Clustering & Global Challenges
April 07-09, 2021
Online international conference
Health
Smart Energy
Quantum Tech.
Advanced Materials

Near-infrared luminescent nanoprobes for bioimaging and nanothermometry

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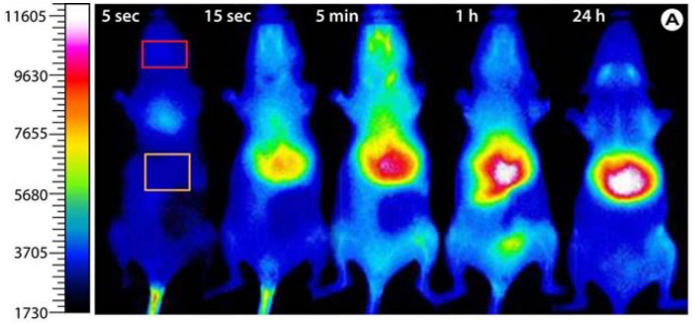
M. Matulionyte, F. Vetrone

L.Q.J. Maia

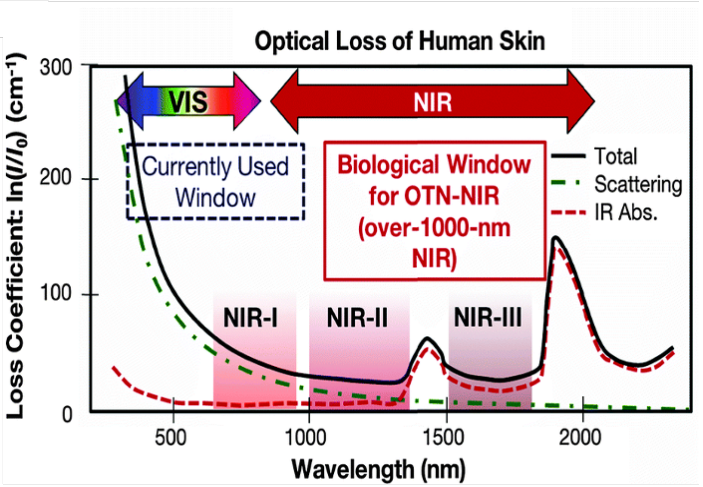
Invited presentation, **Friday, 9th April 2021**

NIR luminescent nanoprobes

➢ Nanoprobes for *in-vivo* diagnosis

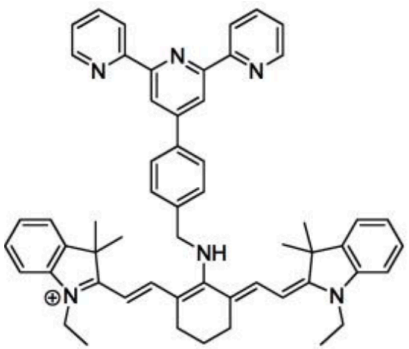


Molecules ***2012****, 17, 14067-1409*



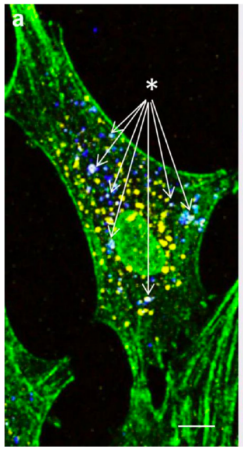
Nanoscale Horiz. **2016**, 1, 168-184

NIR Dyes



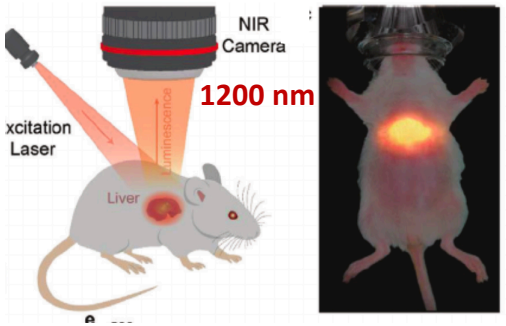
Curr Opin Chem Biol. **2010**; 14(1): 64.

Harmonic nanoparticles ($LiNbO_3$, $BiFeO_3$)



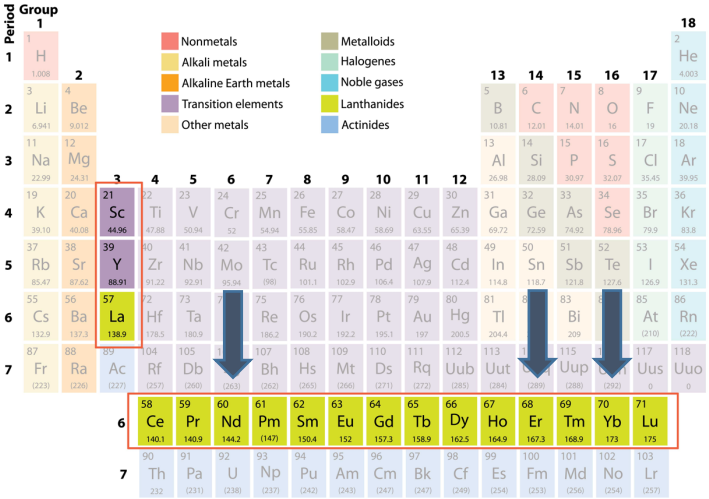
Mol. Pharmaceutics **2013**, 10, 783−792

Quantum dots (InP, Ag_2S)



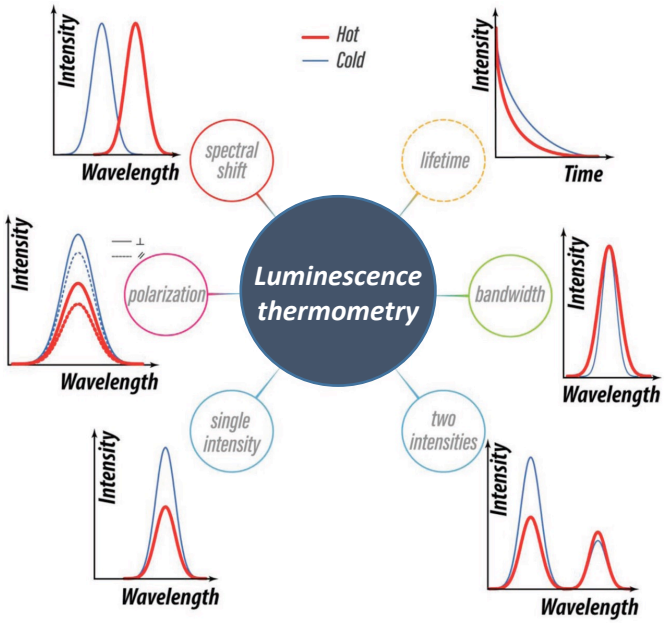
Adv. Sc. **2021**

Rare-earth doped luminescent nanoprobes for bio-imaging and nanothermometry



- ✓ Numerous emission bands in the NIR
- ✓ Narrow emission bands -> spatial discrimination
- ✓ « Long » lifetimes -> temporal discrimination

