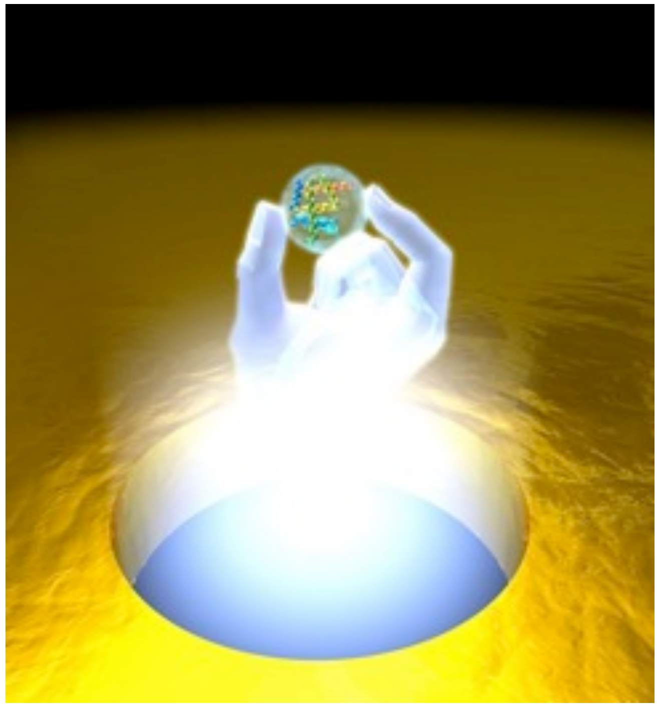
BioPlasmonics:
Developing novel nanotools for biosciences & medicine



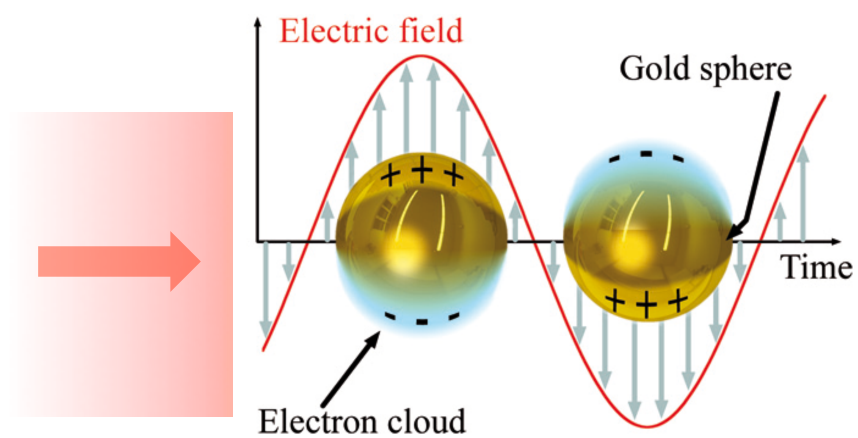
Romain Quidant

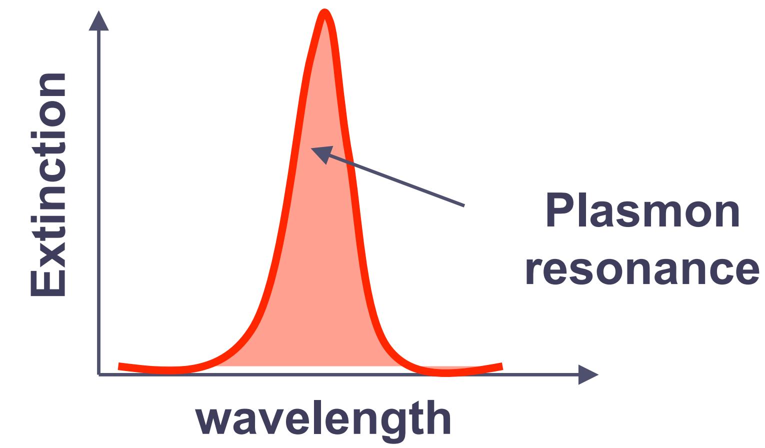
ICFO-Institut de Ciencies Fotòniques &
ICREA-Institució Catalana de Recerca i Estudis Avançats

The protagonist? A gold nanoparticle

GOLD NANOPATICLE

LOCALIZED SURFACE PLASMONS





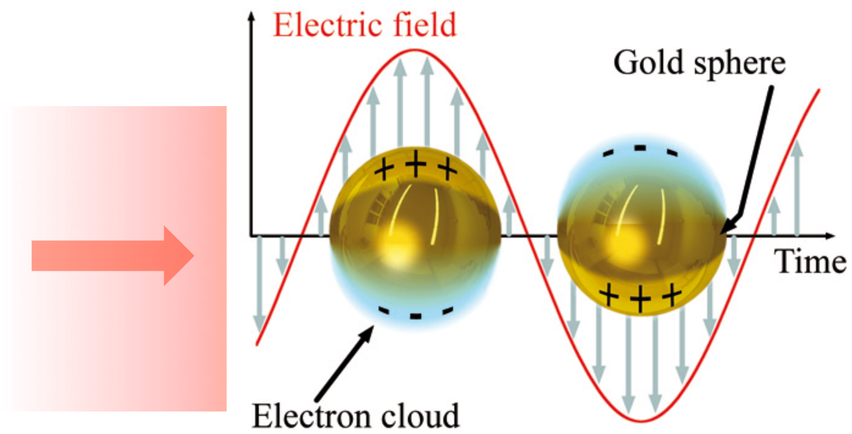
Enhanced Scattering → **Nano-source of light**

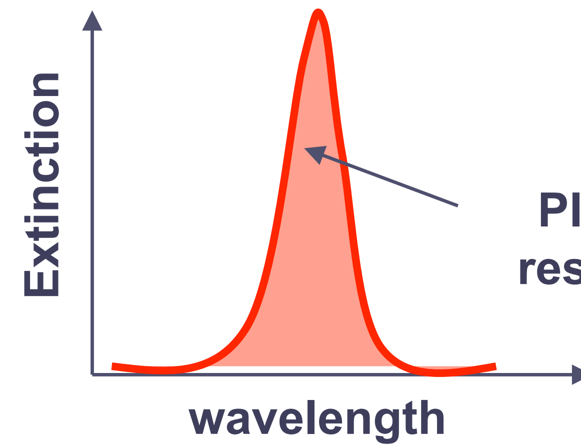
Enhanced Absorption → **Nano-source of heat**

The protagonist? A gold nanoparticle

GOLD NANOPATICLE

LOCALIZED SURFACE PLASMONS





Enhanced Scattering → **Nano-source of light**

Enhanced Absorption → **Nano-source of heat**

Outline

- Part 2 -
ThermoPlasmonics : Using metallic NP as heat nanosources

- Heat generation in plasmonic NPs
- Probing heat at the nanoscale: Thermal Nanoscopy
- Applications

ICFO
Institut de Ciències Fotòniques

Heat generation at the nanoscale

Heat generation in plasmonic nanostructures

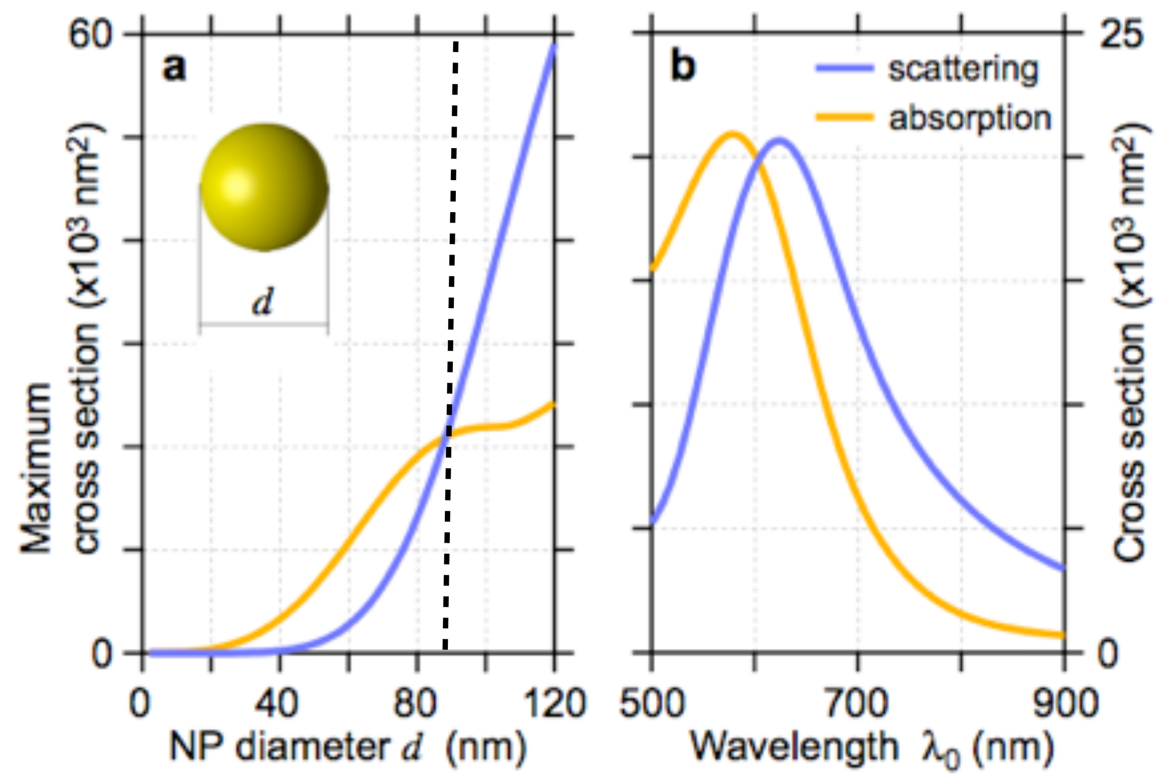
Enhanced absorption at resonance

$$\alpha(\omega) = 4\pi R^3 \frac{\varepsilon(\omega) - \varepsilon_s}{\varepsilon(\omega) + 2\varepsilon_s}$$

$$\sigma_{ext} = \sigma_{abs} + \sigma_{scat}$$

$$\sigma_{\text{scat}} = \frac{k^4}{6\pi}|\alpha|^2$$

$$\sigma_{\text{abs}} = k\,\text{Im}(\alpha) - \frac{k^4}{6\pi}|\alpha|^2$$



Generated heat power

$$Q = \sigma_{\text{abs}}\, I$$

or

Heat source density

$$Q = \int_V q(r)\, d^3r \quad \text{with} \quad q(\mathbf{r}) = \frac{\omega}{2}\text{Im}(\varepsilon(\omega))\varepsilon_0|\mathbf{E}(\mathbf{r})|^2$$

Heat generation is thus directly proportional to the square of the electric field inside the metal.

