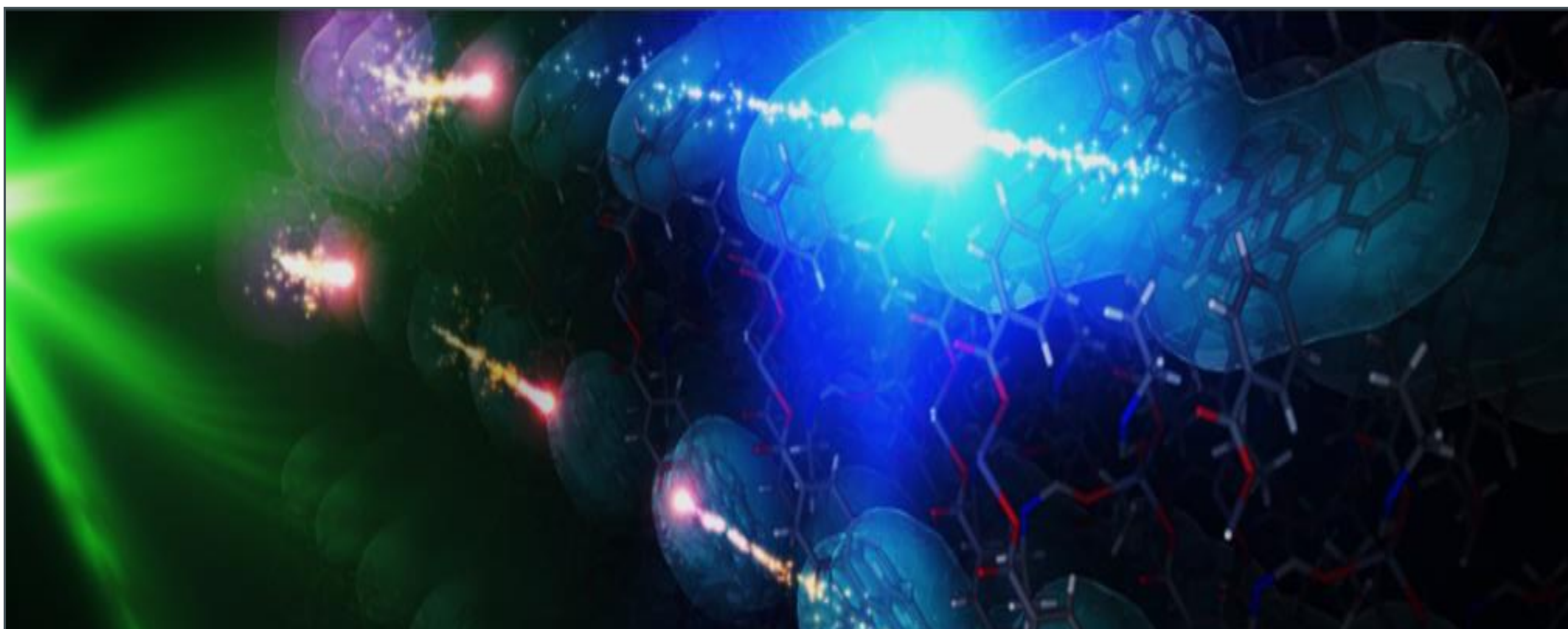
PHOTOPHYSICS OF MOLECULAR MATERIALS AND SEMICONDUCTOR NANOSTRUCTURES

UNIVERSITÀ DEGLI STUDI MILANO-BICOCCA



RESEARCH TOPICS:
PHYSICS OF LUMINESCENT NANOMATERIALS

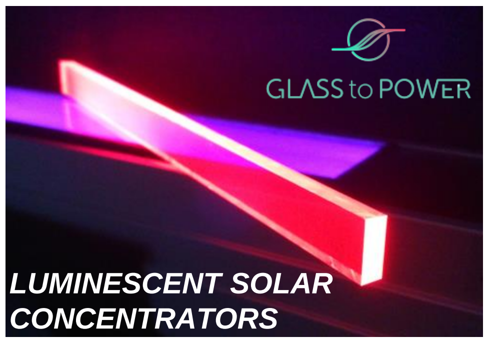
Prof. F. Meinardi Prof. S. Brovelli Dr. A. Monguzzi

DIPARTIMENTO DI SCIENZA DEI MATERIALI U5

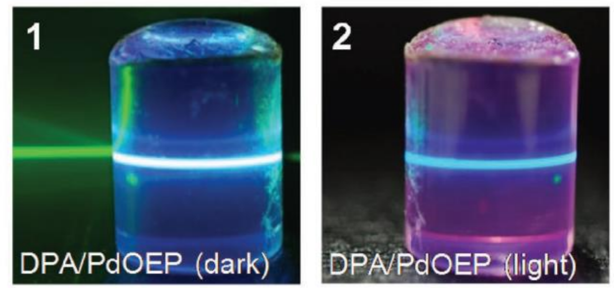
- Semiconductor Nanostructures
- Organic and Hybrid Nanoparticles and Nanotubes
- Metal Quantum Clusters

RESEARCH TOPICS: APPLICATIONS

- Photon managing for Solar Technologies (DOWN and UP photon conversion)



PHOTONS UPCONVERTERS

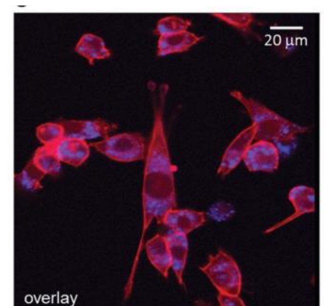


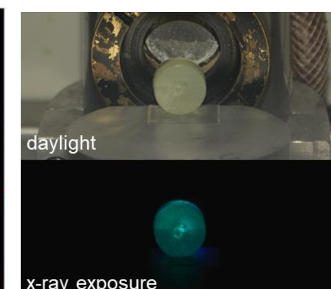
- Luminescent Materials for Photonics and Imaging Applications

(LED, Scintillationg, Bioimaging)

