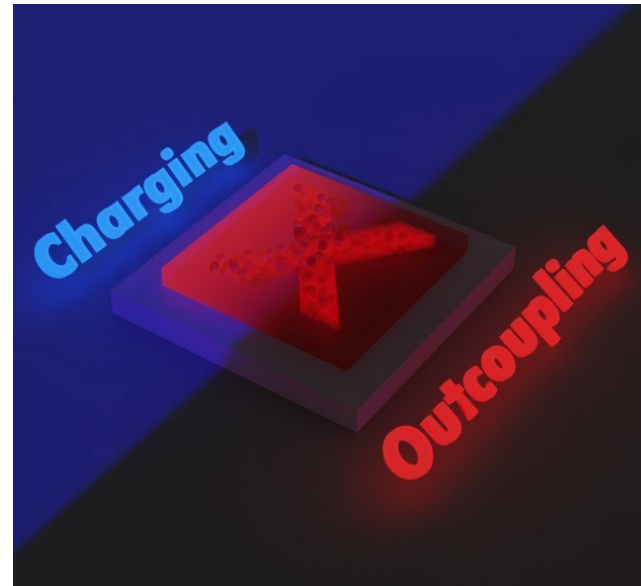




# Wet-deposition of nanophosphor particles: an alternative method to obtain translucent films with original optical properties.



Victor Castaing, M. Romero, G. Lozano, H. Míguez  
Institute of Materials Science of Seville (CSIC-US)

06/10/2023

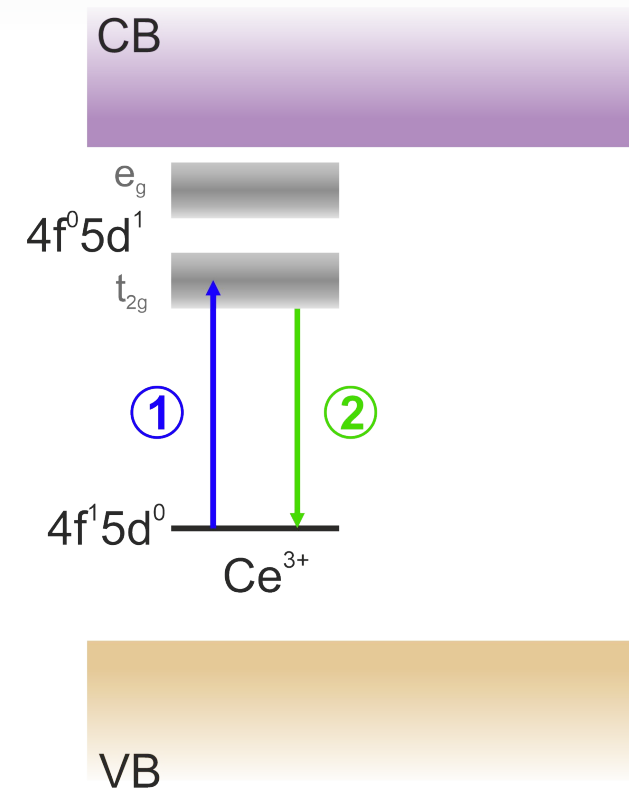
1



## PHOSPHORS & PERSISTENT PHOSPHORS :



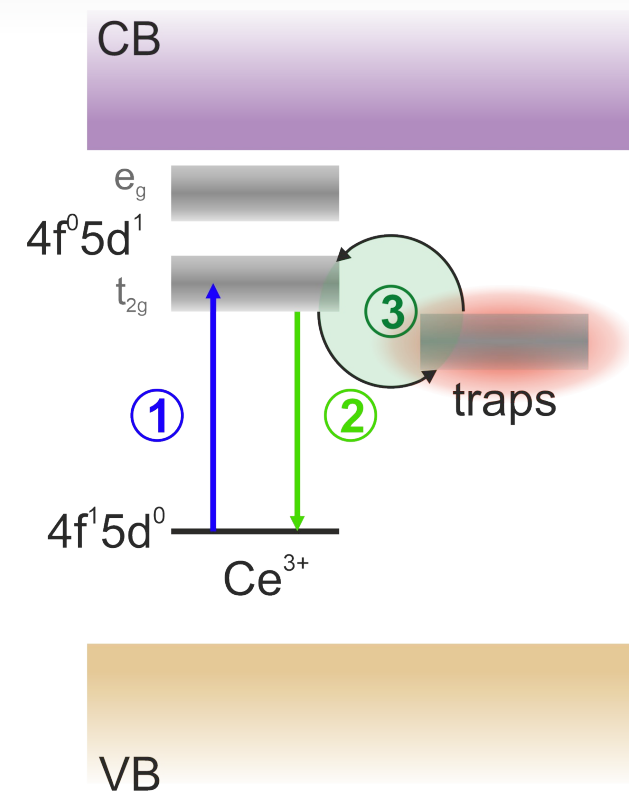
Orléans / Sevilla



- TM- or RE-doped inorganic matrices
- High efficiency
- Tuneable emission properties



## PHOSPHORS & PERSISTENT PHOSPHORS :

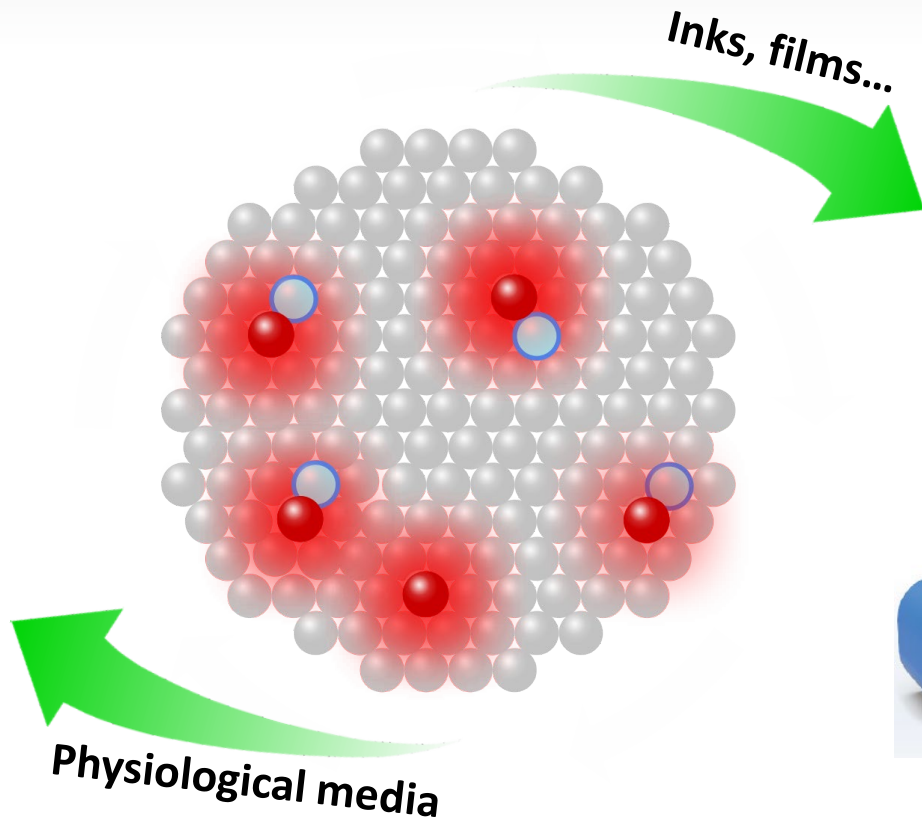
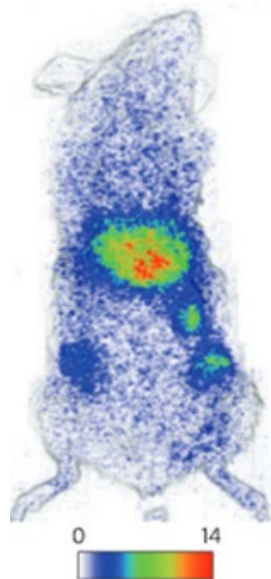