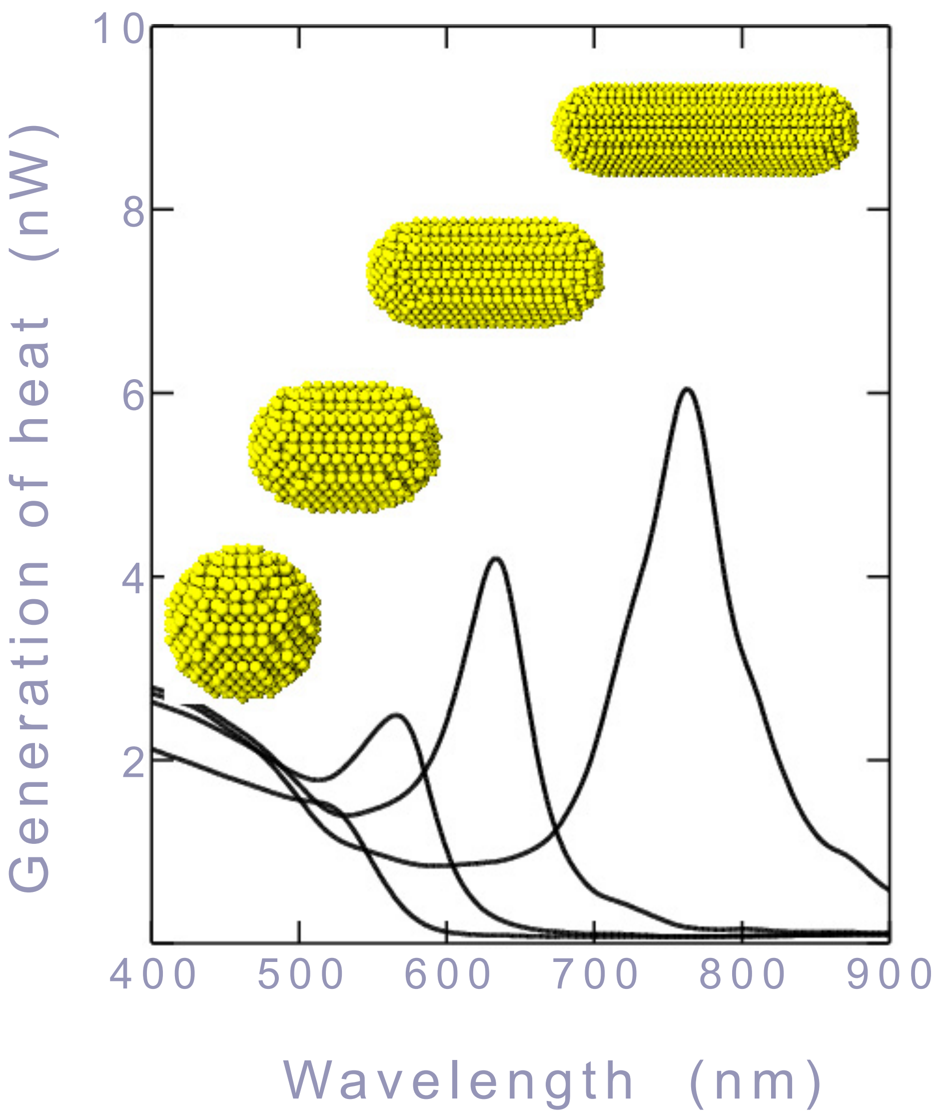
G. Baffou, C. Girard and R. Quidant, APL **94**, 153109 (2009)

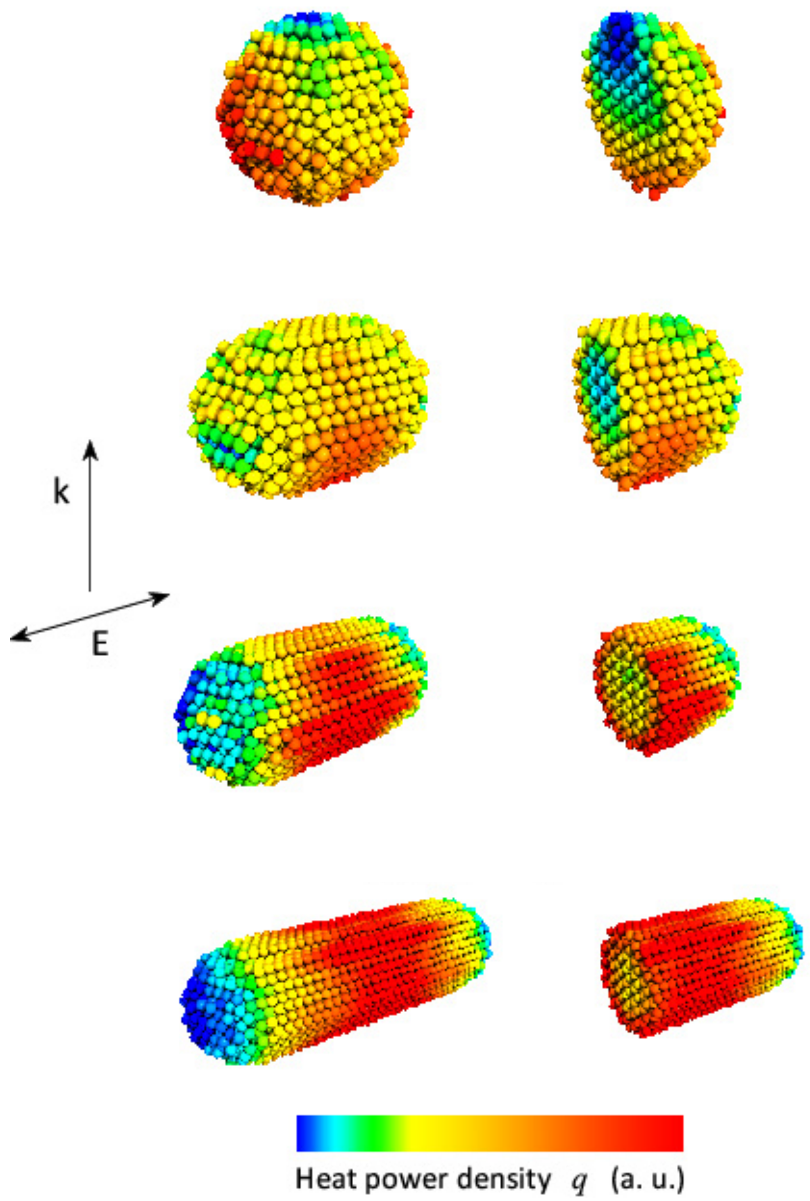
G. Baffou, R. Quidant, J. Garcia de Abajo, ACSnano **4**, 709-716 (2010)

G. Baffou and R. Quidant, Laser and Photonics Review, available online (2012)

Designing efficient heat nano-sources

Guillaume
Baffou

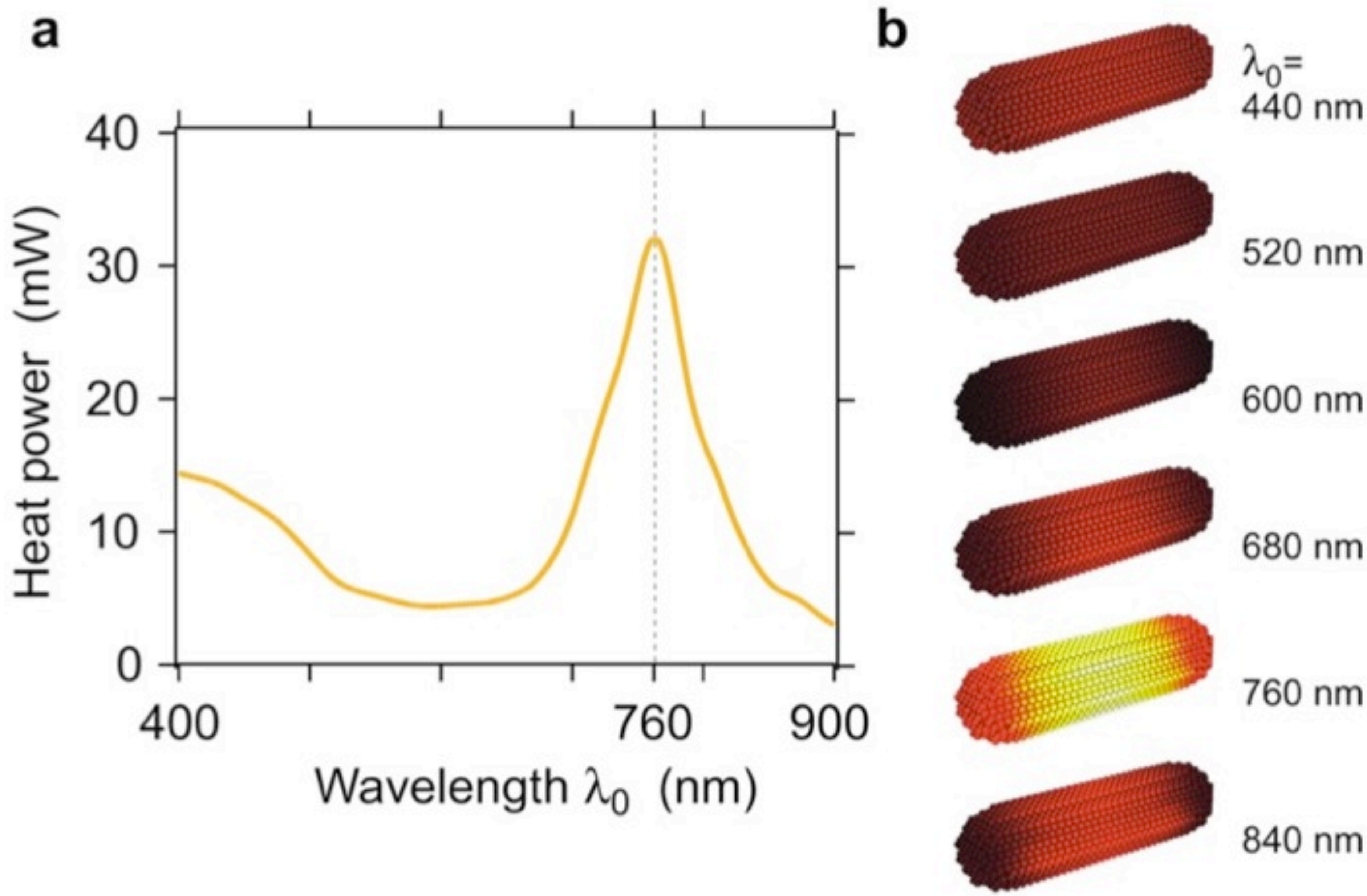




G. Baffou, C. Girard and R. Quidant, APL **94**, 153109 (2009)

Designing efficient heat nano-sources

Guillaume Baffou



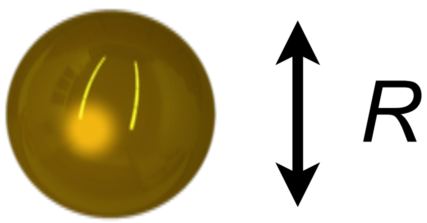
Heat is generated in the rod center where the currents flow (unlike light accumulated at the rod edges)

G. Baffou, C. Girard and R. Quidant, APL **94**, 153109 (2009)

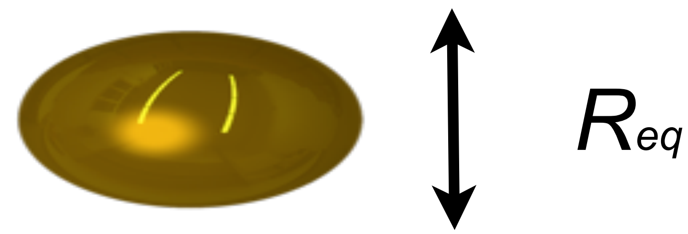
Temperature increase and spatial profile

Guillaume Baffou

Spherical NP



Non-spherical NP



T decay in 1/r away from the particle

$$\delta T(r) = \delta T_{NP} \frac{R}{r}, \quad r > R,$$

$$\delta T(r) \approx \delta T_{NP}, \quad r < R$$

T is homogeneous within the particle

where

$$\delta T_{NP} = \frac{Q}{4\pi \kappa_s R}$$

Temperature increase of the nanoparticle

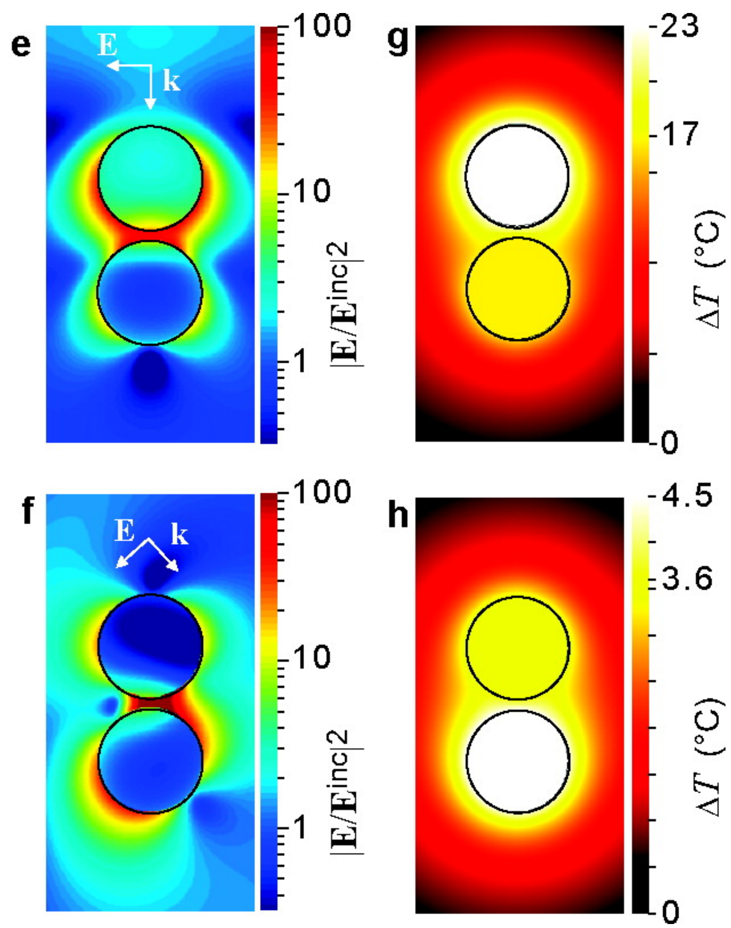
$$\delta T_{NP} = \frac{Q}{\beta \, 4\pi \kappa_s R_{eq}}$$