➢ Measure temperature at the nanoscale with a contactless process

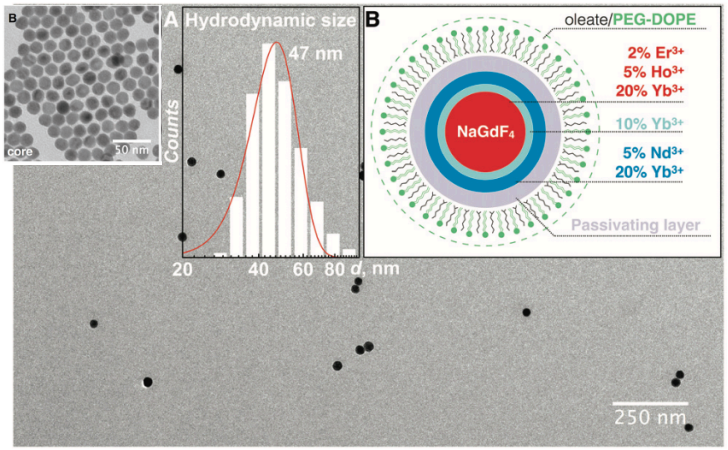


- ✓ High spatial resolution (< 1 µm)
- ✓ Short acquisition time (< 1 ms)
- ✓ High thermal sensitivity (> 1%.K^{-1})

D. Jaque & F. Vetrone *Nanoscale*, 4, **2012,** 4301
C.D.S. Brites et al. *Adv. Opt. Mater*, **2018,** 1801239

Targeted nanomaterials: garnet nanocrystals

➢ Nd^{3+}-doped **fluorides**

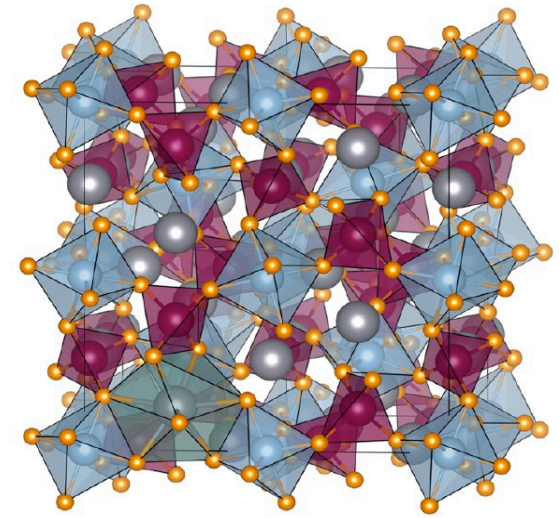


Lots of Nd^{3+}-doped **fluorides** (LaF_3, $NaYF_4$, …) because of their strong photoluminescence related to their low phonon energy < 600 cm^{-1}

But: Dissolution ? Toxicity ?

➢ Nd^{3+}-doped **garnets**

$Y_3Al_5O_{12}$ (YAG)



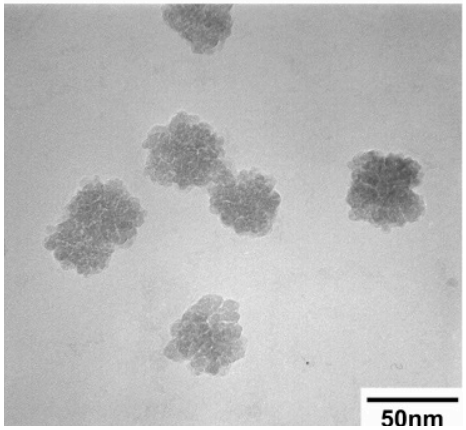
Y^{3+} Al^{3+} Al^{3+} O^{2-}

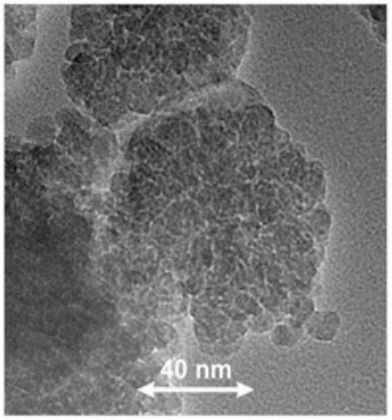
- ✓ Phonon energy (< 900 cm^{-1})
- ✓ Chemical robustness
- ✓ Ability to incorporate RE^{3+}
- ✓ Versatile matrices

Phys.Chem.Chem.Phys., **2017**, 19, 11825

Synthesis of YAG nanocrystals by solvothermal method

$$3\ Y(acetate)_3 + 5\ Al(O\text{-}i\text{-}Pr)_3 \xrightarrow[t = 2\text{-}3\ hours]{Butanediol,\ 300°C} YAG\ nanocrystals$$





- Suspension in ethanol
- but bad crystallinity affects the PL

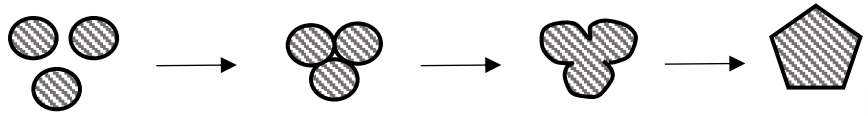
- Improved crystal quality
- Colloidal stability in water
- High photoluminescence intensity
- High thermal resolution

R. Kasuya et al. *J. Alloys Comp. 408* **(2006)** 820
R. Kasuya *J. Phys. Chem. B* **2005**, 109, 22126
M. Vorsthove, Mat. Res. Bull. 46 **(2011)** 1761

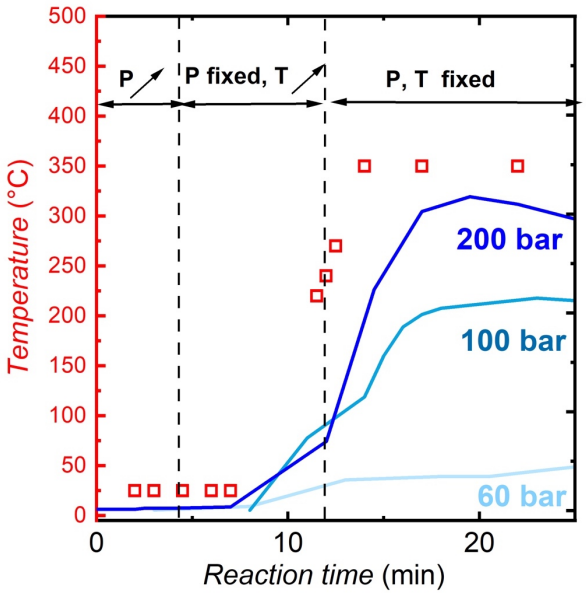
Adaptation of the solvothermal process to obtain well-crystallized nanocrystals

- Home-made autoclaves
- Large T/P ranges:
  - ✓ T : 0-1000°C
  - ✓ P: 0-800 bar
- Fixed P

- Optical windows for *in situ* photoluminescence experiments



Nucleation burst | Self-oriented aggregation | Coalescence | Nano-single-crystal



Testemale *et al. Rev. Sci. Inst.* **76**, 043905 **(2005)**
Dantelle et al. *RSC Advances* 8 **(2018)** 26857-26870

