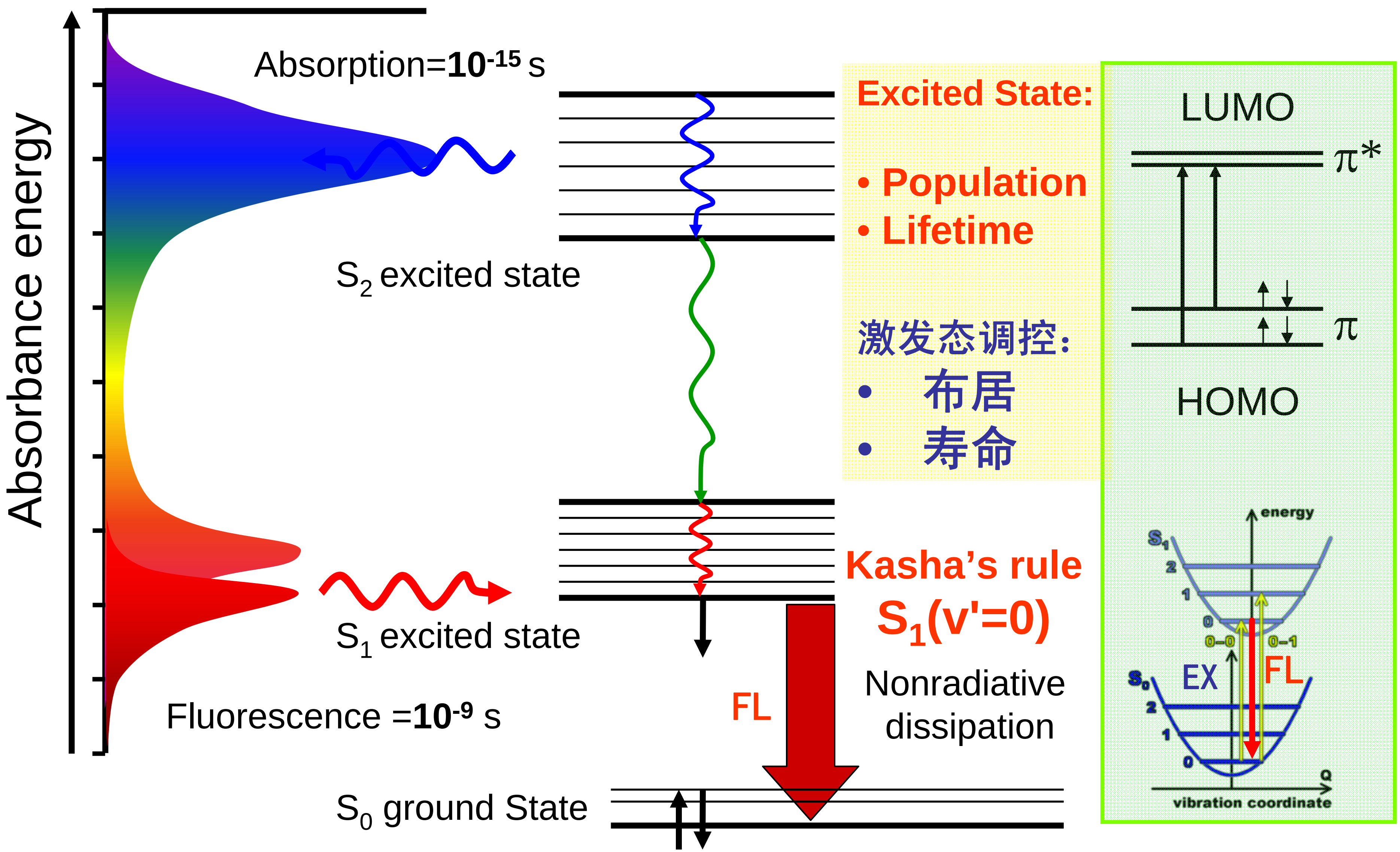
Play with the competition
between
Quenching and Enhancement

Tuning of quantum states:

$$H\ \Psi(\mathbf{r},\mathbf{t}) = \underline{E}\ \underline{\Psi(\mathbf{r},\mathbf{t})}$$

能量 空间 时间

Excitation and Emission of Molecules

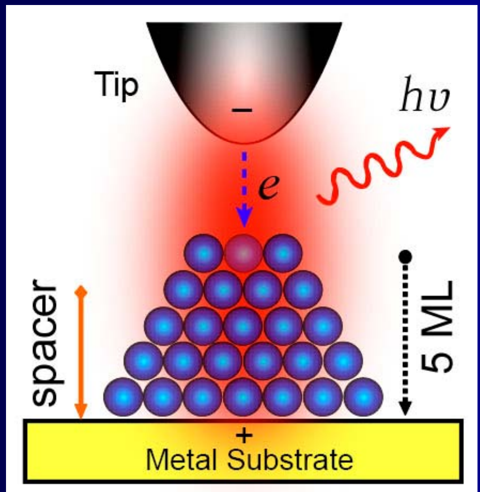


Fluorescence: $S_1 \rightarrow S_0$

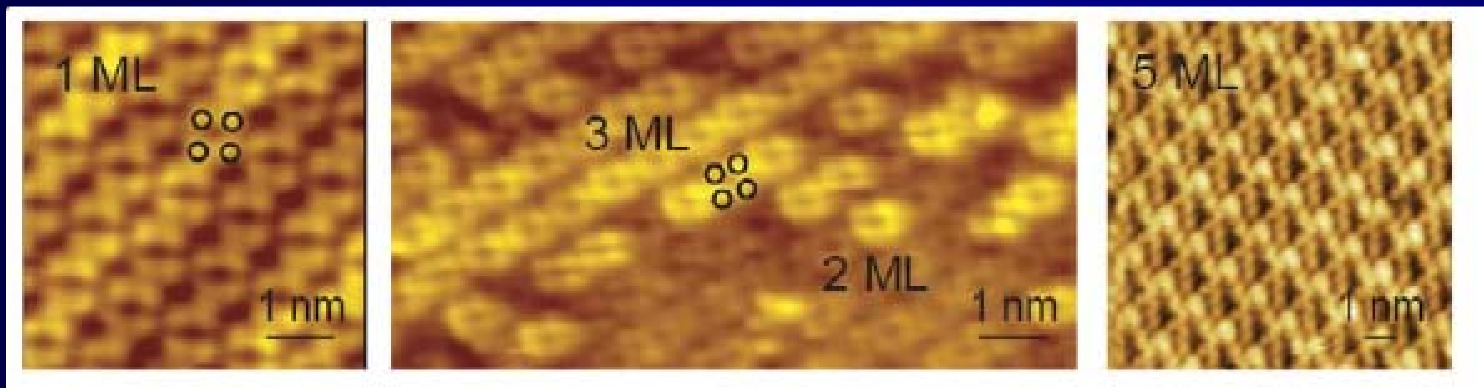
Single Molecular Electroluminescence?