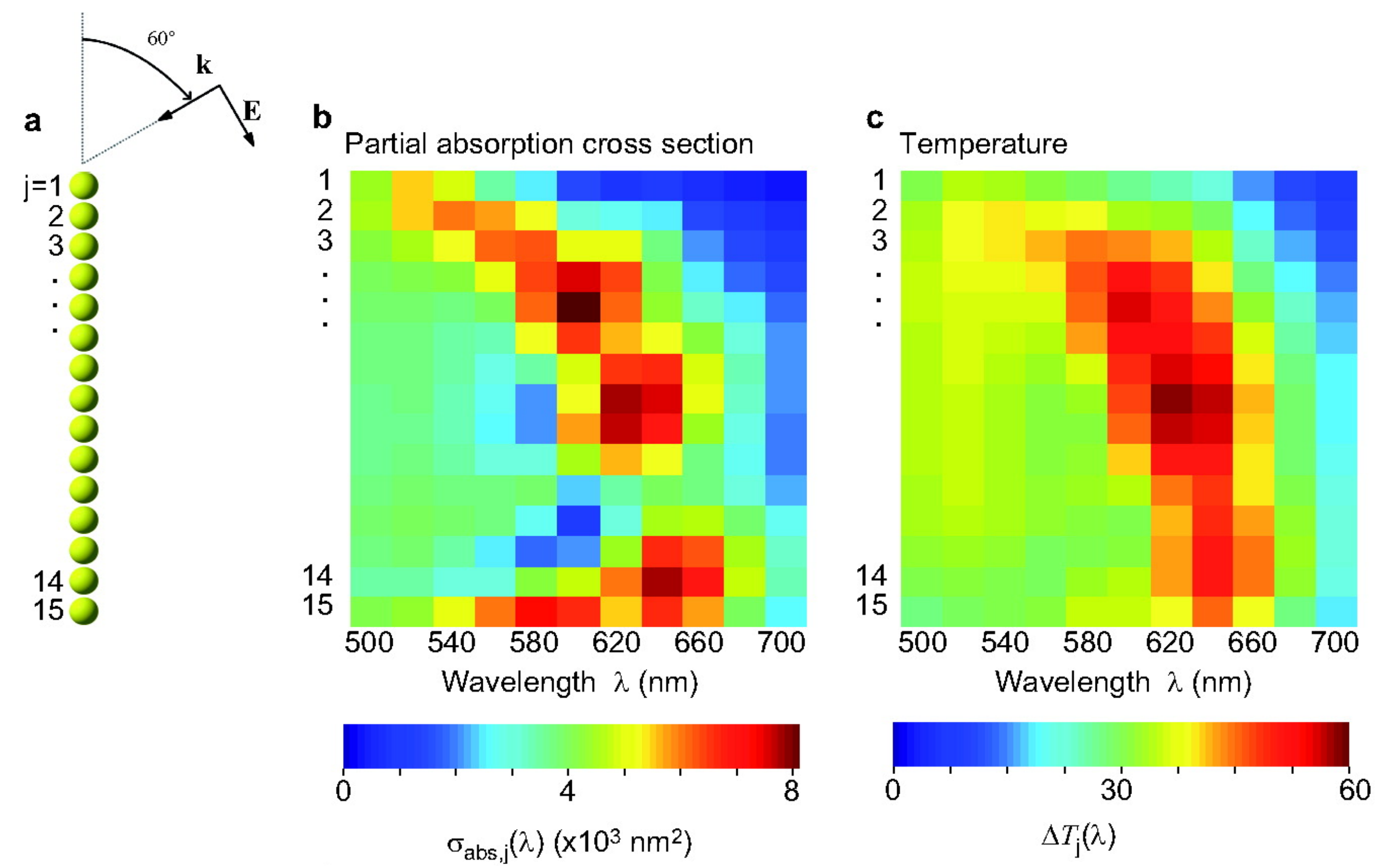
G. Baffou, R. Quidant, F. J. G. de Abajo, ACSnano **4**, 709-716 (2010)

Nanoscale heat control in plasmonic ensembles

Guillaume Baffou

In collaboration with Javier Garcia de Abajo (CSIC Madrid)





G. Baffou, R. Quidant, F. J. G. de Abajo, ACSnano **4**, 709-716 (2010)

Probing heat at the nanoscale

Probing temperature at the nanoscale?

Probing temperature at the nanoscale is fundamentally a complicated task mainly because of the non- propagative nature of heat

Fluorescence intensity

quantum dots, thermo-sensitive dyes

+ Simple
- Low reliability (quenching, photobleaching etc..) & Invasive (bio)

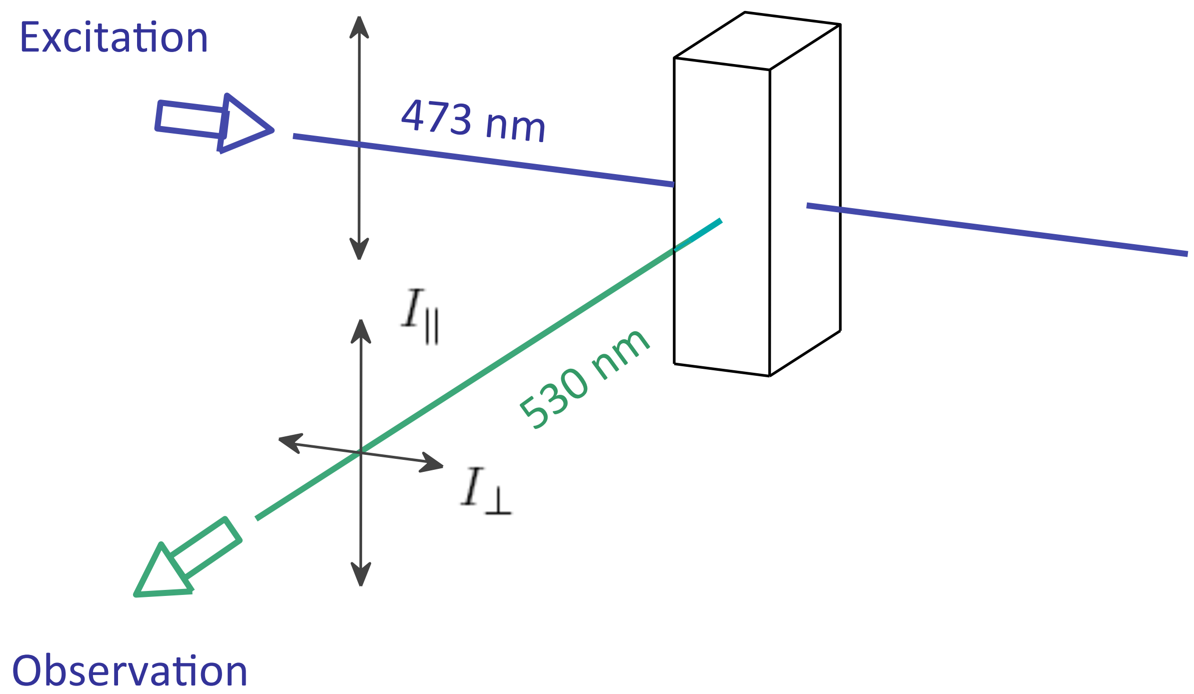
Spectroscopic techniques

Fluorescence: Change in the spectrum

Raman: Change in the ratio between stoke and anti-stoke signal

+ Reliable
- Slow and usually limited to single point measurement

Probing temperature with Fluorescence Polarization Anisotropy (FPA)



Polarization Anisotropy

$$r = \frac{I_{\|} - I_{\perp}}{I_{\|} + 2\, I_{\perp}}$$

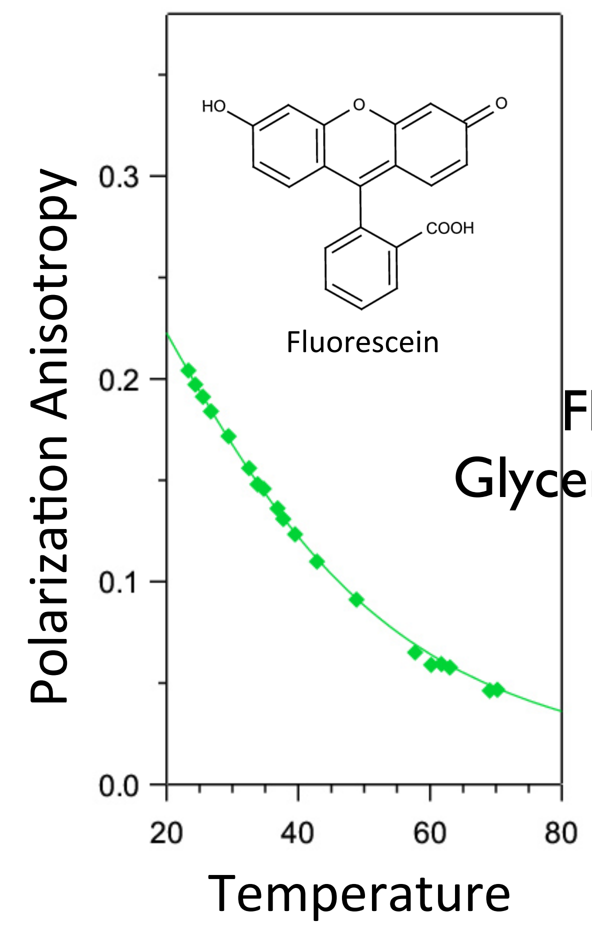
FPA is maximum when:

τR (rotation time) ≈ τF (fluorescence life time)

Typical fluorescent molecule (≈1nm):

τR= 10−10 s ≠ τF= 10-9 s

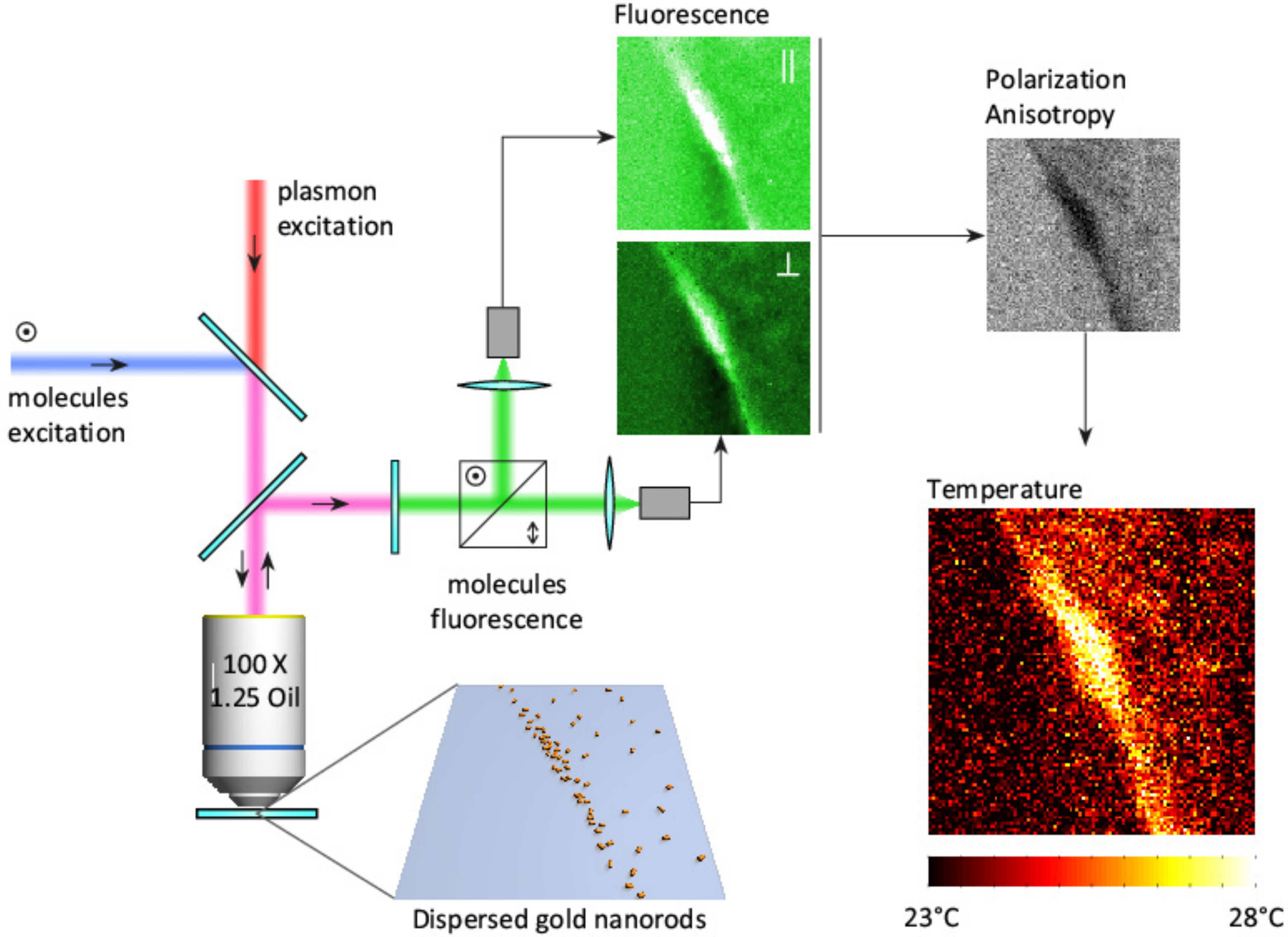
→ Need to increase the fluid viscosity to slow the molecules down