- Defects can be used to store light
- PersL = delayed and long-lasting emission
- PersL used for decoration and signalling



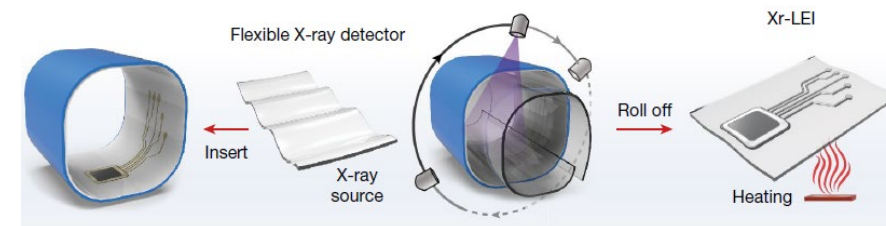
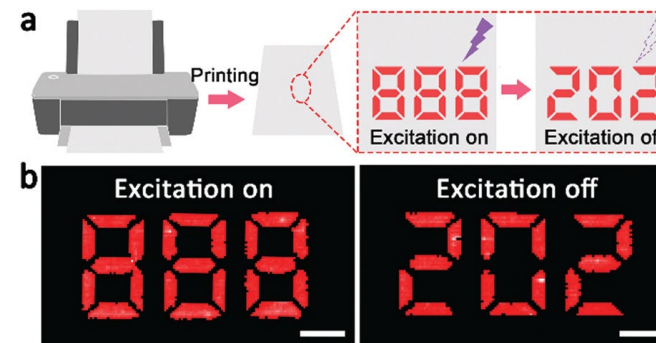
## PERSISTENT NANOPHOSPHORS APPLICATIONS :

Imaging  
Sensors  
Therapy



**Colloidal stability**  
**Bright and devised properties**

### Dynamic anticounterfeiting



### Flexible X-ray imaging screen

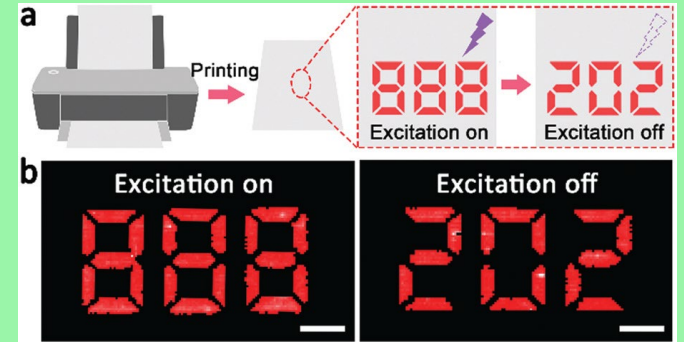
*Nat. Mater.* **2014**, 13, 418-426  
*Nature* **2021**, 590, 410-415  
*Chem. Commun.* **2020**, 56, 6660



## ANTICOUNTERFEITINGS :



### Dynamic anticounterfeittings



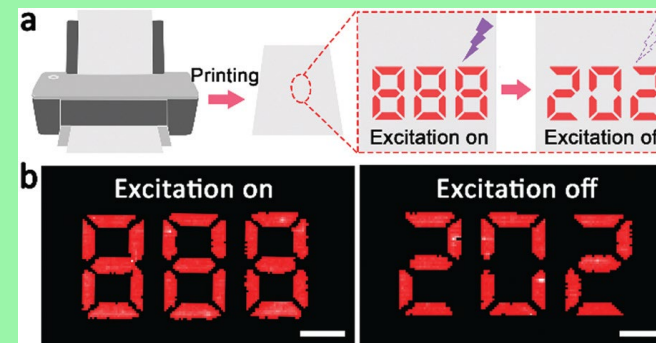
Invisible with naked eyes → Inks, thin films...



## ANTICOUNTERFEITINGS :



### Dynamic anticounterfeittings



Invisible with naked eyes → Inks, thin films...  
Reveal under stimulus → PL, EL, ML ...

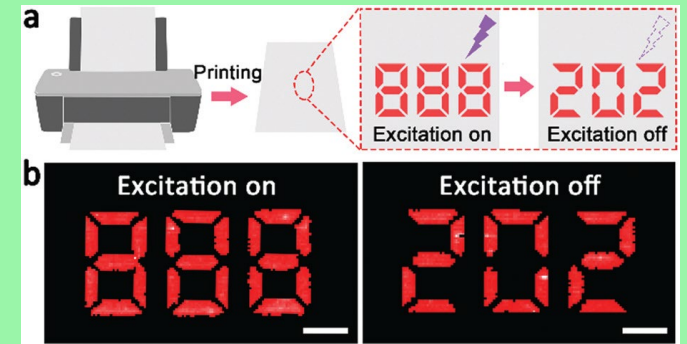
<https://www.ecb.europa.eu/euro/banknotes/current/security/html/index.en.html#additionalFeatures>



## ANTICOUNTERFEITINGS :



### Dynamic anticounterfeittings

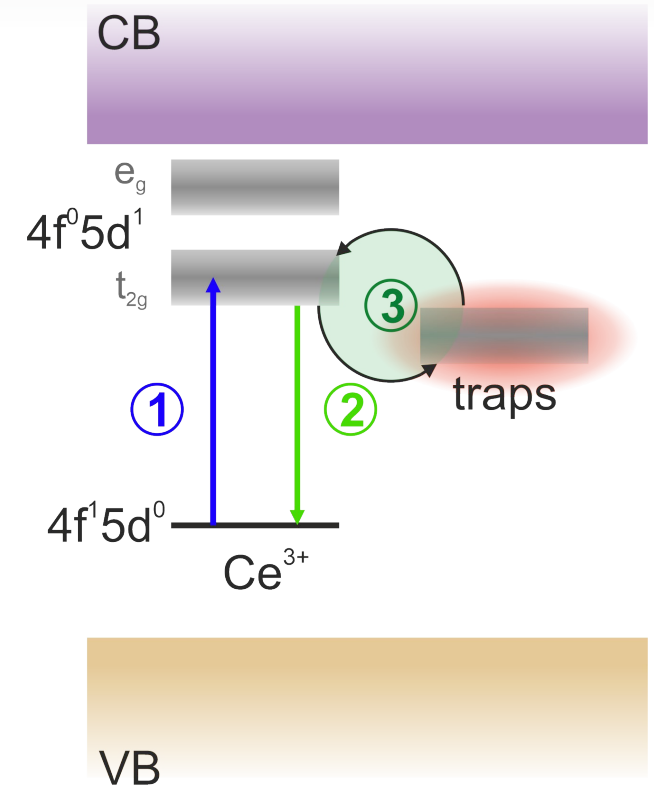
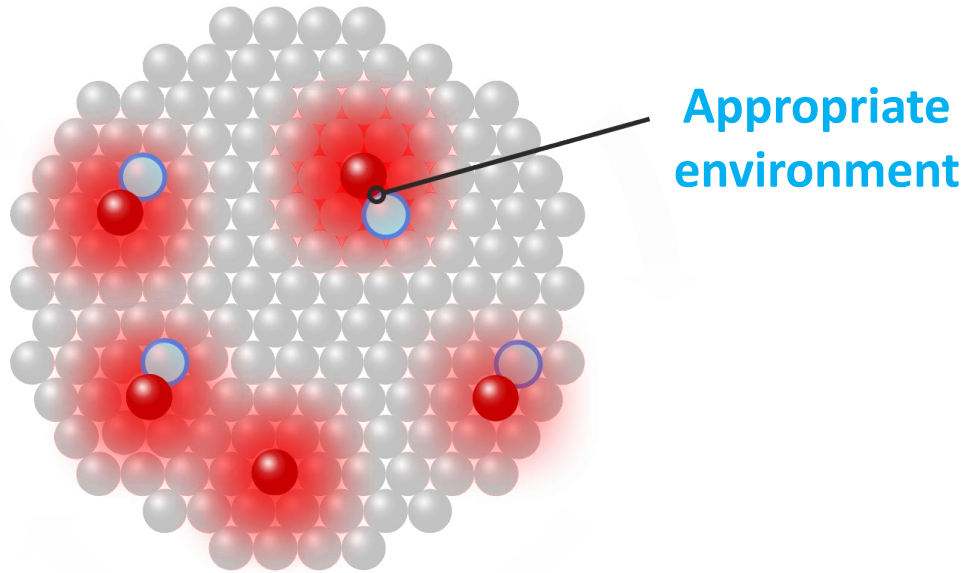


