High-Performance Spectral-Conversion Luminescent Nanoprobes: What's Ahead ?

Xiaogang Liu, National University of Singapore

LED/OLED

Solar Cells

DNA Sensing
Biolabeling
Super-resolution imaging

Optogenetics
Cancer therapy

Thermometers
Anti-counterfeiting

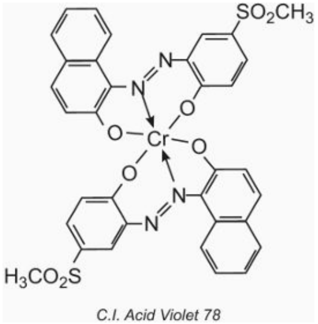
Nanophotonics
Optical Communications

What New Science and Technology are Possible?

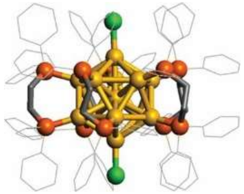
Outline

- Introduction
  - Lanthanide-doped Nanophosphors, Growth Techniques
- Photon Upconversion Tuning
  - The Concentration Effect, Surface Control, Energy Migration
- Excitation Source Selection
  - Neodymium for 800 nm Excitation, Helium Ion Beam Excitation, Pulsed Excitation
- Emerging Applications
  - Therapy, Axon Transport Tracking, 3D Printing etc.
- Acknowledgments

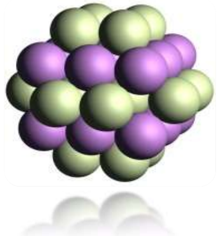
Luminescent Materials for Future Imaging

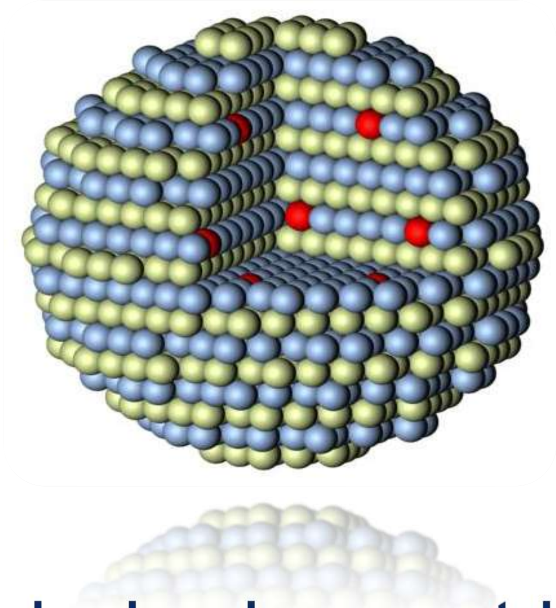


Metal-complex probes



Colloidal Clusters





Organic dyes	1 nm	**Quantum dots**	10 nm	**Ln-doped nanocrystals**
FITC, RhB, Cy5 etc.		CdS, CdSe, Ag_2S, $CsPbBr_3$ Carbon, graphene, etc.		YVO_4:Eu, $NaYF_4$:Yb/Er, $Gd_3Ga_5O_{12}$:Cr/Nd, etc.

Science Needed:

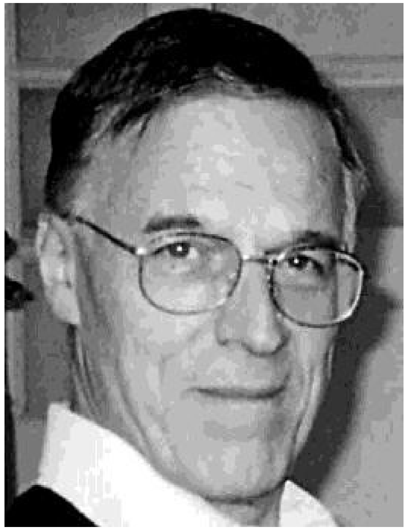
Versatile, Unconventional Materials

Better Photostability and Less Cytotoxicity

Suitable for multi-modal integration (MRI, PET, SPECT…)

Photon Upconversion

addition de photon par transferts d'energies, APTE



Compteur quantique par transfert d’energie entre deux ions de dans un tungstate mixte et dans un verre
F. Auzel, ***CR. Acad, Sci.*** (Paris) (1966)

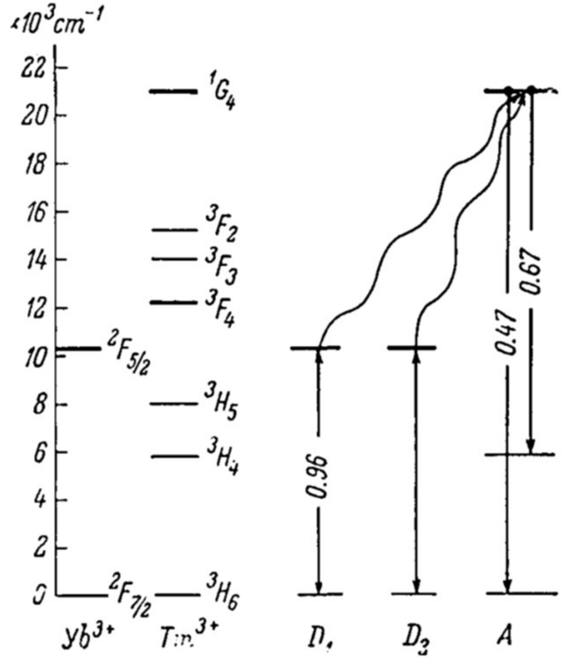


Fig. 4. Term diagram of Yb^{3+} and Tm^{3+} ions and cooperative sensitization by Yb^{3+} ions of Tm^{3+} emission.

Cooperative Luminescence of Solids
P. P. Feofilov and V. V. Ovsyankin ***Applied Optics*** (1967)

Synthesis of Lanthanide-doped Phosphors

Solid-State Reaction
Combustion synthesis

Hot injection and
hydrothermal reaction

$NaYF_4$: Yb,Er—an efficient upconversion phosphor*

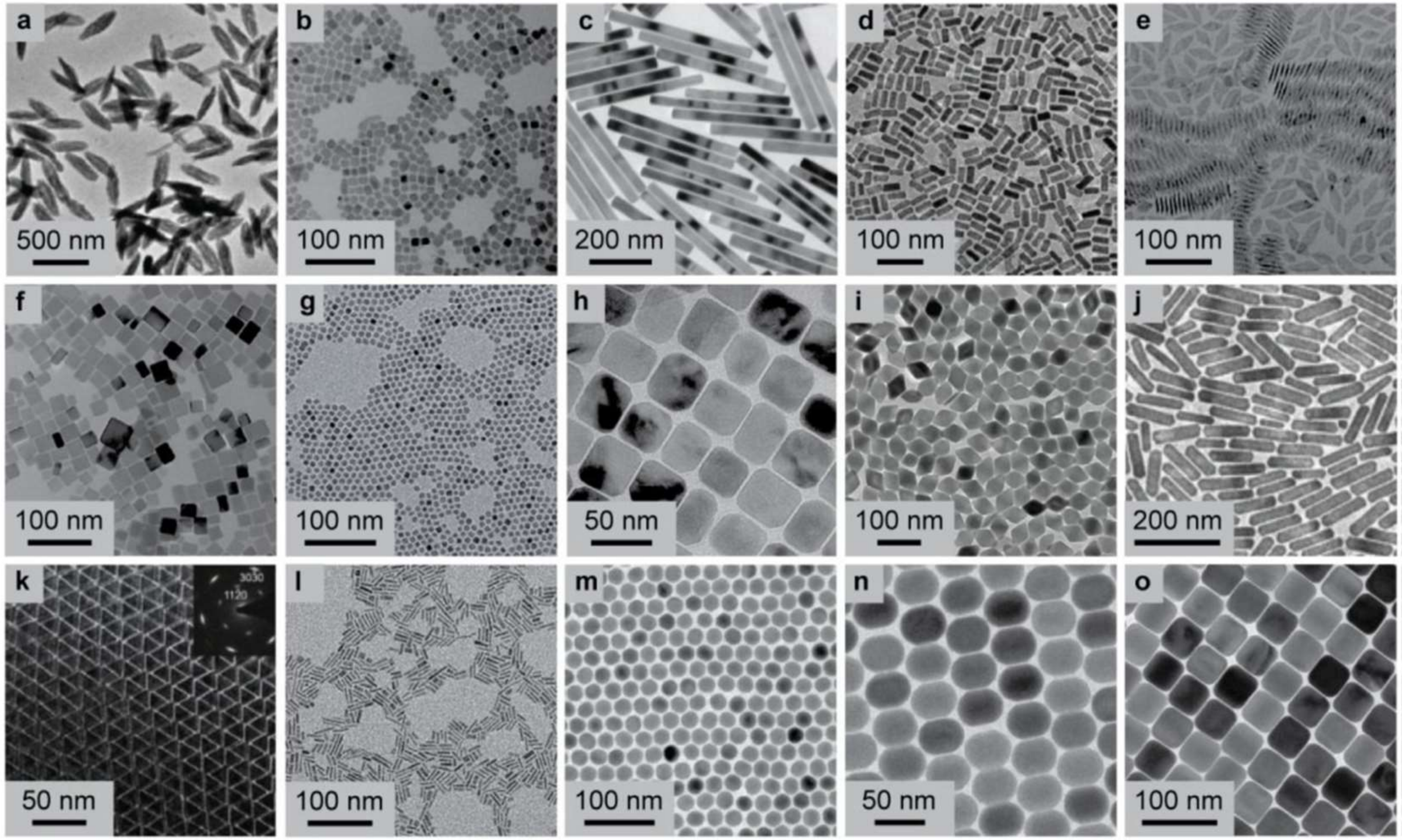
N. Menyuk, K. Dwight, and J.W. Pierce
Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts 02173

(Received 30 May 1972)

Studies of the infrared-pumped visible luminescence of $NaYF_4$:Yb,Er show it to have at least twice the visible output of YF_3:Yb,Er when pumped with a narrow-band excitation source at the optimum frequency. It is also free from saturation effects until very intense excitation levels are reached. The mechanism for red upconversion appears to change with increasing excitation from a two-step process to one involving a significant amount of three-step upconversion, which change is accompanied by an increase in the response time for visible emissions.

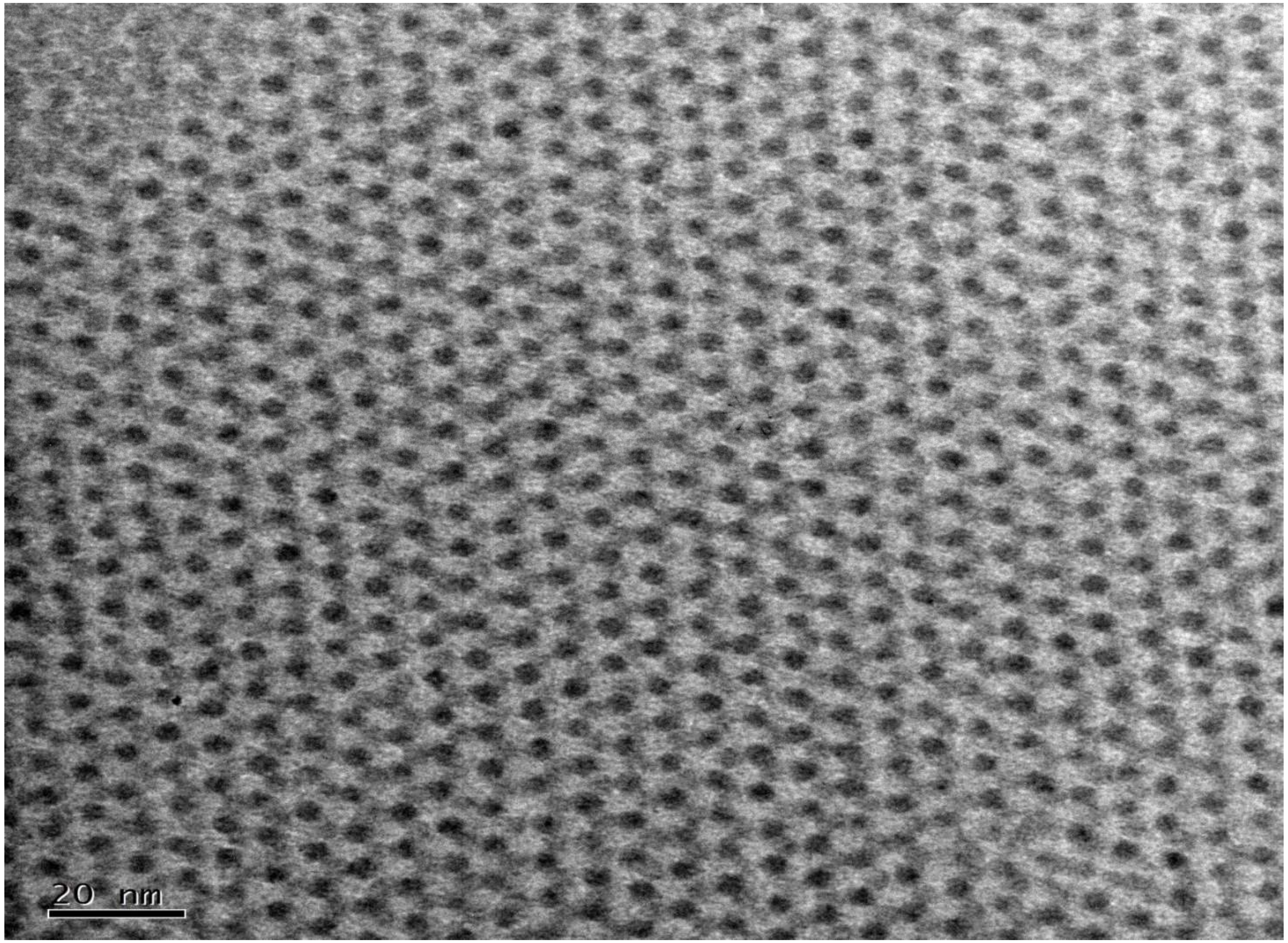
Appl Phys Lett 21, 159 (1972)

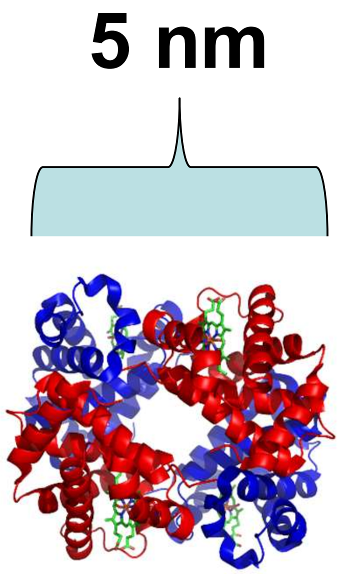
Challenges for Nanophosphor Synthesis



A. A. Bol, R. van Beek and A. Meijerink, ***Chem Mater*** 2002, 14, 1121; J. A. Capobianco, F. Vetrone, T. D' Alesio, G. Tessari, A. Speghinib and M. Bettinelli ***Phys Chem Chem Phys*** 2000, 2, 3203; S. Heer, K. Ko¨mpe, H. U. Gudel and M. Haase, ***Adv Mater*** 2004, 16, 2102; X. Wang, J. Zhuang, Q. Peng, Y. Li, ***Nature*** 2005, 437, 121; H. Mai, Y. Zhang, R. Si, Z. Yan, L. Sun, L. You and C. Yan, ***JACS*** 2006, 128, 6426; J. C. Boyer, F. Vetrone, L. A. Cuccia and J. A. Capobianco, ***JACS*** 2006, 128, 7444.

Size Matters!





Hemoglobin

Scale-down to sub-protein dimensions

Upconversion Signatures of Bulk & Nano forms

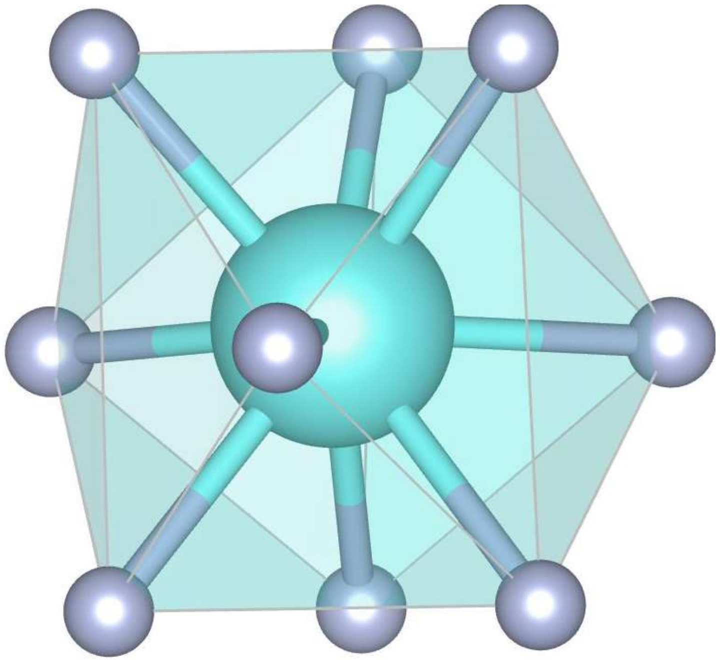
	Bulk	Nano (sub-10 nm)
Brightness	Relatively high	Extremely low
PLQY	~ 0.1	< 0.001
Lifetime	> 150 μs	< 50 μs
Irradiance-dependency	Higher fluence → shorter lifetime	Invariant lifetime
Quenching mechanism	• Cross-relaxation • Energy migration to defect	Surface-related loss: unsaturated coordination, H_2O, OH^-, and ligand

High-doping Design:

Under high-power (10^5 –10^7 W/cm^{-2}) irradiation, heavy doping of activators leads to enhanced emission, while doping of sensitizers becomes less important.

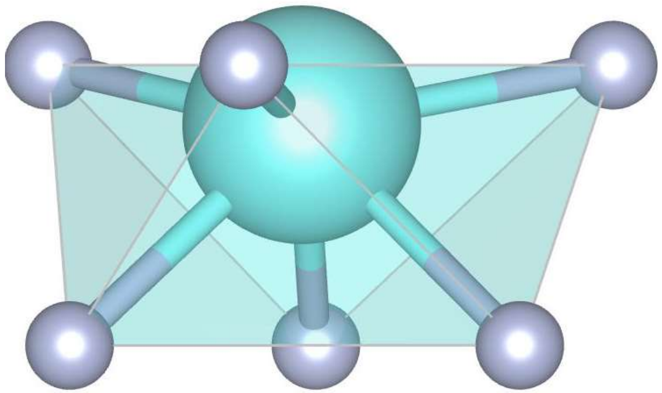
Nature Nanotechnology 8, 729 (2013) and 9, 300 (2014).