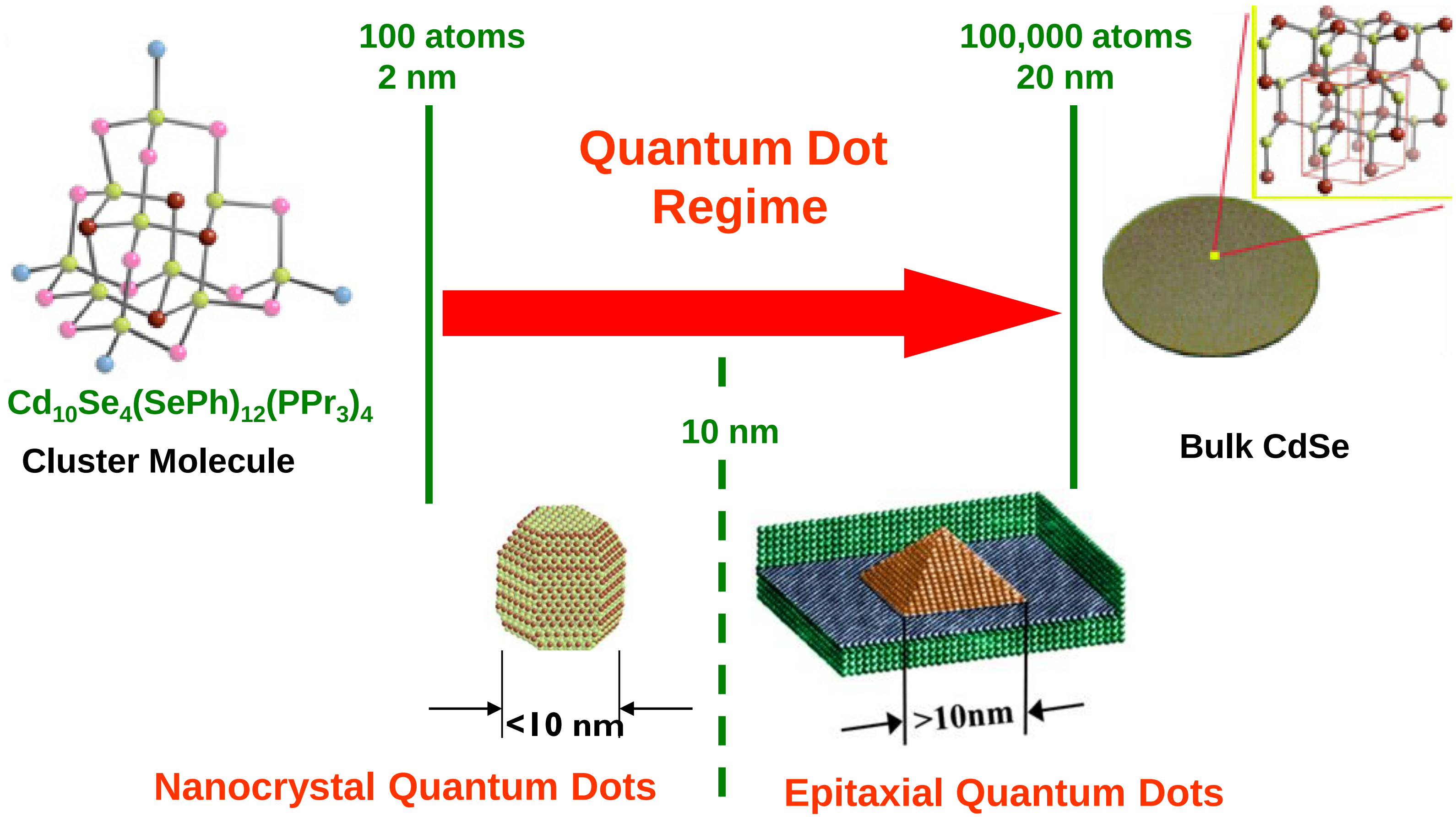
MATERIALS FOR PHOTONICS

LED, OLED



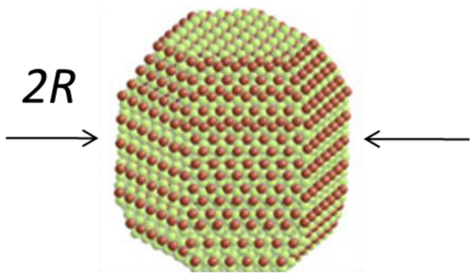


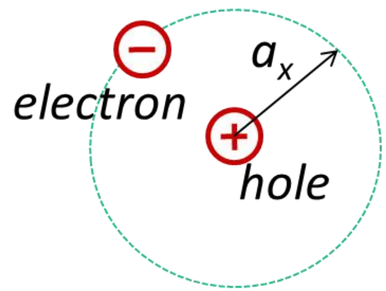
SEMICONDUCTOR NANOCRYSTALS



SEMICONDUCTOR NANOCRYSTALS

- **Nanocrystal Size vs. Exciton Bohr Radius**





- **Exciton Bohr radius**

$$a_x = \varepsilon \frac{m_0}{m_{eh}} a_B \qquad m_{eh} = \frac{m_e m_h}{m_e + m} \qquad a_B = \frac{\text{h}}{m_0 e^2} = 0.053\,nm$$

free electron mass (m_0)

Bohr radius of hydrogen atom (a_B)

dielectric constant (ε)

electron-hole reduced mass (m_{eh})

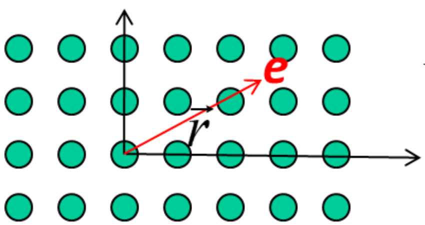
- **Examples: CdSe** $m_{eh} = 0.10m_0$; $e_0 = 9.4$; $a_x = 4.9$ nm