Invisible with naked eyes → Inks, thin films...  
Reveal under stimulus → PL, EL, ML ...  
Changing stimulus changes response → added security dimension

<https://www.ecb.europa.eu/euro/banknotes/current/security/html/index.en.html#additionalFeatures>



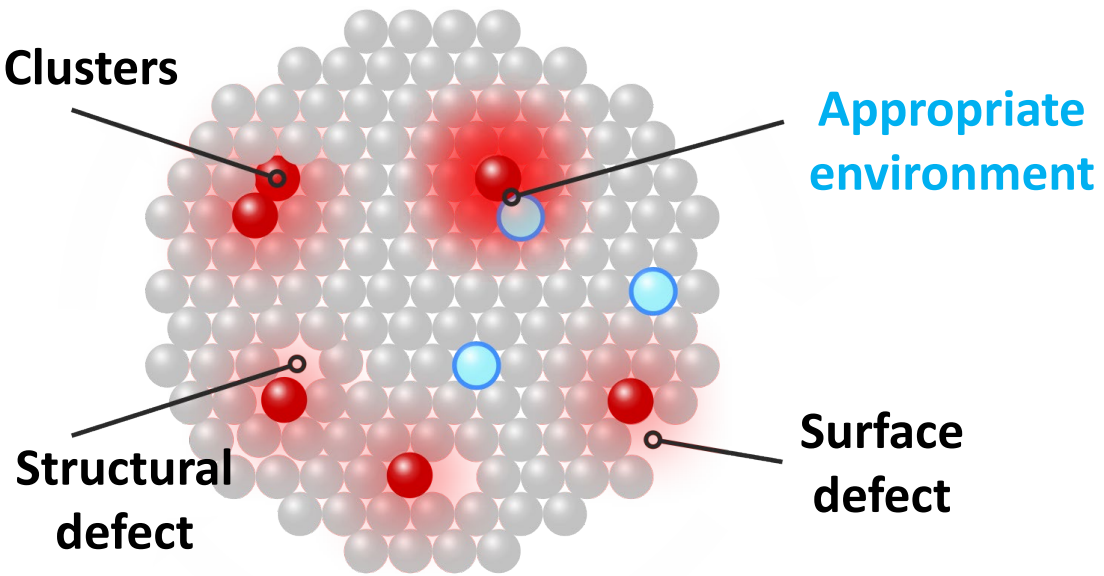
## PERSISTENT NANOPHOSPHORS CHALLENGES :