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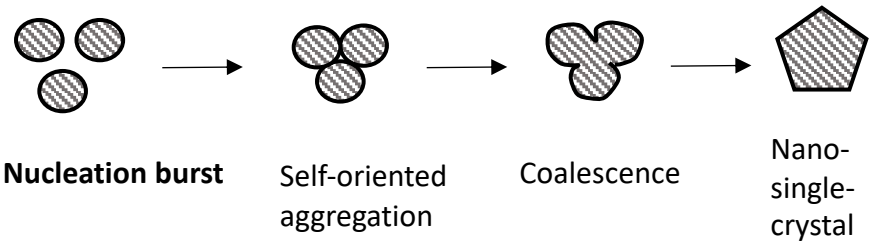
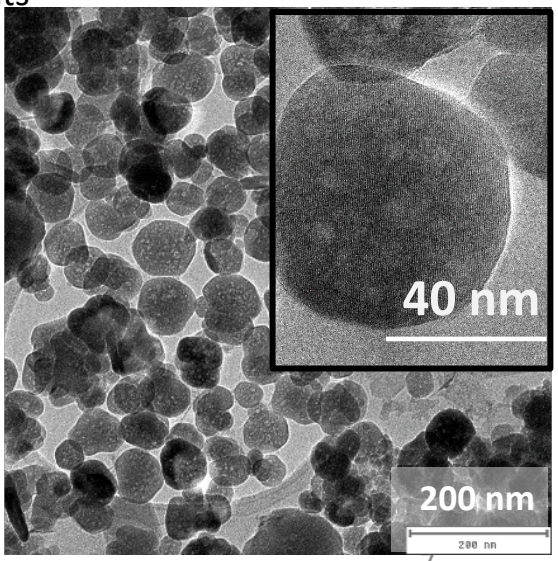


Nucleation burst | Self-oriented aggregation | Coalescence | Nano-single-crystal

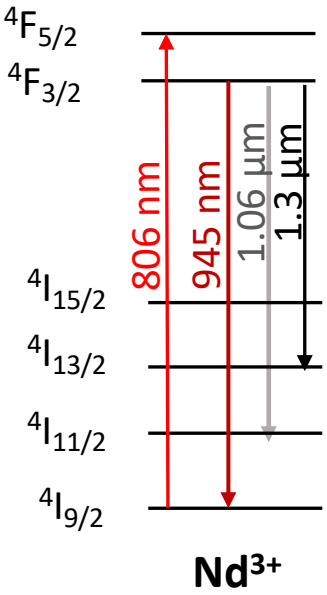
➢ Fine control of the nanocrystallisation process

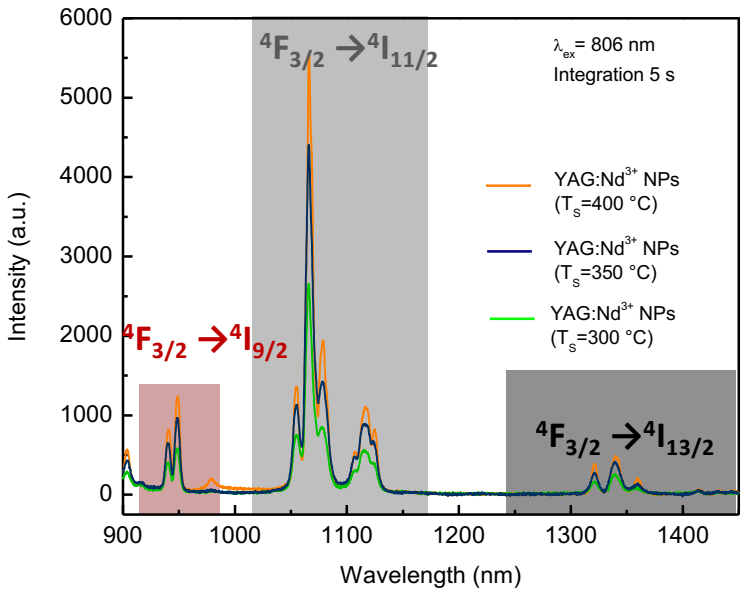


200 bar, 400°C

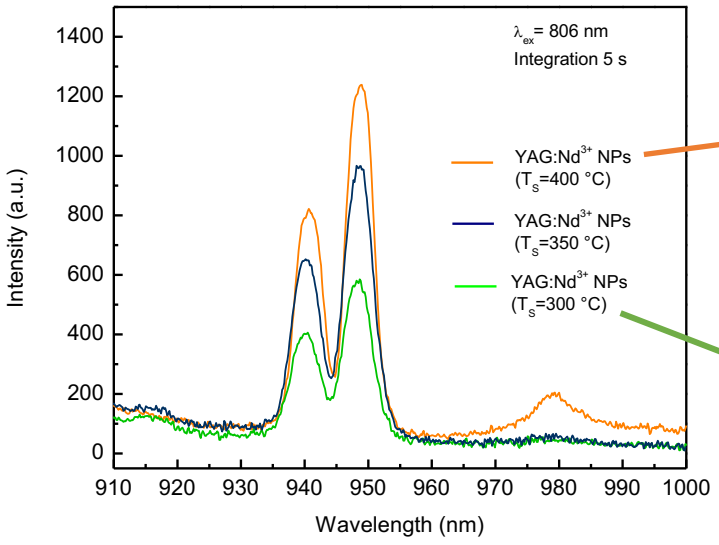
Testemale *et al. Rev. Sci. Inst.* **76**, 043905 **(2005)**
Dantelle et al. *RSC Advances* 8 **(2018)** 26857-26870

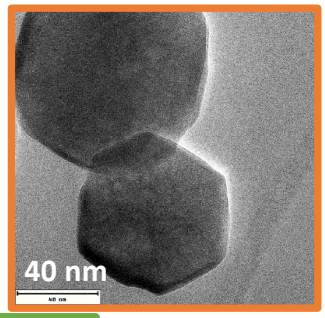
Improved optical properties in the NIR

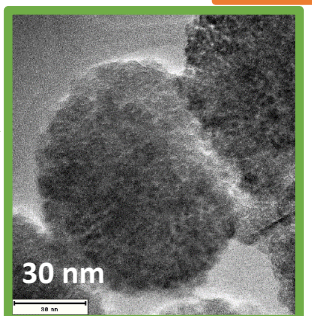




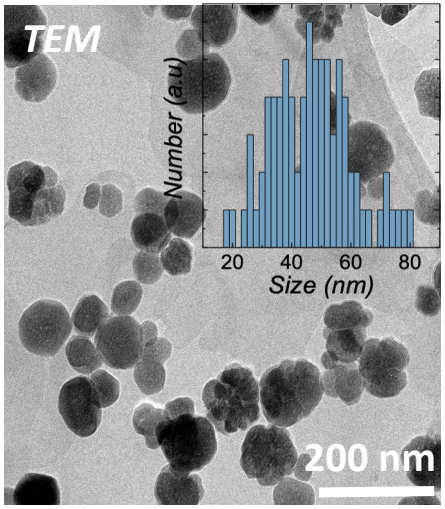
- Narrow emission lines
- Enhanced intensity with improved crystal quality