Starting from simple and easier systems: Thin Film Structures.

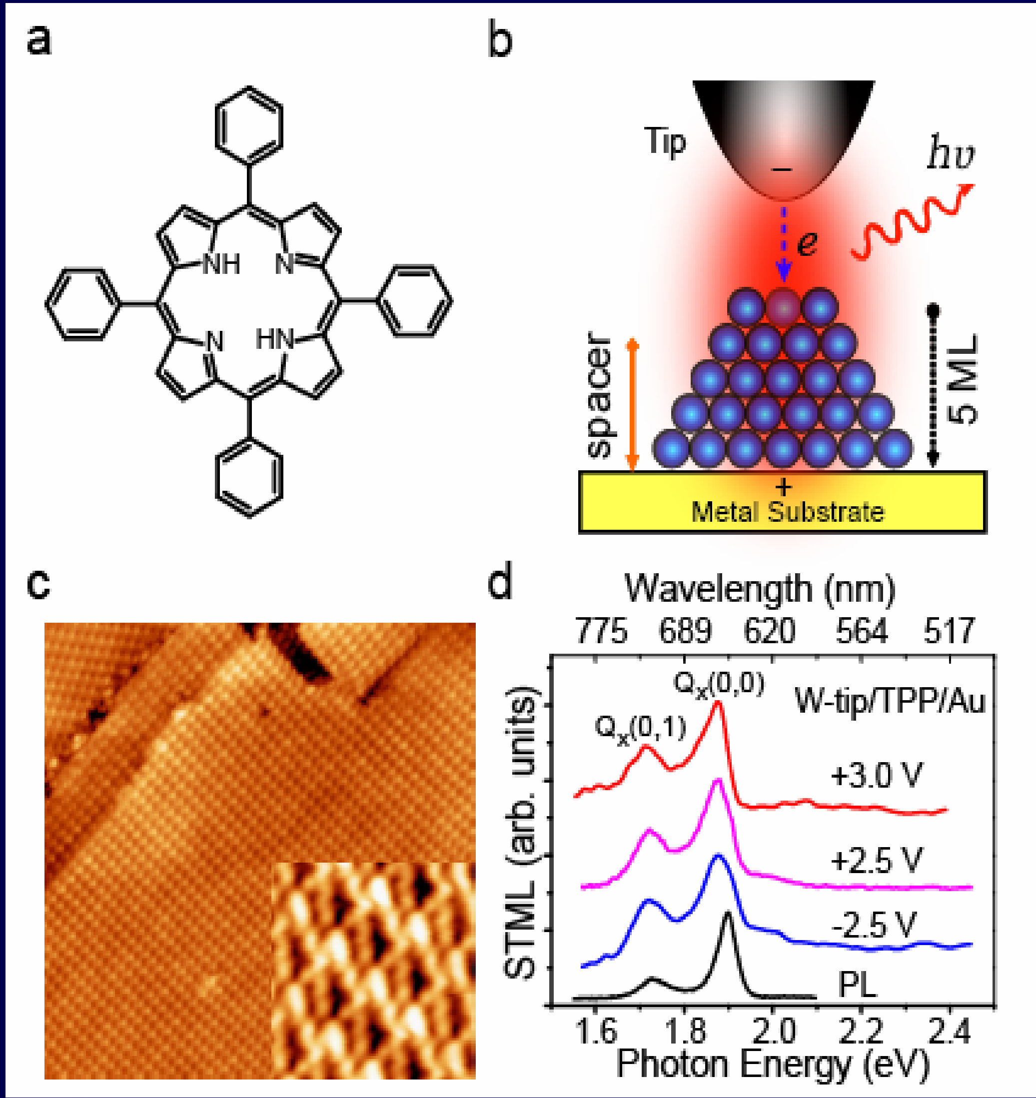
Example **Decoupling + NCP enhancement**



- **Feasibility?**
- **Mechanism?**



layer-by-layer Growth



Porphyrin:

Molecule-specific double Q-band EL!

Beating Fluorescence Quenching!