Fluorescein in a Glycerol/water (4:1) mix

Probing temperature with Fluorescence Polarization Anisotropy (FPA)

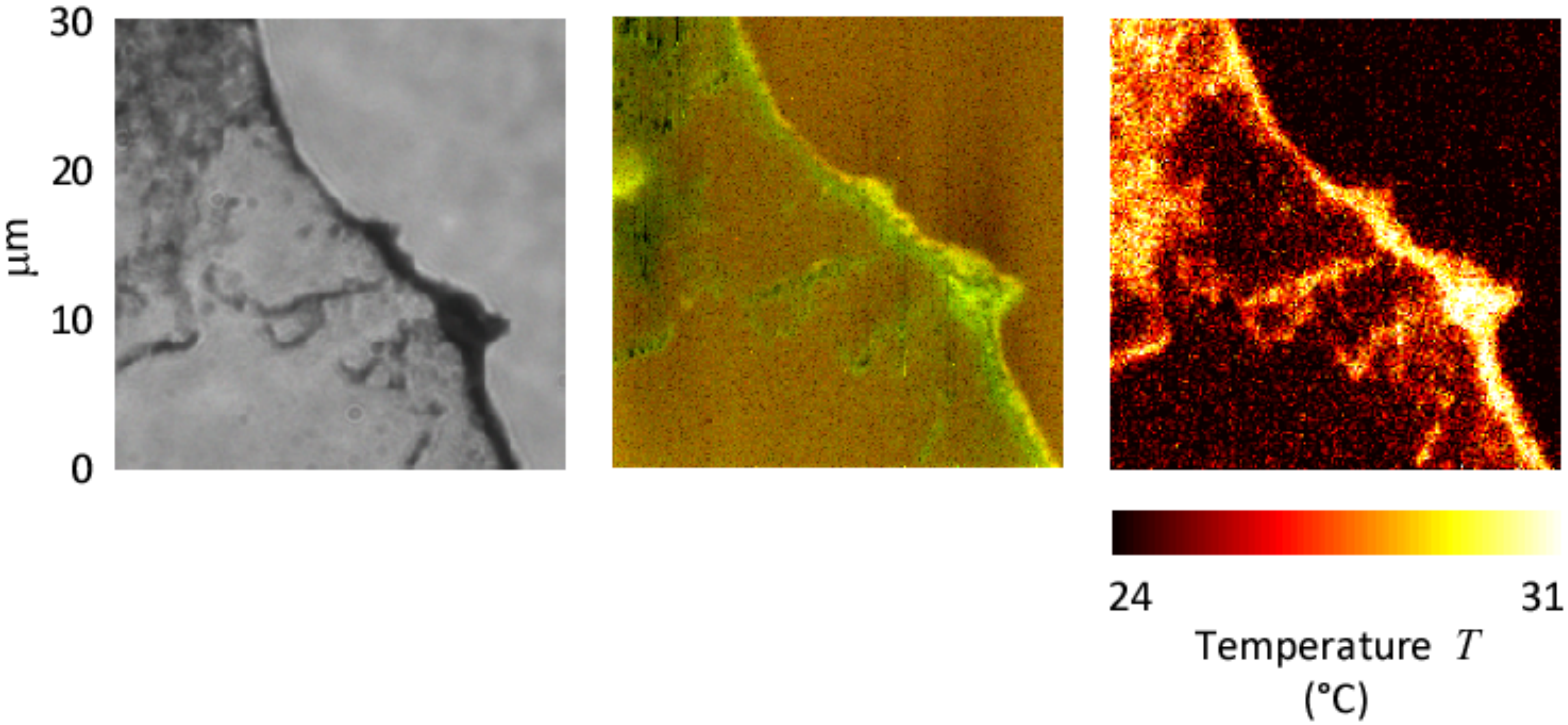
Guillaume Baffou



Probing temperature with Fluorescence Polarization Anisotropy (FPA)

Guillaume Baffou

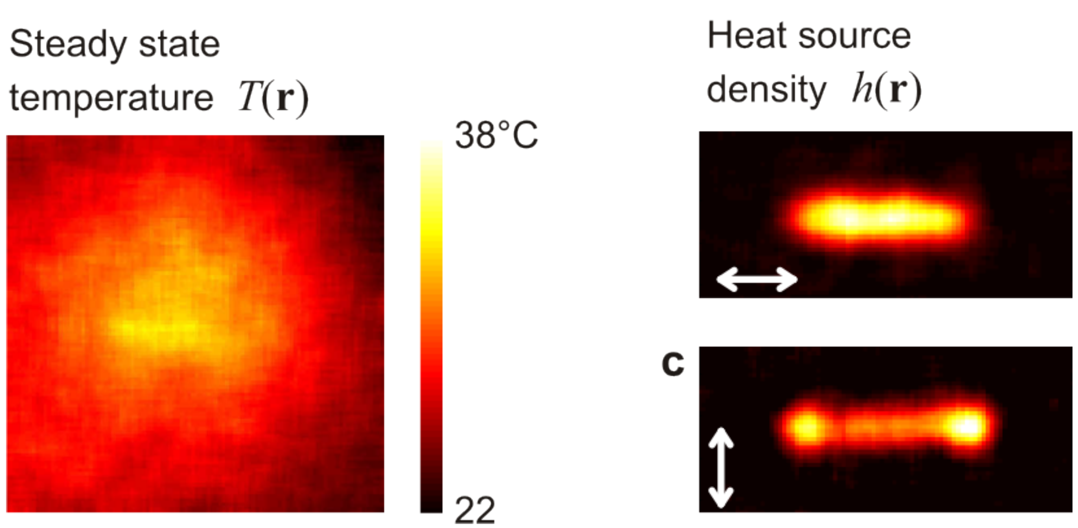
Baffou et al, Optics express **17**, 3291-2398 (2009)