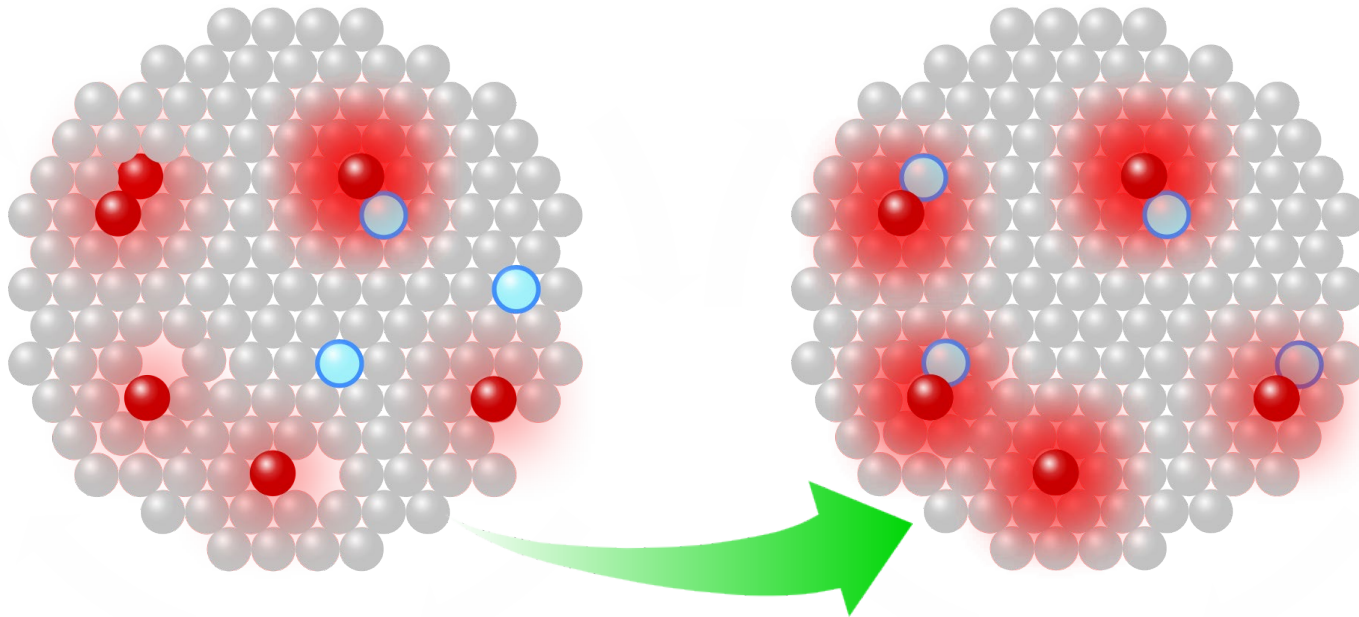


## PERSISTENT NANOPHOSPHORS CHALLENGES :





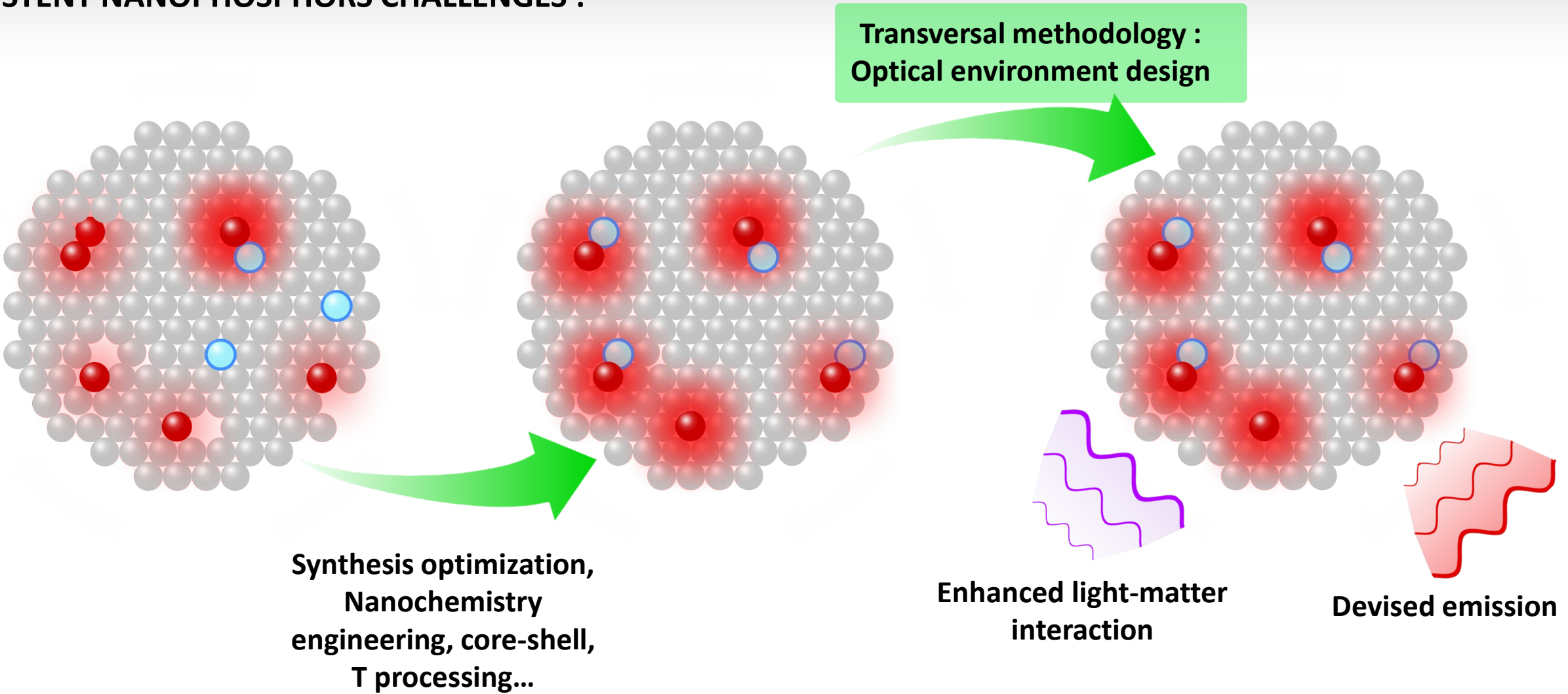
## PERSISTENT NANOPHOSPHORS CHALLENGES :



**Synthesis optimization,  
Nanochemistry  
engineering, core-shell,  
T processing...**



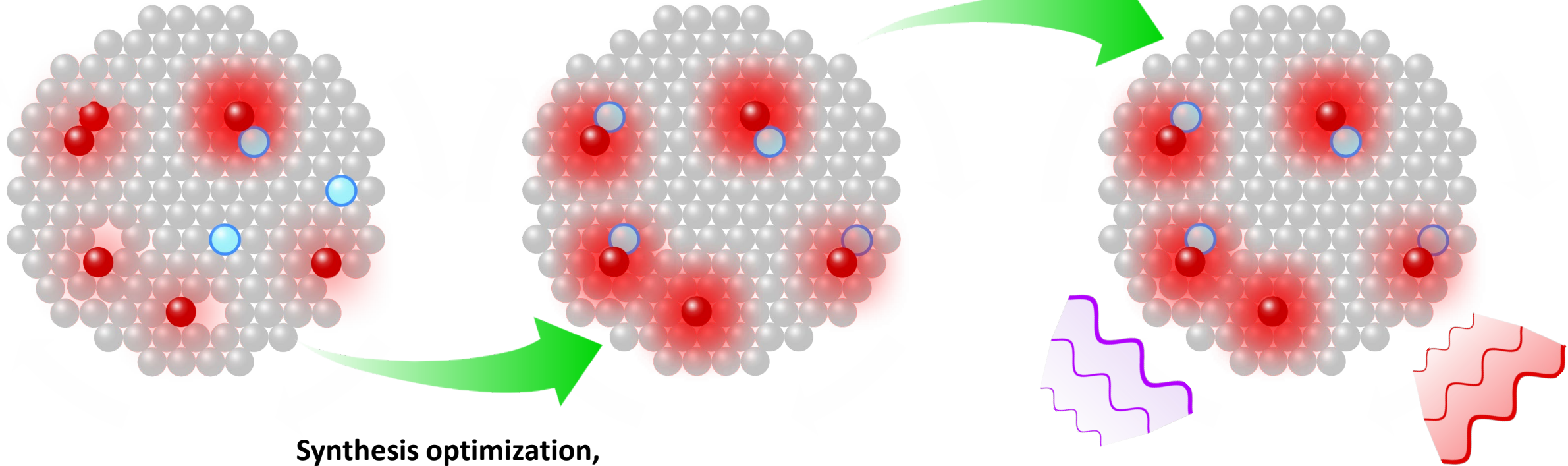
## PERSISTENT NANOPHOSPHORS CHALLENGES :





## PERSISTENT NANOPHOSPHORS CHALLENGES :

Transversal methodology :  
Optical environment design



Synthesis optimization,  
T processing...

**1. Preparation**

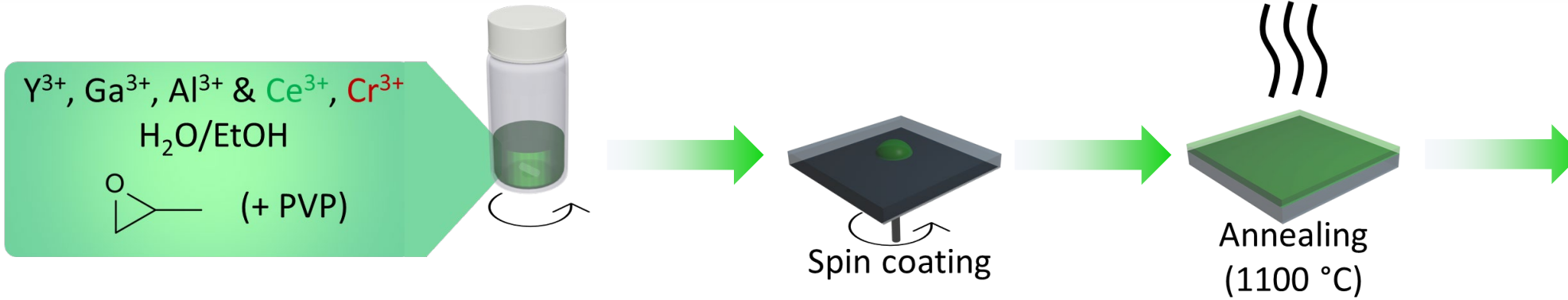
**2. Optical design**

**3. Application opportunities**



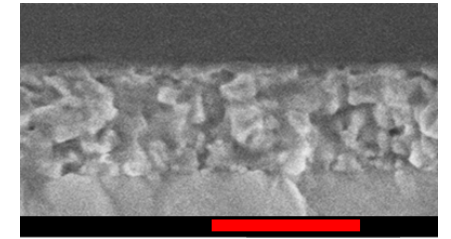
## PERSISTENT NANOPHOSPHOR PREPARATION :