  PbSe $m_{eh} = 0.038m_0$; $e_0 = 210$; $a_x = 292$ nm

  CuCl $a_x = 1$ nm

SEMICONDUCTOR NANOCRYSTALS

- **Carrier motion in an infinite periodic lattice (Bloch's theorem)**



$$\Psi_{n\vec{k}}(\vec{r}) = u_{n\vec{k}}(\vec{r})e^{i\vec{k}\vec{r}}$$

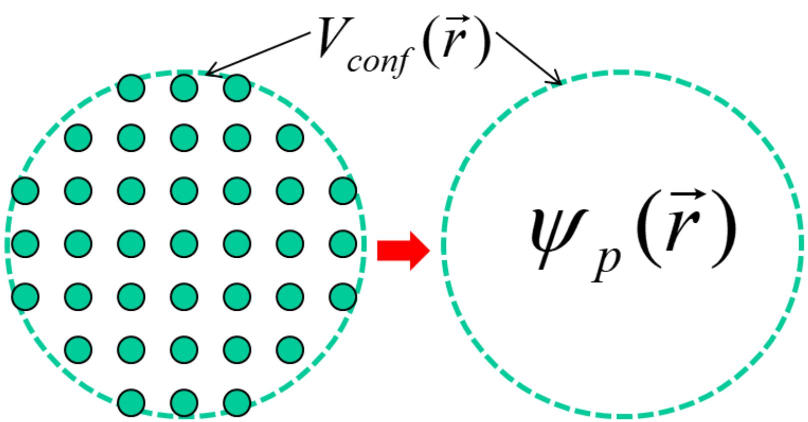
wave vector

plane wave

periodic function – Bloch function

- **Carrier motion in a finite crystal: envelope function approximation →**

The wavefunction is a linear combination of Bloch functions



$$\Psi_{np}(\vec{r}) = \sum_{\vec{k}} C_{p\vec{k}} u_{n\vec{k}}(\vec{r}) e^{i\vec{k}\vec{r}} \approx$$

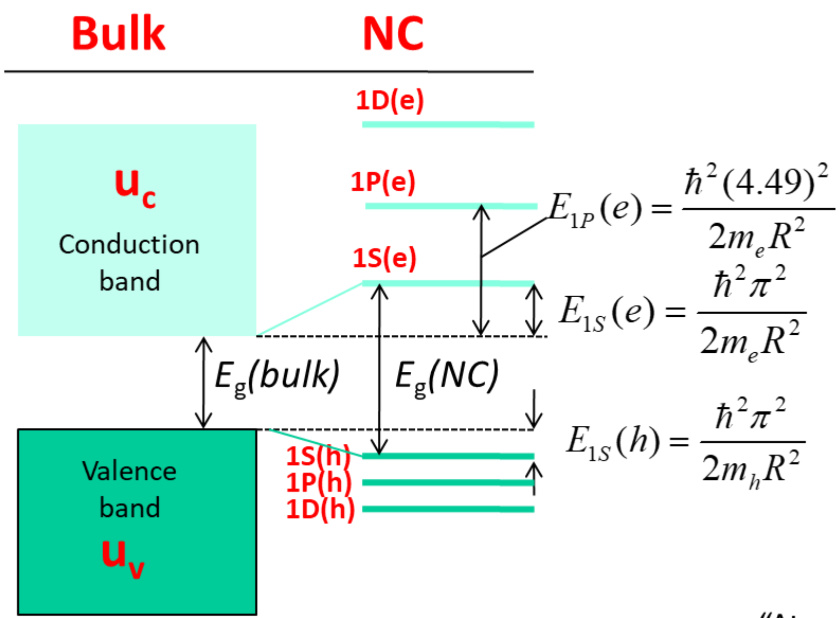
$$\approx u_{n0}(\vec{r}) \sum_{\vec{k}} C_{p\vec{k}} e^{i\vec{k}\vec{r}} = u_{n0}(\vec{r}) \psi_p(\vec{r})$$

Expansion coefficient   Bloch function at *k* = 0

envelope function

SEMICONDUCTOR NANOCRYSTALS

Size-Dependent Energy Gap



- ***NC energy gap***

$$E_g(NC) = E_g(bulk) + \frac{\hbar^2 \pi^2}{2m_e R^2} + \frac{\hbar^2 \pi^2}{2m_h R^2}$$

$$= E_g(bulk) + \frac{\hbar^2 \pi^2}{2m_{eh} R^2}; \quad m_{eh} = \frac{m_e m_h}{m_e + m}$$

- ***NC confinement energy***

$$E_{conf} = \frac{\hbar^2 \pi^2}{2m_{eh} R^2} = \pi^2 \frac{a_B^2}{R^2} \frac{m_0}{m_{eh}} I_0$$

"Atomic" units: a_B = 0.053 nm, I_0 = 13.6 eV

- ***Estimation for PbSe NCs***

E_g(bulk) = 0.28 eV; m_{eh} = 0.038m_0

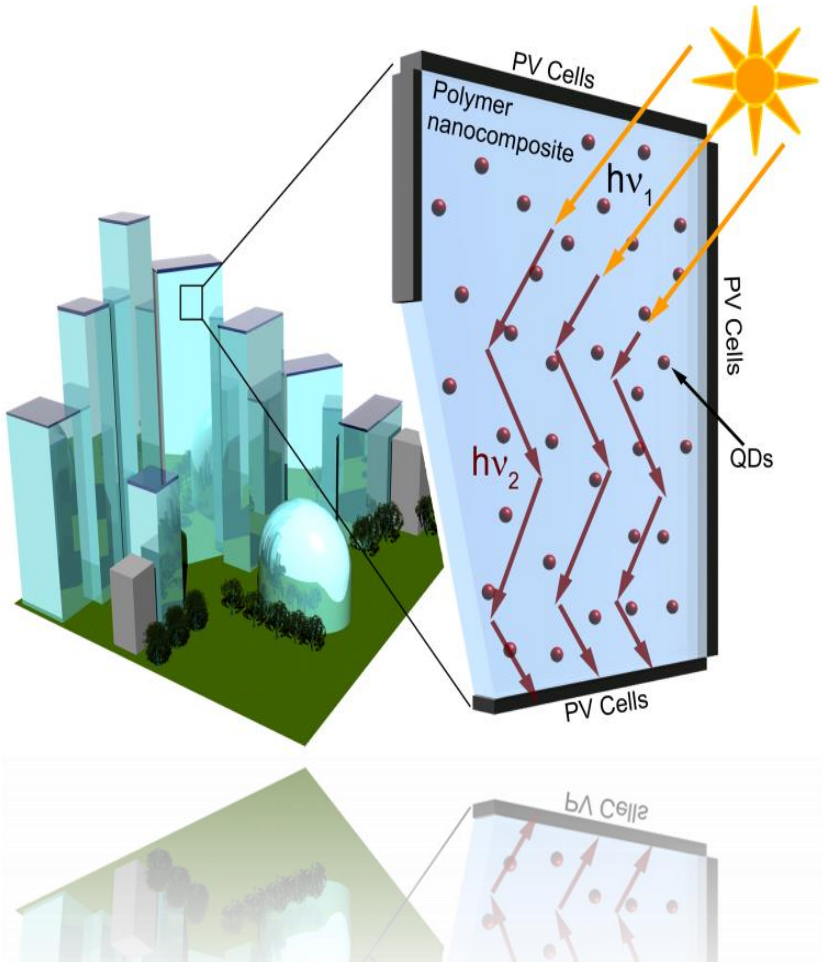
R = 4 nm; E_{conf} = 0.62 eV; E_g(NC) = 0.9 eV