Surface Properties



Bulk $NaYF_4$
CN = 9

(0001) facet

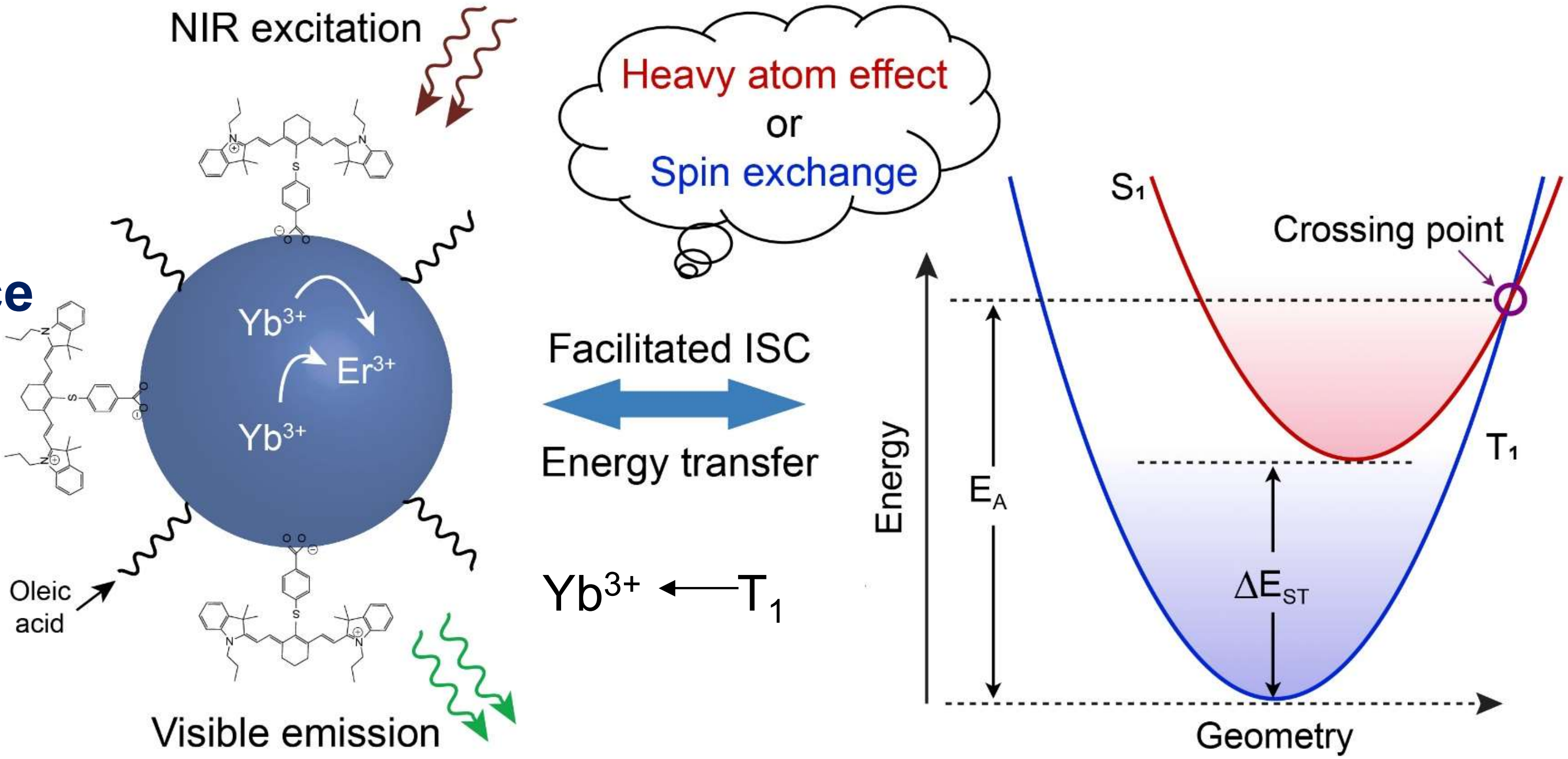


Surface Topology $NaYF_4$
CN = 6

Surface Engineering for Upconversion Enhancement

Strategies:

- **Core-shell structure**
- **High-power irradiance**
- **Dye-sensitization**
- **Other methods ??**



Challenge:

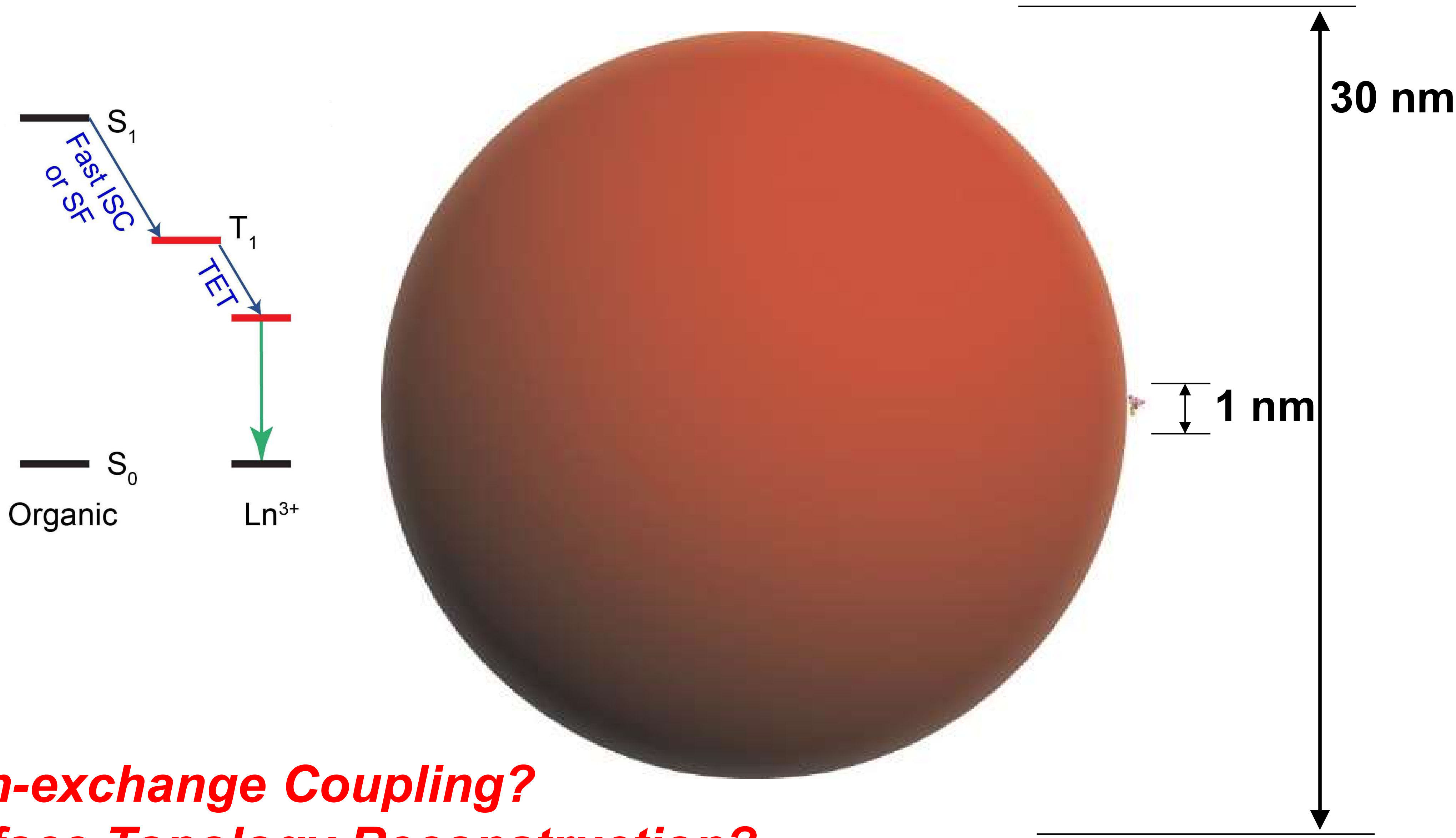
Preparation of ultrasmall, bright nanocrystals.

Mechanistic Investigations.

Nature Photonics, 2018, 12 402

Unanswered Questions

Energy Transfer from Small Molecules to 'Large' Nanocrystals



Spin-exchange Coupling?

Surface Topology Reconstruction?

Energy Migration through Sublattices

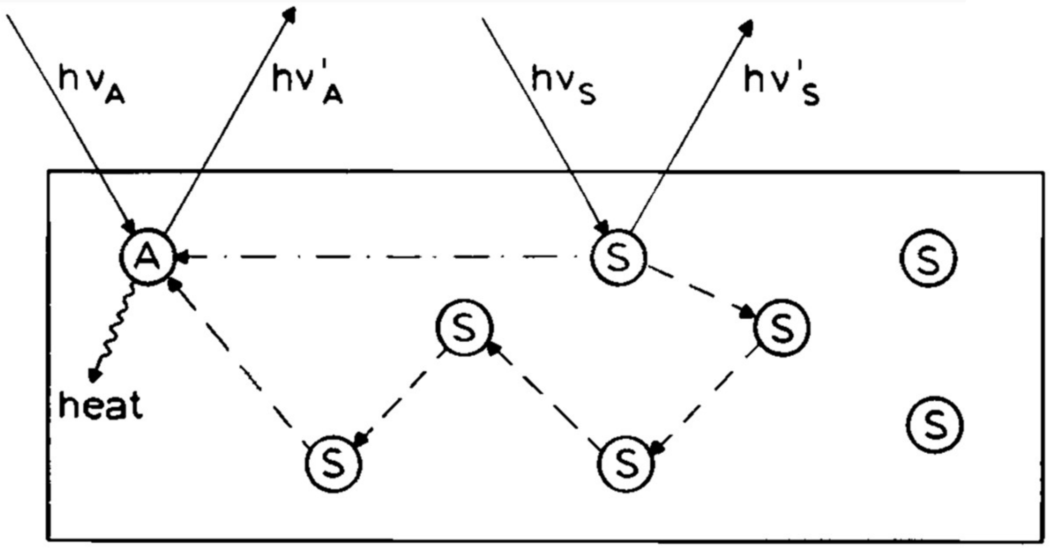
Journal of Luminescence
Volume 29, Issue 3, May–June 1984, Pages 243-260

LUMINESCENCE AND ENERGY MIGRATION IN A TWO-DIMENSIONAL SYSTEM: $NaEuTiO_4$

P.A.M. BERDOWSKI and G. BLASSE

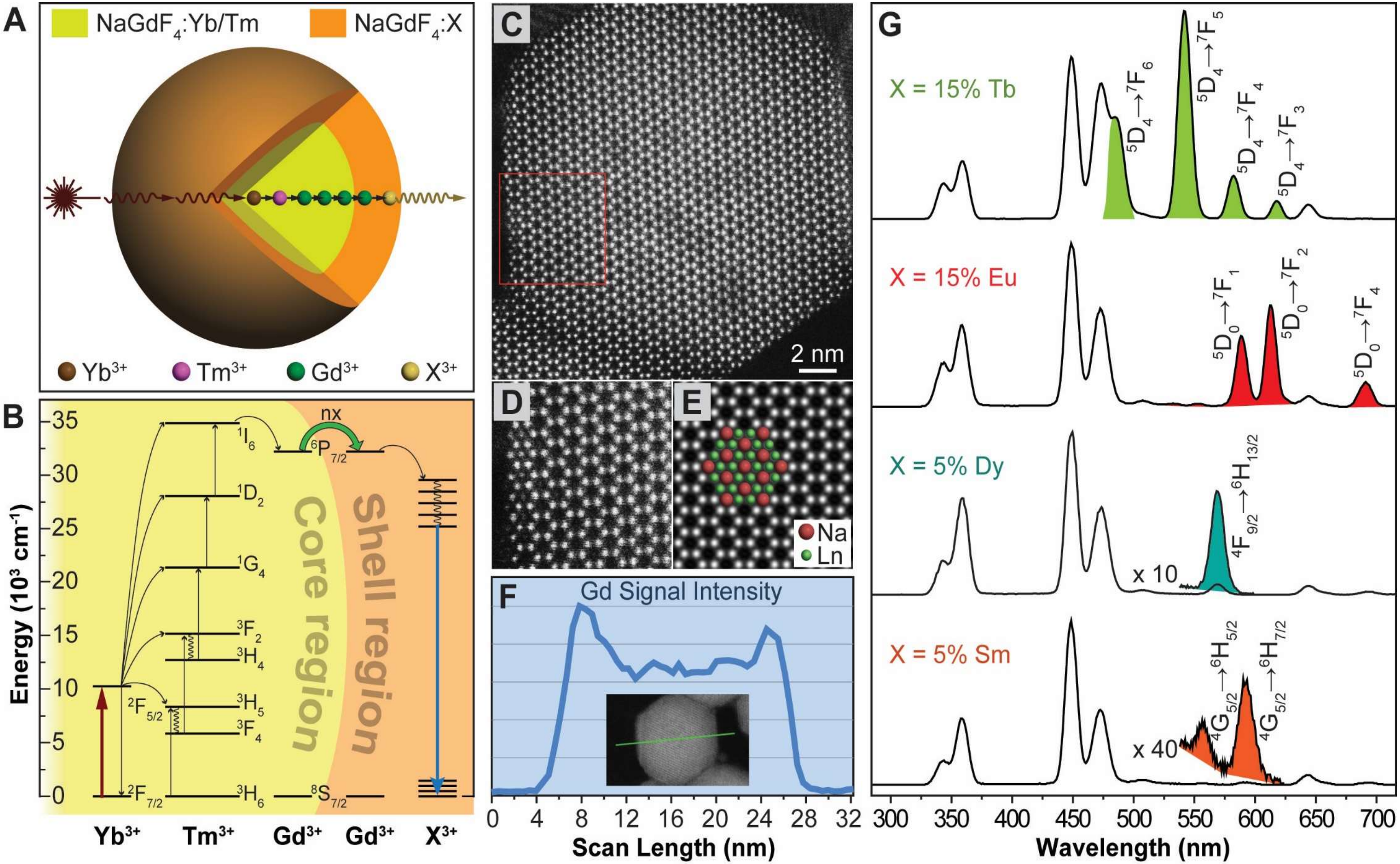
Solid State Department, Physics laboratory, Utrecht University, P.O. Box 80.000, 3508 TA Utrecht, The Netherlands

Received 5 January 1984



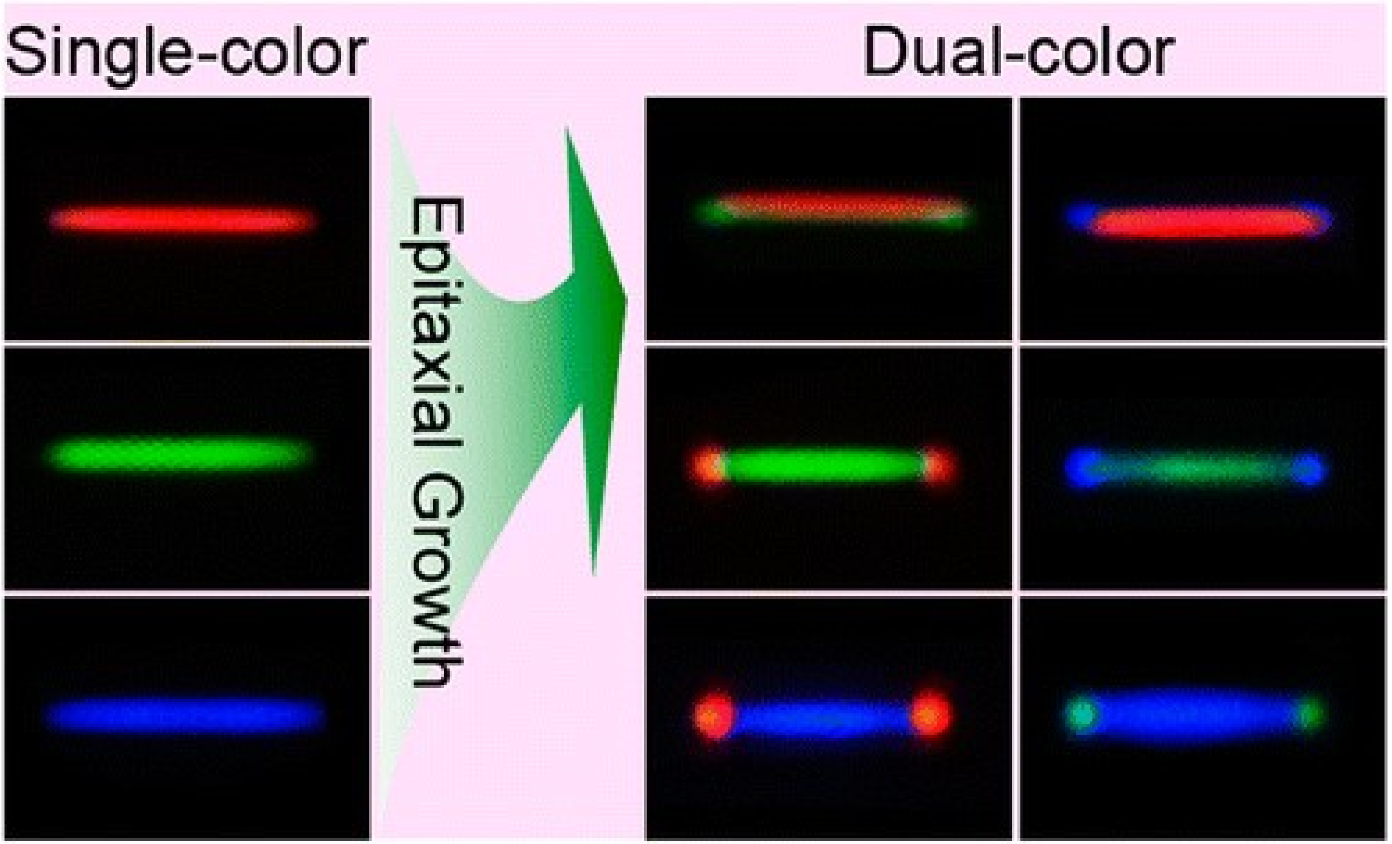
G. Blasse ***Red. Trav. Chim. Pays-Bas*** 105, 143-149 (1986)