$Y_3Al_2Ga_3O_{12}:Ce^{3+},Cr^{3+}$  sol-gel synthesis



 : Soft proton scavenger → controlled condensation

PVP : water-soluble polymer → ease deposition process

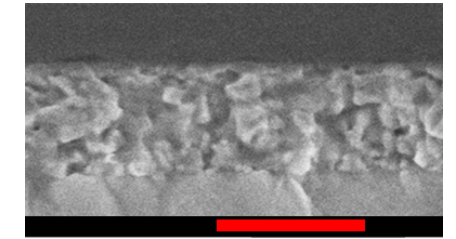
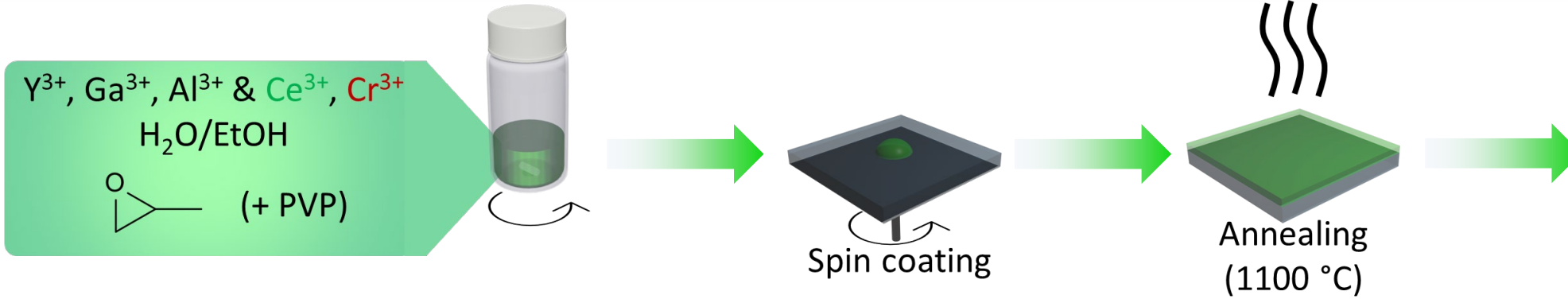


500 nm

**SOL-GEL SYNTHESIS ↔ TRANSPARENT PHOSPHOR FILMS**

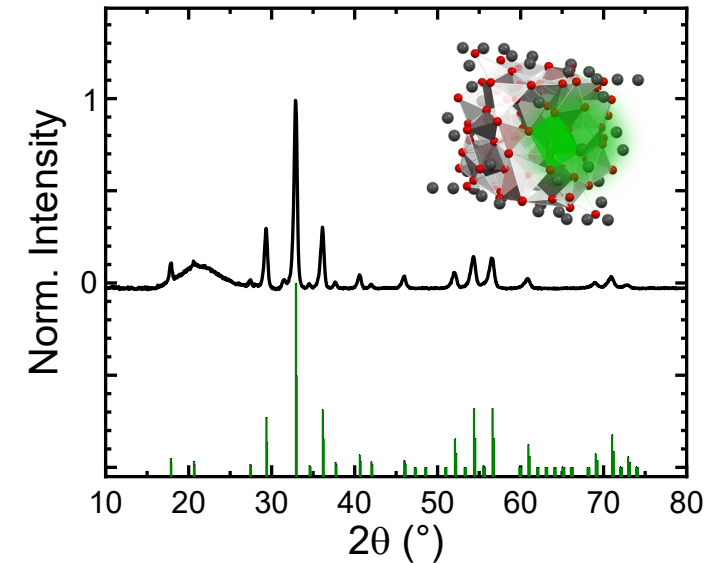
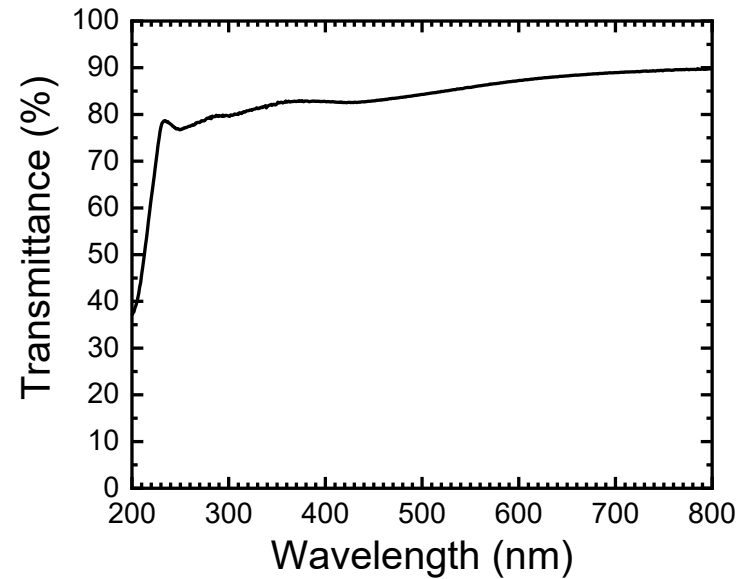


**PERSISTENT NANOPHOSPHOR PREPARATION :**  
*Y<sub>3</sub>Al<sub>2</sub>Ga<sub>3</sub>O<sub>12</sub>:Ce<sup>3+</sup>,Cr<sup>3+</sup> thin film characterization*