SEMICONDUCTOR NANOCRYSTALS

TUNABLE OPTICAL, LUMINESCENCE and MAGNETIC PROPERTIES

vs composition, size, shape and doping

SMART WINDOWS



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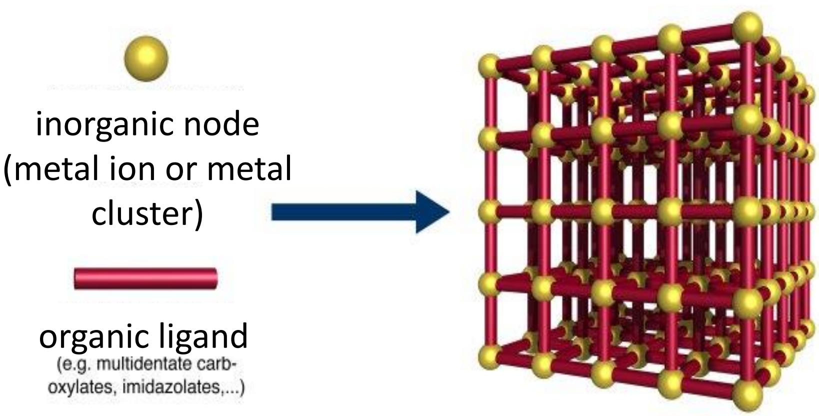
Highly efficient luminescent solar concentrators based on earth-abundant indirect-bandgap silicon quantum dots

Francesco Meinardi[1,2*†], Samantha Ehrenberg[3†], Lorena Dhamo[1], Francesco Carulli[1], Michele Mauri[1,2], Francesco Bruni[1,2], Roberto Simonutti[1], Uwe Kortshagen[3*] and Sergio Brovelli[1,2*]

HYBRID NANOMATERIALS: FLUORESCENT METAL ORGANIC FRAMEWORKS

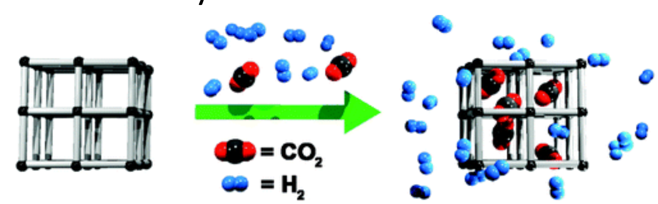


Metal-Organic Framework

O.M. Yaghi, H.L. Li, *J. Am. Chem. Soc.* 1995, **117**, 104010

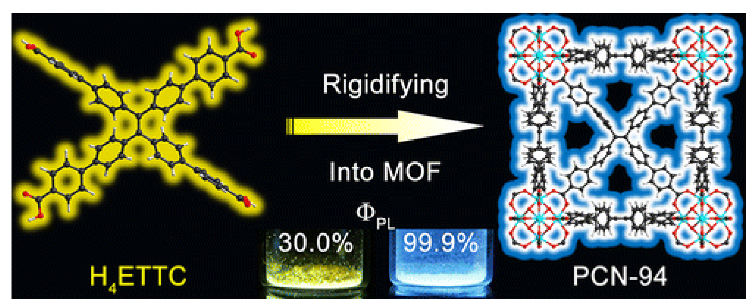
Optically inert MOFs = modulable porous systems

- Gas storage
- Molecular sensors
- Chemical catalysis

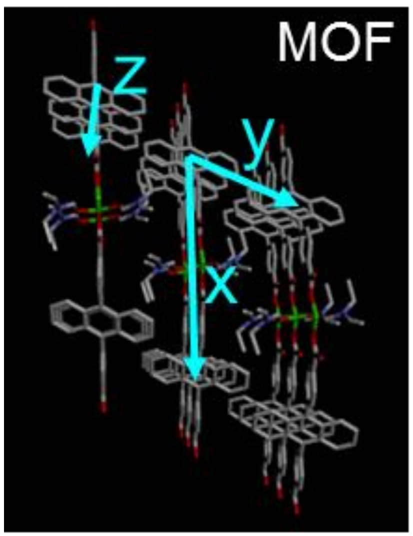


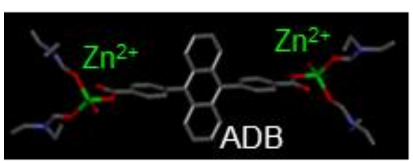
Luminescent MOFs:

- From ions
- From Ligands

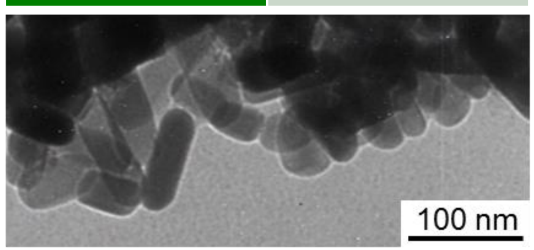


RECOMBINATION MECHANISMS OF MOLECULAR EXCITONS IN MOFS

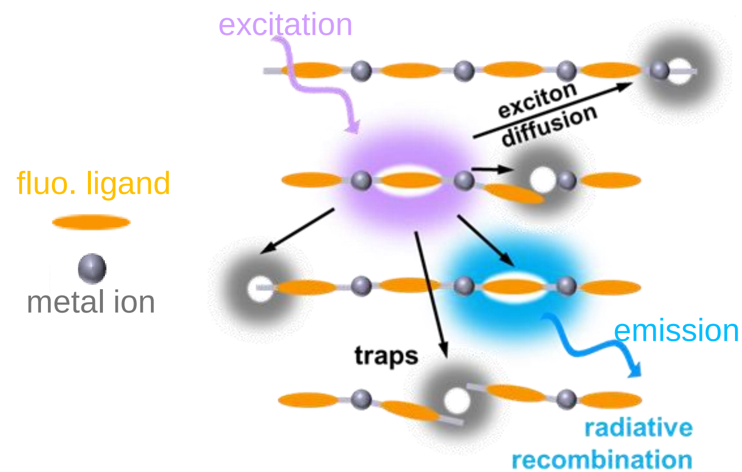




	MOF
Symmetry	Monoclinic
a (Å)	16.7
b (Å)	6.9
c (Å)	28.3
β	90.6
Volume (Å^3)	3252
Molecules per unit cell	4

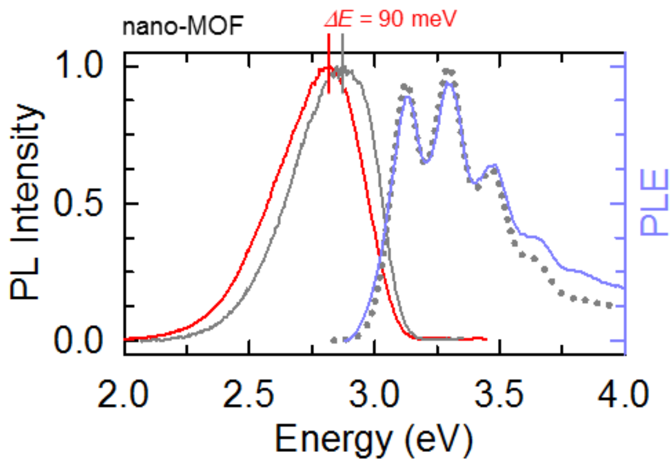


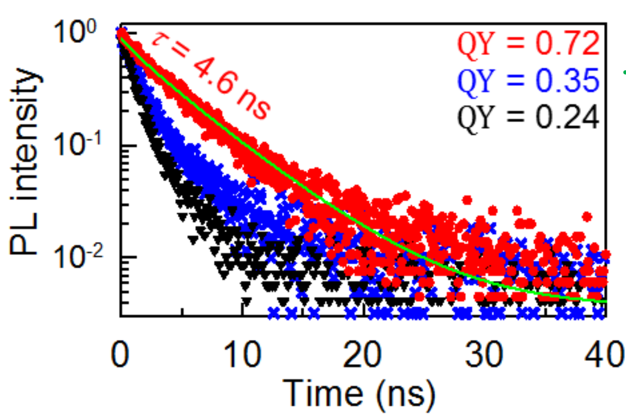
Molecular excitons migrate within the framework reaching energetic traps



RECOMBINATION MECHANISMS OF MOLECULAR EXCITONS IN MOFS

Absorption/Photoluminescence Properties





Einstein Coefficients

Stickler-Berg
relationship

$$\frac{1}{\tau_{rad}} = 2.88 \cdot 10^{-9}\, n^2\, \frac{\int PL(\nu) d\nu}{\int \frac{PL(\nu)}{\nu^3} d\nu} \int \frac{\varepsilon(\bar{\nu})}{\bar{\nu}}\, d\bar{\nu}$$

$$QY = \frac{\tau_{exp}}{\tau_{rad}}$$

RECOMBINATION MECHANISMS OF MOLECULAR EXCITONS IN MOFS

1. Excitation light penetration length (*x*)

Lambert-Beer ⟶ $\frac{I}{I_0} = 10^{-A} = e^{-\varepsilon M x}$

	x (nm)	*d* (nm)
MOF	**924**	**~100**
MOF-bpy	629	~50
MOF-dabco	564	~200

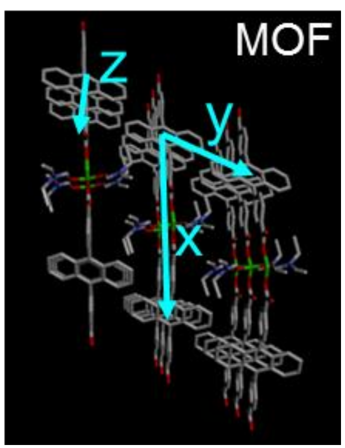
$x/d >> 1$

2. Singlet diffusion length (L)

$$L_i = (D_i \tau)^{0.5}$$

$$D_i = \left(k_{hop} R^2\right)_i$$

Axis	R (Å)	Θ^2	R_0 (nm)	k_{hop} (THz)	D ($cm^2 s^{-1}$)	L (nm)
x	9.2	4	6.0	$3.5 \cdot 10^{1}$	0.30	**252**
y	9.0	1	4.7	9.9	$8.1 \cdot 10^{-2}$	**131**
z'	6.0	1	4.7	$1.1 \cdot 10^{2}$	0.41	**296**



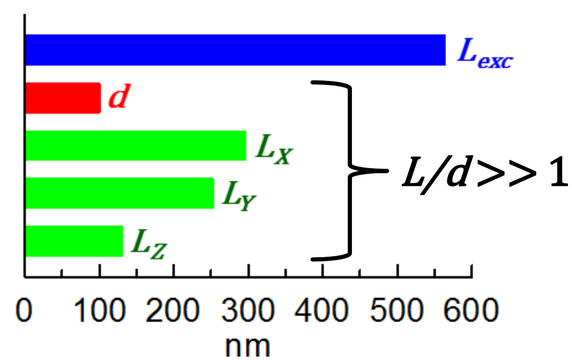
XRD analysis

Förster Rate $k_{hop} = k_{Fs} = \frac{1}{\tau_D}\left(\frac{R_0}{R}\right)^6$

Förster Radius $R_0 = 0.211\left(\theta^2 \cdot n^{-4} \cdot QY \cdot J(\lambda)\right)^{1/6}$