5ML TPP on Au

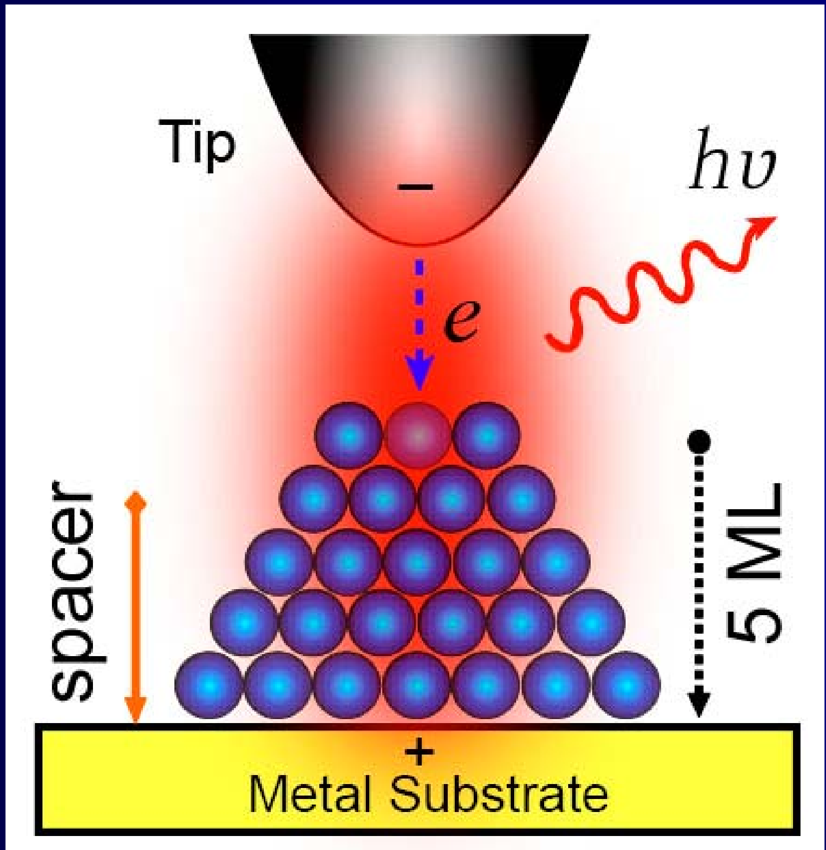
Layer-by-layer growth
STML acquired

at low current:
200 pA

Multimonolayer decoupling approach

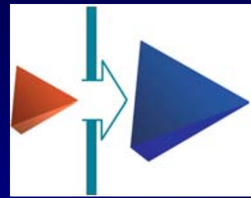
Dong et al., Phys. Rev. Lett. 2004

New Optoelectronic Phenomena at the Nanoscale



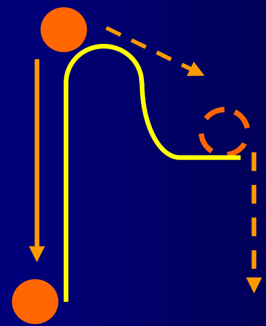
Nature Photonics, 2010

上转换



Upconversion Electroluminescence

热荧光



Hot-Electroluminescence

频谱调控

Spectral Tunability

Three Conventional Characteristics of Molecular Photoluminescent Spectra
分子光致发光光谱的三个普遍特性 (PL)

1. Stokes Shifts

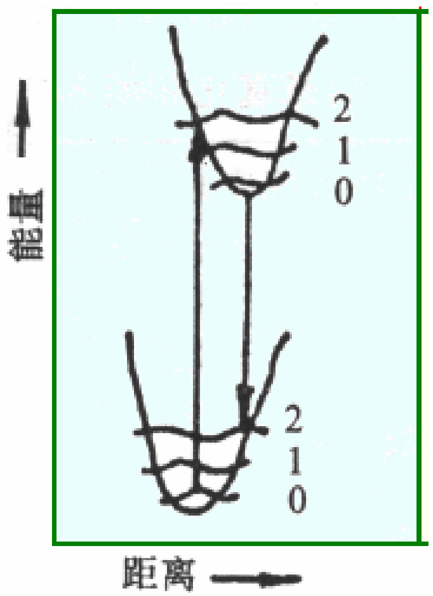
λem > λex! Energy dissipation via vibrational relaxation,

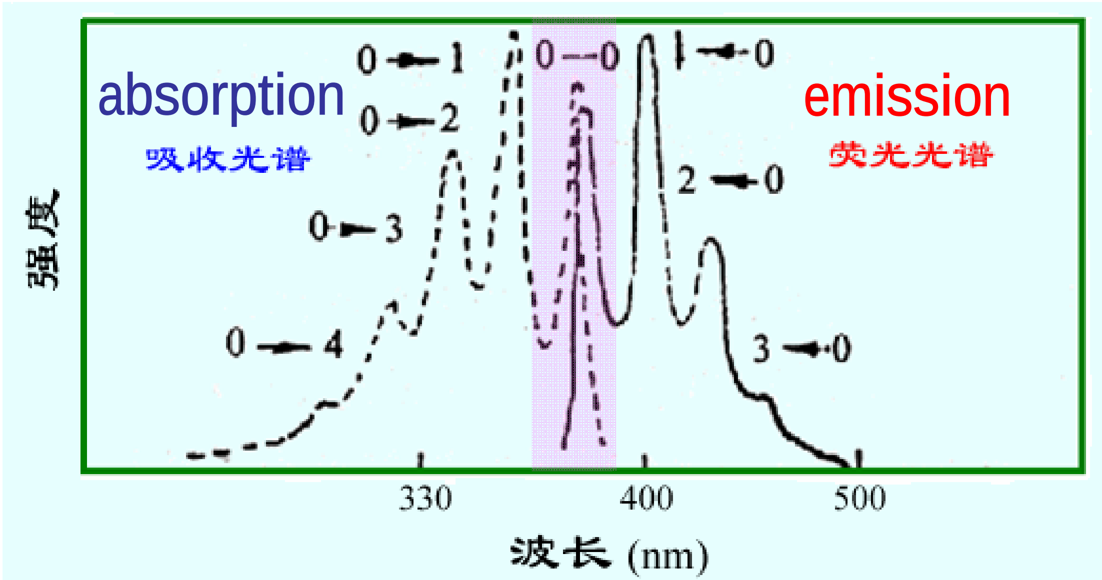
2. λ_{ex} independent emission spectra

Kasha's rule: Emission always occurs from the lowest vibronic level $S_1(v=0)$, the thermally equilibrated state, due to fast vibrational relaxation.

3. Mirror Symmetry

Consequence of the **Franck-Condon principle**! Similarity in the vibronic structure!





(0,0) transition:
E_{min} for absorption
E_{max} for emission

Could be different for fs-laser excitation!