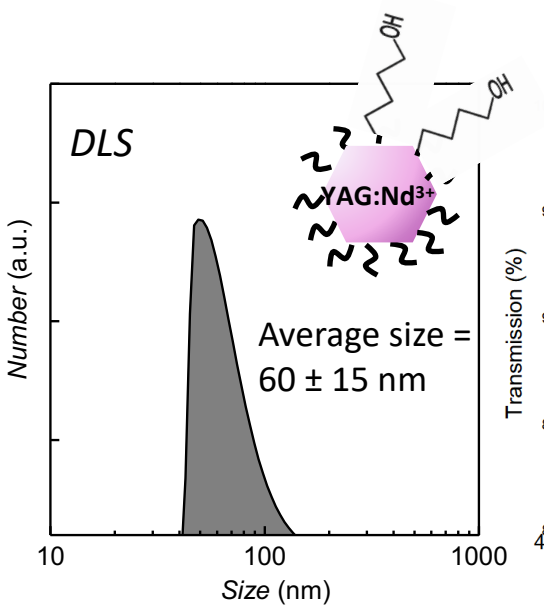


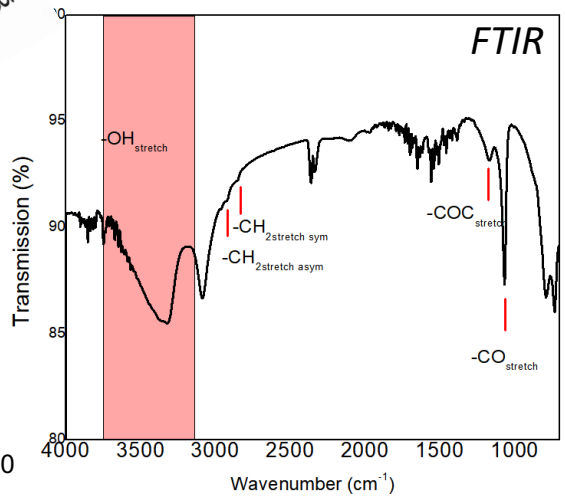


Colloidal suspension of YAG:Nd^{3+} nanocrystals in ethanol



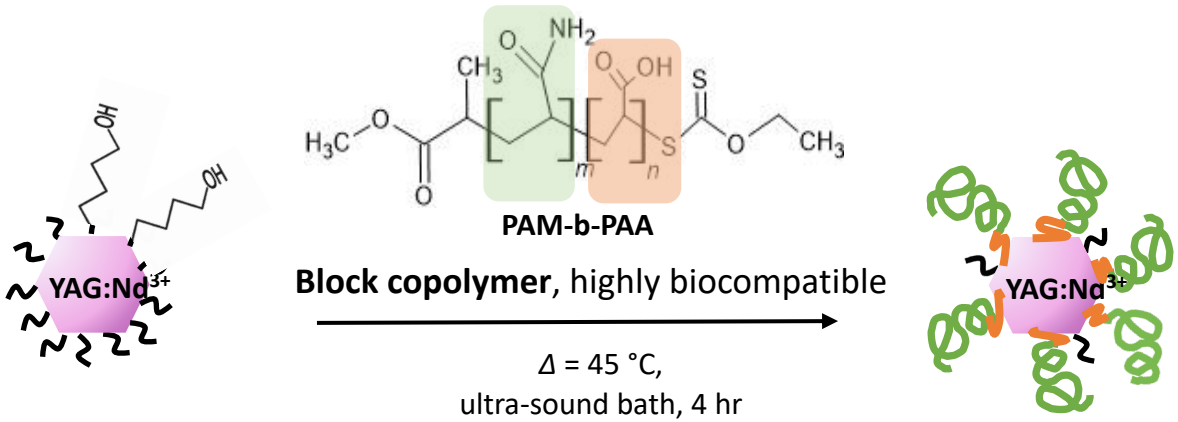
Average size = 55 ± 15 nm





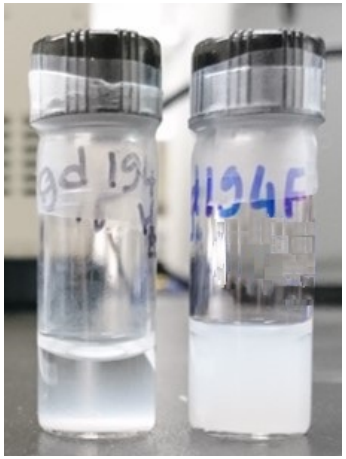
- Butanediol groups grafted at the nanocrystal surface
- Stabilizes the nanocrystals in EtOH but not in water

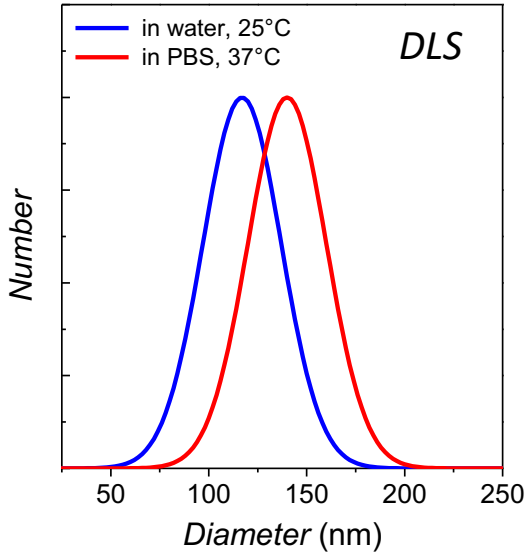
Copolymer grafting for stabilization in water and in PBS



Observation after 1 hour

Before After

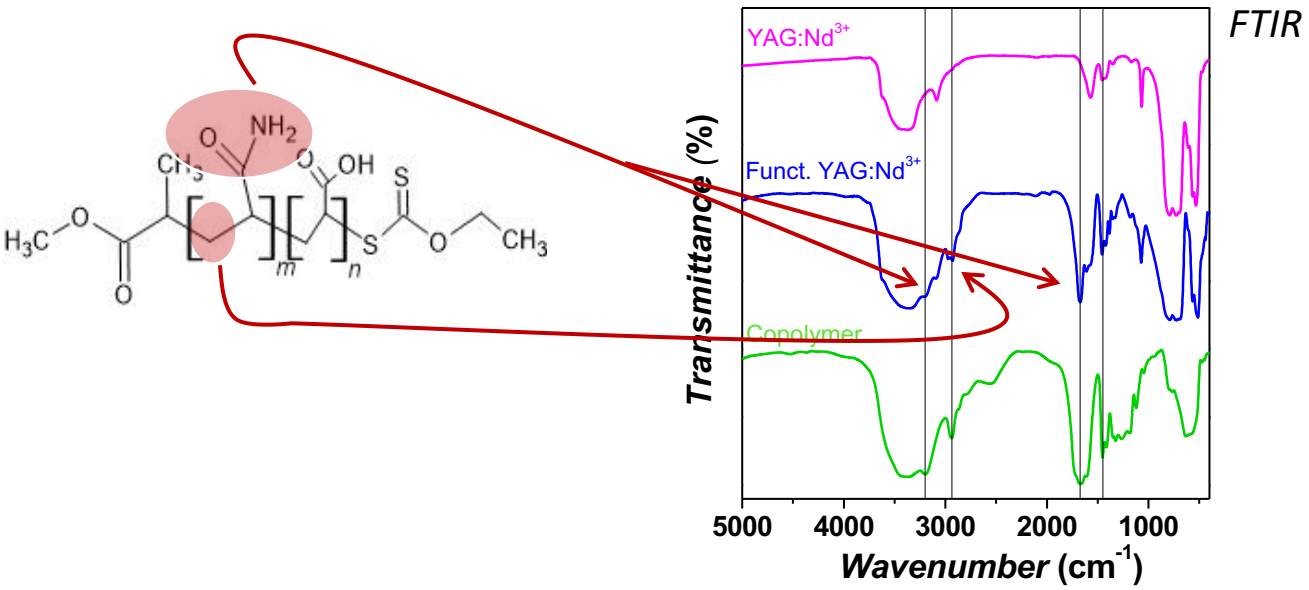




➢ Copolymer grafting drastically increases colloidal stability in water

C. Gérardin et al, *Angewandte Chemie Int. Ed.* **2003**, 42, 3681-3685
A. Cantarano … G. Dantelle, *ACS Appl. Mater. Interfaces* 12 **(2020)**