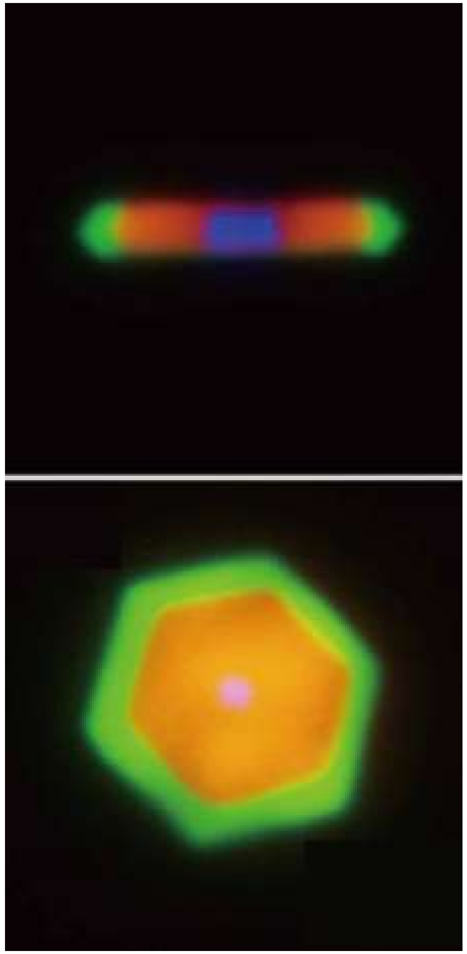
Energy Migration within Core-Shell Structures



F. Wang et al. ***Nature Materials***, 2011, *10*, 968.

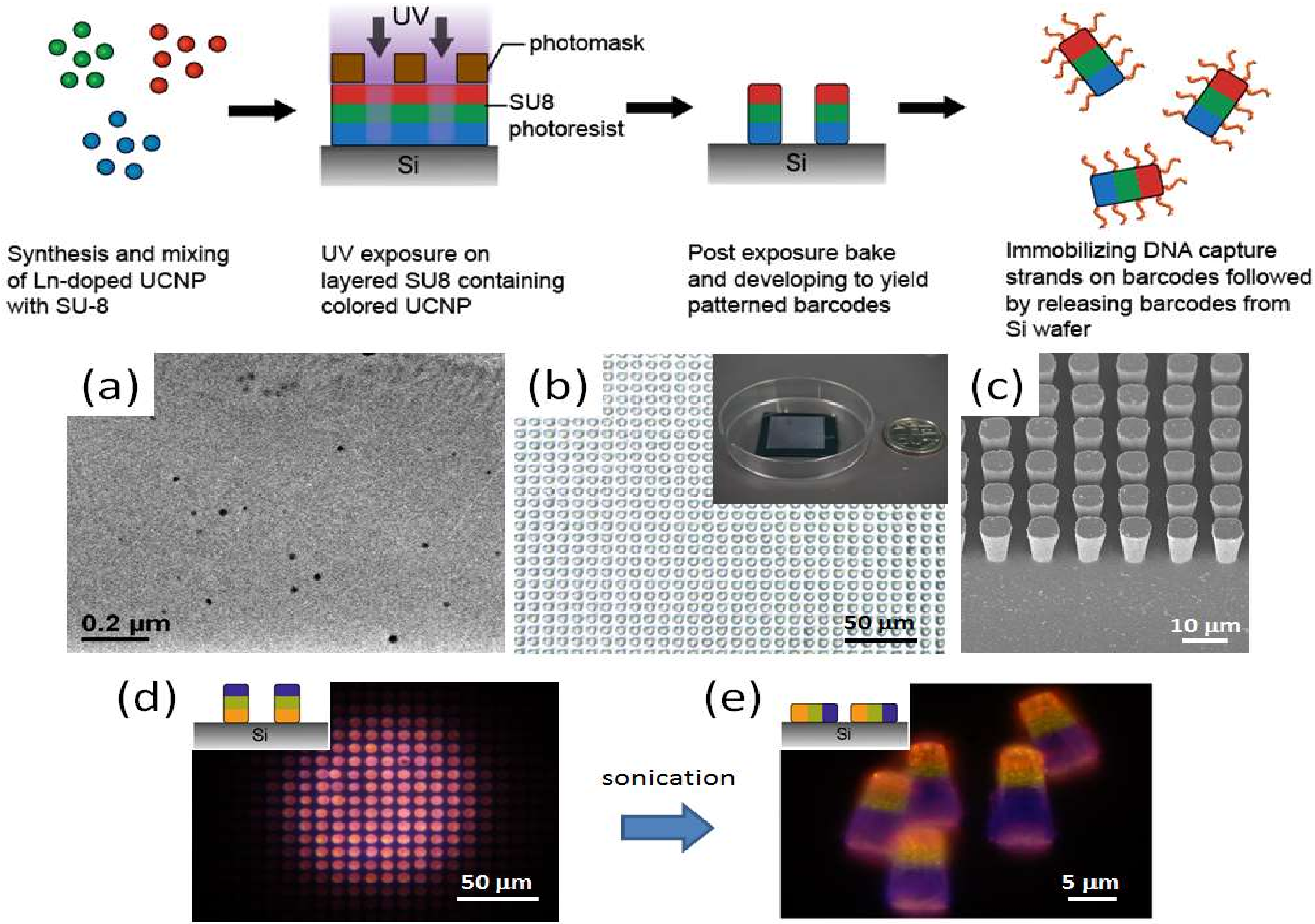
Multicolor Barcoding at Single-Crystal Resolution





J. Am. Chem. Soc., **2014**, *136*, 4893–4896.

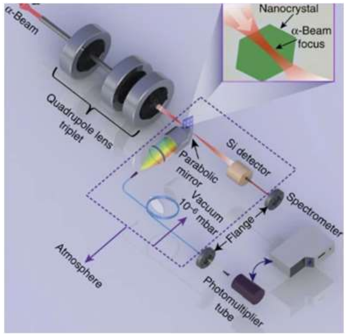
Photolithographic Fabrication



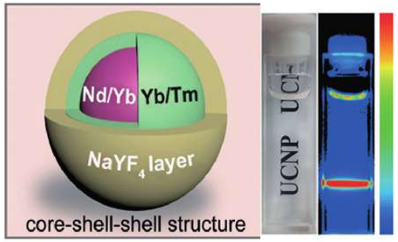
Adv Opt Mater **2020**

Choice of Excitation

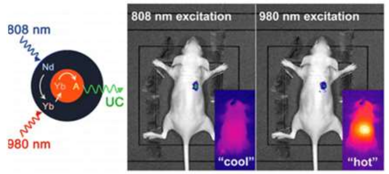
Nat. Commun. '15



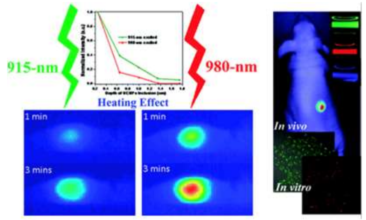
Adv. Mater. '15
Chem. Eur. J. '16



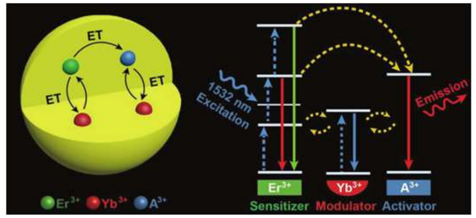
ACS Nano '13
JACS "13



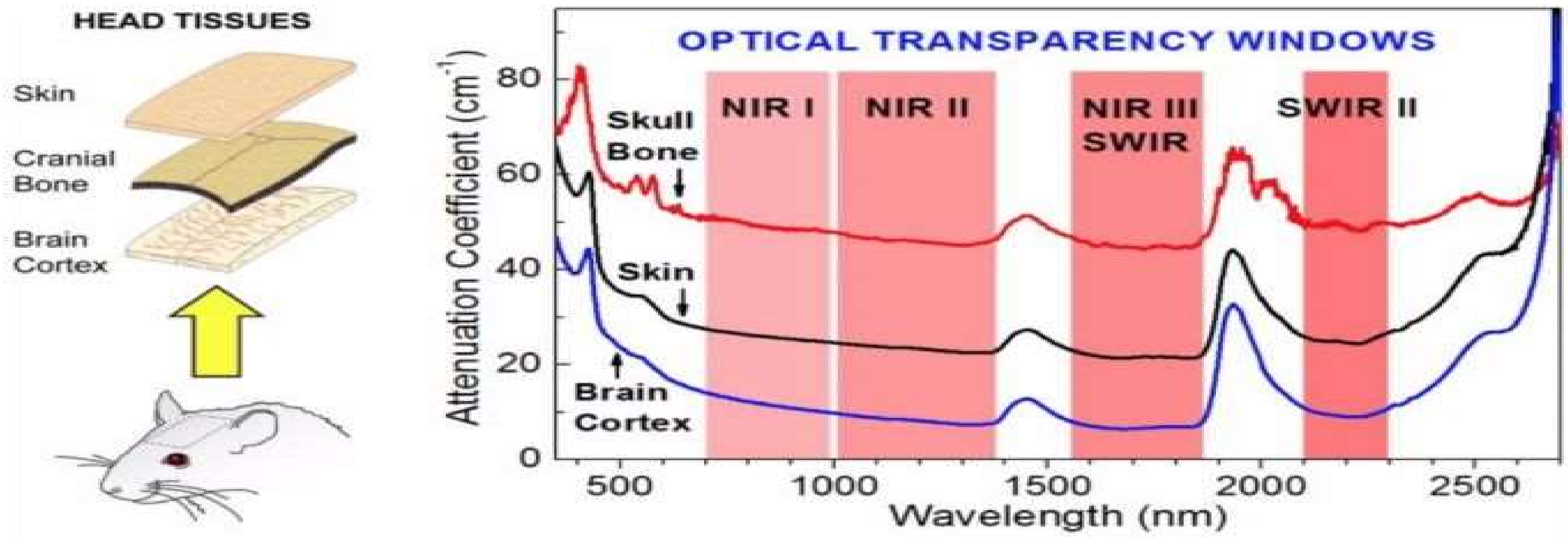
ACS Nano '11



Angew. Chem. '17
Adv. Funct. Mater. '18

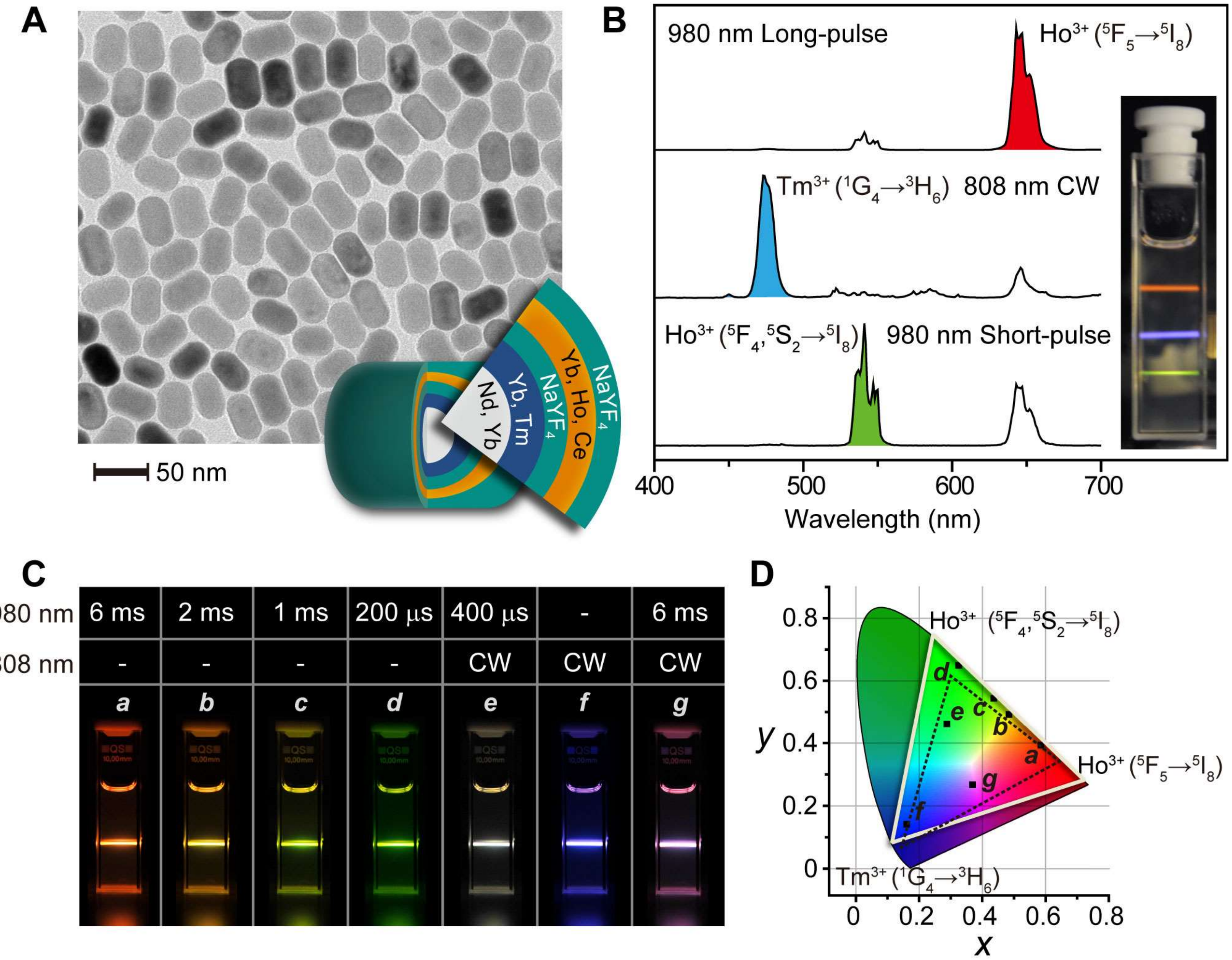


Ion beam | **740 nm** | **800 nm** | **915 nm** | **980 nm** | **1530 nm**



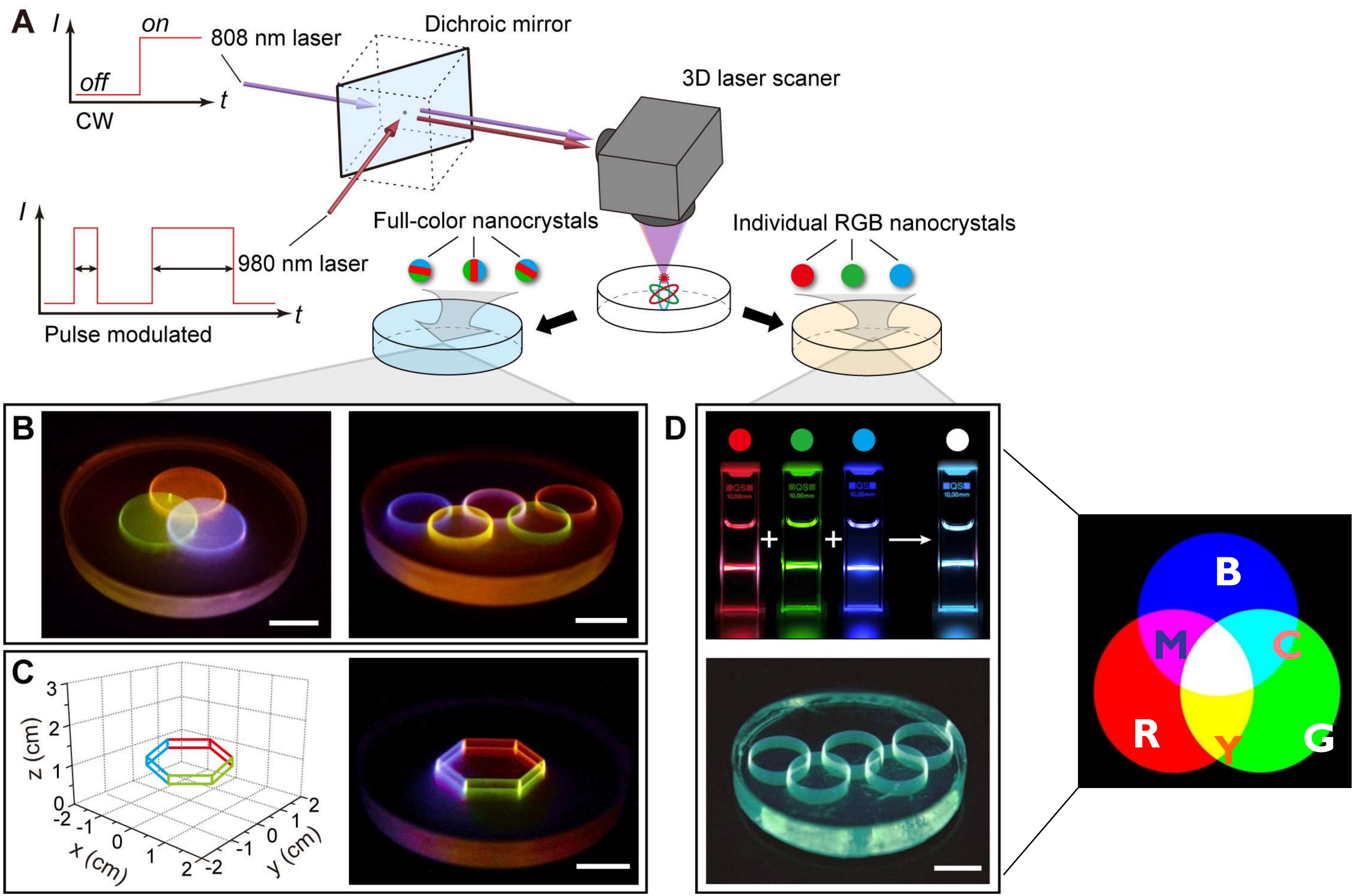
***J. Biophotonics.* *11*,** e201800141 (2018)