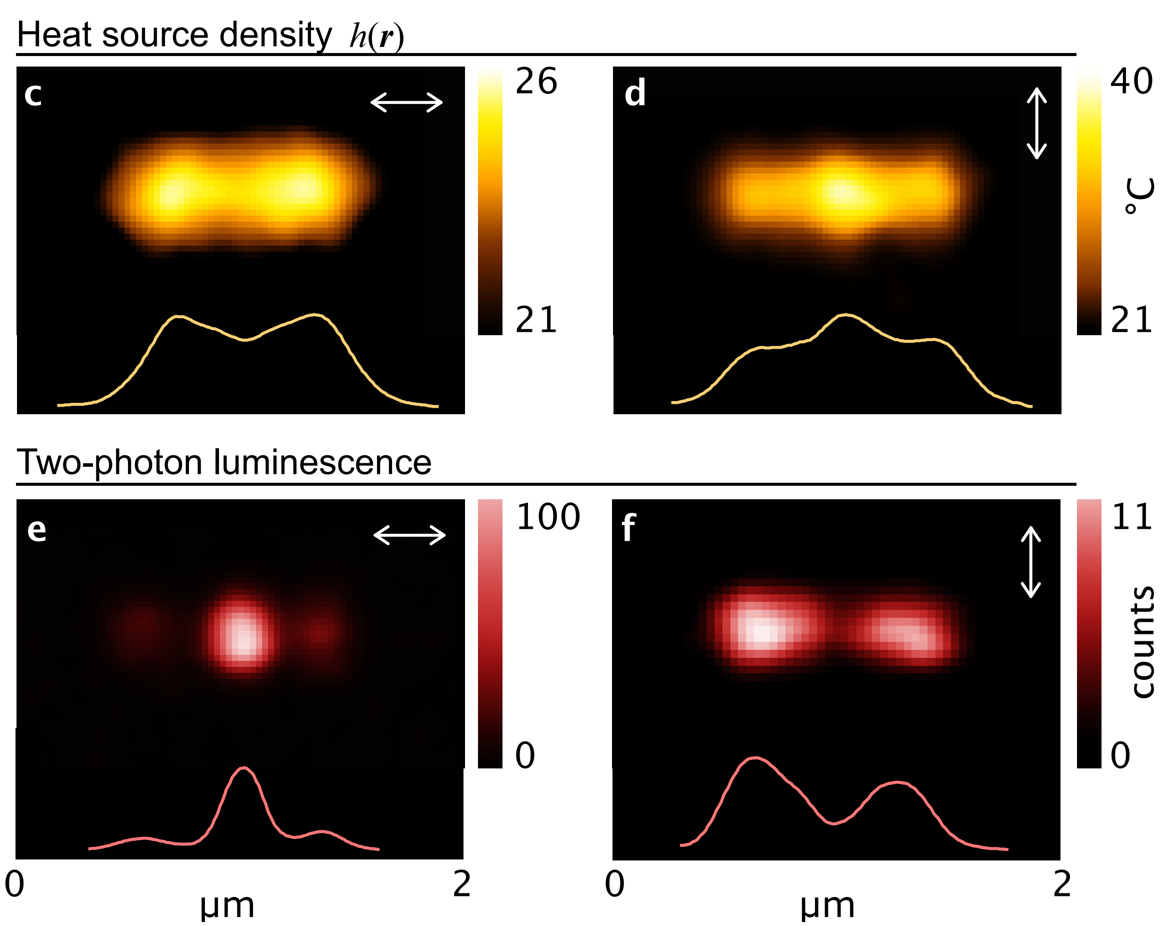
Temperature versus heat source density

Guillaume Baffou

Two thermal imaging modes



Optimizing light and heat in plasmonic nanostructures requires different recipes



G. Baffou, C. Girard & R. Quidant, 104, 136805 Phys. Rev. Lett. (2010)

Temperature mapping in living cells using GFP

Jon Donner

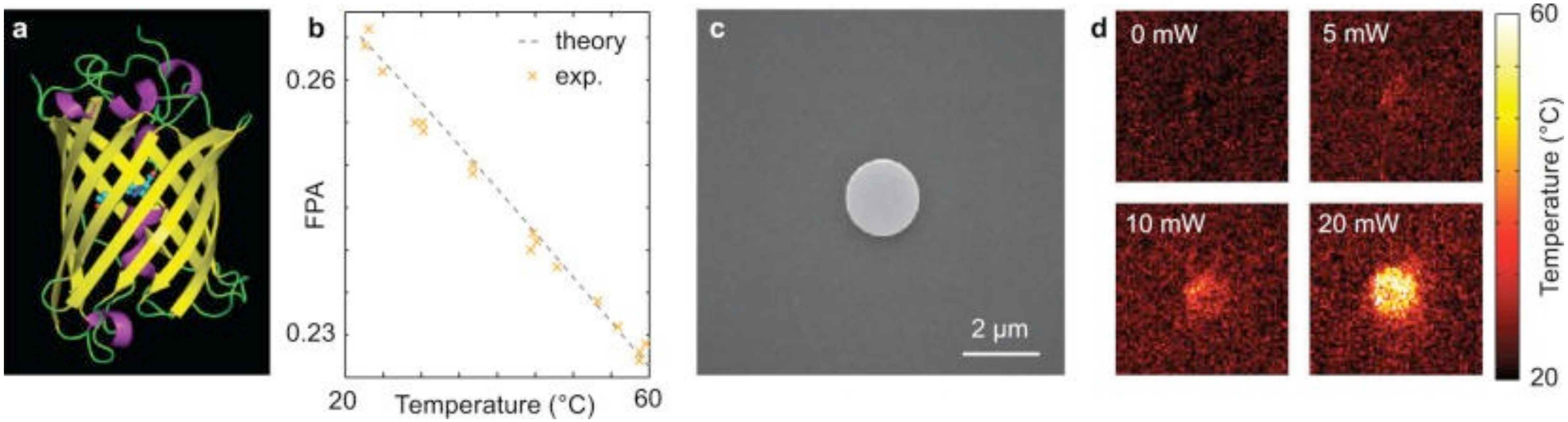
Sebas Thompson

The use of Glycerol is prohibited when considering living cells

Characteristic size of 3.5 nm ->

τ_R = 4.1 ns in water ~ τ_F= 2.5 ns

Proof of concept on a plasmonic nanostructure



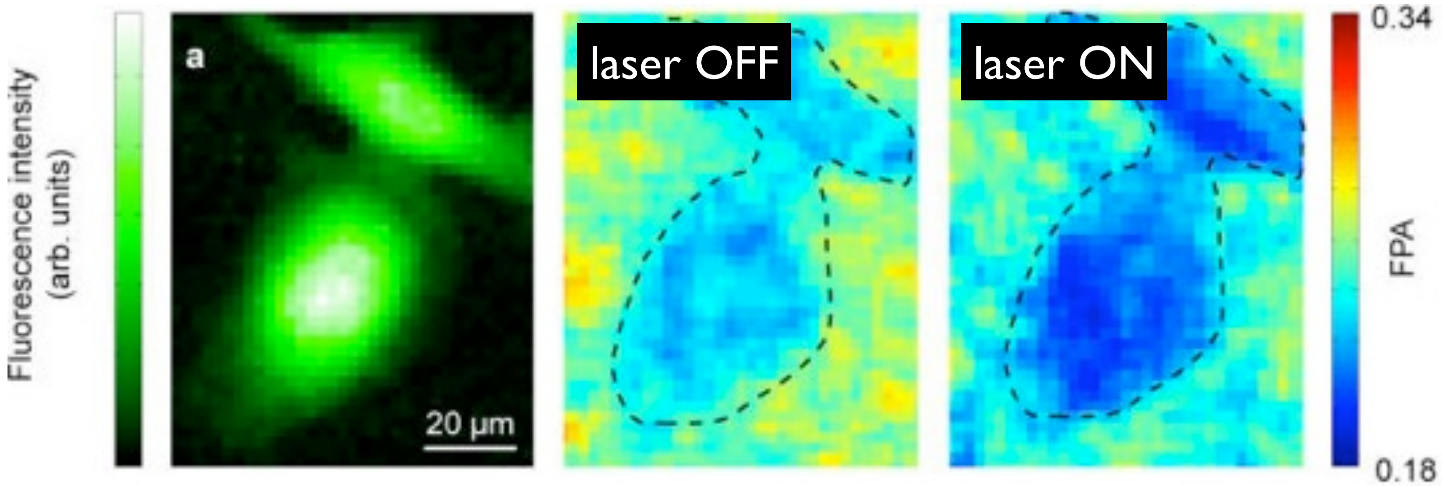
Donner, S. A. Thompson, M. P. Kreuzer, G. Baffou, R. Quidant,
Nano Lett. **12**, 2107-2111 (2012)

GFP Fluorescence Polarization Anisotropy in cells

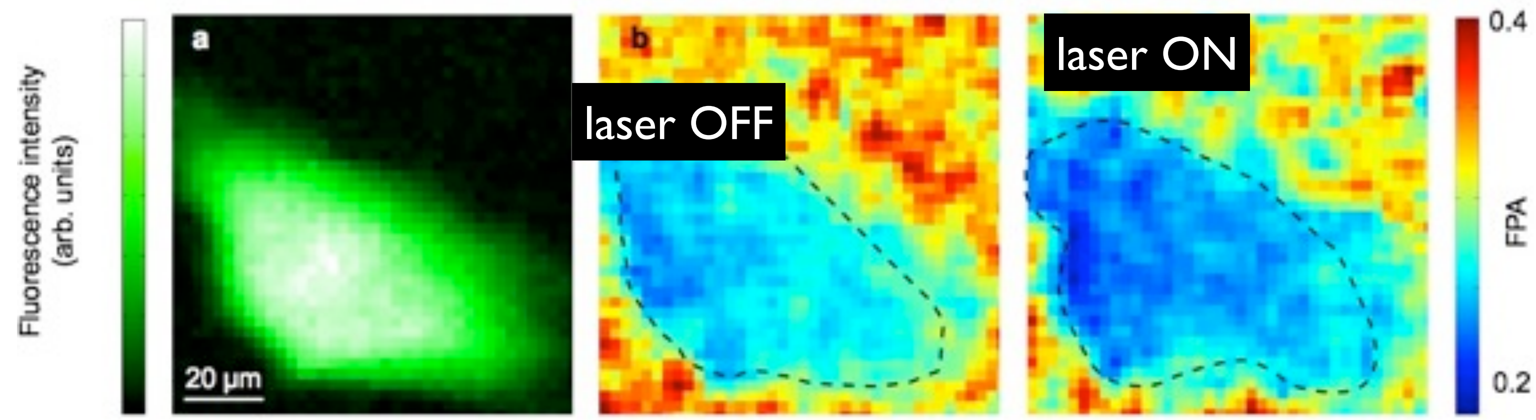
Jon
Donner

Sebas
Thompson

Hela cells



U-87 MG cells



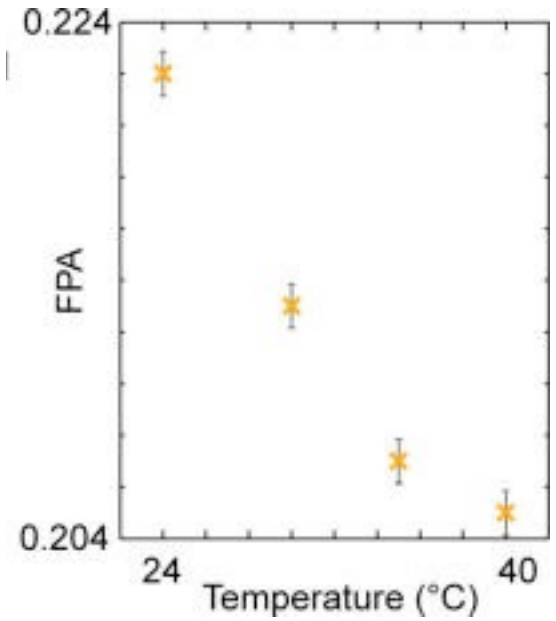
Donner, S. A. Thompson, M. P. Kreuzer, G. Baffou, R. Quidant,
Nano Lett. **12**, 2107-2111 (2012)