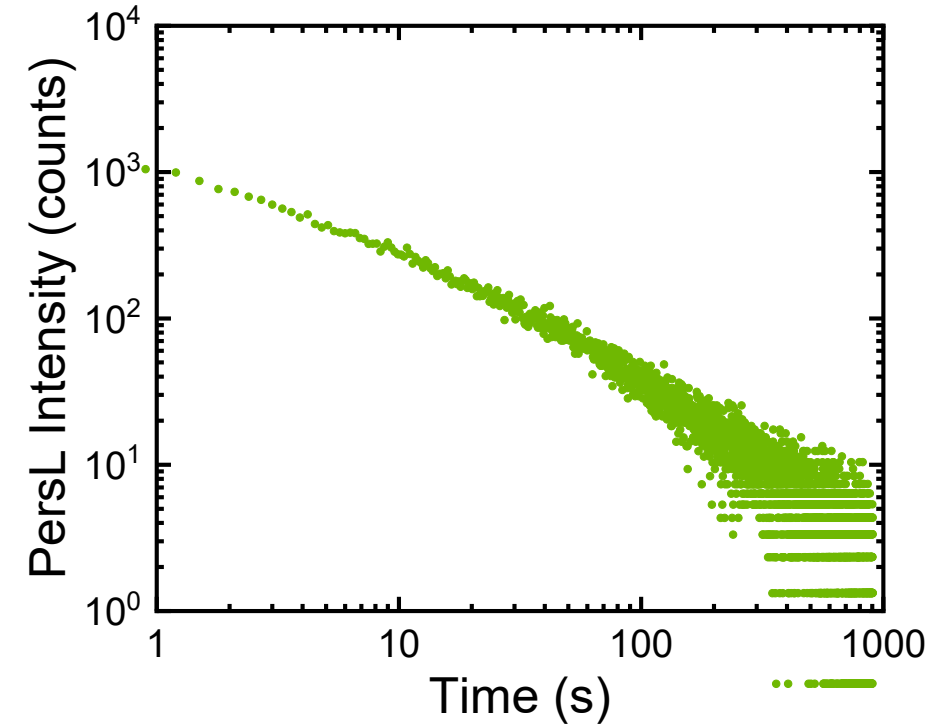
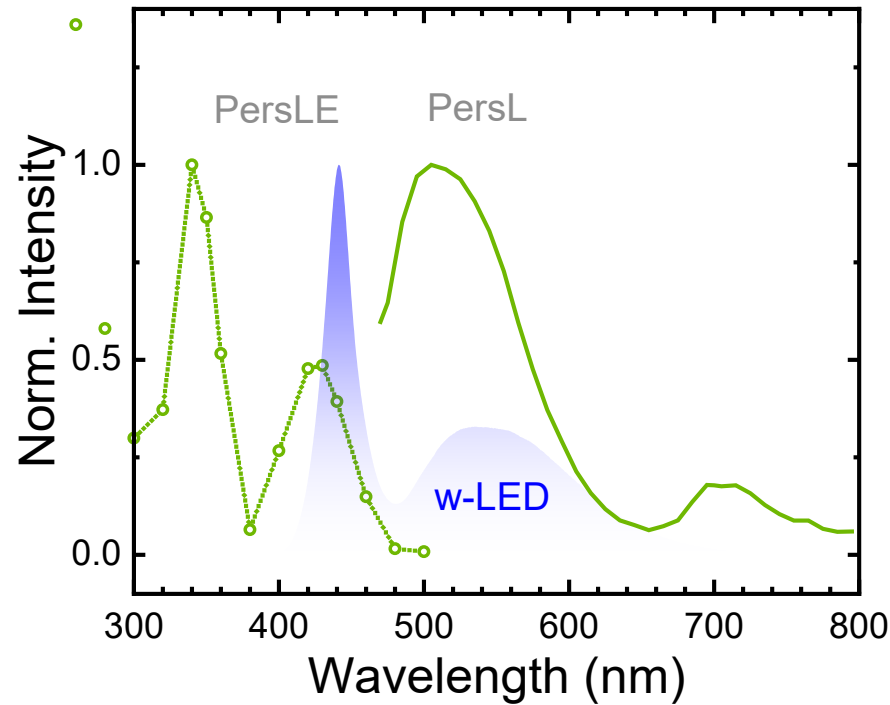
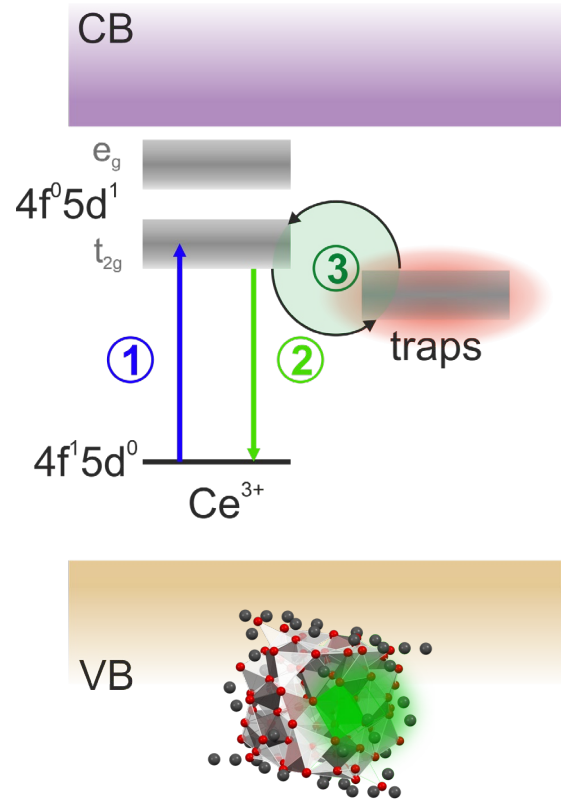
500 nm

- 300 nm thick
- Average transparency > 80 %
- Porosity (~ 15 %)
- Annealing to crystallize





# PERSISTENT NANOPHOSPHOR PREPARATION : $Y_3Al_2Ga_3O_{12}:Ce^{3+},Cr^{3+}$ thin film characterization

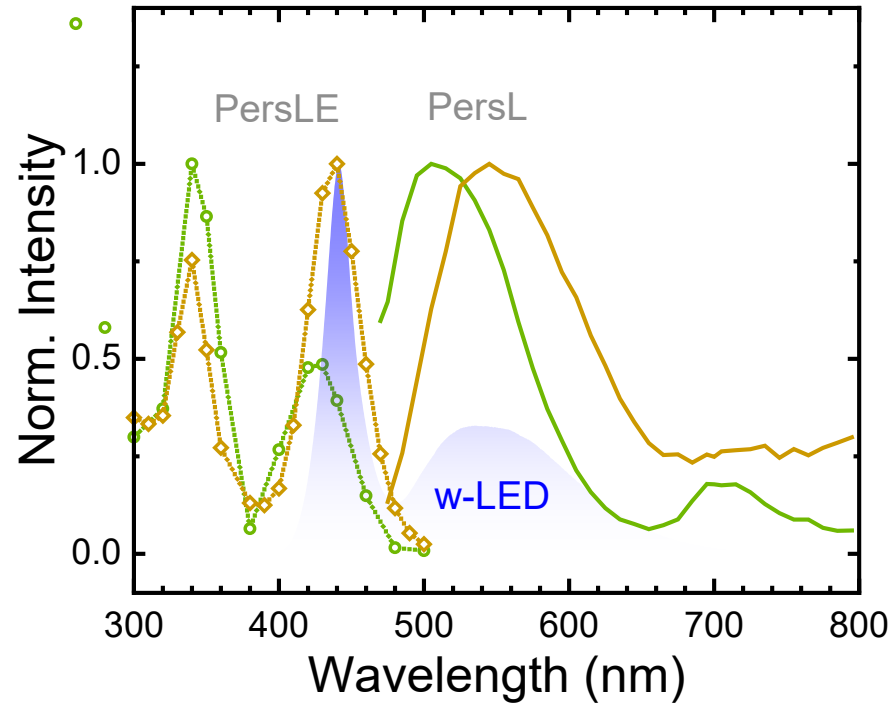
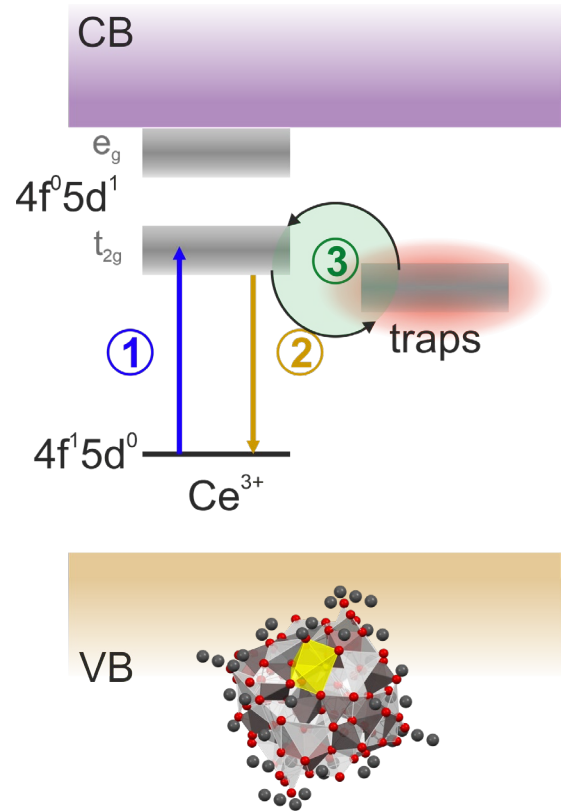