Remote Color Tuning On Demand

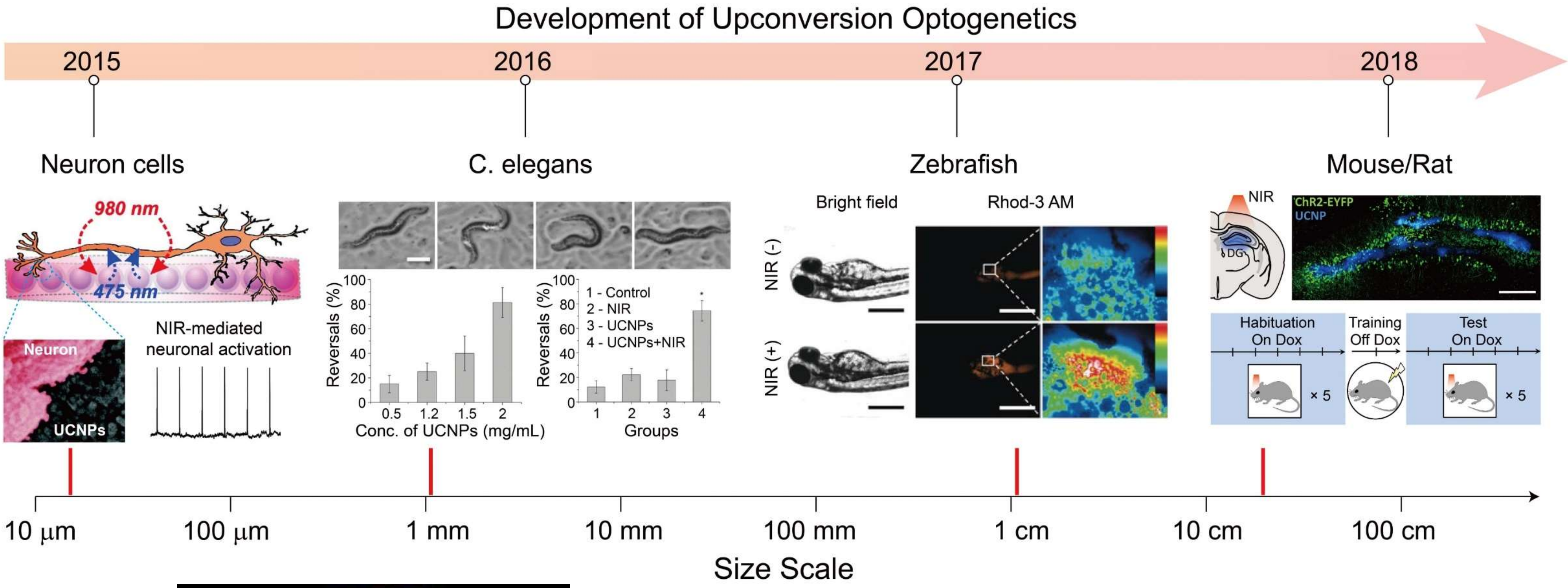


Deng *et al.* ***Nature Nanotech.*** **2015**

Volumetric 3D Display in Full Color

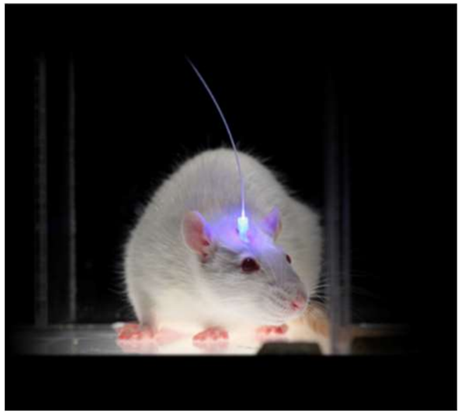


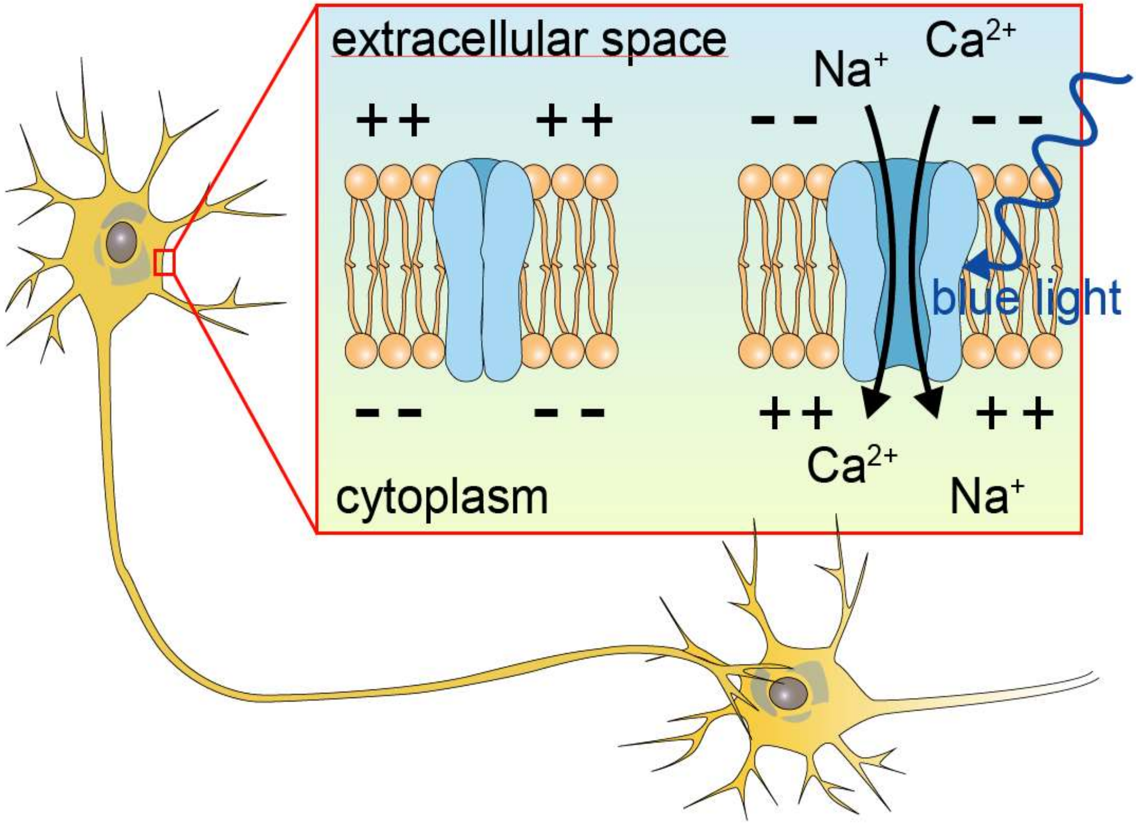
Deng *et al.* ***Nature Nanotech.*** 2015



Parkinson's disease,
Essential tremor,
Dystonia,
Chronic pain,
Major depression,
Obsessive–compulsive disorder
...

Understanding the Brain



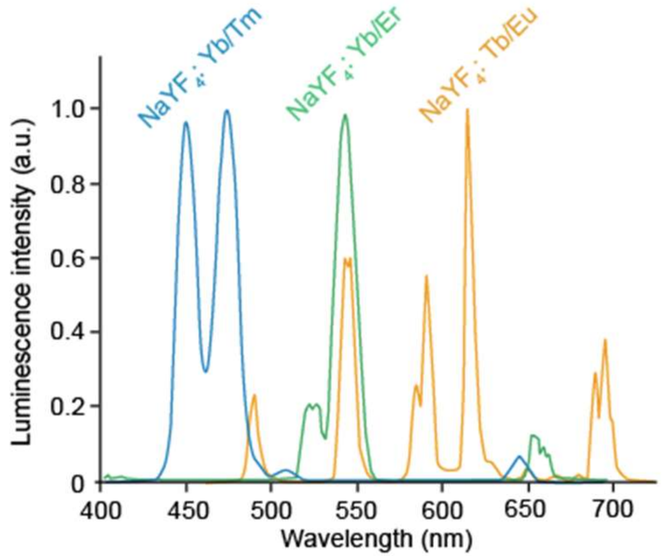


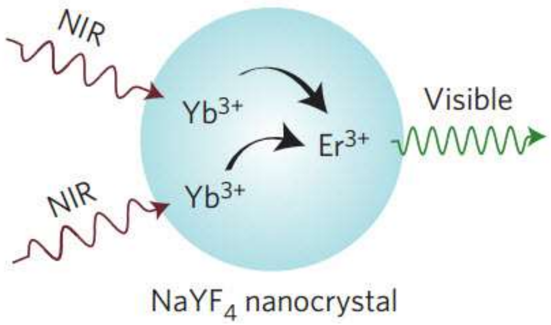
Oka et al., *Nature*, 520, 349

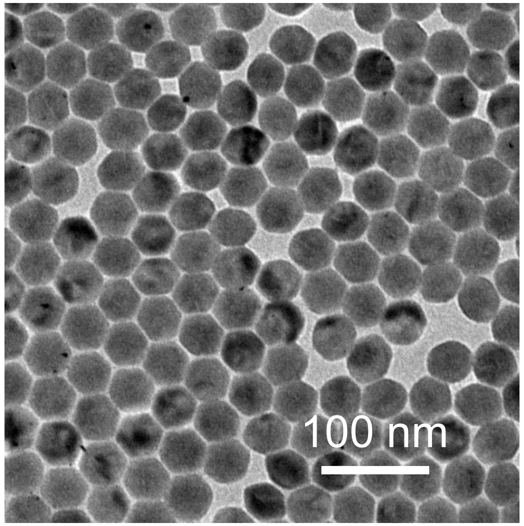
Near-infrared (NIR) Optogenetics

Convert NIR light to visible light

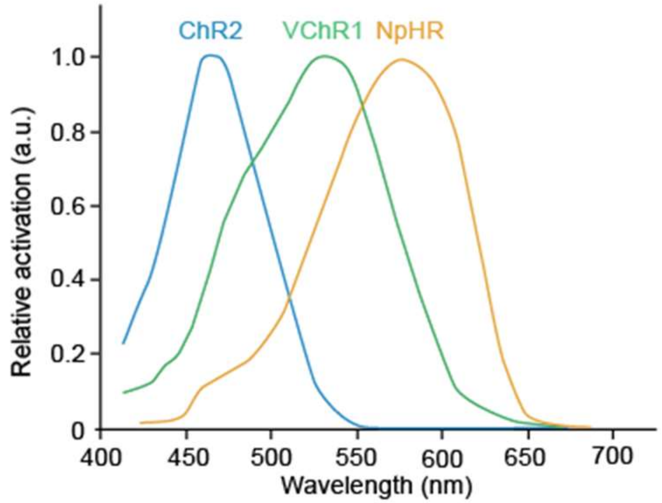
UCNP emission wavelength







Opsin excitation wavelength

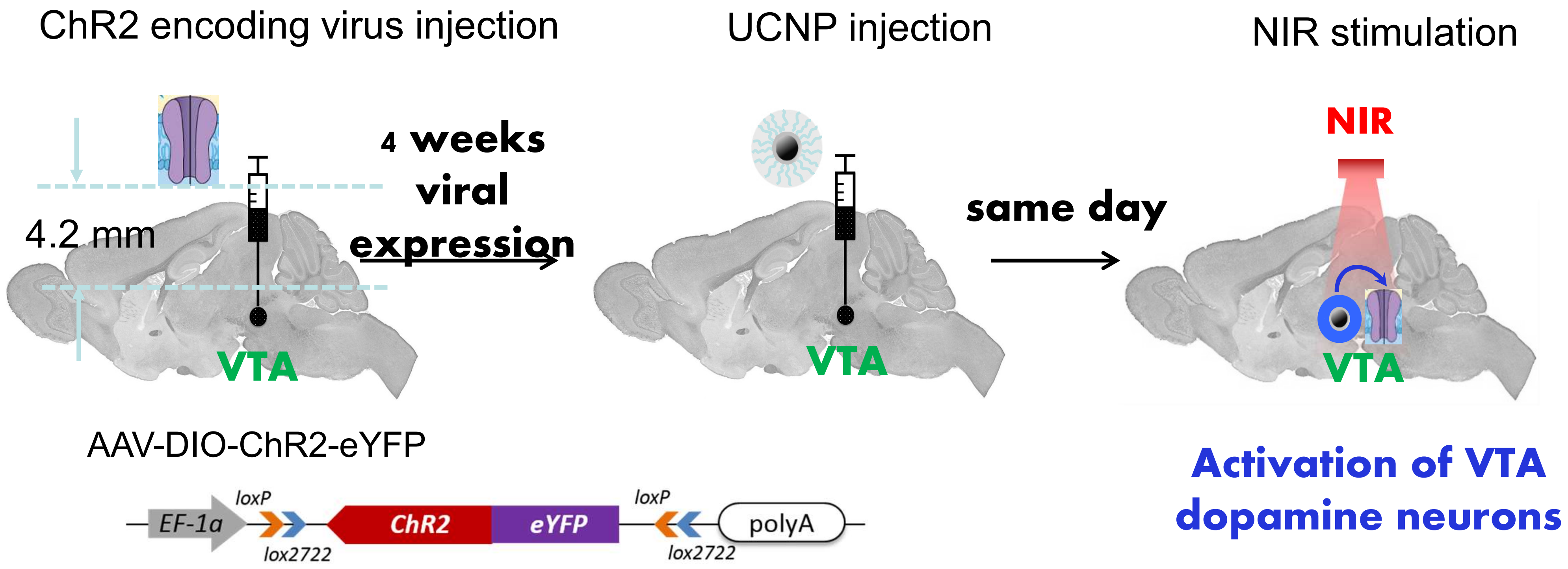


Chen et al. *Science* **2018**

NIR optogenetics for deep brain stimulation in rodents

Stimulating dopamine (DA) neurons at Ventral Tegmental Area (VTA) brain region

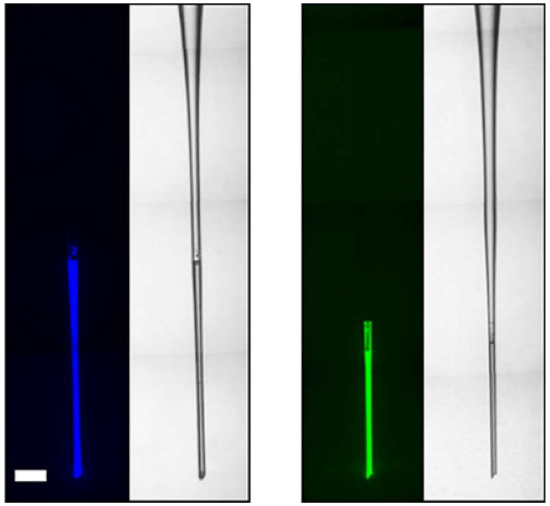
Related to the reward mechanism



Chen et al., *Science* **2018**

Near-Infrared Control of Brain Activity

Activation in C1V1-Mouse



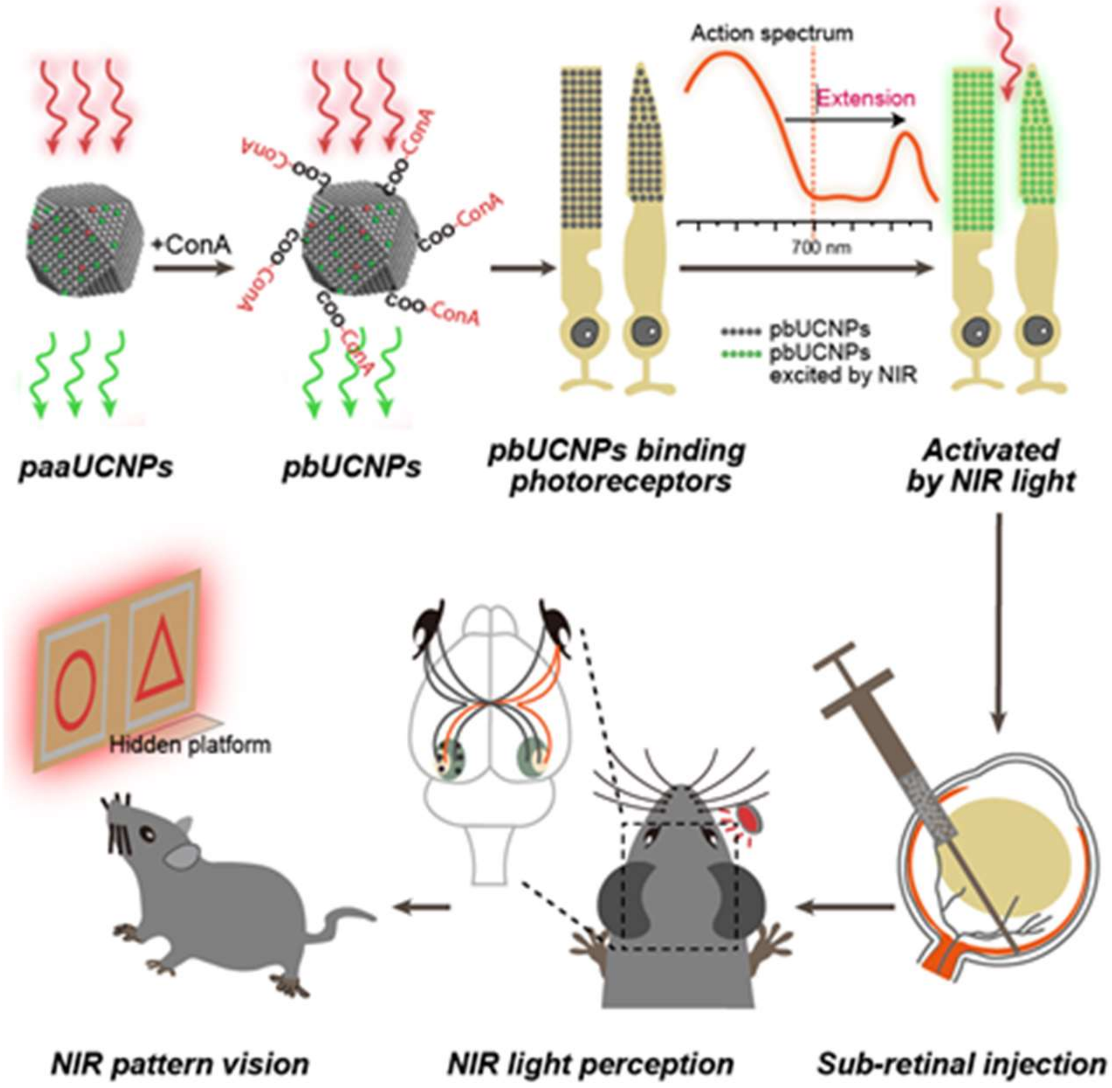
Shi et al. *Biomaterials*, 2017, 142, 136;
Nano Letters, 2018, 18, 948.