Intracellular temperature mapping

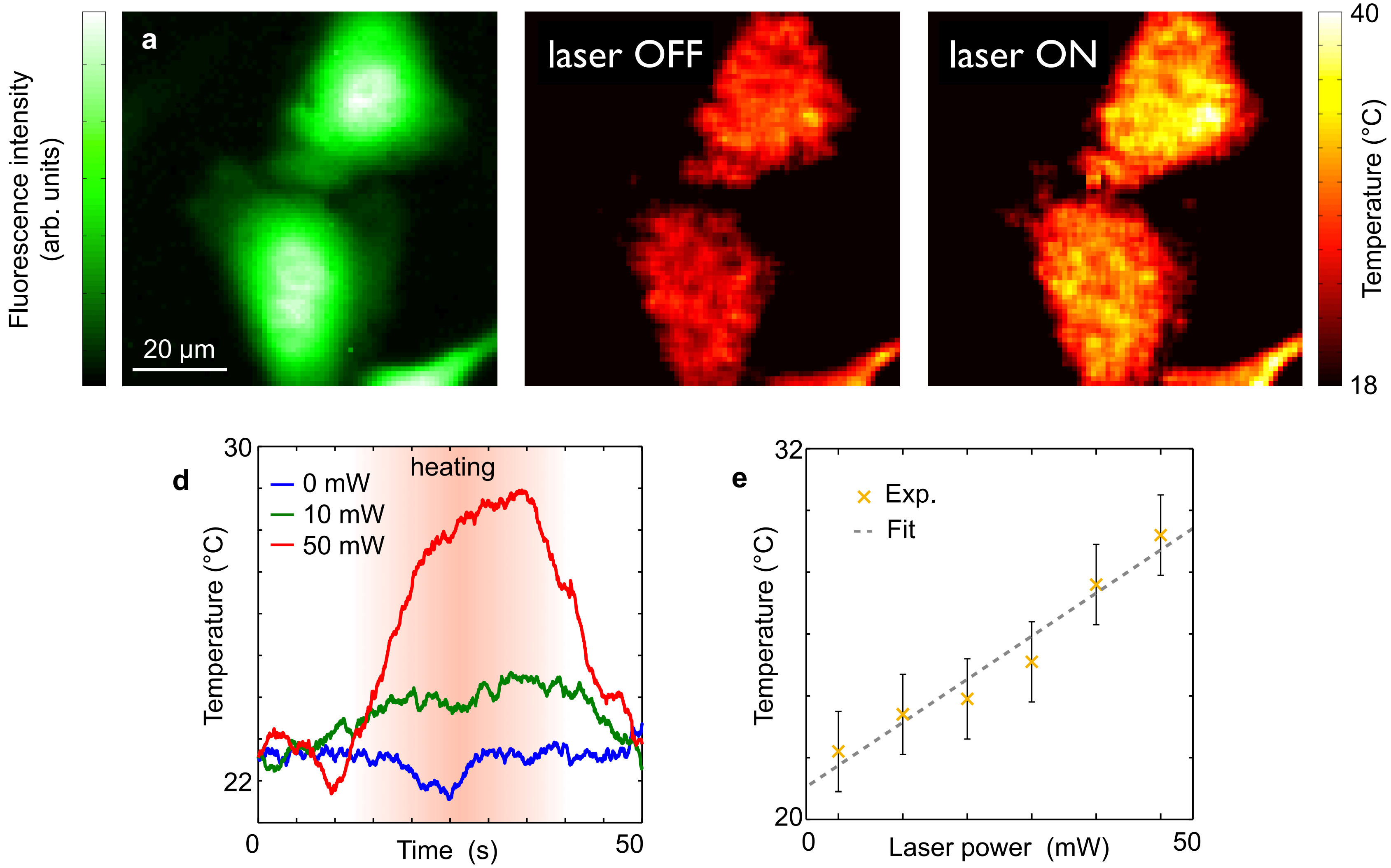
Jon Donner

Sebas Thompson

FPA/Temperature Calibration



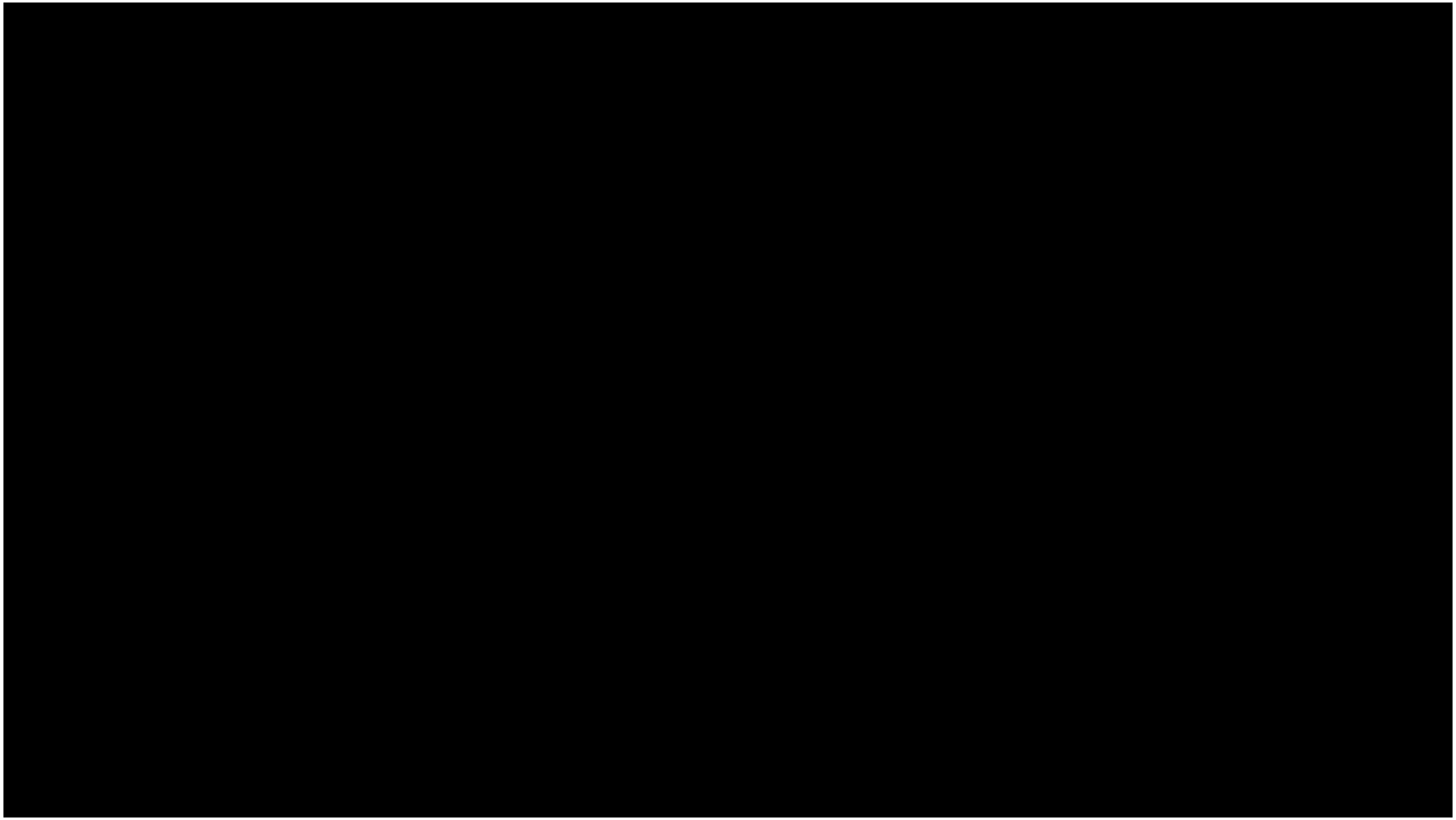
Thermal images



Donner, S. A. Thompson, M. P. Kreuzer, G. Baffou, R. Quidant,
Nano Lett. **12**, 2107-2111 (2012)

Applications

Photothermal Cancer Therapy



Original proprosal by West & Halas (Rice Univ)

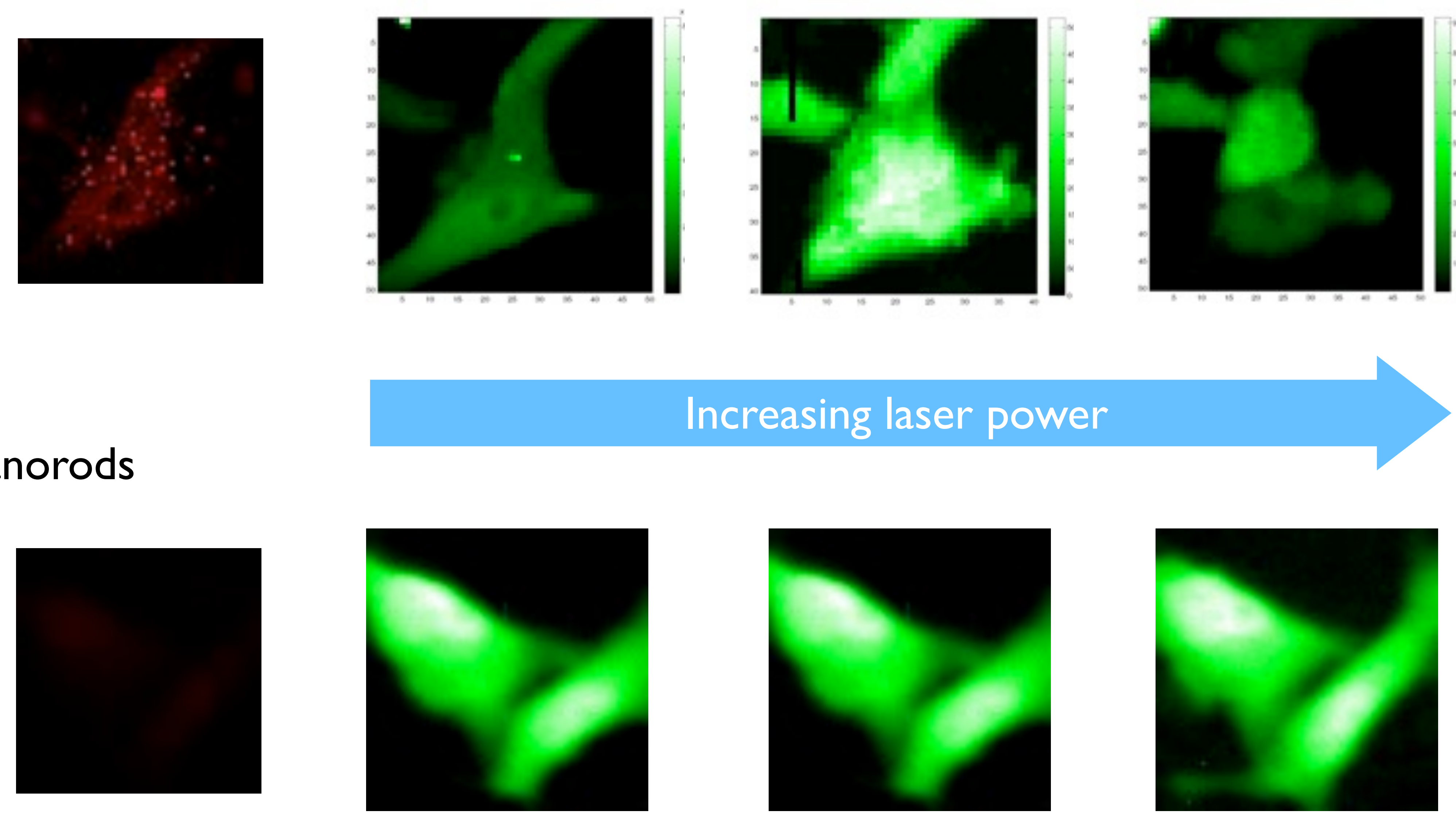
See for instance: Proc. Natl Acad. Sci. 100 (23), 13549 (2003)