"Photonics: Forbidden light" ------ Nature China

Tuning molecular electroluminescence by resonant nanocavity plasmons

New optoelectronic effects:

Hot electroluminescence

Upconversion electroluminescence

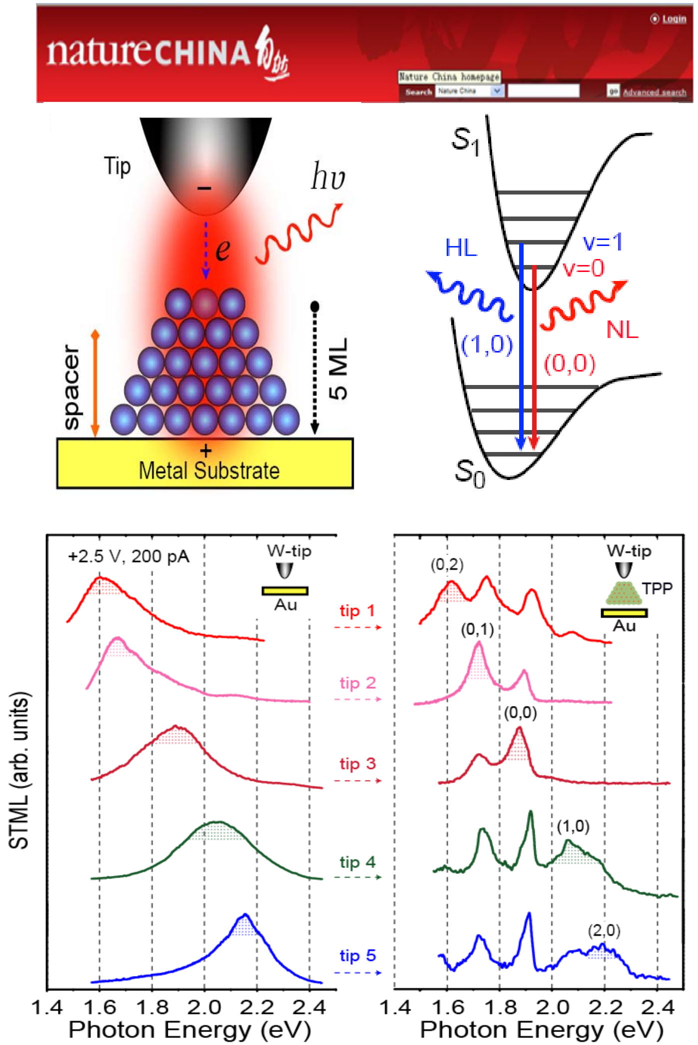
Dramatic spectral shaping

Plasmonic light:
A coherent optical source!

Nanoscale light sources?

Towards plasmo-electronic integration?

Dong et al.
Nature Photonics 4, 50-54 (2010)

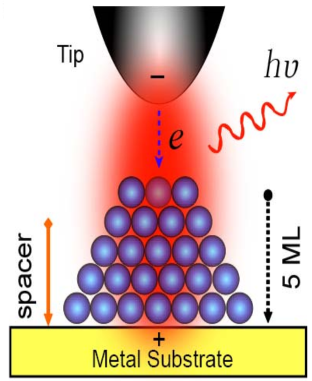


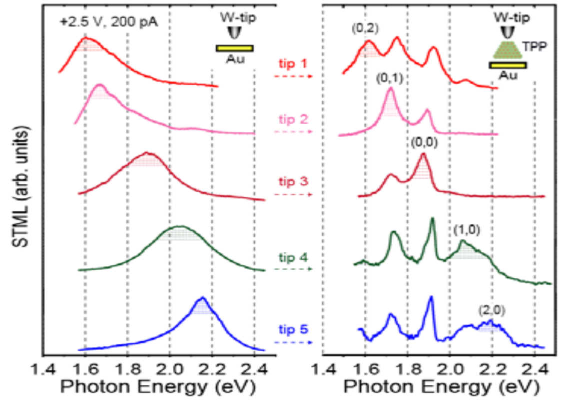
Role of Plasmons in SMEL？

- **Metal Substrate**

  Strong NCP fields

  → Resonant molecular EL

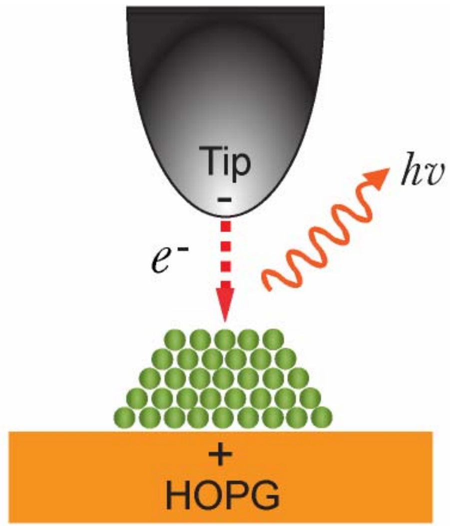




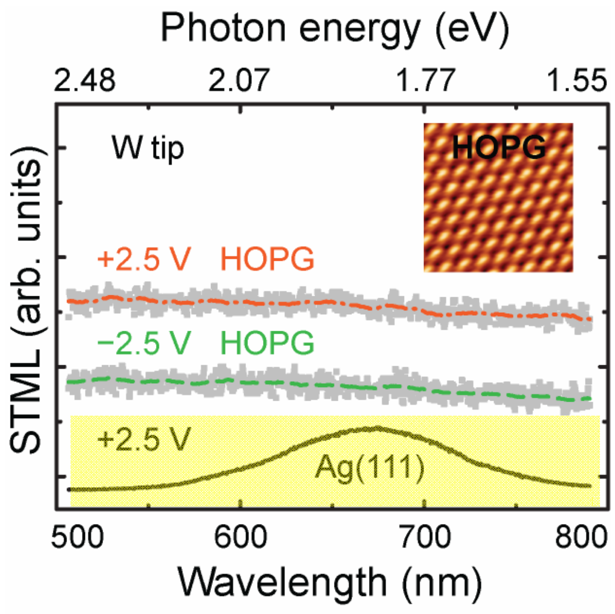
What happens when substrate is non-plasmonic?