UCNP-based Micro-Optrodes

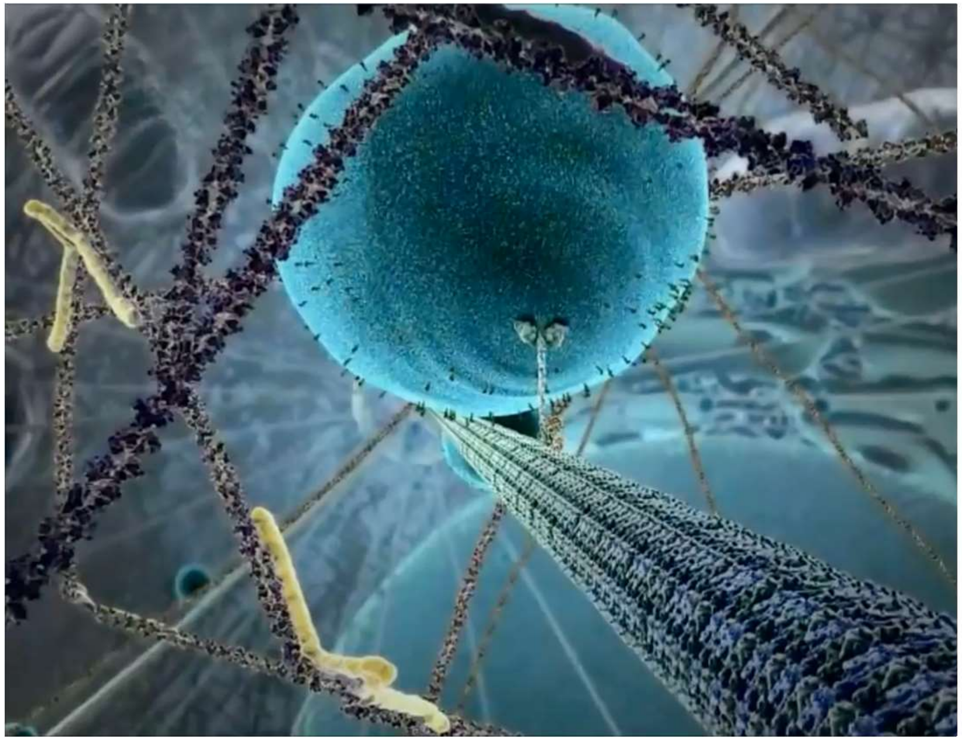
Inhibition in eNpHR-Mouse

Mammalian Near-Infrared Image Vision through Injectable and Self-Powered Retinal Nanoantennae

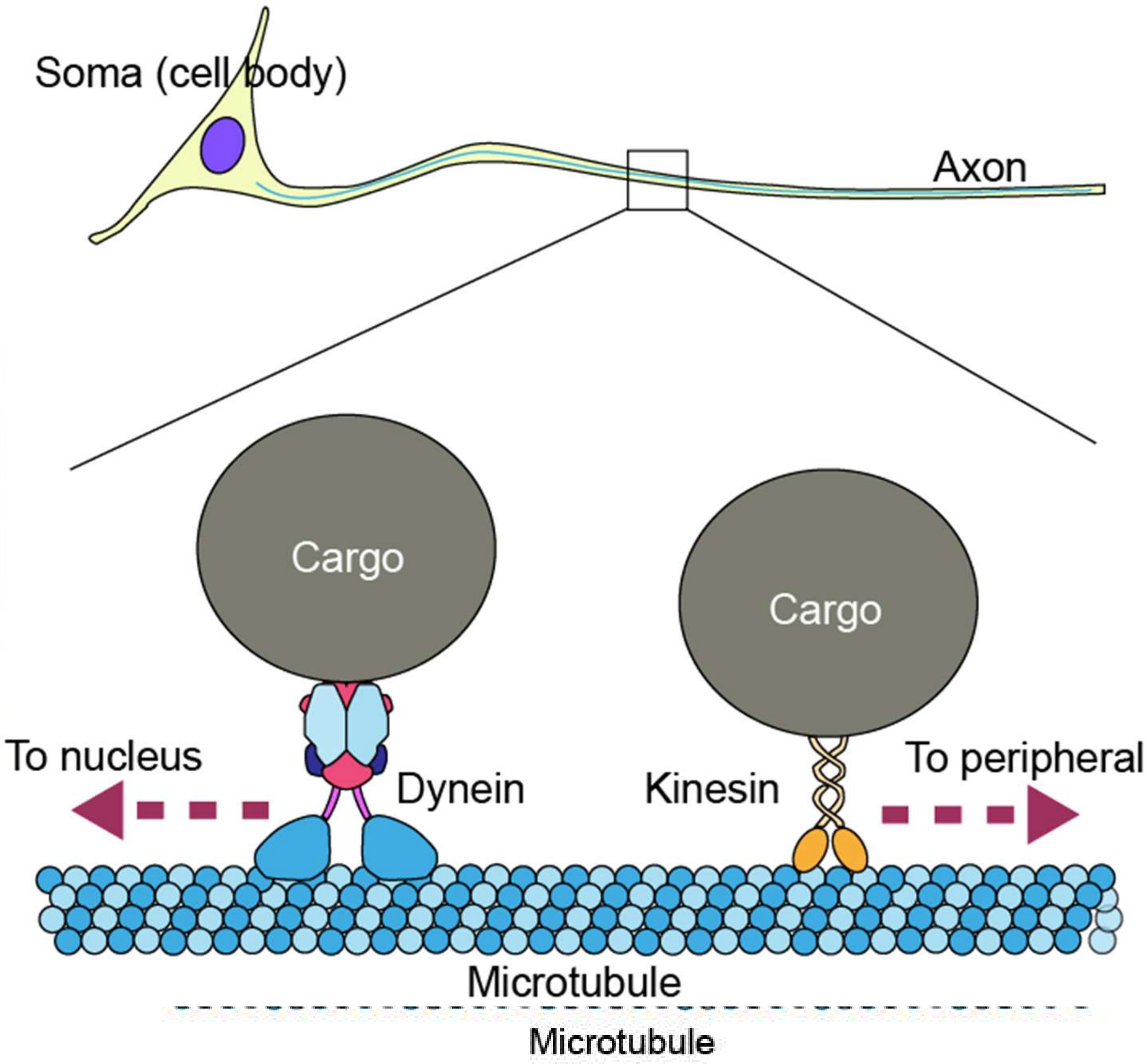
Ma et al. *Cell* **2019**, 177, 243-255.



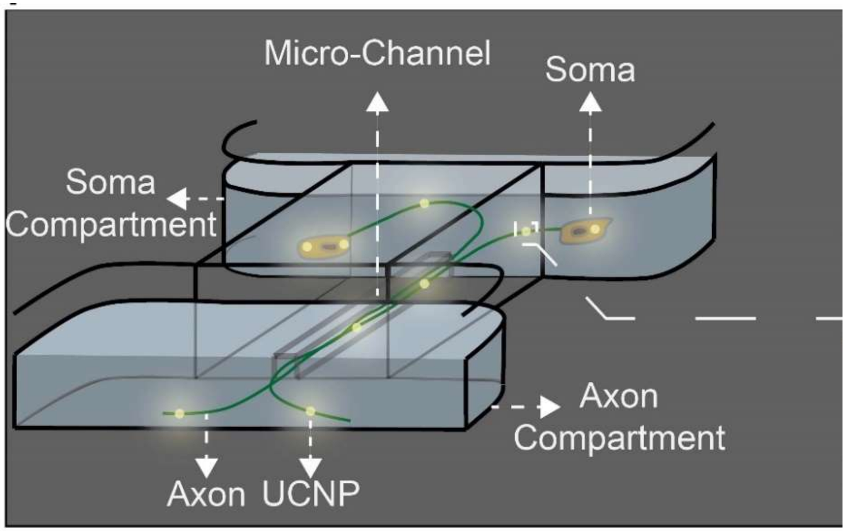
Imaging motor protein with UCNPs

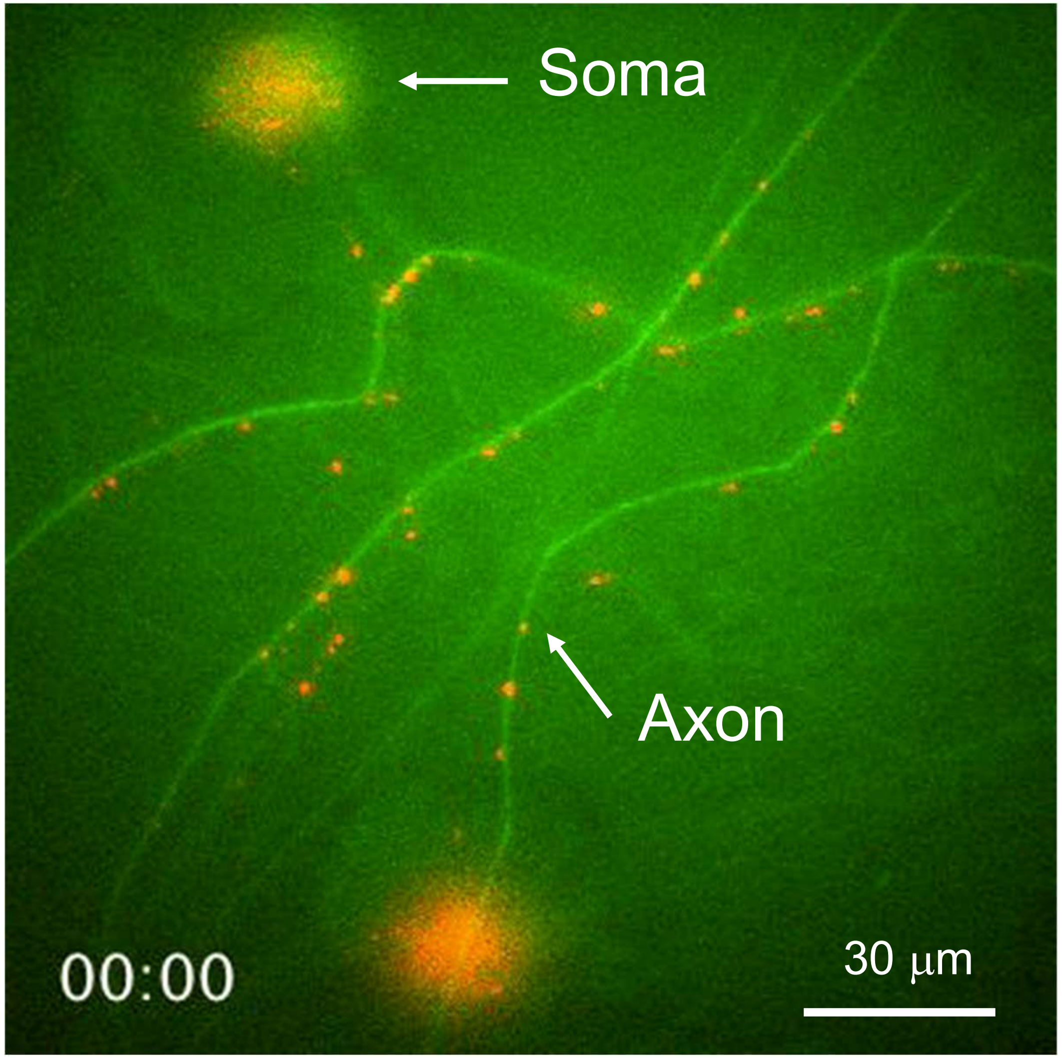


Video from http://www.studiodaily.com
'The Inner Life of a Cell'