Hyperthermia of targeted cancer cells

Sebas Thompson

With Nanorods

Cell death

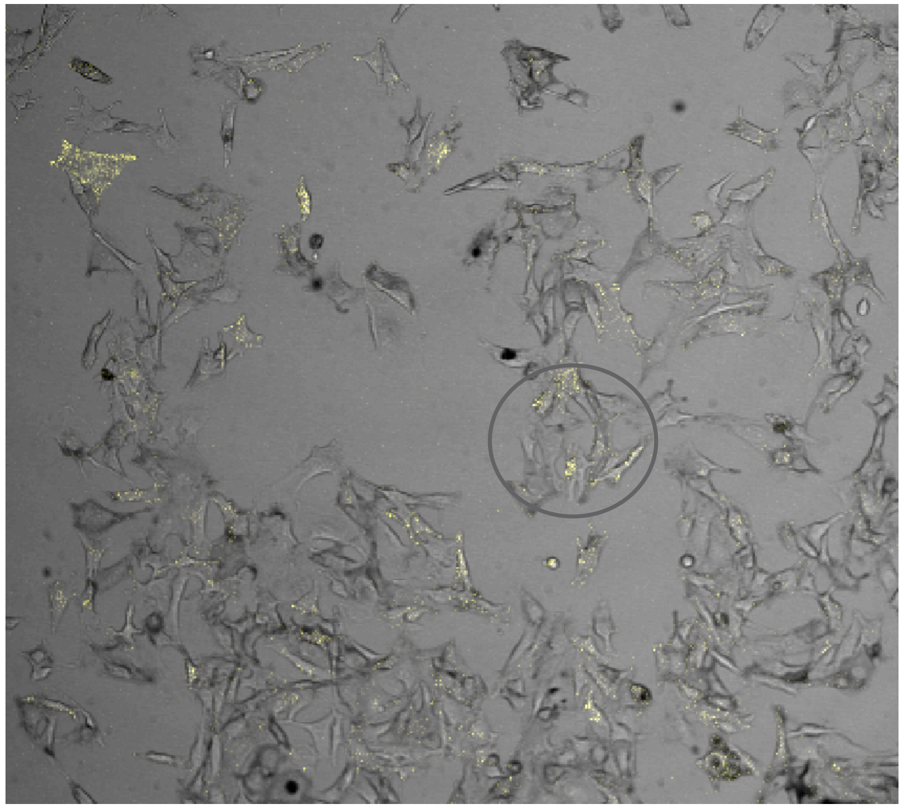


No Nanorods

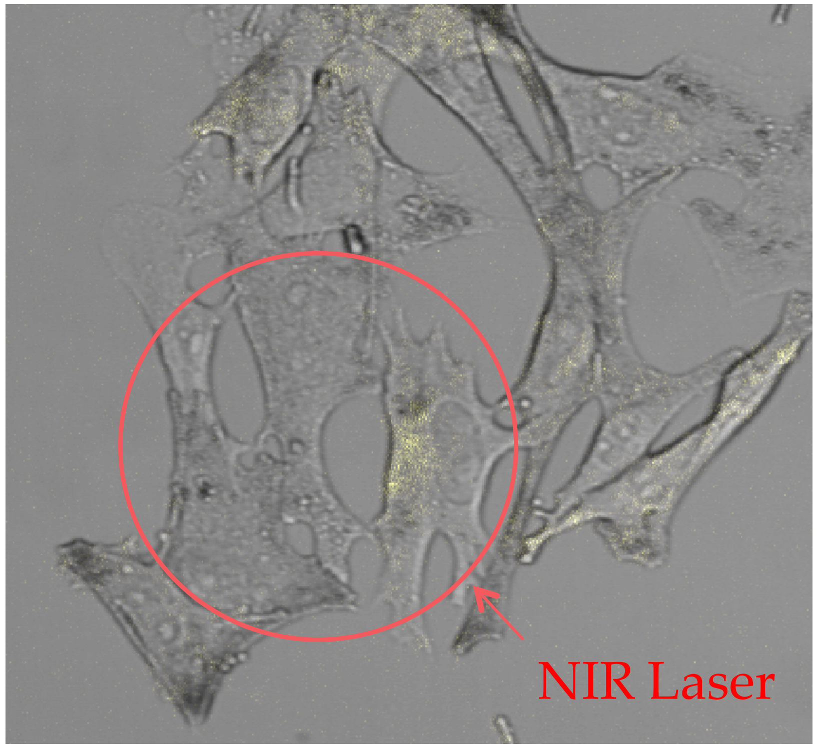
No cell damage

Hyperthermia in a mixed population

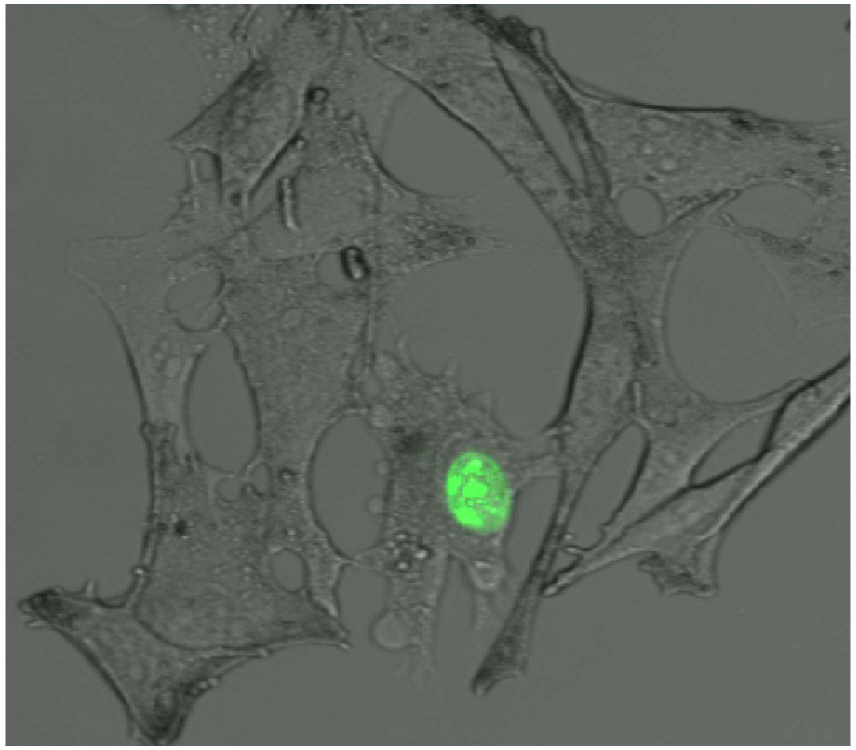
Sebas Thompson



Before illumination

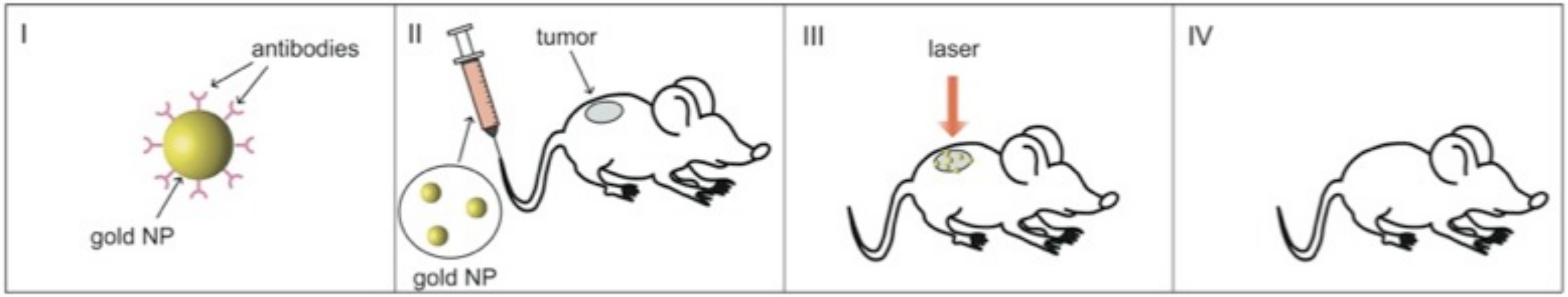


After illumination



Necrosis of the targeted cells

Illustration of PTT in mice model



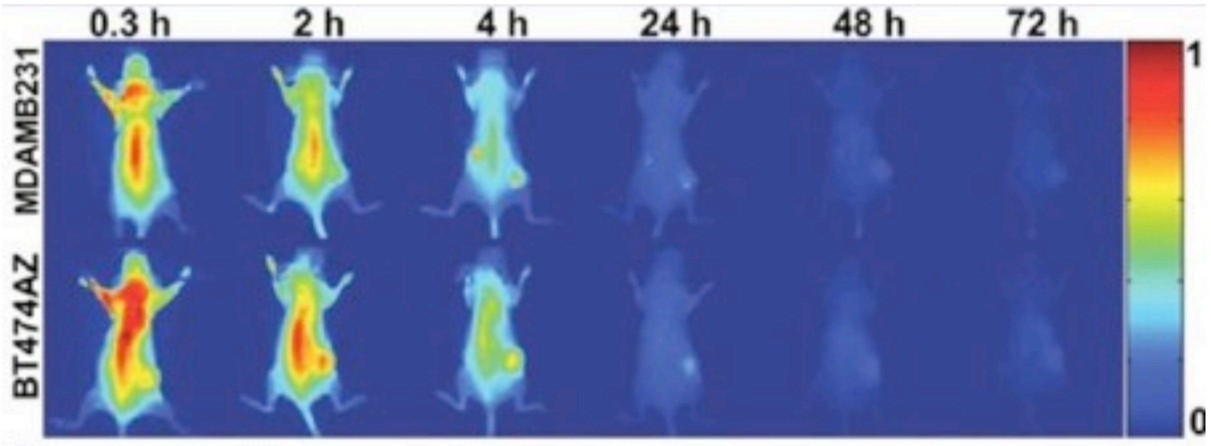
Before treatment

After 21 days of treatment

J. M. Stern, J. Stanfield, W. Kabbani, J. T. Hsieh, and J. A. Cadeddu, J. Urol. 179, 748 (2008)

Still a lot to do…

- Improving targeting in vivo



Halas' group, Rice University (Texas)

- Further toxicity studies

Gold is biocompatible but...

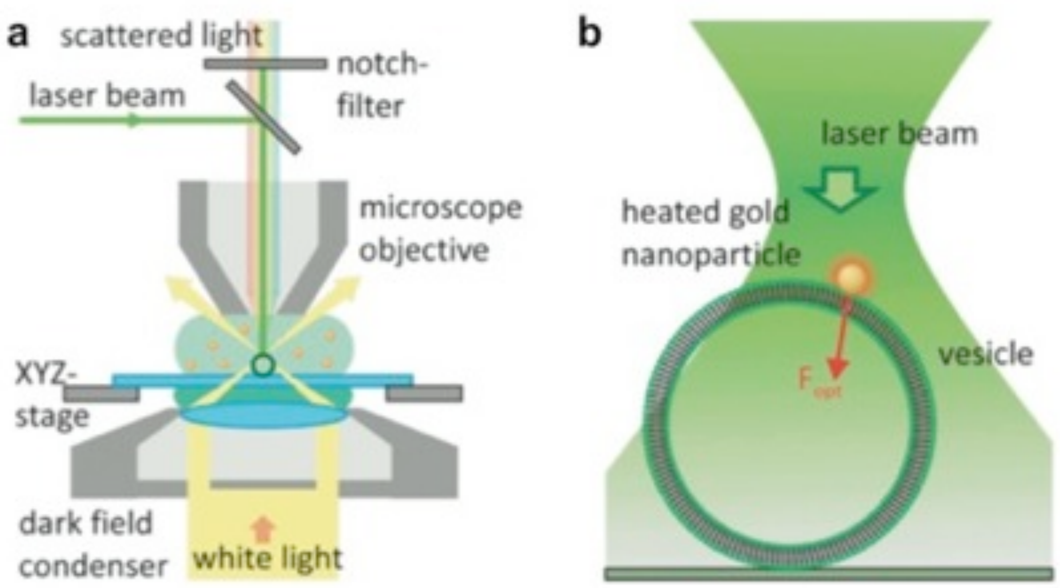
- up to a certain concentration

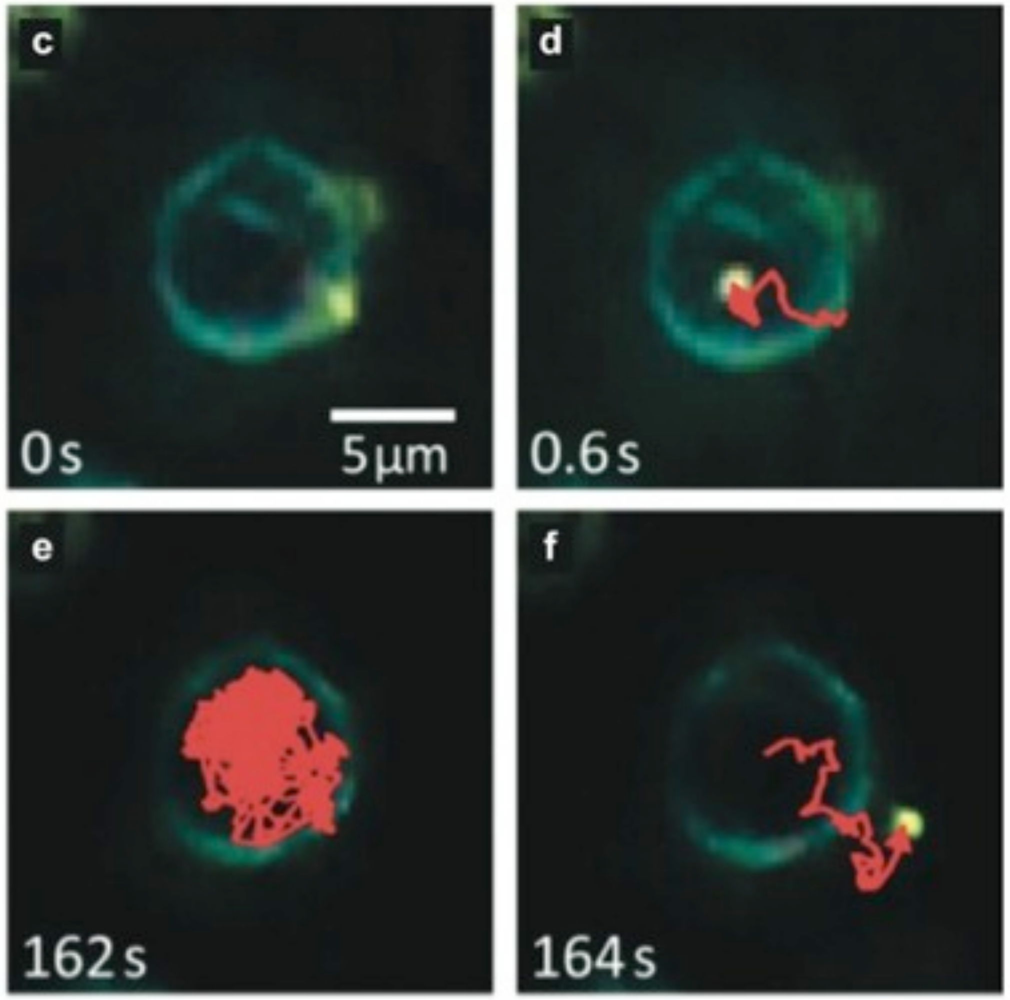
- Surface chemistry does matter

Nanosurgery, Cell transfection

Perforation of a phospholipid membrane
using a trapped single gold NP

Feldmann's group



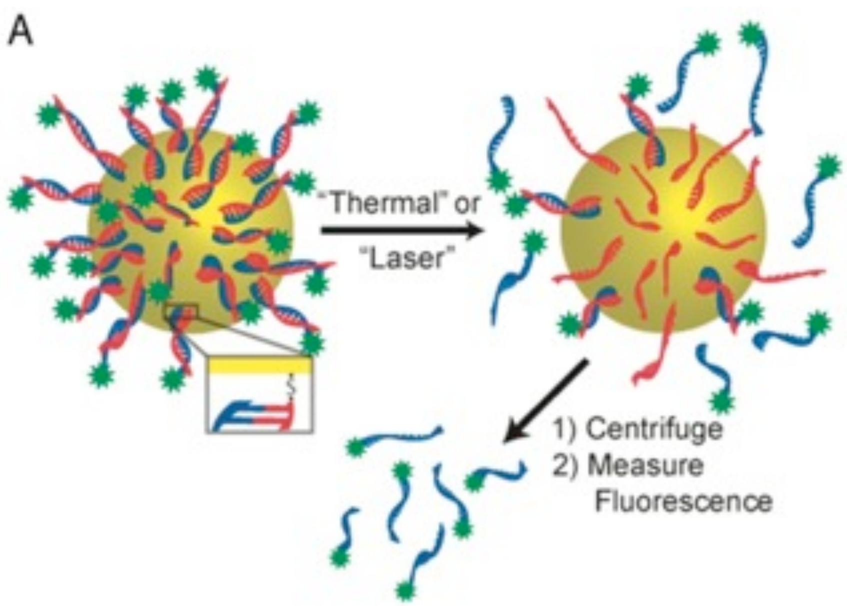


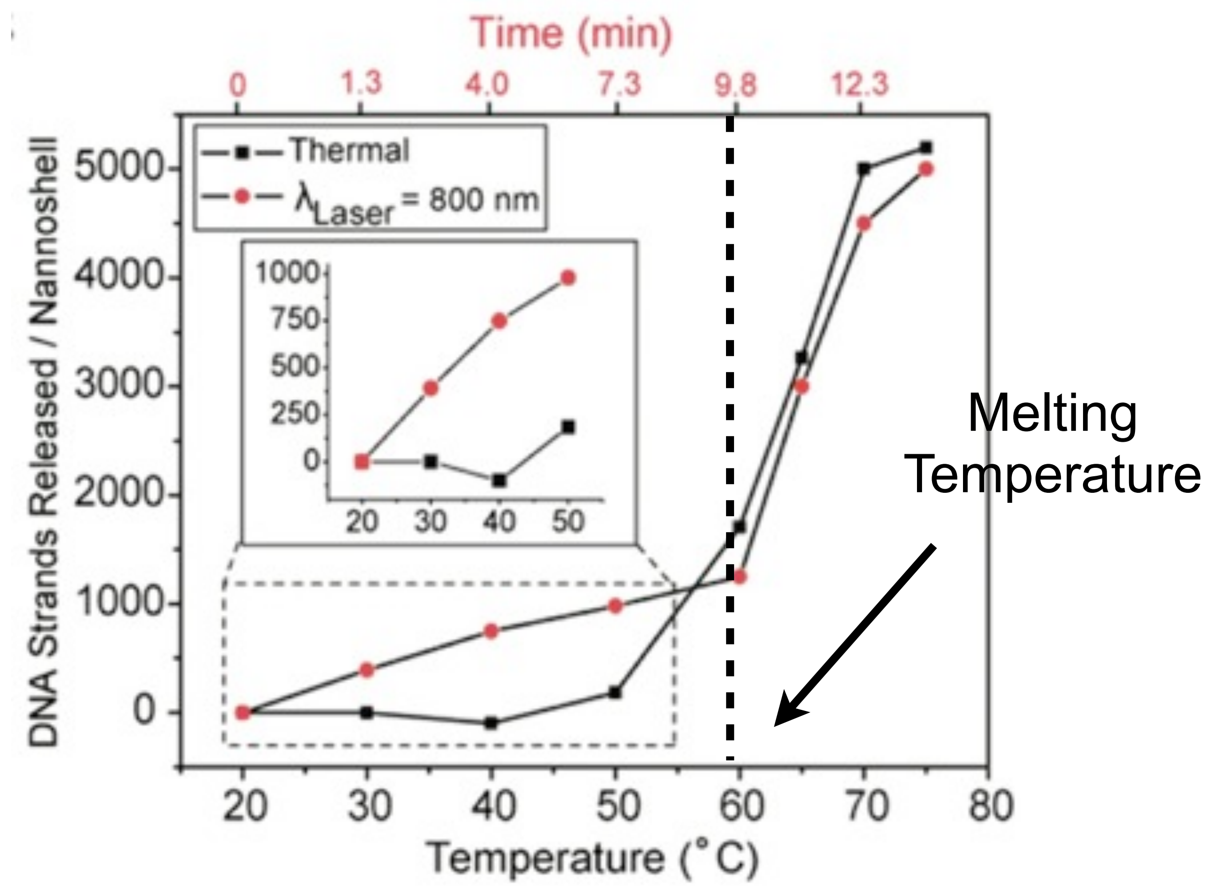
A. Urban et al , ACS Nano 5(5), 3585 (2011))