Spectral Overlap $J(\lambda) = \int_0^\infty PL(\lambda) \cdot \varepsilon_A(\lambda) \cdot \lambda^4 \, d\lambda$

spectroscopy



ENGINEERED MOFS FOR LOW POWER PHOTON UPCONVERSION

NANO LETTERS
Letter
Cite This: Nano Lett. XXXX, XXX, XXX−XXX
pubs.acs.org/NanoLett

Quasi-thresholdless Photon Upconversion in Metal−Organic Framework Nanocrystals

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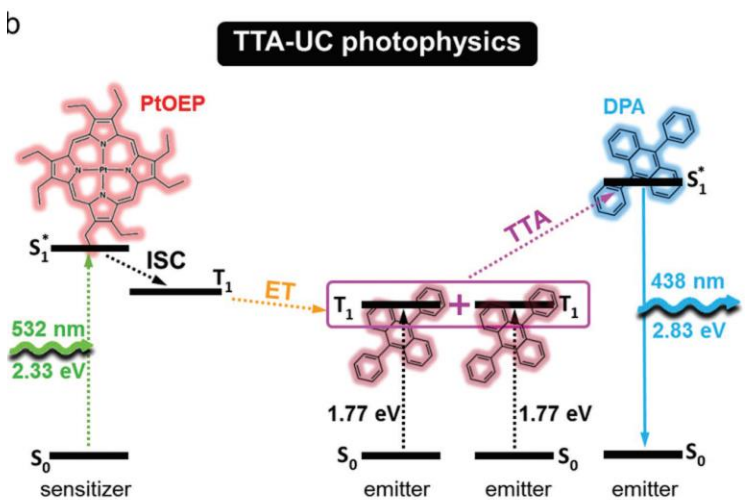
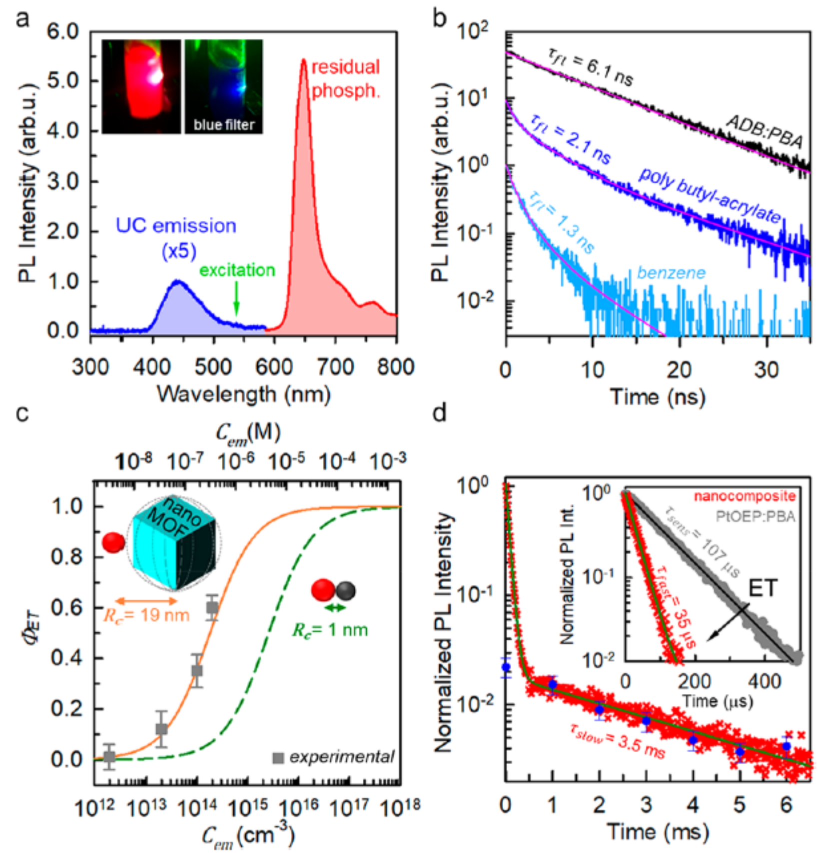


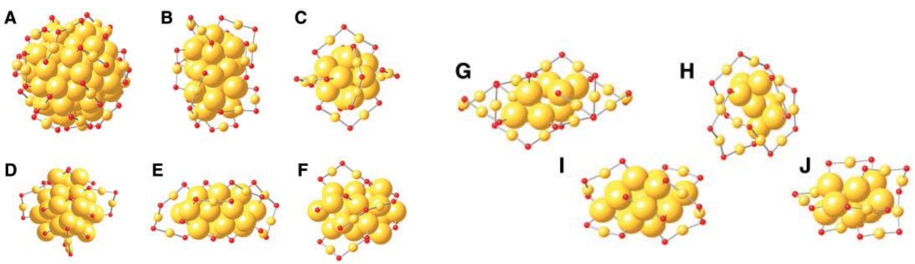


METAL QUANTUM CLUSTERS

BRIDGING THE GAP BETWEEN ATOMS AND COLLOIDAL NANOPARTICLES

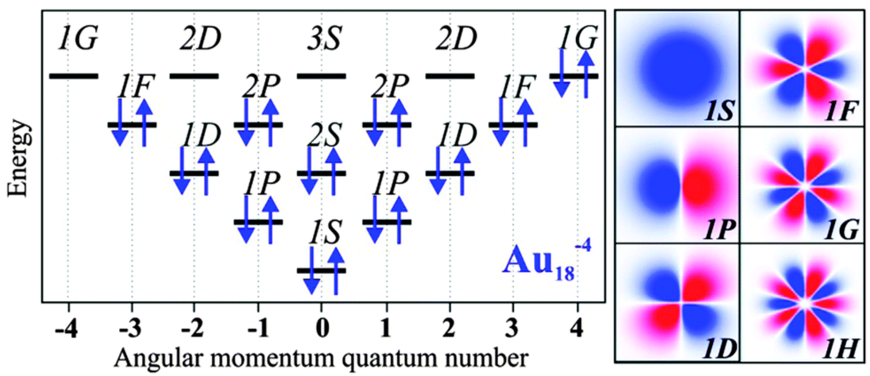
M_n clusters combine molecule-like electronic structure with quantum confinement effects