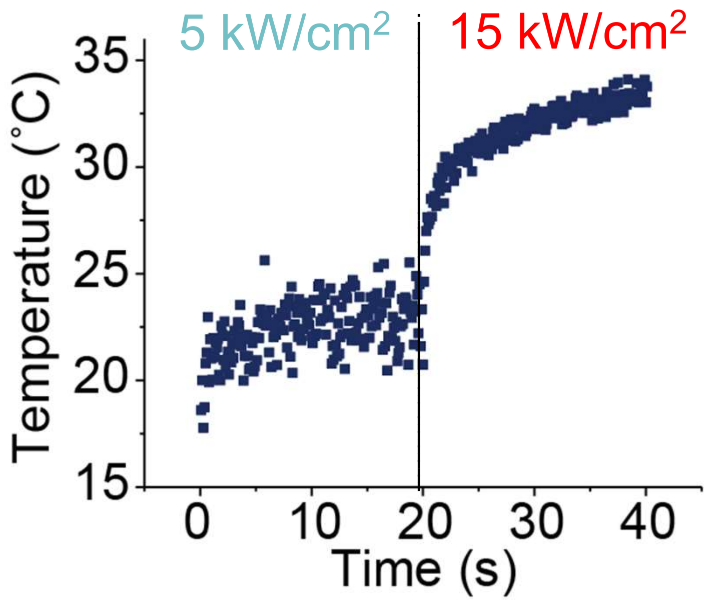
Video recording in soma chamber

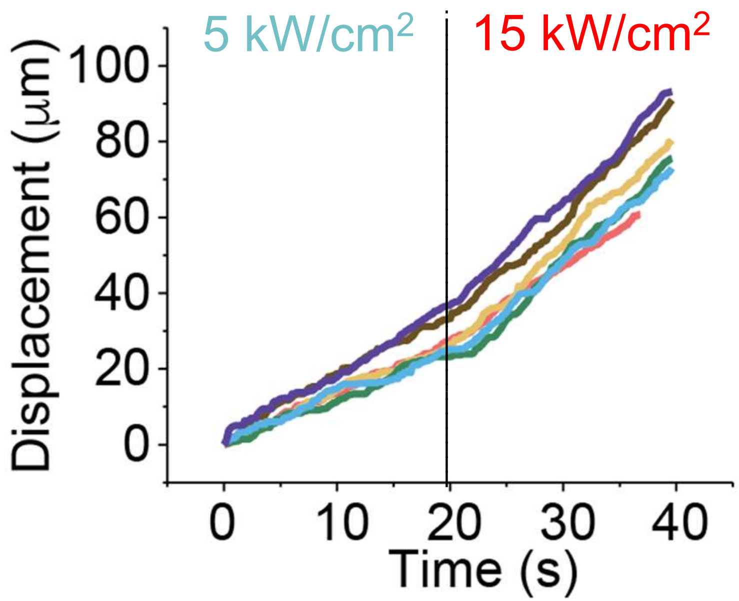


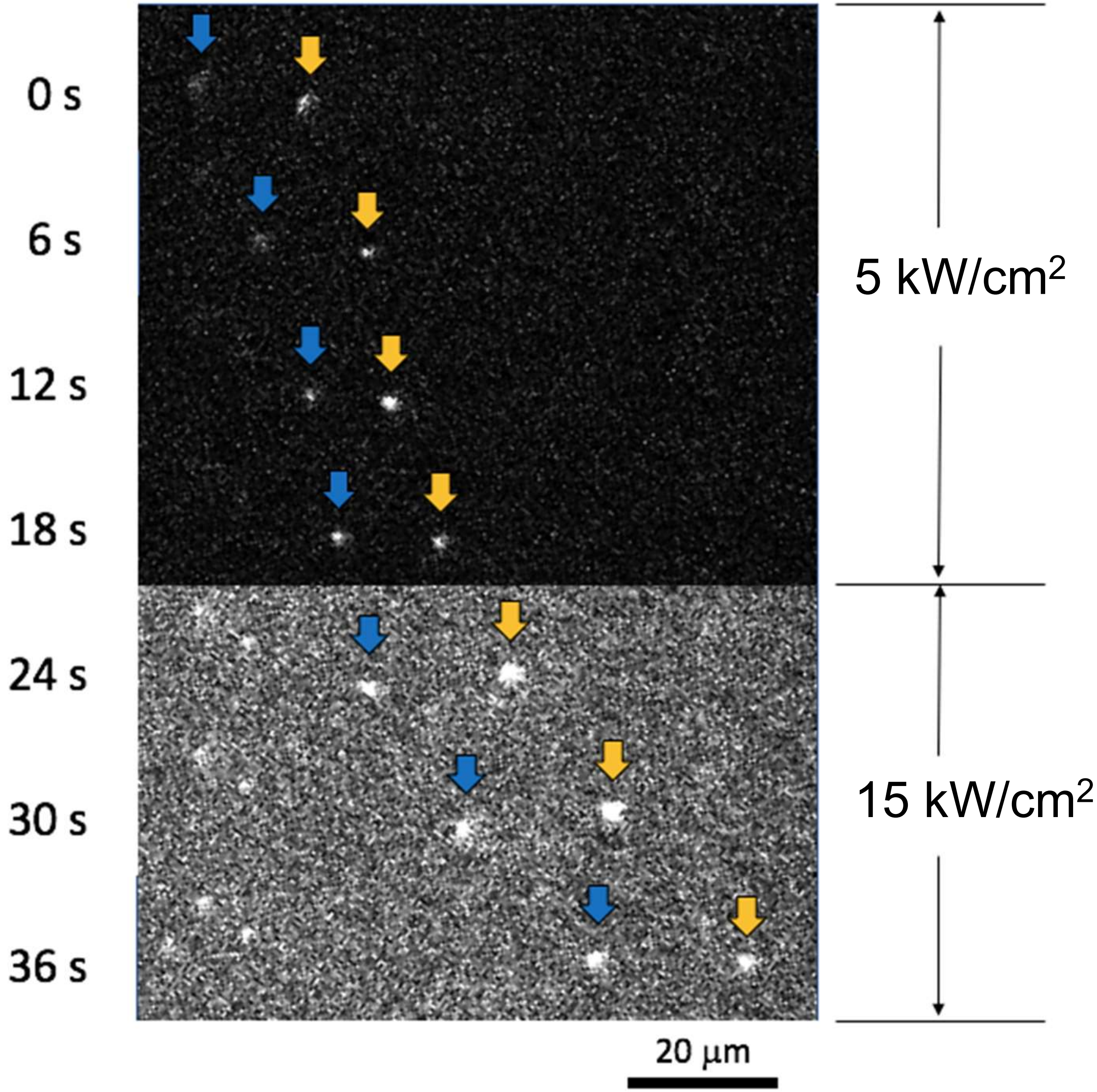


Zeng et al. ***Angewandte Chemie*** 2019

Probing Dynein Behavior

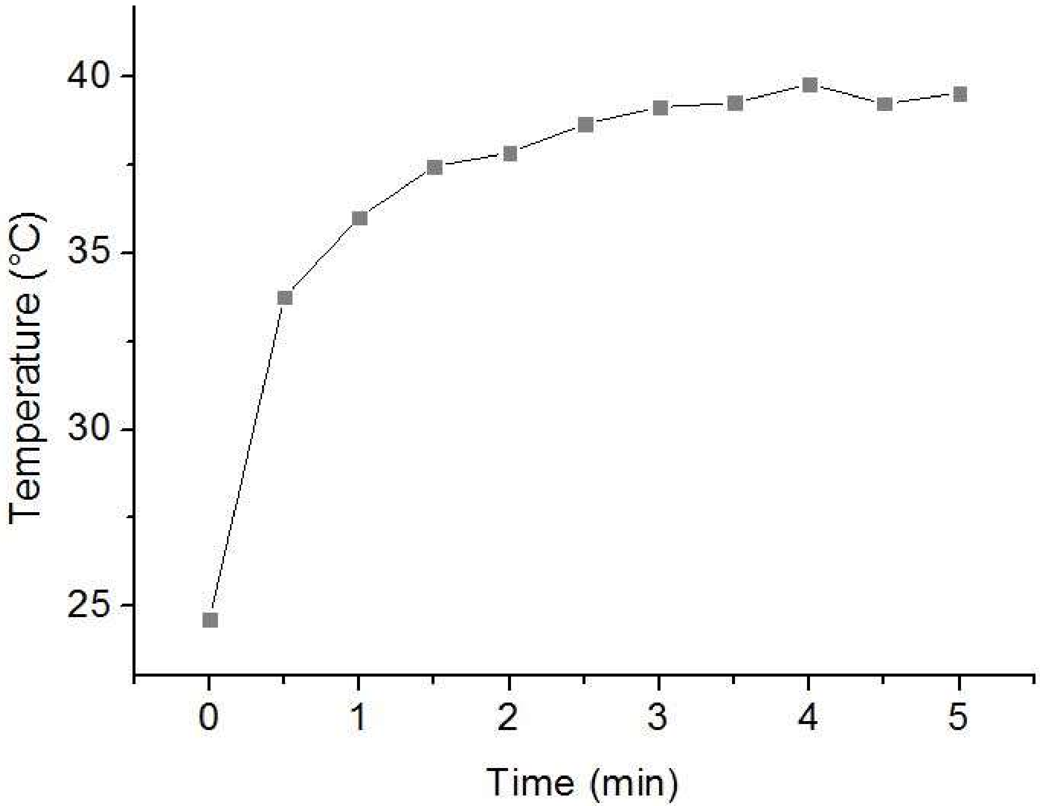


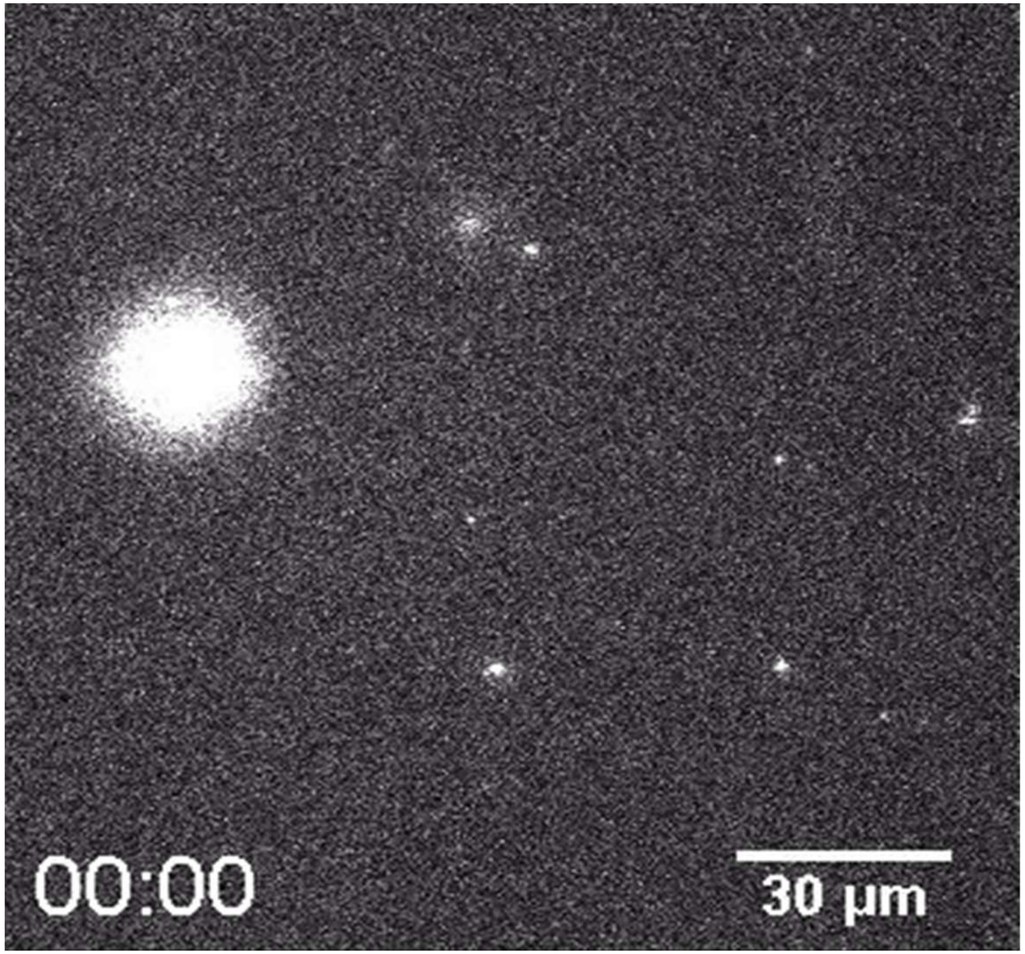




Temperature rise under 980 nm illumination

980 nm at 15 kW/cm^2





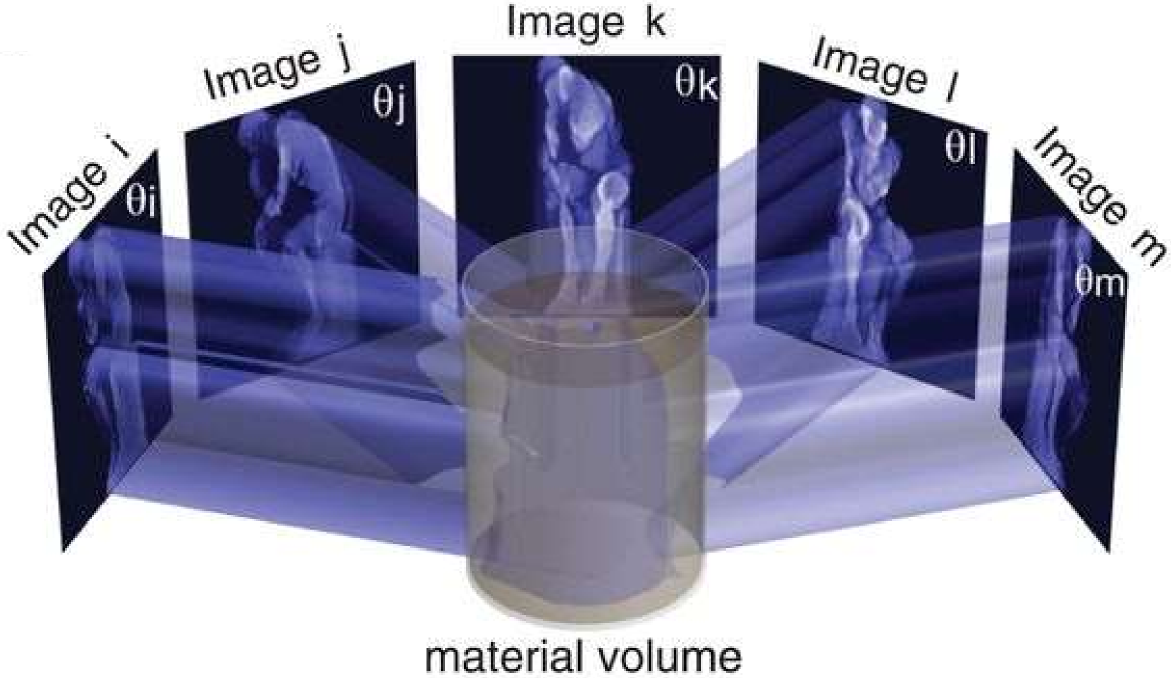
The Optical Path to 3D Printing

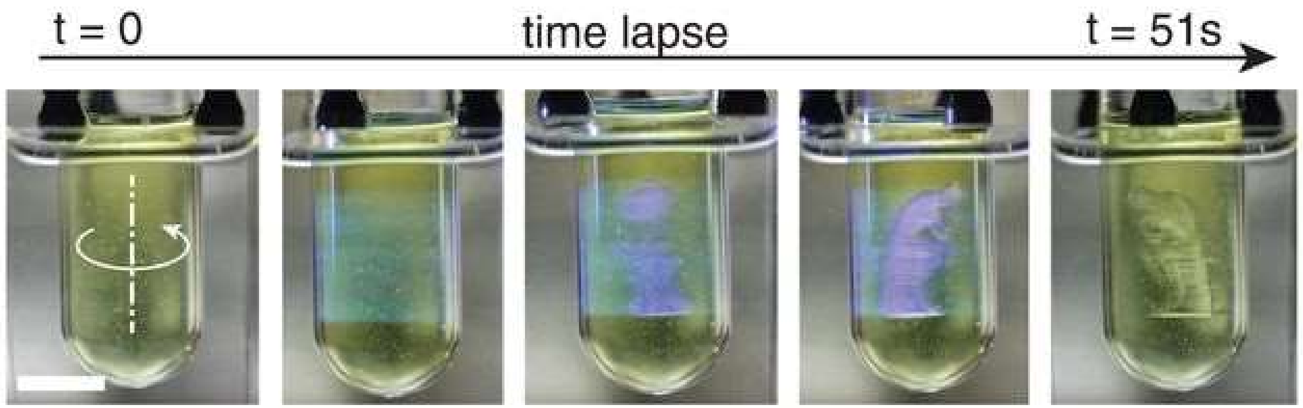
The Computed Axial Lithography (CAL) Approach

Challenges for 3D printing

- Slow build rates
- Layering artifacts
- Geometric constraints
- Equipment and manufacturing costs
- Post-processing requirements

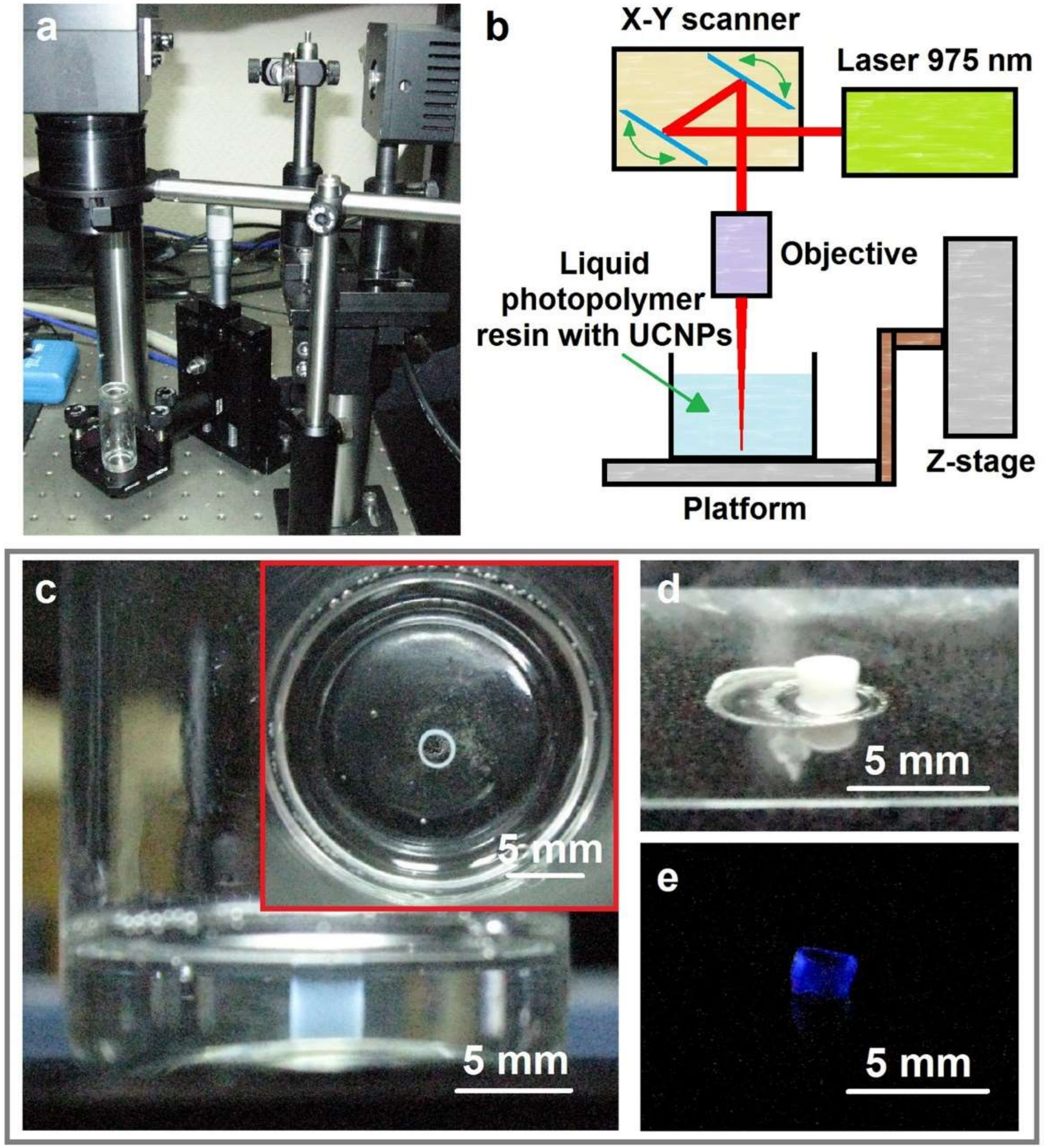
https://www.instructables.com/id/3D-Printed-Cycle





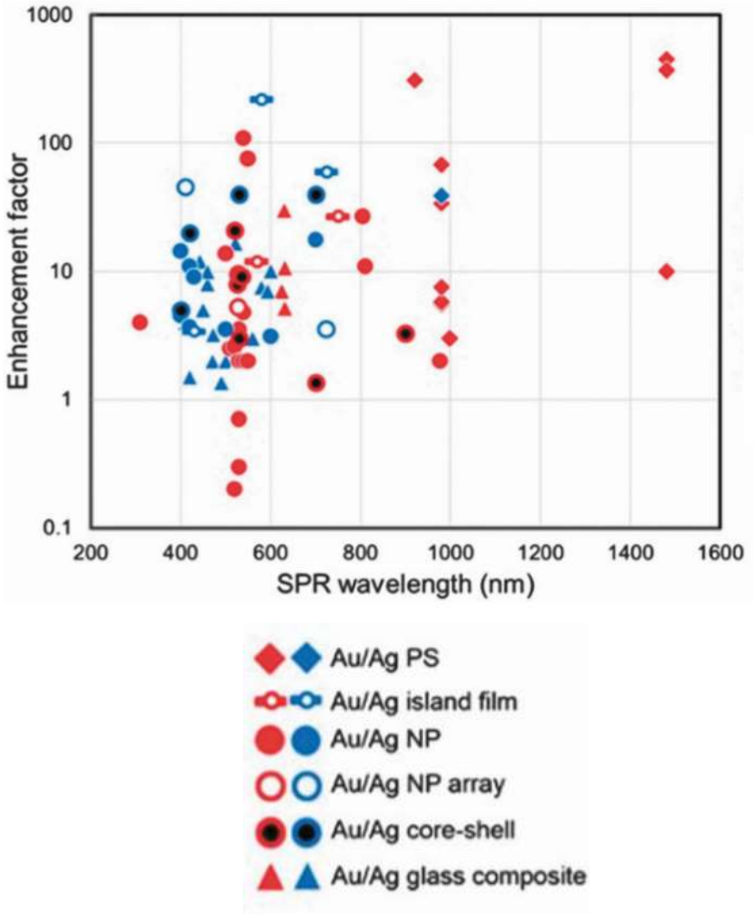
Science 08 Mar 2019

3D Photopolymerization Using Upconversion Nanoparticles



Scientific Reports **volume 8**,
Article number: 3663 (2018)

Plasmon-Coupled Upconversion Enhancement



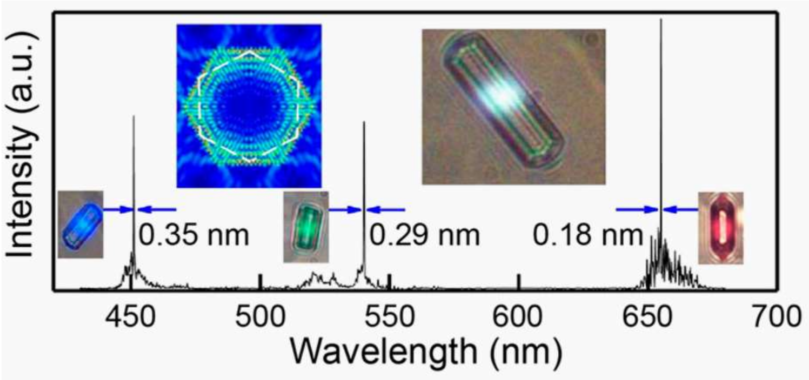
Challenges:

- ***Insufficient optical density of states within localized 'hot spots' or inefficient spatial coupling between nanoparticles and optical resonators***
- ***Scattering due to surface roughness***
- ***Large-scale assembly of UCNPs into well-defined plasmonic circuitry with single-particle resolution***