Thermal-induced drug release

Halas' group

NP= cargo + heat source





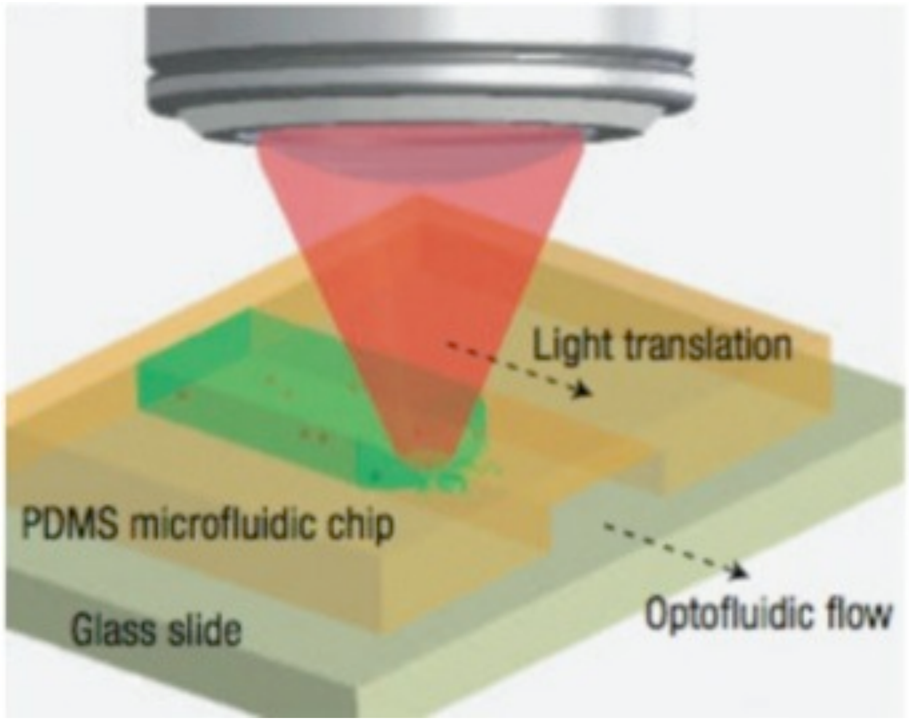
Huschka et al , JACS 133, 12247 (2011))

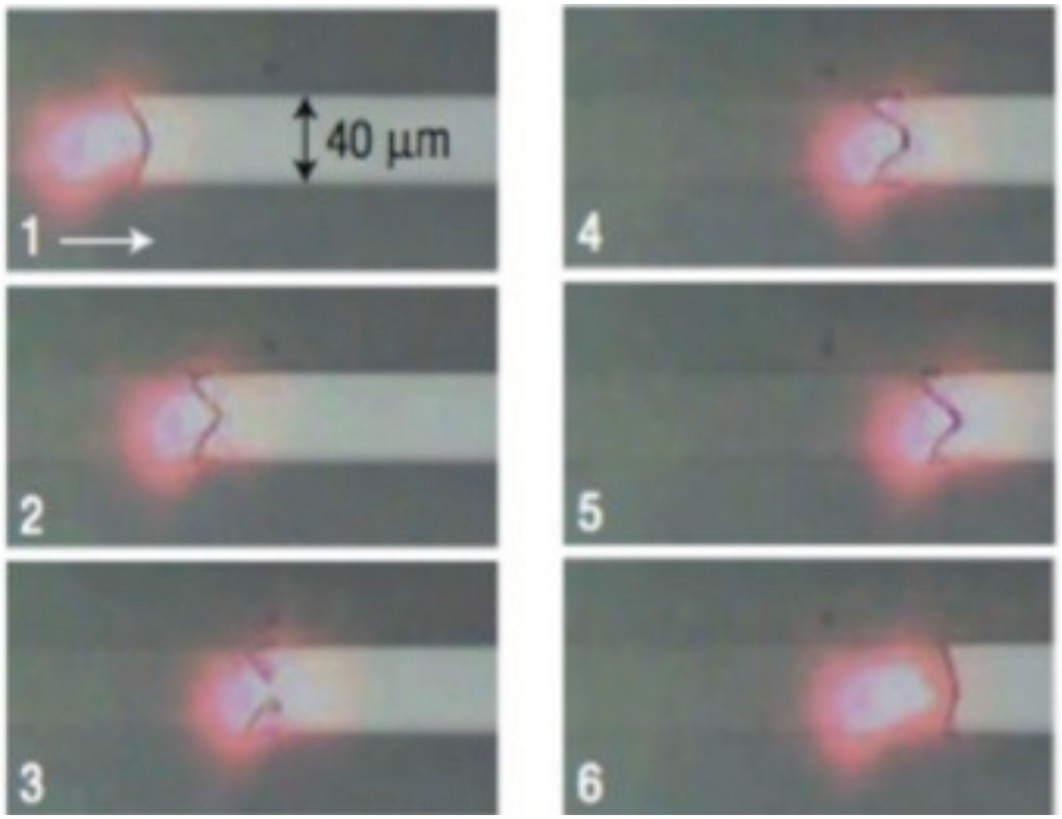
P. K. Jain et al, JACS 128, 2426 (2007)

H. Takahashi et al, Chem. Commun. 2247 (2005)

Plasmon-based Optofluidics

Lee's group



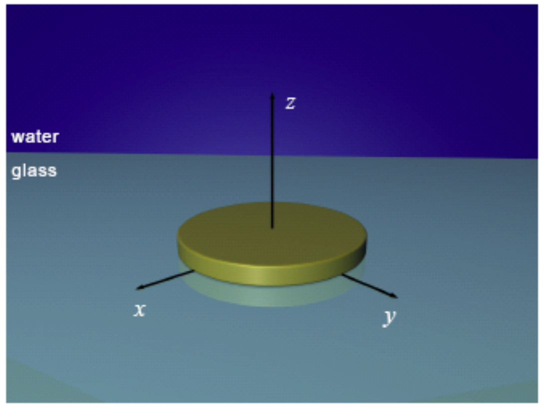


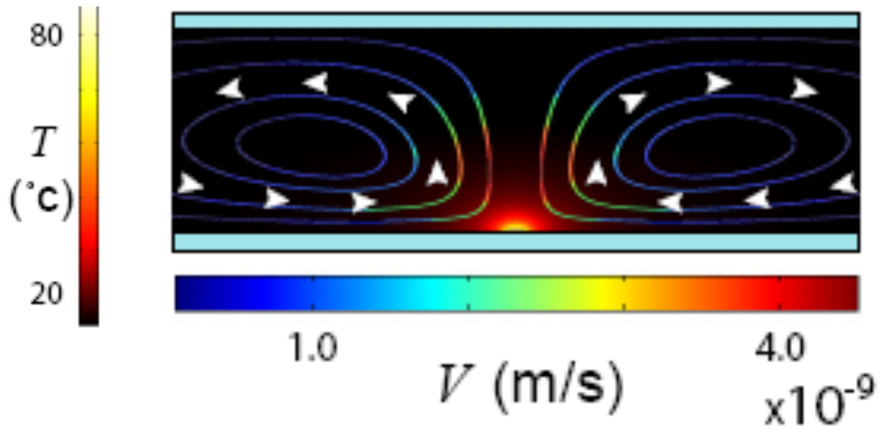
Temperature dependence of the surface tension at the fluid/air interface

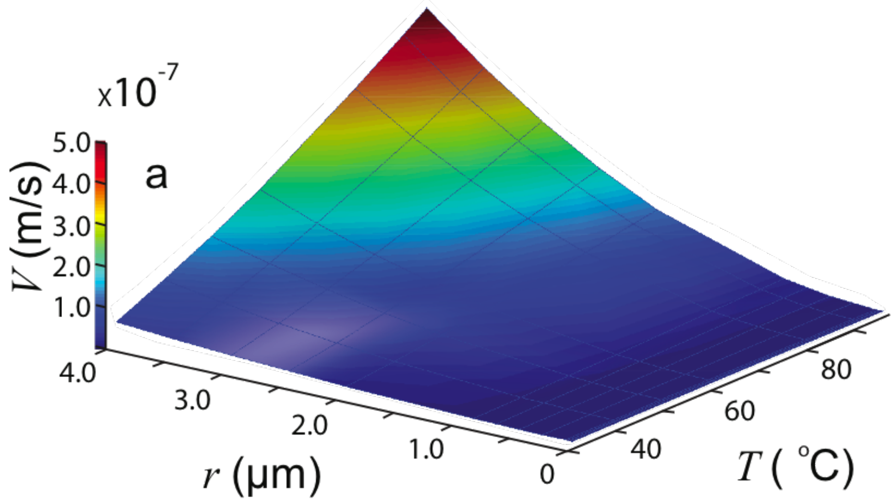
G. L. Liu, J. Kim, Y. Lu, and L. P. Lee, Nature Mater. 5, 27 (2006)

Plasmon-based Optofluidics

Jon Donner







-> **A way to develop optofluidic functionalities at the micro/nano-scale**

-> **Assessing the contribution of photothermal effects in plasmonic experiments**

J. Doner et al, ACS nano 5, 5457-5462 (2011)

WILEY ONLINE LIBRARY

Early View publication on wileyonlinelibrary.com
(issue and page numbers not yet assigned;
citable using Digital Object Identifier – DOI)

LASER & PHOTONICS REVIEWS

Laser Photonics Rev., 1–17 (2012) / **DOI** 10.1002/lpor.201200003

Abstract Recent years have seen a growing interest in using metal nanostructures to control temperature on the nanoscale. Under illumination at its plasmonic resonance, a metal nanoparticle features enhanced light absorption, turning it into an ideal nano-source of heat, remotely controllable using light. Such a powerful and flexible photothermal scheme is the basis of *thermo-plasmonics*. Here, the recent progress of this emerging and fast-growing field is reviewed. First, the physics of heat generation in metal nanoparticles is described, under both continuous and pulsed illumination. The second part is dedicated to numerical and experimental methods that have been developed to further understand and engineer plasmonic-assisted heating processes on the nanoscale. Finally, some of the most recent applications based on the heat generated by gold nanoparticles are surveyed, namely photothermal cancer therapy, nano-surgery, drug delivery, photothermal imaging, protein tracking, photoacoustic imaging, nano-chemistry and optofluidics.

Thermo-plasmonics: using metallic nanostructures as nano-sources of heat

Guillaume Baffou[1,*] **and Romain Quidant**[2,3,*]

THE PLASMON NANOOPTICS GROUP@ICFO

romain.quidant@icfo.es

ICFO Institut de Ciències Fotòniques · spedoc · erc · GOBIERNO DE ESPAÑA MINISTERIO DE CIENCIA E INNOVACIÓN · Fundació Privada CELLEX · icrea Institució Catalana de Recerca i Estudis Avançats