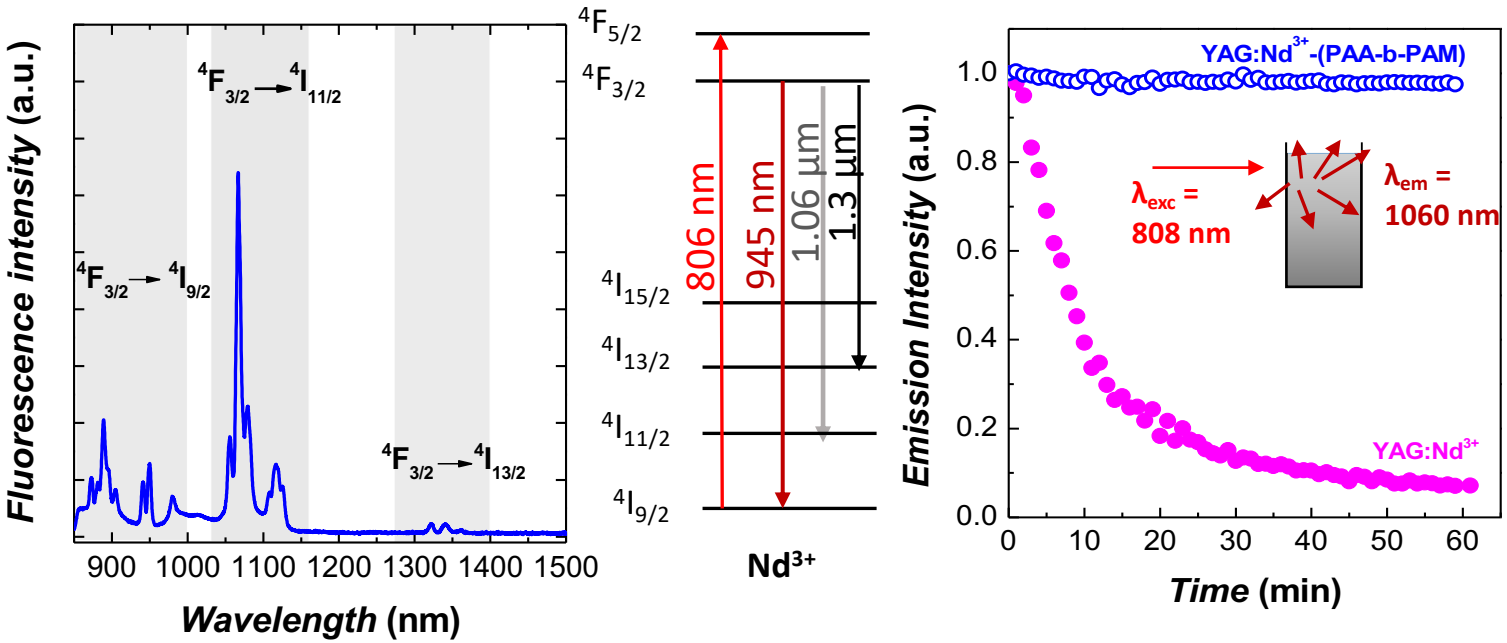
Copolymer grafting for stabilization in water and in PBS



- Proofs of copolymer surface grafting

A. Cantarano … G. Dantelle, *ACS Appl. Mater. Interfaces* 12 **(2020)** *51273*

NIR luminescence of (copo)-YAG:Nd^{3+} and *in-vivo* imaging



A. Cantarano … G. Dantelle, *ACS Appl. Mater. Interfaces* 12 **(2020)** *51273*

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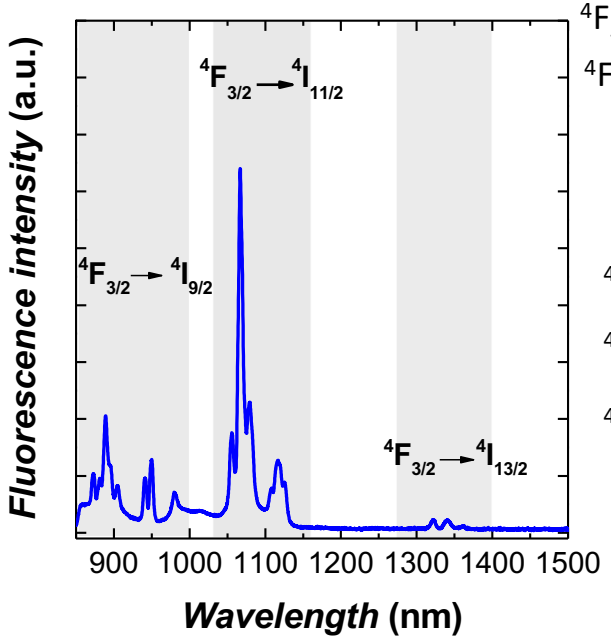
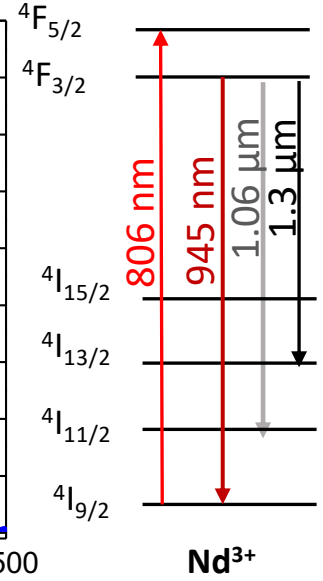
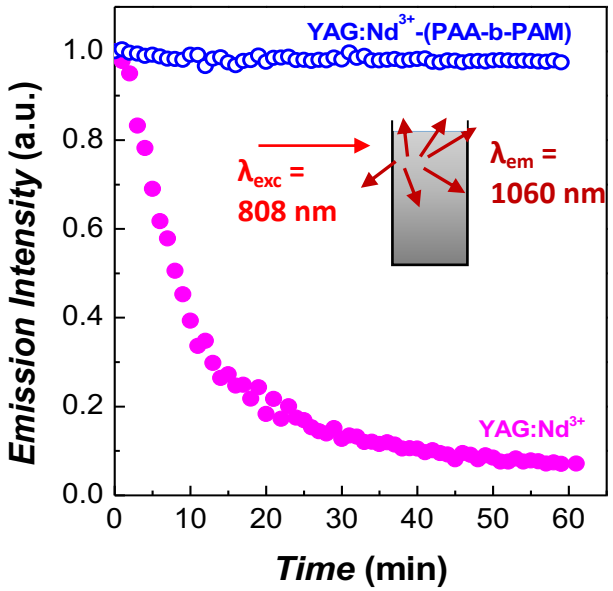
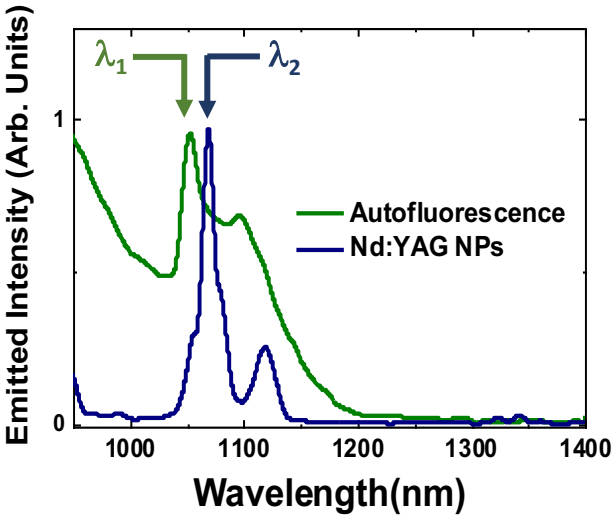
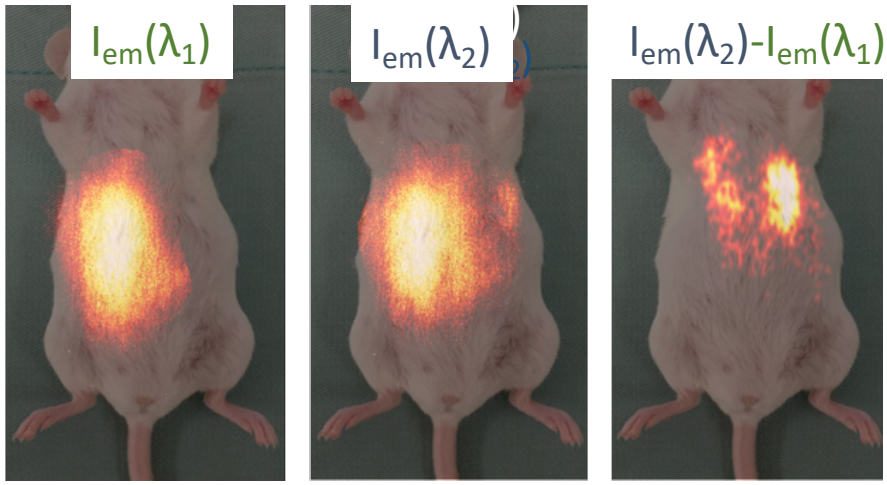