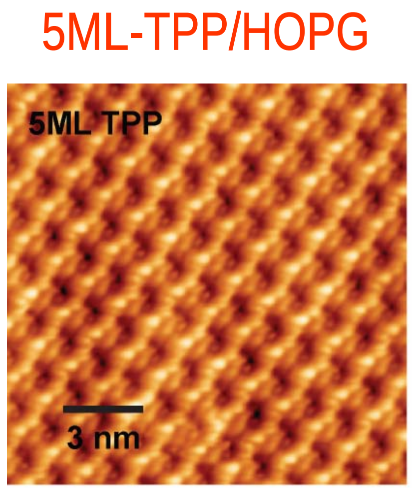
Is molecular EL still possible?

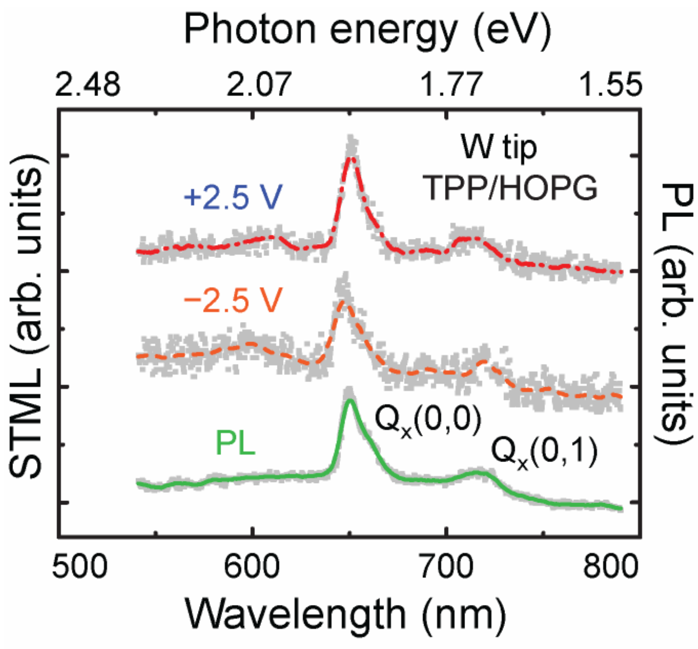
- **Half-metal Substrate, e.g., HOPG**
- **Semiconductor Substrate, e.g., Si（100）**



STM Induced Molecular EL on HOPG: OK



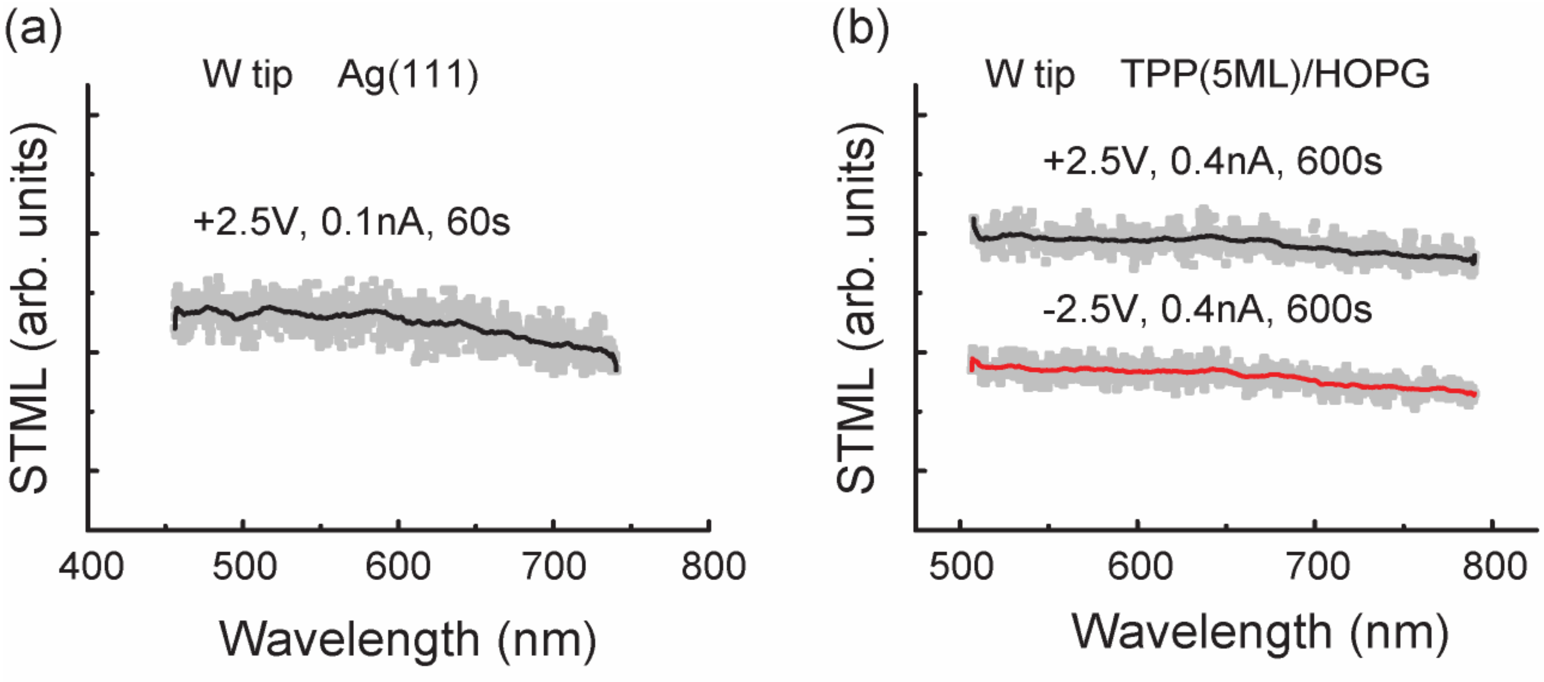




When tip is plasmonically bright!