Chemical Society Reviews, 2015, 44, 2940

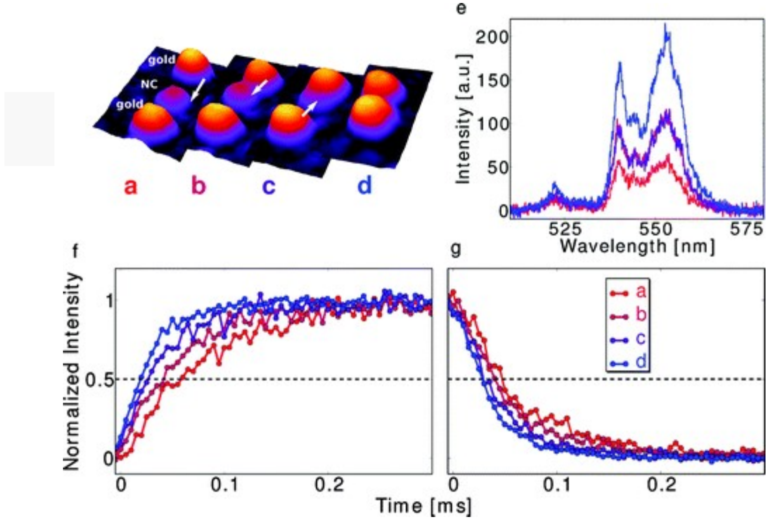
Single Nanoparticle/Molecular Manipulation

White-light single-particle upconversion lasing

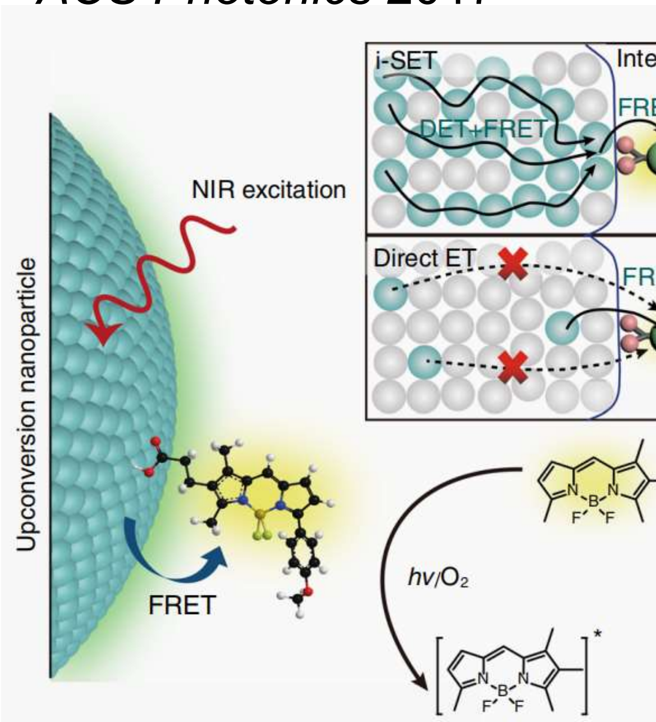


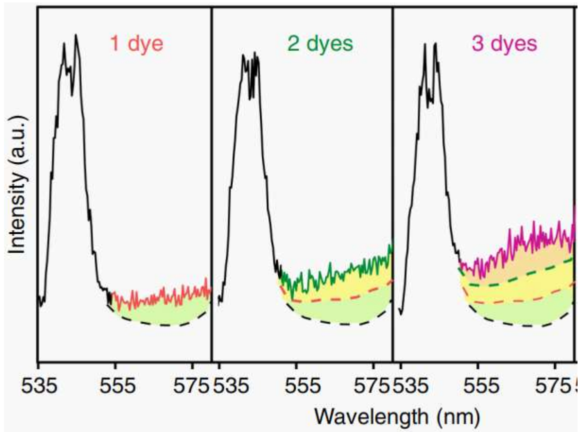
ACS Photonics 2017

Plasmon-Enhanced Upconversion



Nano Lett. 2010



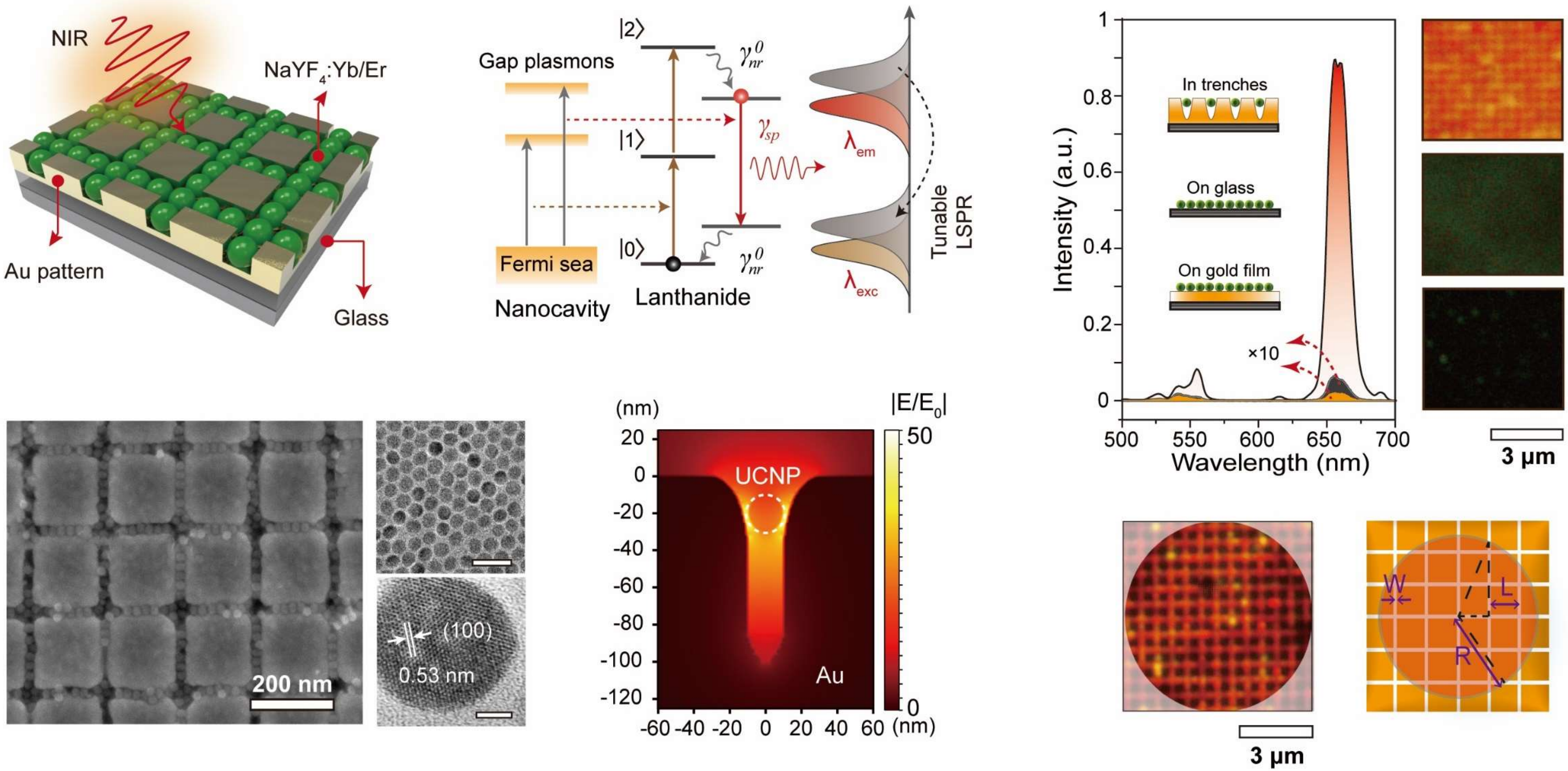


Single upconversion nanoparticle-based molecular sensing

$NaYbF_4$:Tb@$NaTbF_4$

Nat. Commun., 2020

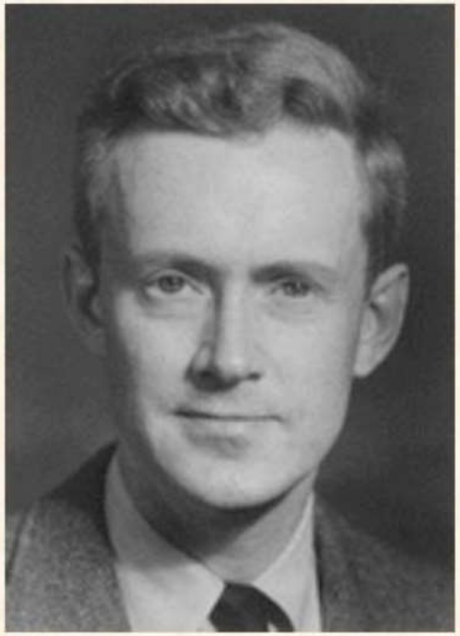
Deep-subwavelength Near-field Confinement toward Giant Upconversion Emission



Manuscript under consideration in *Adv. Mater.*

Purcell effect

1946 - E. M. Purcell predicts modification of spontaneous emission rates in complex media



Edward M. Purcell
1912-1997

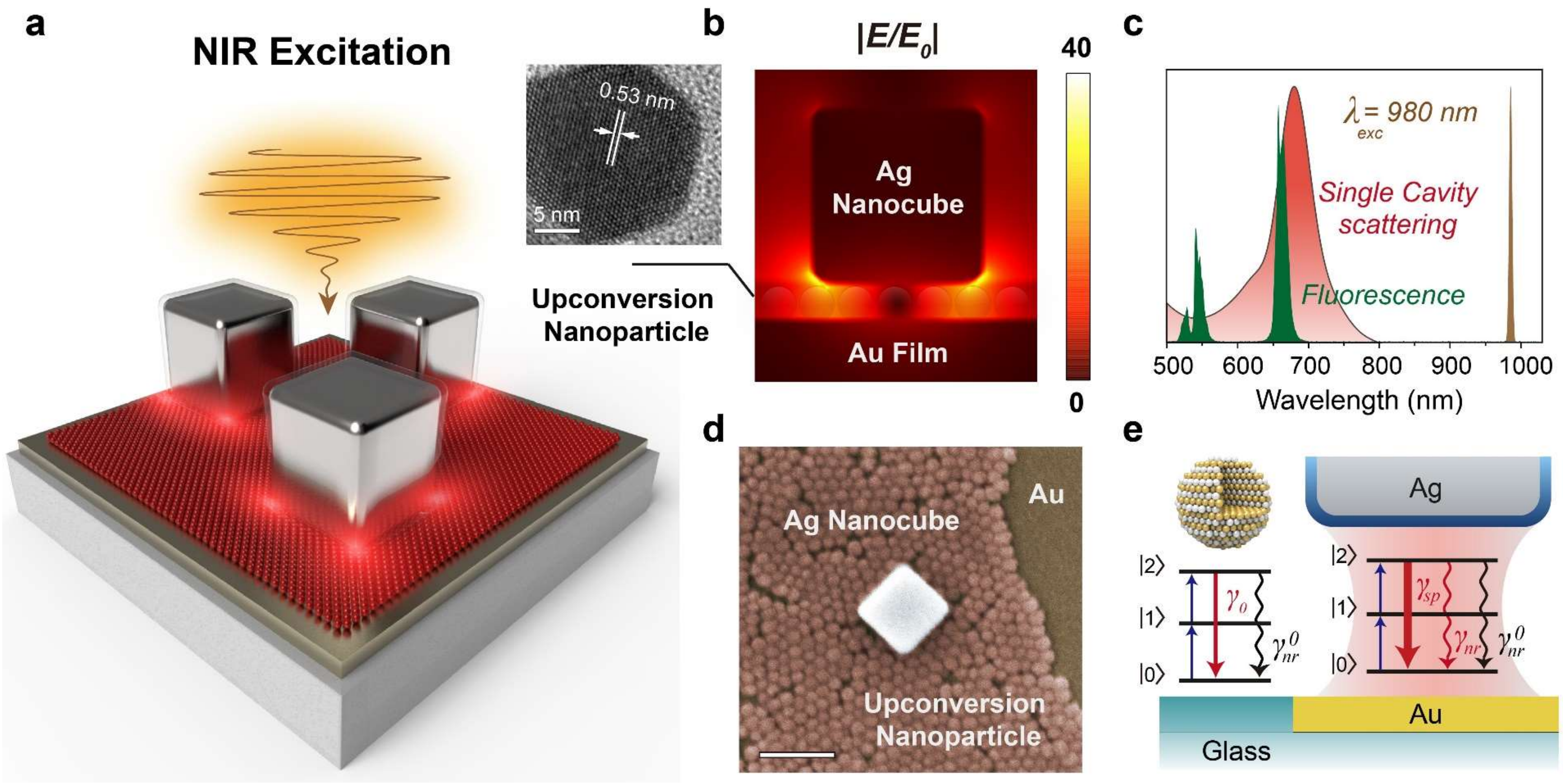
B10. Spontaneous Emission Probabilities at Radio Frequencies. E. M. PURCELL, *Harvard University.*—For nuclear magnetic moment transitions at radio frequencies the probability of spontaneous emission, computed from

$$A_\nu = (8\pi\nu^2/c^3)h\nu(8\pi^3\mu^2/3h^2)\ \mathrm{sec.}^{-1},$$

is so small that this process is not effective in bringing a spin system into thermal equilibrium with its surroundings. At 300°K, for $\nu = 10^7$ sec.$^{-1}$, $\mu = 1$ nuclear magneton, the corresponding relaxation time would be 5×10^{21} seconds! However, for a system coupled to a resonant electrical circuit, the factor $8\pi\nu^2/c^3$ no longer gives correctly the number of radiation oscillators per unit volume, in unit frequency range, there being now *one* oscillator in the frequency range ν/Q associated with the circuit. The spontaneous emission probability is thereby increased, and the relaxation time reduced, by a factor $f = 3Q\lambda^3/4\pi^2V$, where V is the volume of the resonator. If a is a dimension characteristic of the circuit so that $V\sim a^3$, and if δ is the skin-depth at frequency ν, $f\sim\lambda^3/a^2\delta$. For a non-resonant circuit $f\sim\lambda^3/a^3$, and for $a<\delta$ it can be shown that $f\sim\lambda^3/a\delta^2$. If small metallic particles, of diameter 10^{-3} cm are mixed with a nuclear-magnetic medium at room temperature, spontaneous emission should establish thermal equilibrium in a time of the order of minutes, for $\nu = 10^7$ sec.$^{-1}$.

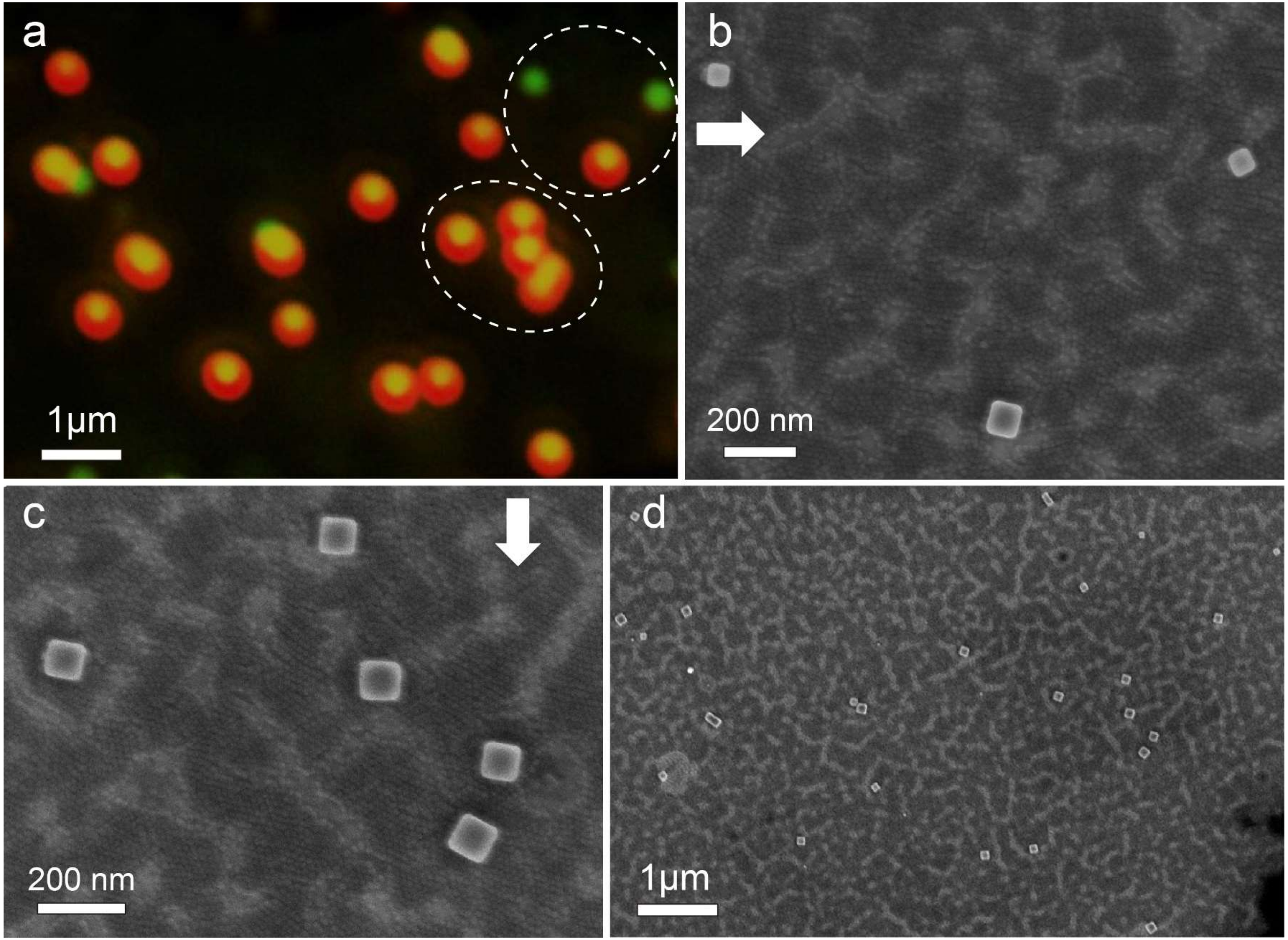
Phys. Rev. **69**, 681 (1946)