- Composition optimization
- Green PersL
- Visible charging

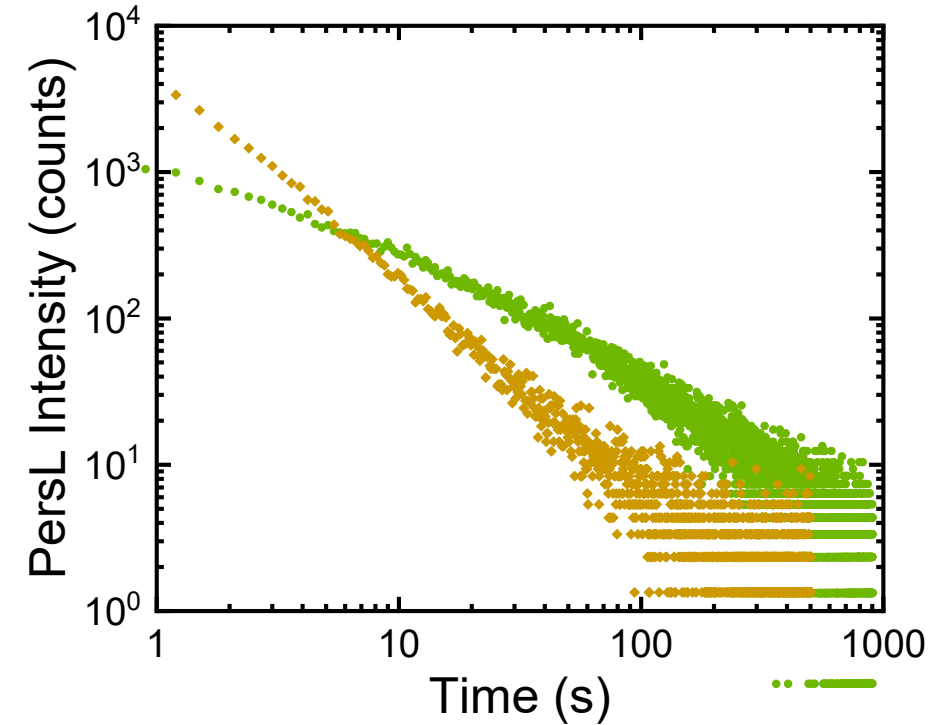


# PERSISTENT NANOPHOSPHOR PREPARATION :

*Gd<sub>3</sub>Al<sub>2</sub>Ga<sub>3</sub>O<sub>12</sub>:Ce<sup>3+</sup>, Cr<sup>3+</sup> thin film characterization*



- Composition optimization
- Green PersL
- Visible charging



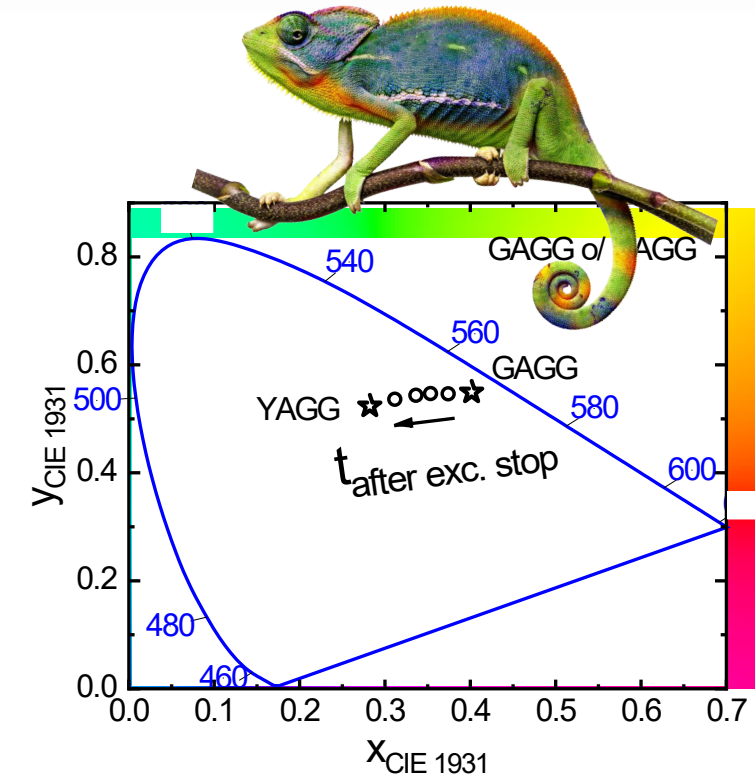
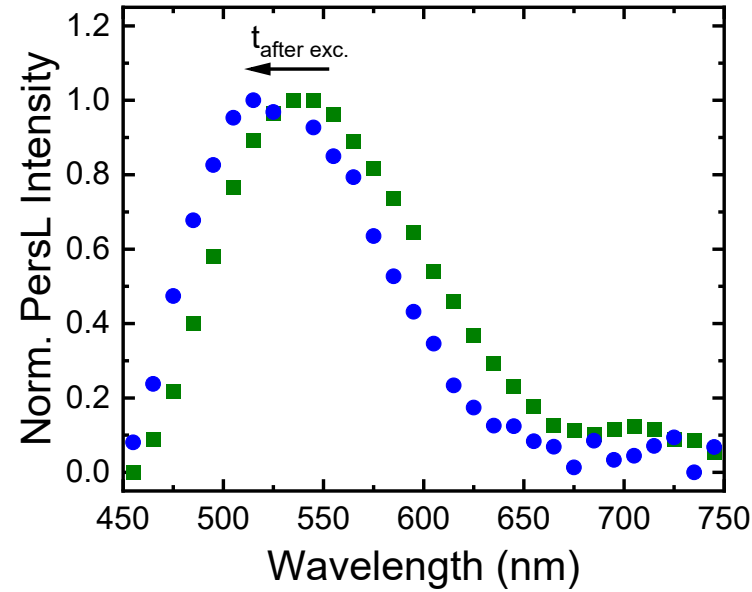
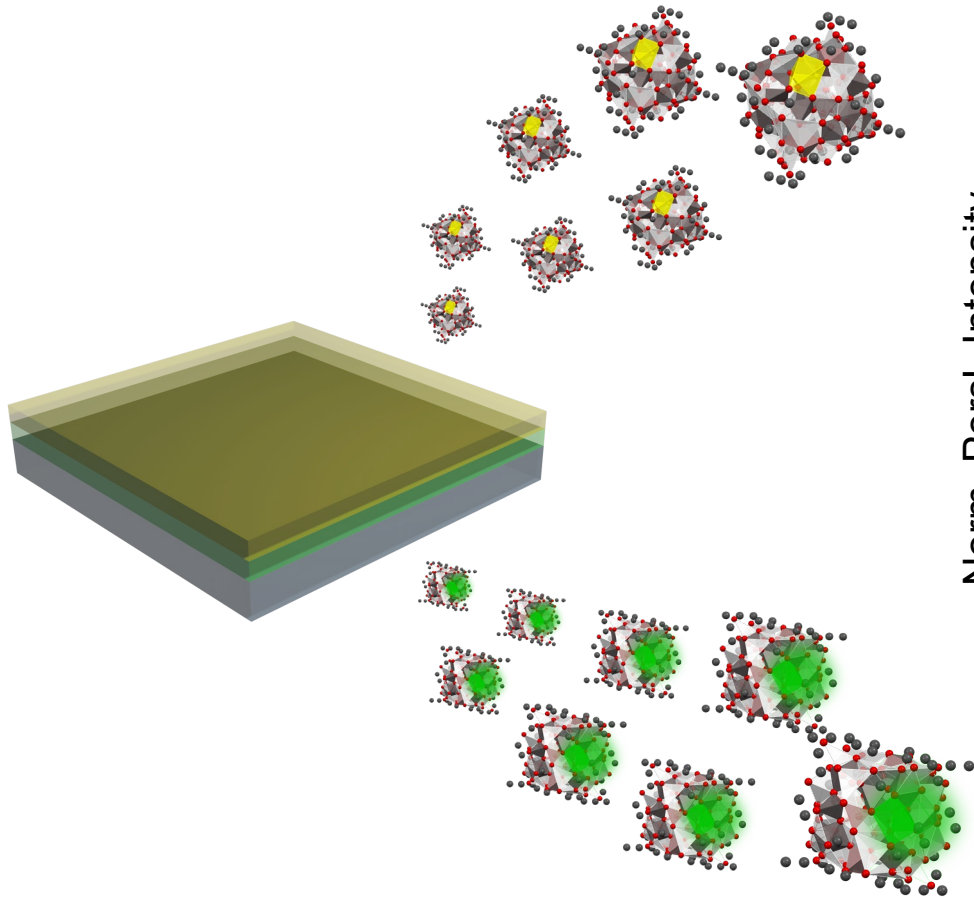
- Matrix modification:
- PersL shift
  - Different kinetics