- 半金属表面上也可以产生STM诱导的本征分子荧光、且具有振动分辨；
- 双极性运作：正负偏压下均可以实现分子发光；
- 光致和电致的激发方式虽然不同，但是分子激发态能量辐射衰退通道相同。

STM Induced Molecular EL on HOPG



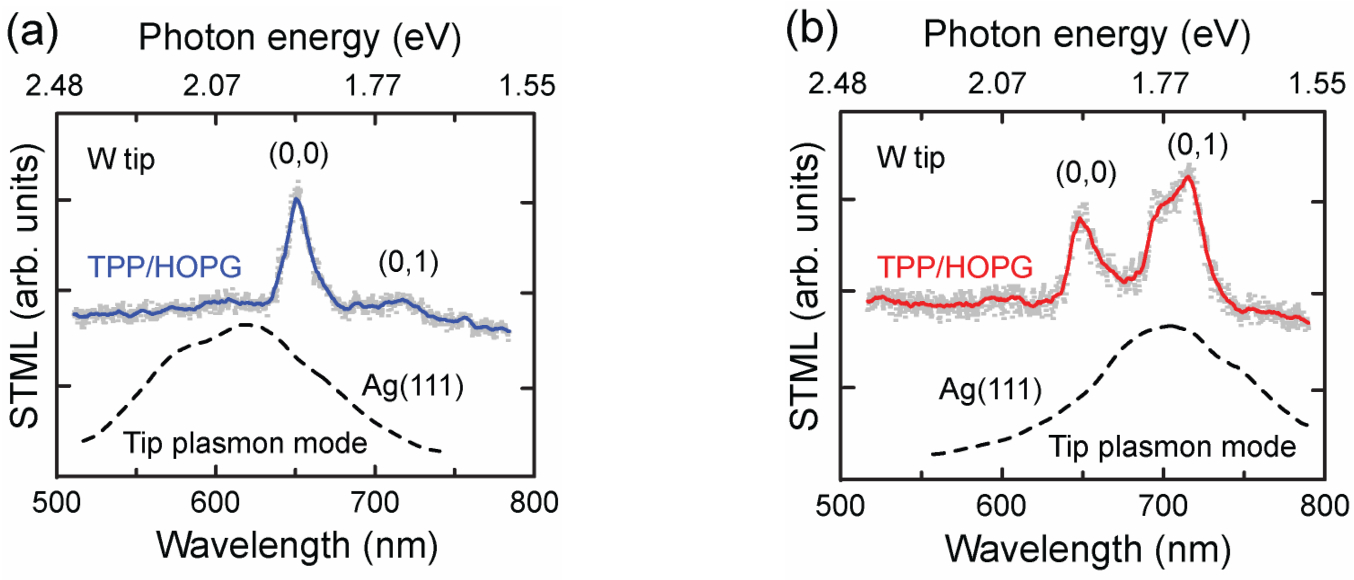
When tip is plasmonically dark,
no molecular electroluminescence!

Plasmon is crucial!

STM Induced Molecular EL on HOPG

Spectral shaping:

Matching of the tip-plasmon modes with molecular vibronic transitions



等离激元对于产生分子电致发光是必不可少的；

等离激元模式对于分子发光频带具有选择性调控作用；

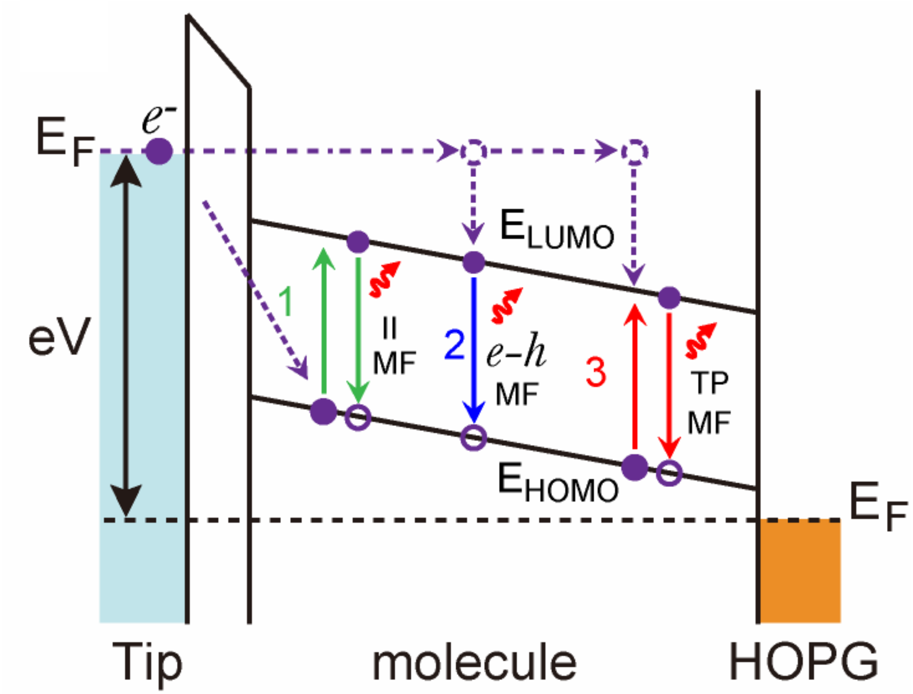
针尖等离激元本身就足以激发分子发光。

HOPG：反射镜面？

C. Zhang *et al.*, APL in press.

STM Induced Molecular EL on HOPG

Mechanism

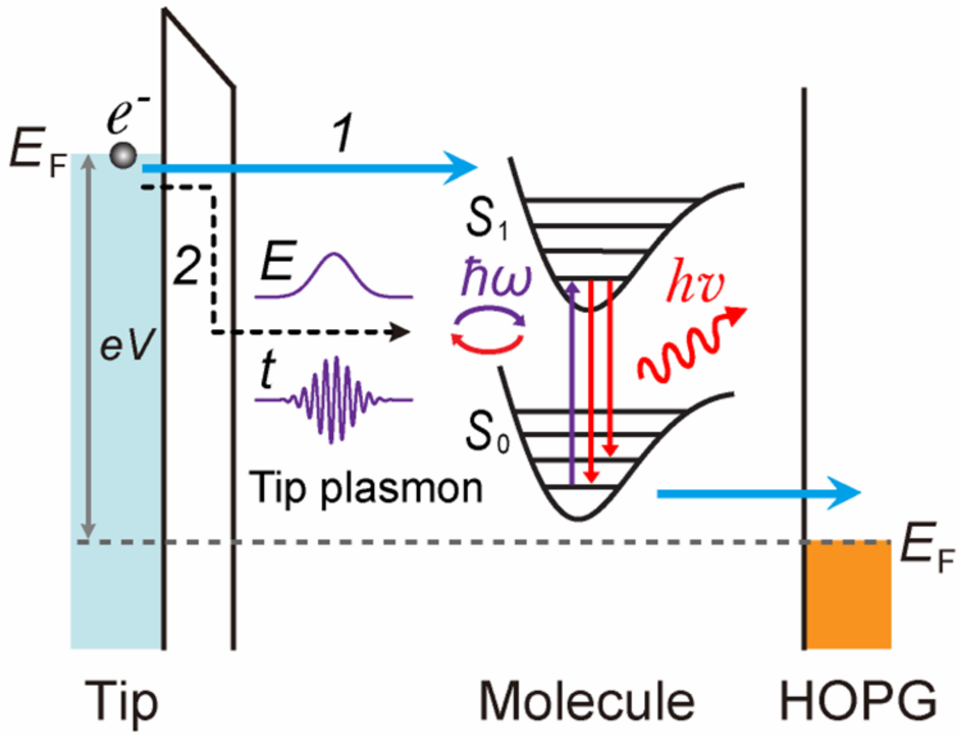


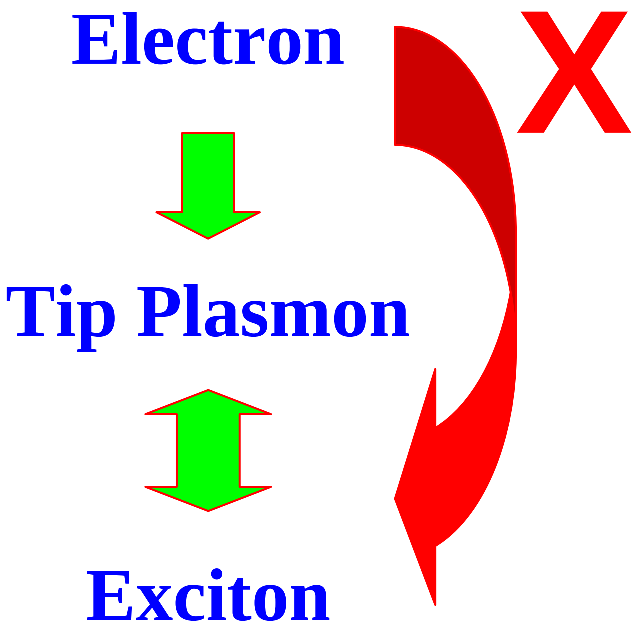
Three Possible Channels (分子发光的三种可能机制):

1. **Impact Ionization (II) Mechanism);**
2. **Hot Electron Injection Type OLED Mechanism;**
3. **Tip Plasmon Mediated Fluorescence Mechanism**

STM Induced Molecular EL on HOPG

Mechanism

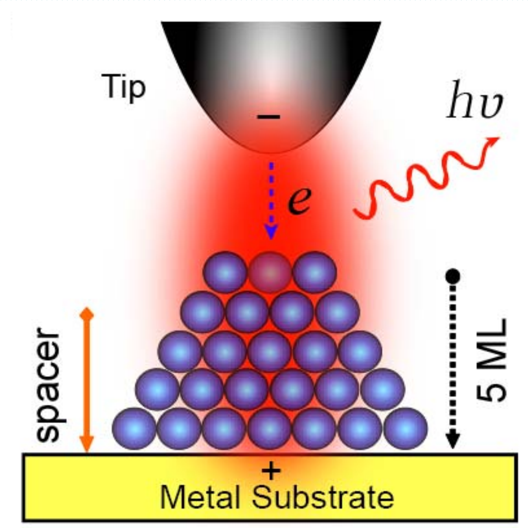


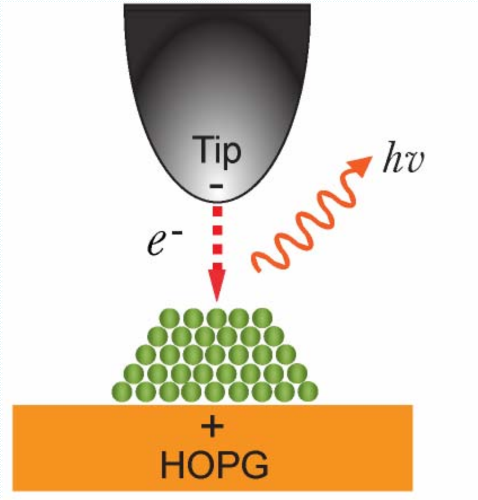


分子发光来源：Plasmon mediated molecular electroluminescence

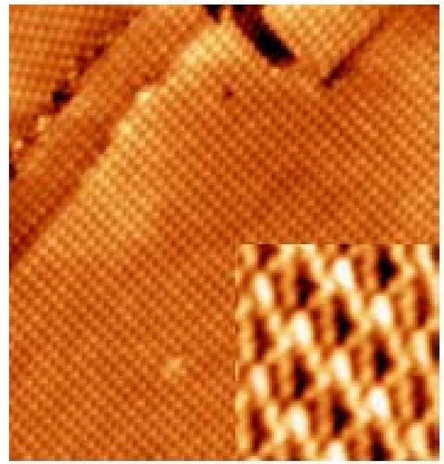
- 探针等离激元对分子的近场激发及共振耦合,
- 电子直接激发分子不能产生分子发光：OLED注入式电子空穴直接复合发光机制不适用。

C. Zhang *et al.*, APL in press.





Ultrathin Film



STM Induced Molecular EL on Thin Films

Single Molecular Electroluminescence (SMEL)？

What are crucial factors governing SMEL？

Plasmon mediated single molecular electroluminescence (SMEL)

What are the key factors that govern the SMEL phenomenon?

Y. Zhang, et al., APL 97 (2010) 243101

Y. Zhang *et al.*, in preparation.

Plasmon mediated single molecular electroluminescence (SMEL)

What are the key factors that govern the SMEL phenomenon?