Nanocavity Coupling



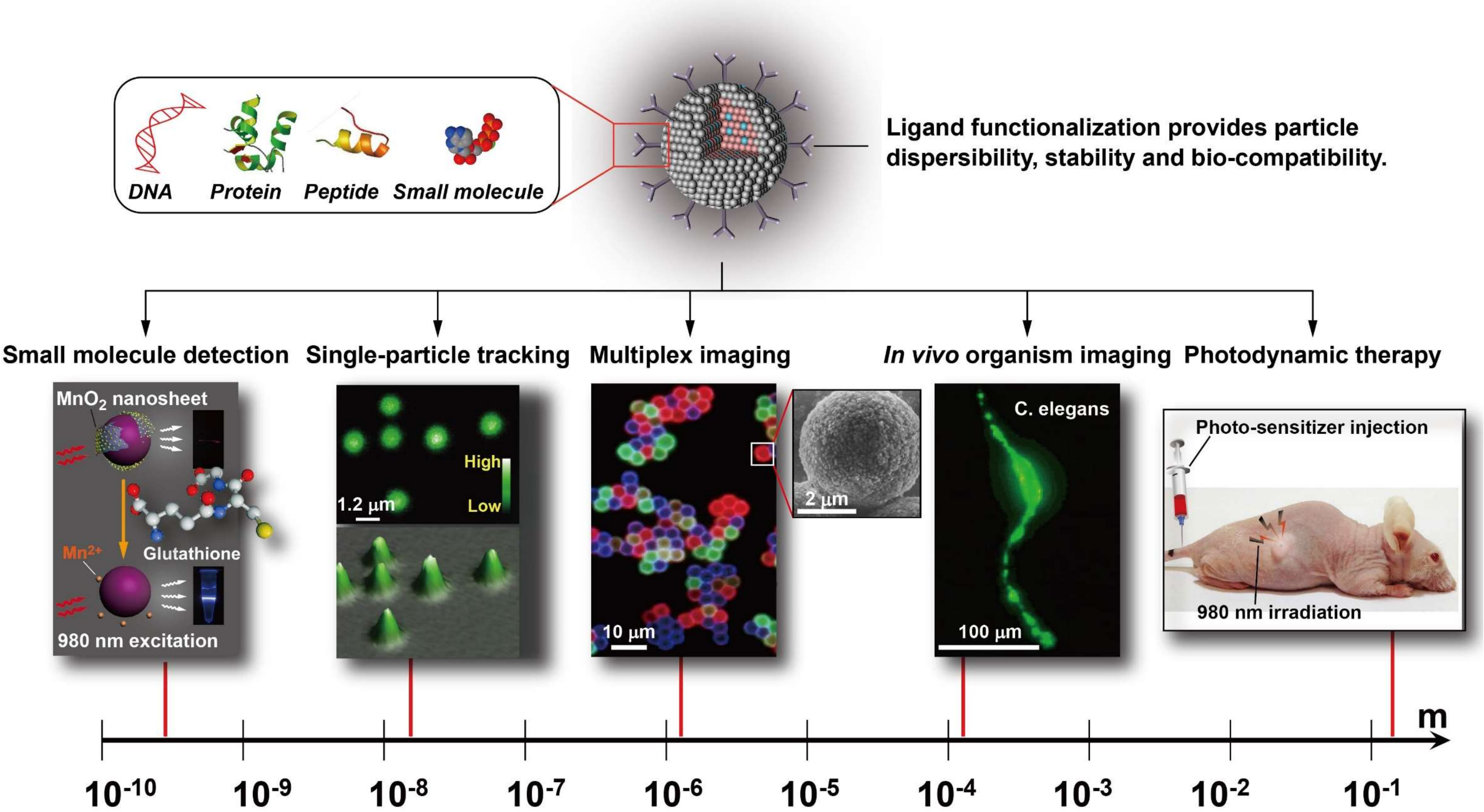
UCNP/plasmonic cavity hybrid comprising a gold film-coupled Ag nanocube with a sandwiched monolayer of UCNPs.

Nat. Nanotech., 2020



Luminescence is color tunable!

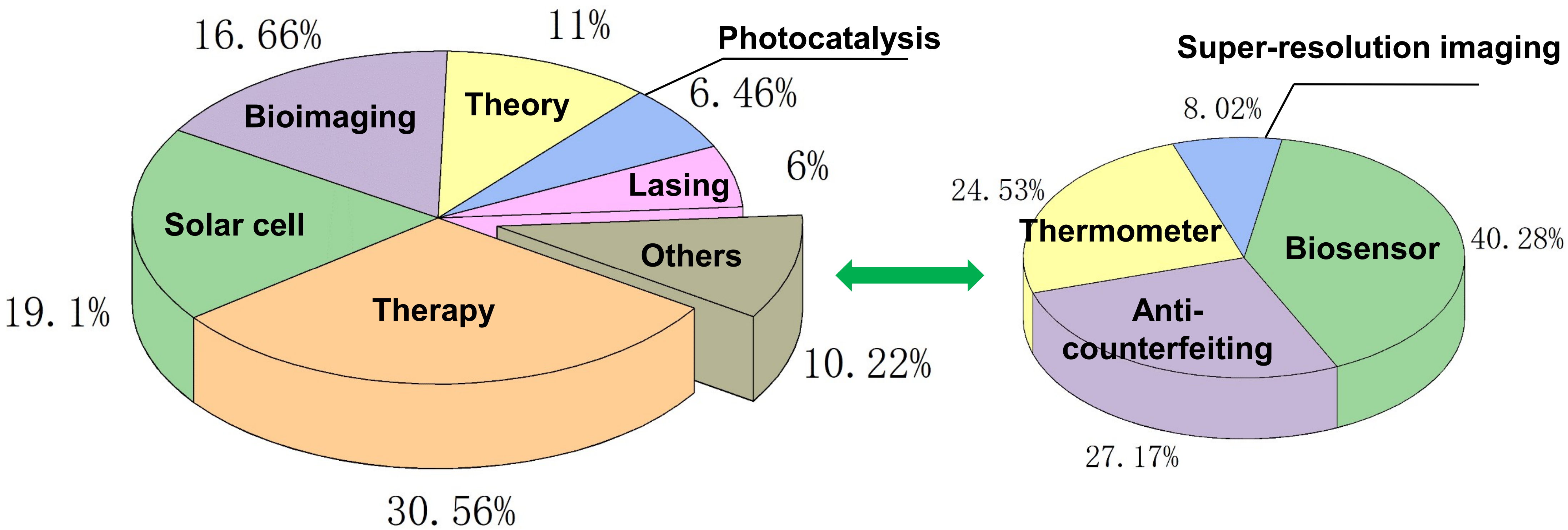
What's next for biological applications?



Bettinelli, Carlos, Liu *Phys. Today* **2015**


Deep penetration
High resolution

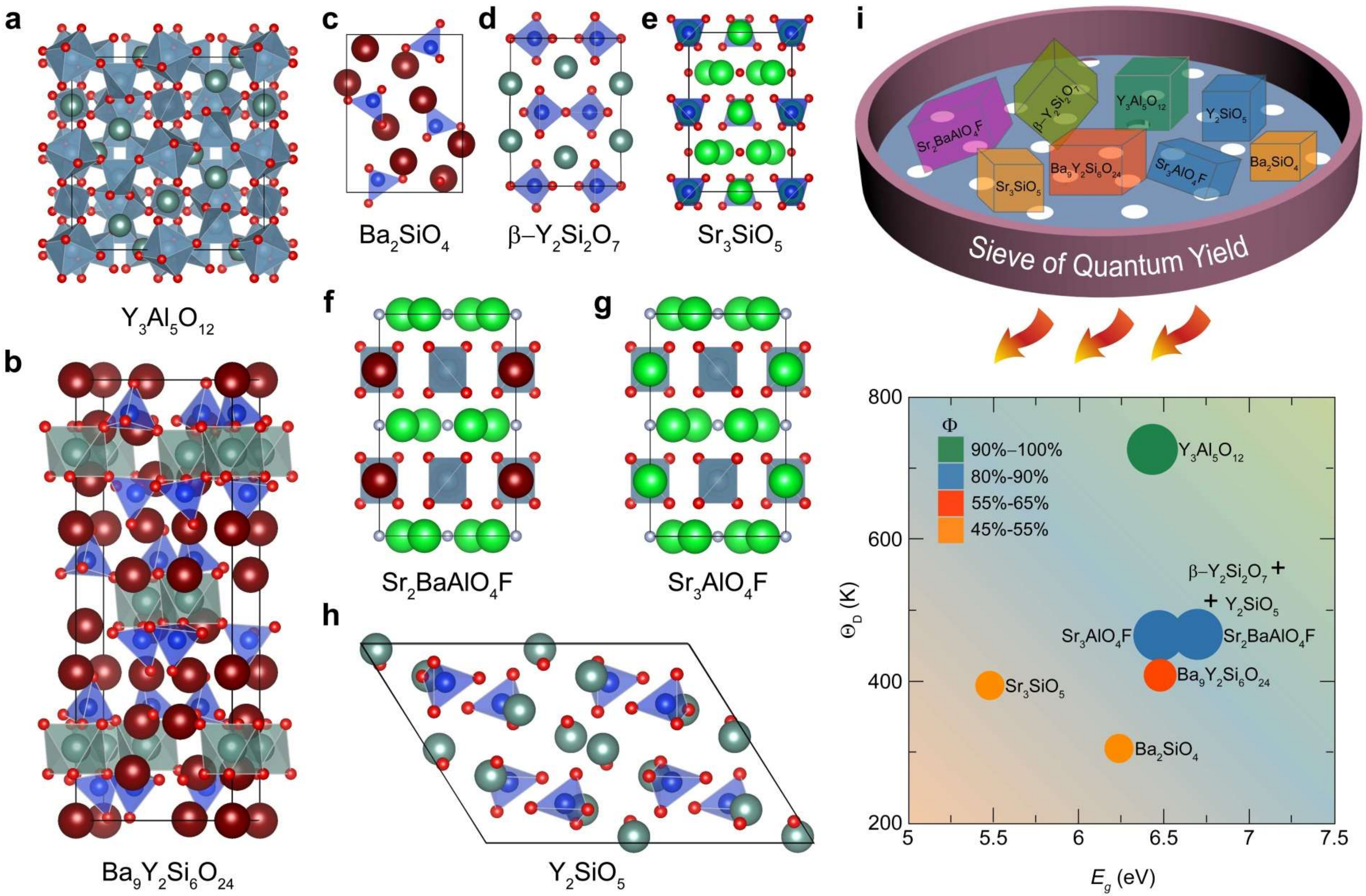
The Evolving Field of Upconversion Nanomaterials



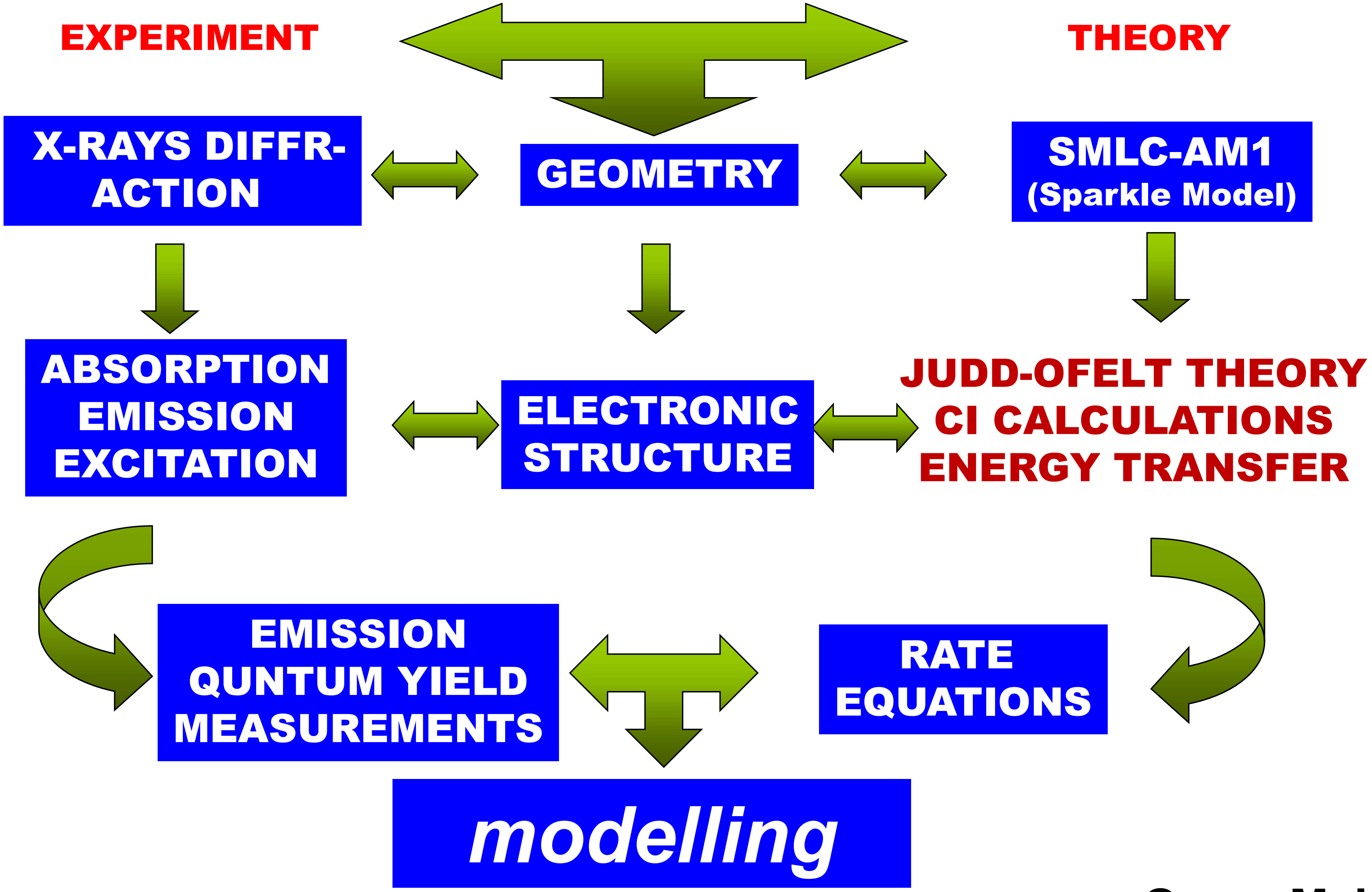
Single-Photon Emitters, Spintronics, 2D Materials, Flexible Electronics, Artificial Intelligence … ?

Open Source Database for Lanthanide Luminescence Spectra ?

Host material screening through quantum calculations

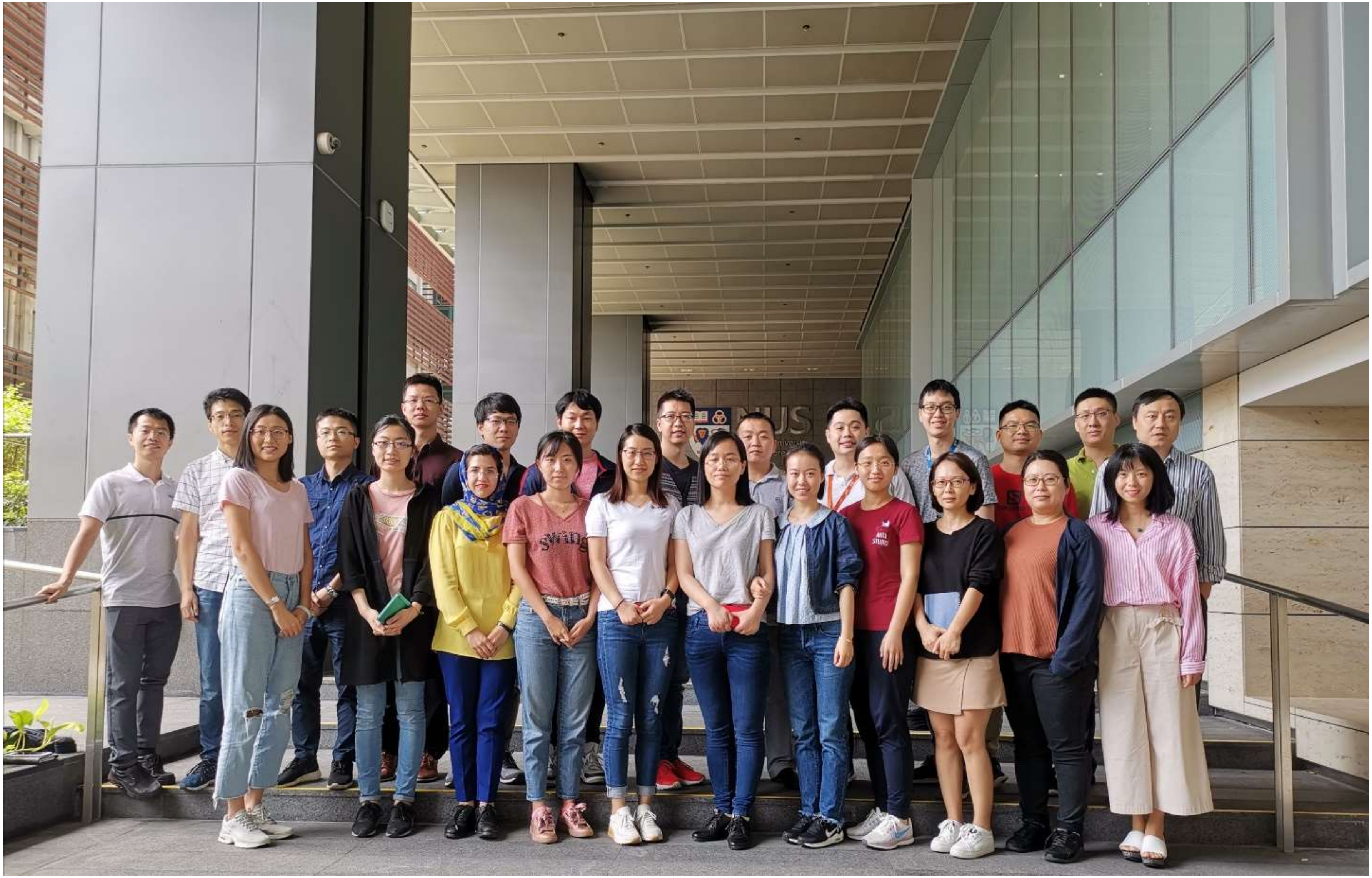


Qin ***Chem Rev*** 2017


EXPERIMENT
THEORY
X-RAYS DIFFR-ACTION
GEOMETRY
SMLC-AM1
(Sparkle Model)
ABSORPTION
EMISSION
EXCITATION
ELECTRONIC STRUCTURE
JUDD-OFELT THEORY
CI CALCULATIONS
ENERGY TRANSFER
EMISSION
QUNTUM YIELD
MEASUREMENTS
RATE EQUATIONS
modelling

Oscar Malta

Acknowledgement



Financial Support: NUS, A*STAR, NRF, MOE


Thank You !