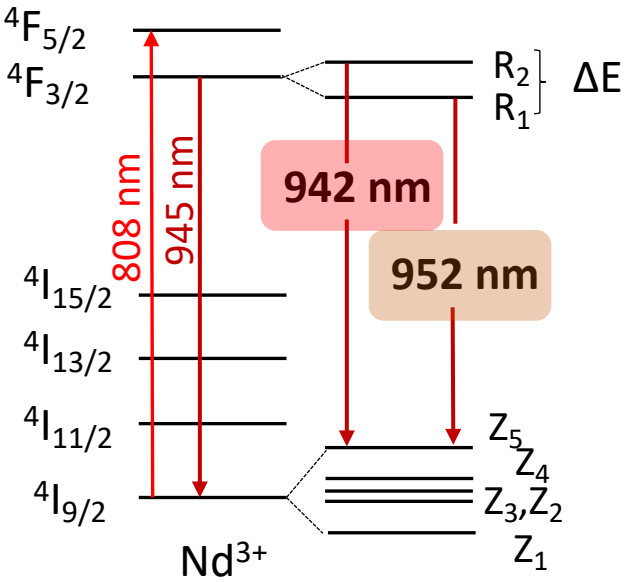




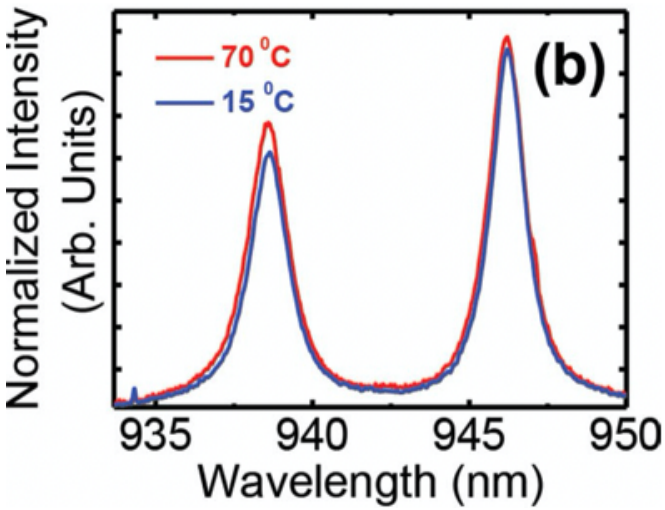
➢ *In-vivo* detection of (copo)-YAG:Nd^{3+}

A. Cantarano … G. Dantelle, *ACS Appl. Mater. Interfaces* 12 **(2020)** *51273*

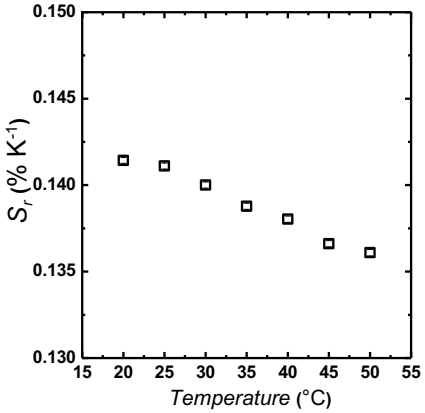
Thermal sensitivity of (copo)-YAG:Nd^{3+}: 0.14 %.K^{-1}



$$(LIR)_T = \frac{I_{942}}{I_{952}}$$



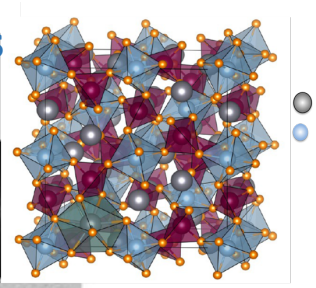
Relative thermal sensitivity: $S_r = \frac{1}{LIR}\frac{\partial LIR}{\partial T}$



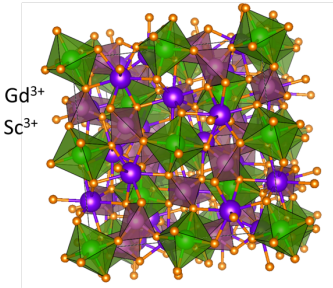
- S_r is directly linked to ΔE, via Boltzman's population rate
- Look for matrices which can provide stronger crystal field splitting