Single Molecular Upconversion Electroluminescence

Plasmon-exciton coupling and amplification

Single Molecular Upconversion Electroluminescence

Injection barrier *independent*: Indirect electron excitation

Plasmon-exciton coupling and amplification

Upconversion molecular electroluminescence: Mechanism

Plasmon assisted Raman scattering (PARS)

上转换分子电致发光机制

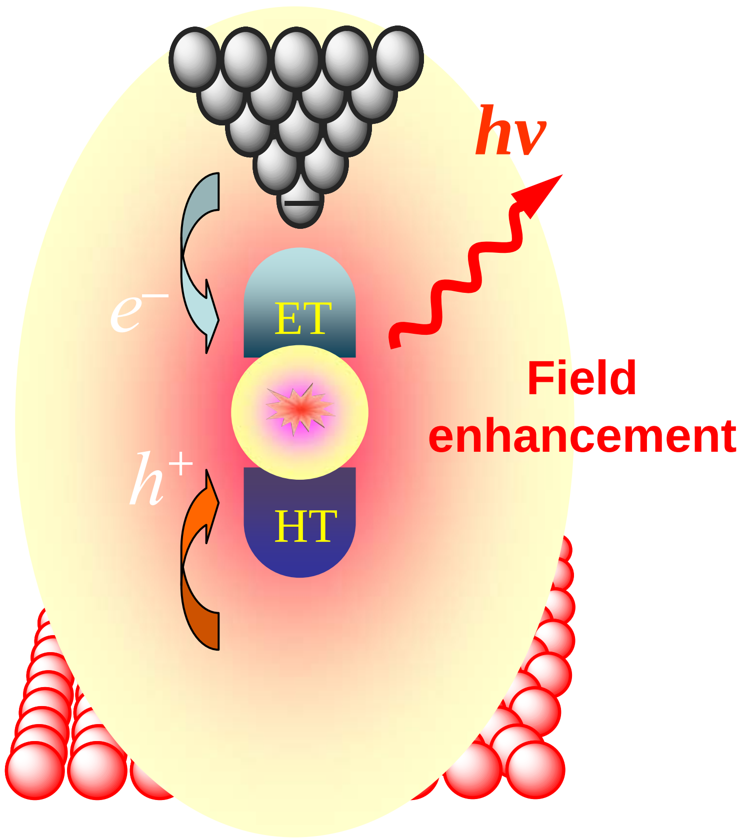
HY Gao et al., in preparation.

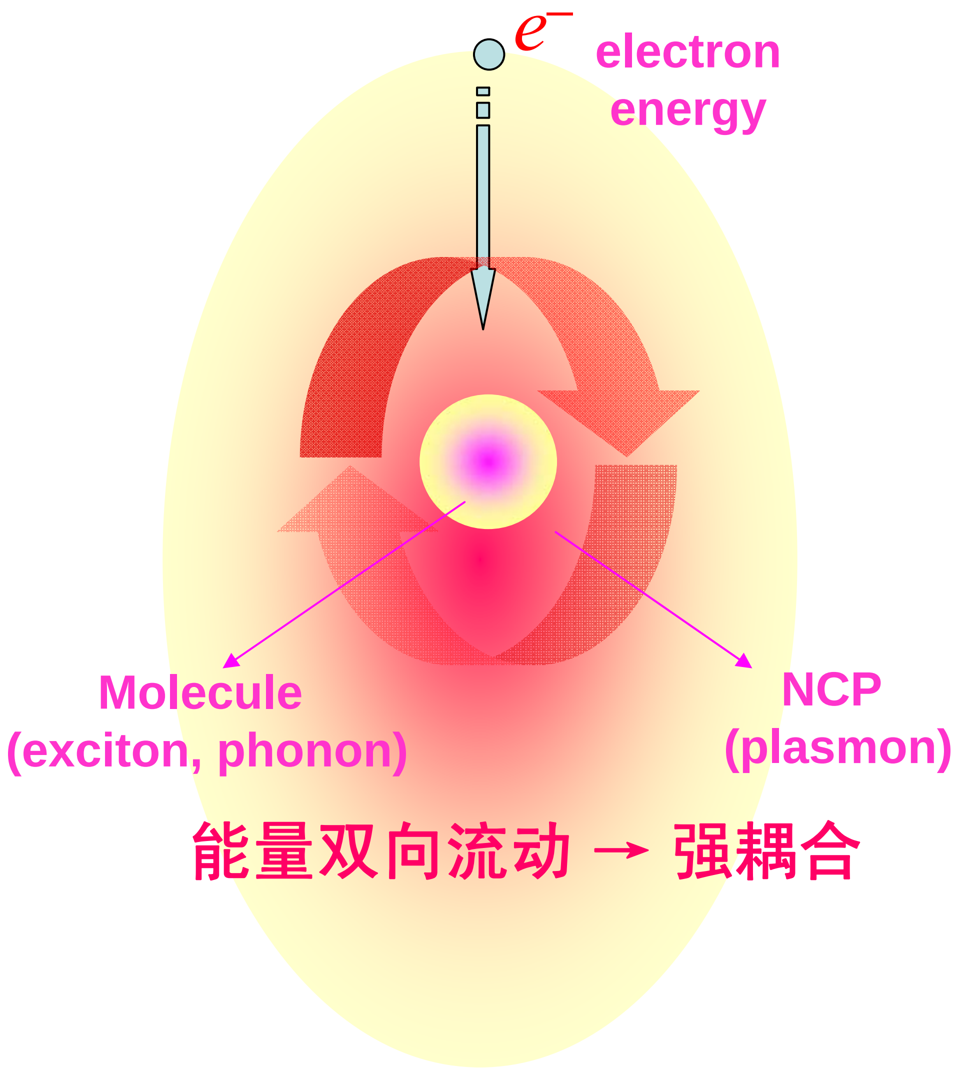
Two key factors that govern the SMEL phenomenon

STM诱导分子发光机制

Y. Zhang *et al.*, in preparation.

Summary





能量双向流动 → 强耦合

Thank you very much!

谢谢！