“***magic” sizes*** and ***electro/magnetic properties*** are dictated by the *s* valence electrons of metal constituents

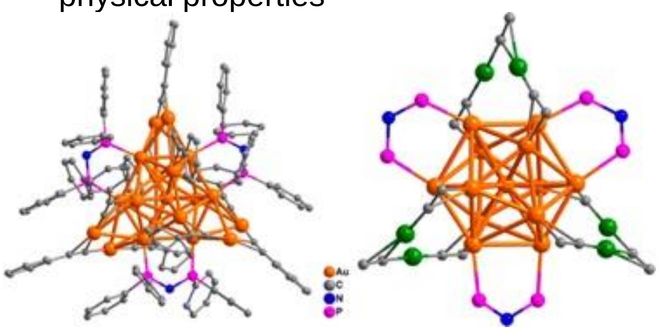


spherical jellium model for s electrons

$$\hat{H} = \hat{H}_{el} + \hat{H}_{back} + \hat{H}_{el-back}$$



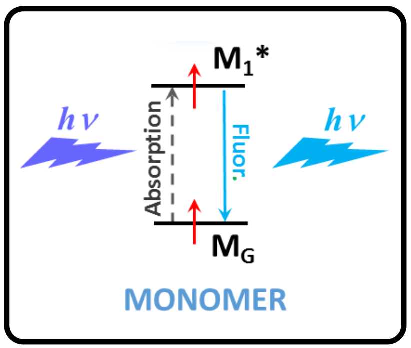
- unmatched flexibility for tailoring their physical properties

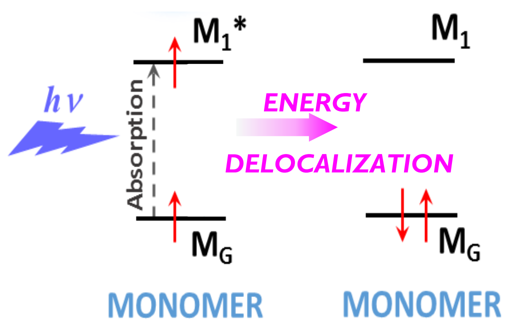


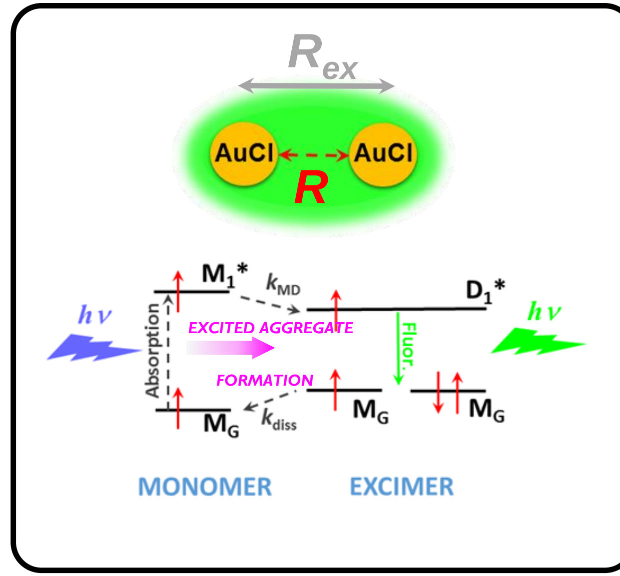
METAL QUANTUM CLUSTERS

EXCITED STATES INTERACTIONS

EXCIMER: *Excited State Aggregate*







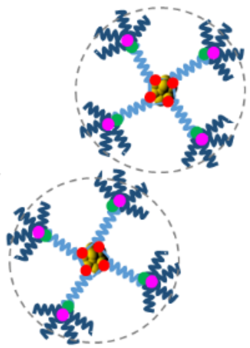
Excimers exhibit the absorption spectrum of their molecular constituents and long-lived non-resonant PL
→ IDEAL large Stokes Shift Emitters

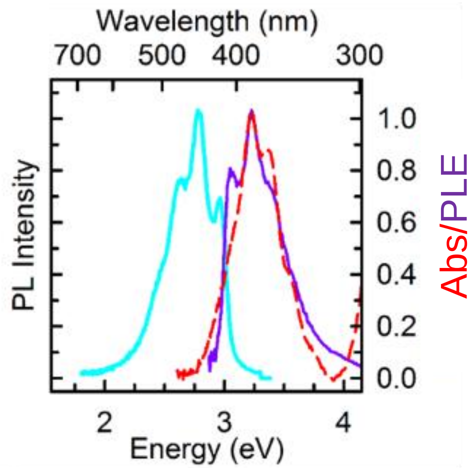
Molecular excimers are typically formed upon collisional interaction between monomers in concentrated solutions
→ In principle not realizable as stable self-standing particles, unless…

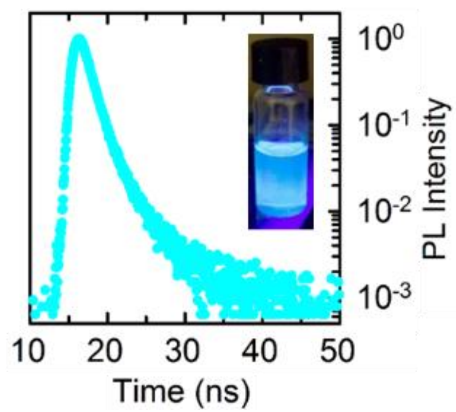
METAL QUANTUM CLUSTERS

EXCITED STATES INTERACTIONS

encapsulated single clusters [Molecular photophysics]