A. Benayas et al. *Adv. Mater.* **2015**, 1, 168
G. Dantelle et al. *PCCP* **2019**, 21, 11132

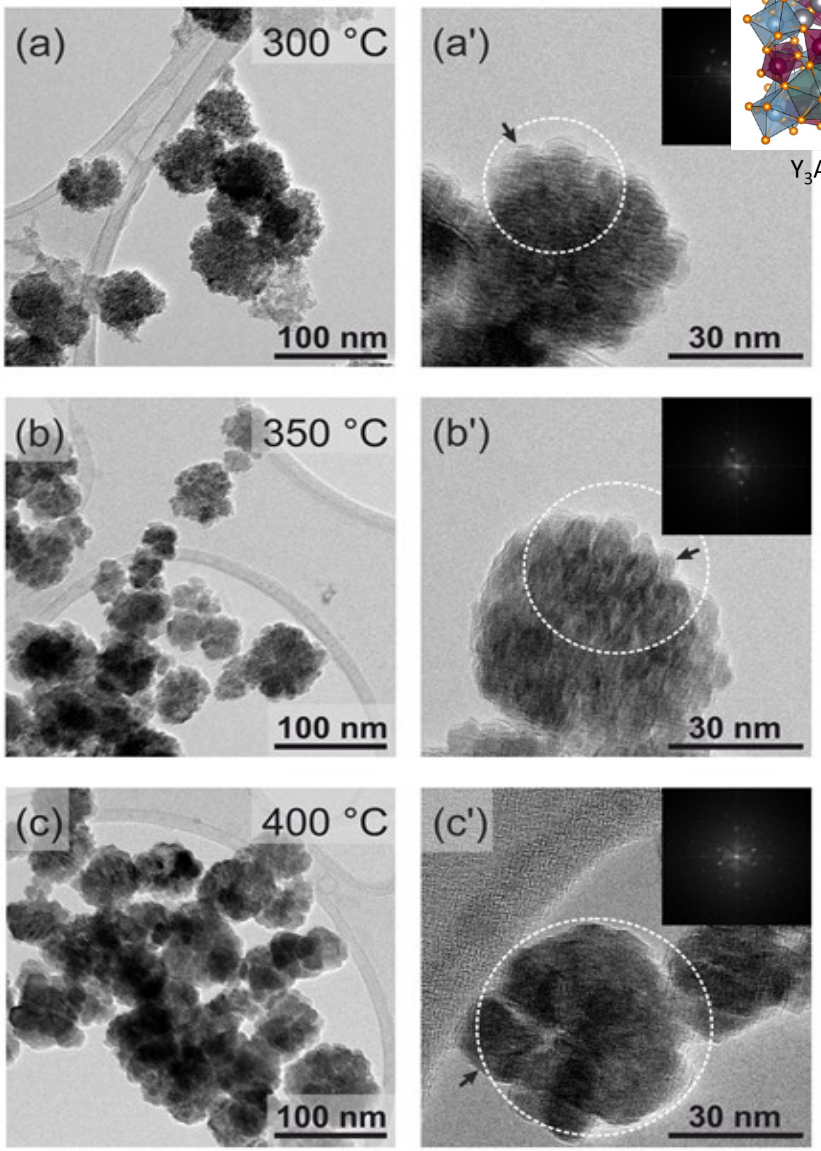
Synthesis of GSAG:Nd^{3+} nanocrystals

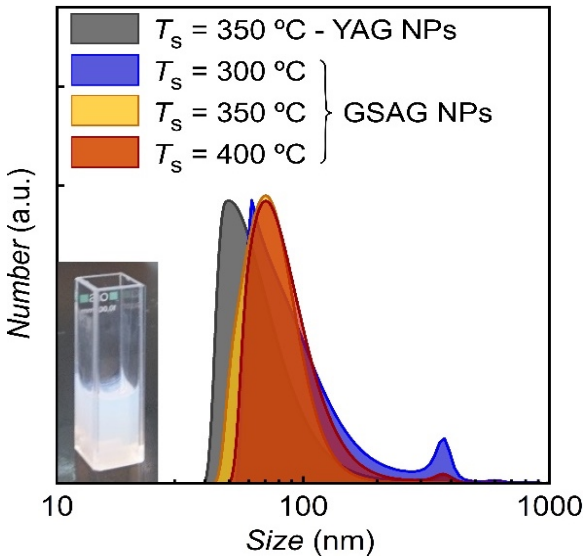


$Y_3Al_5O_{12}$ (YAG)



$Gd_3Sc_2Al_3O_{12}$ (GSAG)

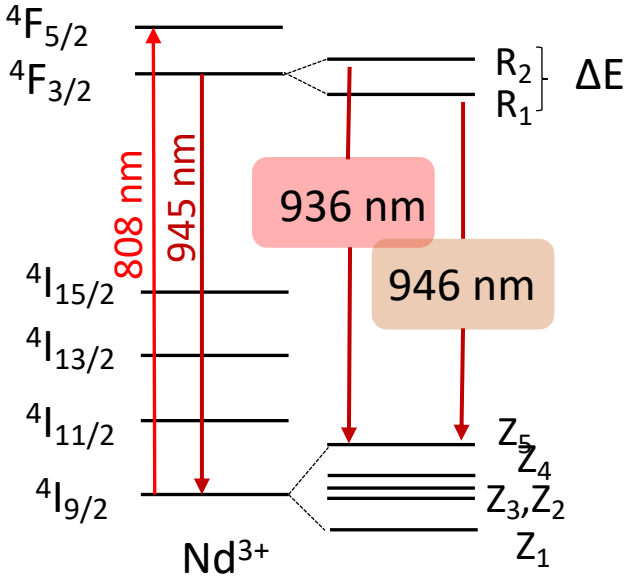


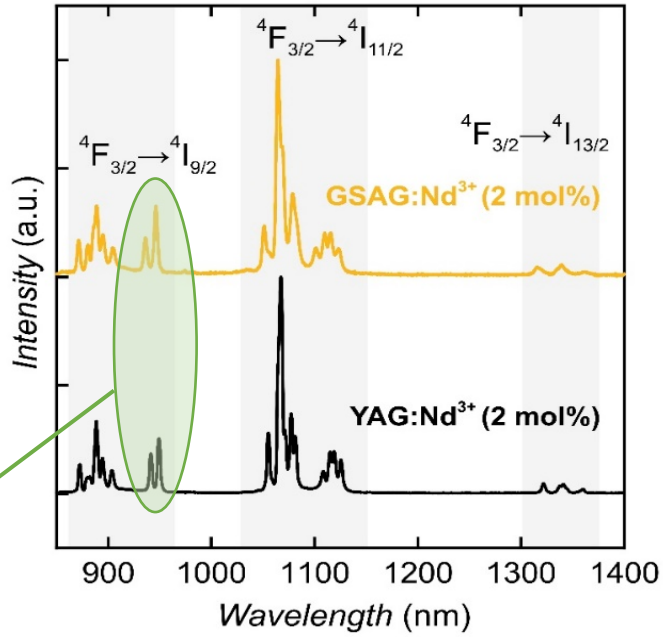


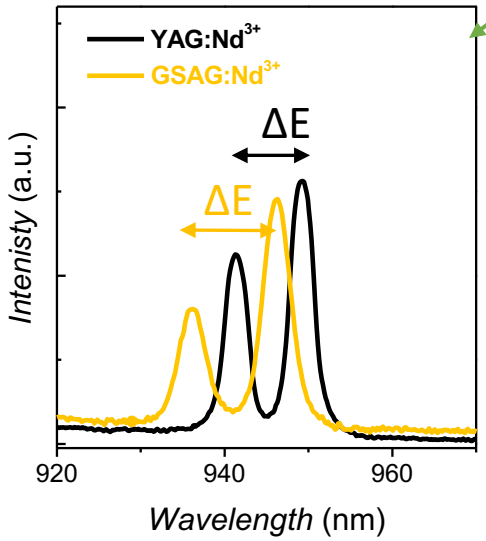
- Elaboration of GSAG nanocrystals
- Stable in ethanol

L. Devys, G. Dantelle et al. *J. Lumin.* 190 **(2017)** 62
G. Dantelle et al. *SPIE* **(2018)** 10533

Thermal sensitivity of (copo)-GSAG:Nd^{3+}







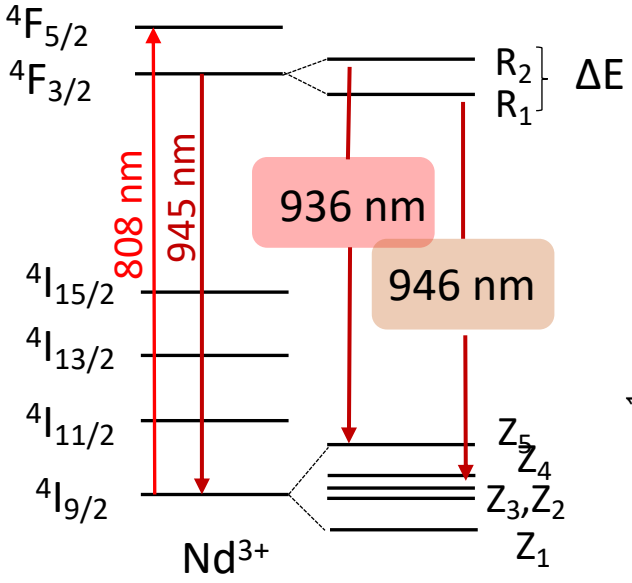
ΔE (YAG:Nd^{3+})= 89 cm^{-1}

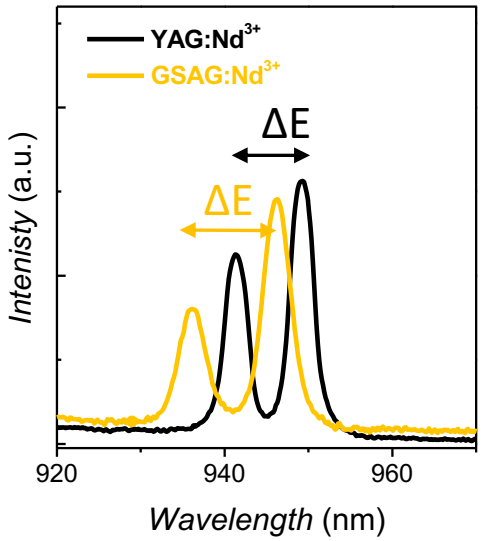
ΔE (GSAG:Nd^{3+})= 114 cm^{-1}

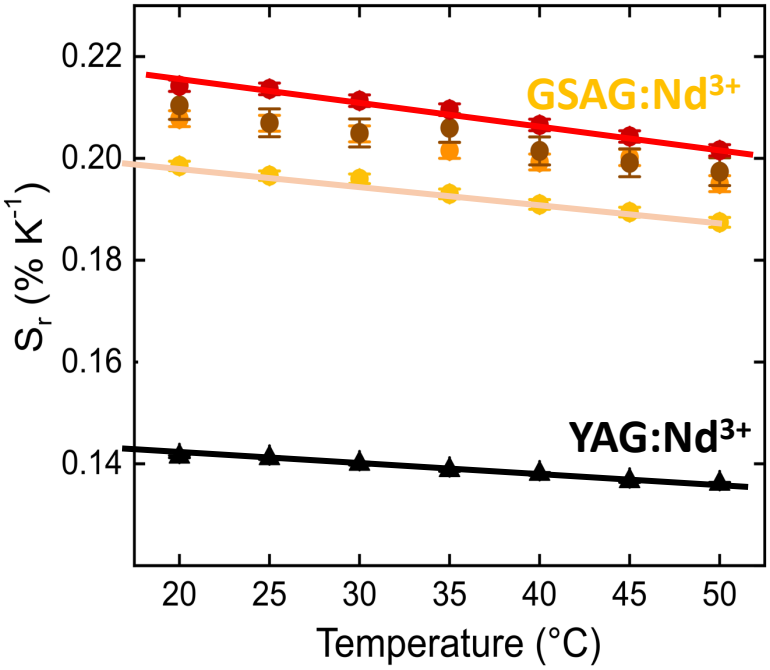
➢ Larger crystal field splitting in GSAG than in YAG

G. Dantelle et al. *PCCP* **2019**, 21, 11132

Thermal sensitivity of (copo)-YAG:Nd^{3+}: 0.22 %.K^{-1}



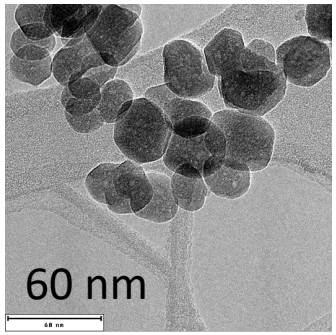




- Higher S_r in GSAG:Nd^{3+} than in YAG:Nd^{3+}
- Consistent with theoretical calculations (M. Suta *et al. Nanomaterials* **2020**, 10, 543)

G. Dantelle et al. *PCCP* **2019**, 21, 11132

Conclusions

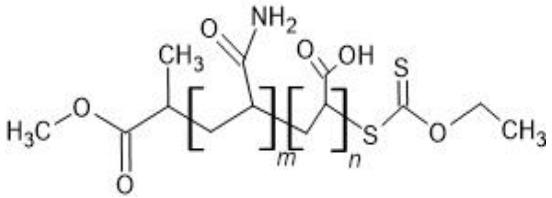


✓ **Original solvothermal synthesis (high P and high T)**

→ Well-crystallized garnet-type nanocrystals
→ Size control in the range 60 to 200 nm
→ Stable colloidal solutions in ethanol

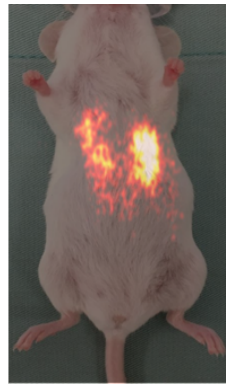
✓ **Robust stabilization process to obtain aqueous colloidal solutions**

→ Effective surface adsorption of block copolymers
→ *Optimization of the process with other copolymers*



✓ **High NIR luminescence and nanothermometry**

→ *In-vivo* bioimaging thanks to autofluorescence removal
→ Competitive S_r (same order of magnitude as Nd^{3+}-doped fluoride nanocrystals)
→ *Need for increasing S_r through the use of different matrices and new codoping systems (Start of a PhD, I. Vallerini-Barbosa between Inst. Néel and UFG, Brazil)*



Thank you for your attention !

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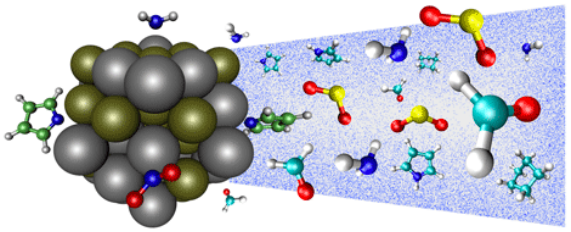

GDRi Nanomateriaux Multifonctionnels Contrôlés

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