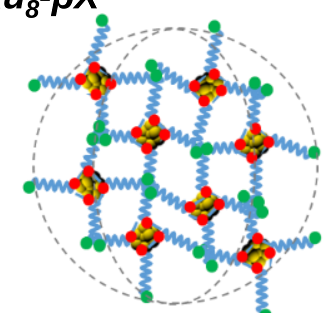


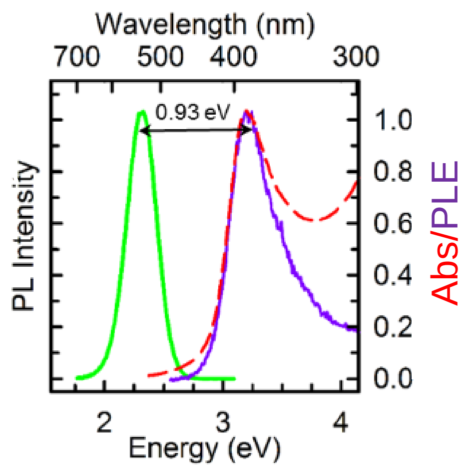


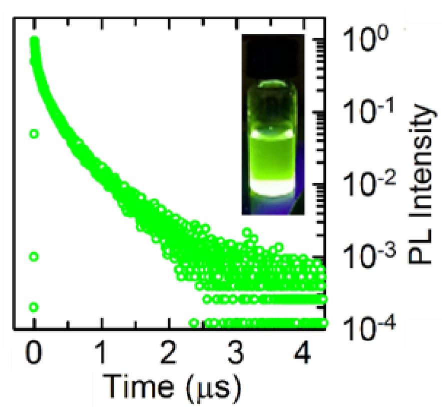


- **ϕ_{PL} = 12%, τ =1.6 ns** **τ_{rad} =13.3 ns** [τ_{rad} (SB) =12 ns]
- Au_8 absorption/PLE
- Mirror symmetry PL, distinct vibronic replica
- ***No LM-CT emission @ 2 eV***

Au_8-pX







- ϕ_{PL} = 4.5%, ultra-slow decay
- ***No LM-CT @ 2 eV***

Au_8 absorption/PLE

Stokes shift 0.93 eV

Largely Stokes Shifted PL

METAL QUANTUM CLUSTERS

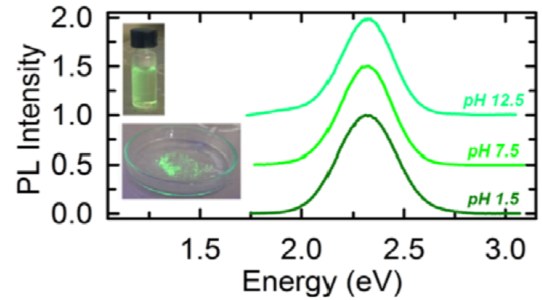
MANIPULATING SECONDARY INTERACITONS FOR BIOIMAGING

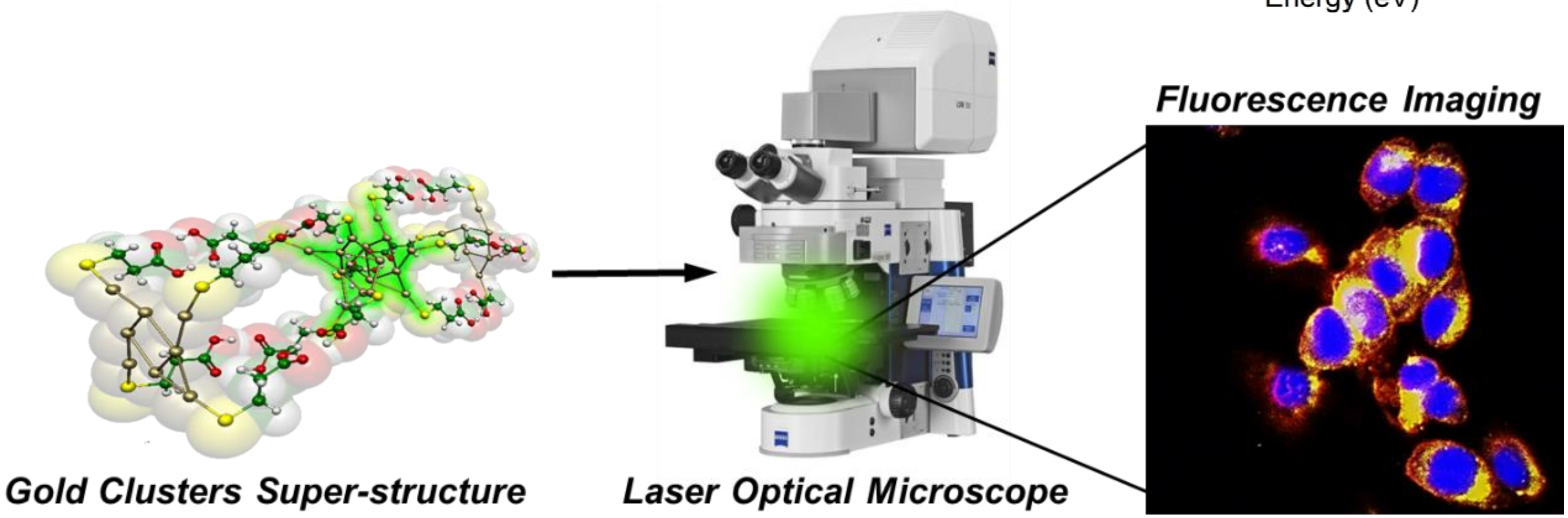
UNIVERSITA' DEGLI STUDI DI MILANO BICOCCA

NANOMATERIALS

Permanent excimer superstructures by supramolecular networking of metal quantum clusters

Beatriz Santiago-Gonzalez,[1]* Angelo Monguzzi,[1]*† Jon Mikel Azpiroz,[2,3] Mirko Prato,[4] Silvia Erratico,[5] Marcello Campione,[6] Roberto Lorenzi,[1] Jacopo Pedrini,[1] Carlo Santambrogio,[7] Yvan Torrente,[5] Filippo De Angelis,[2,4] Francesco Meinardi,[1]† Sergio Brovelli[1]†





SPECTROSCPY LAB

- CW and TR ultrafast photoluminescence spectroscopy
- Close cycle cryostat T ~ 1.5 K
- Magnetic Field Response (fino a 5.5 T)
- Confocal *imaging* micro-photoluminescence