# PERSISTENT NANOPHOSPHOR PREPARATION :

## *Building blocks*



Reduced scattering of stacks:

- Charging of different layers
- Unique time dependent PersL



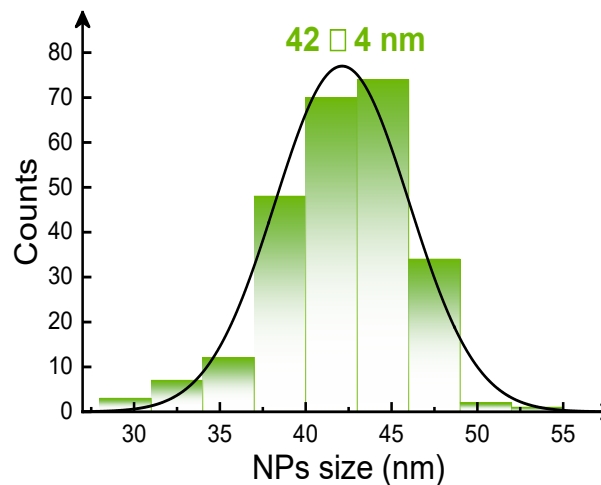
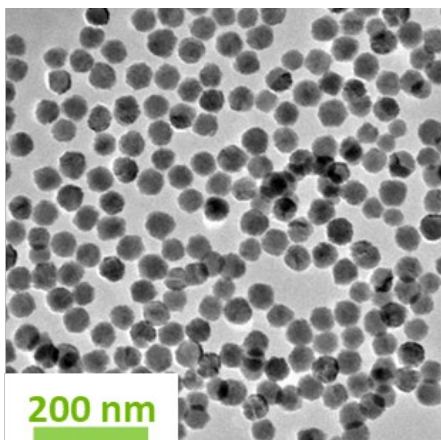
## PERSISTENT NANOPHOSPHOR PREPARATION :

*ZnGa<sub>2</sub>O<sub>4</sub>:Cr<sup>3+</sup> nanoparticle synthesis*

Precursors  
in water



μW



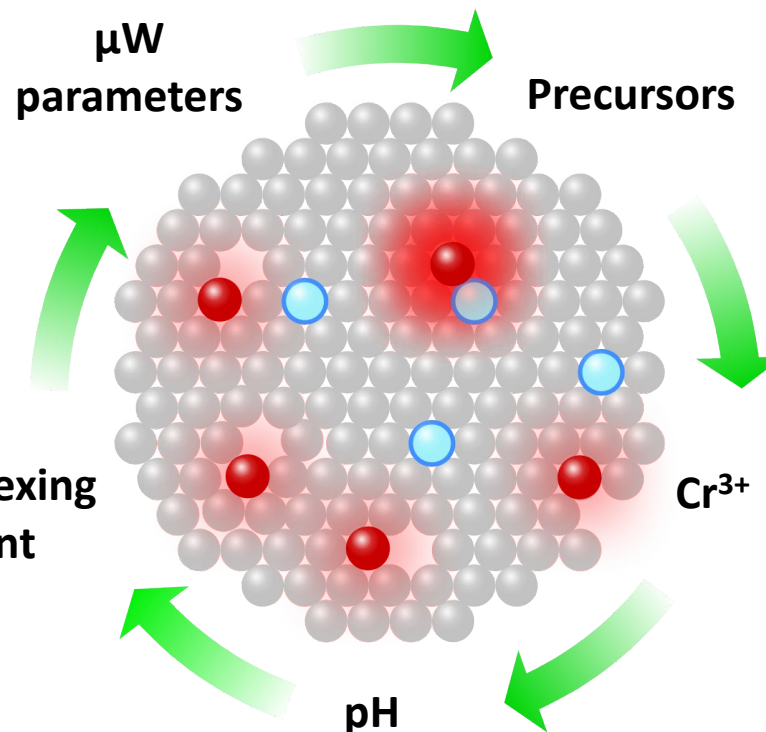
μW  
parameters

Precursors

Complexing  
agent

pH

Cr<sup>3+</sup>

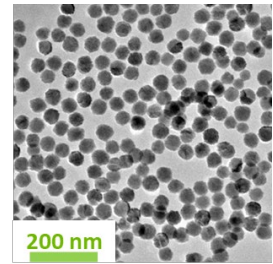


**MW-ASSISTED HYDROTHERMAL SYNTHESIS ↔ COLLOIDALLY STABLE NPs**

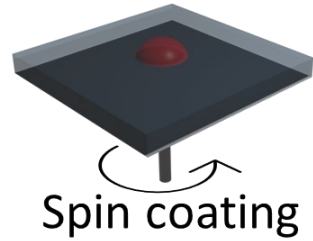


## PERSISTENT NANOPHOSPHOR PREPARATION :

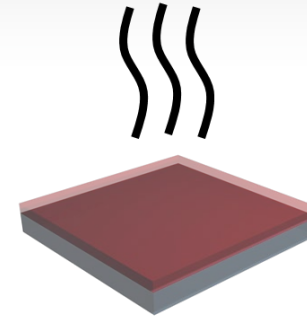
*Wet-deposition*



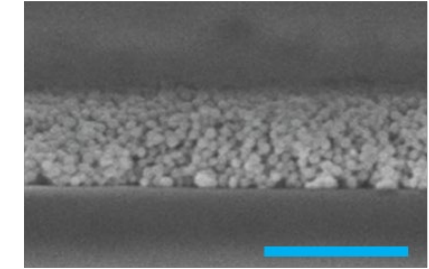
Concentrated  
Volatile solvent



Spin coating



Annealing  
(900 °C)



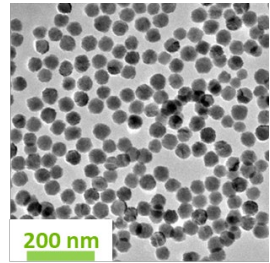
500 nm

< 500 nm

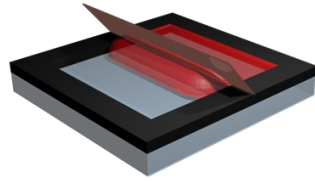


# PERSISTENT NANOPHOSPHOR PREPARATION :

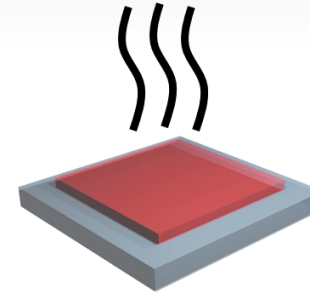
## Wet-deposition



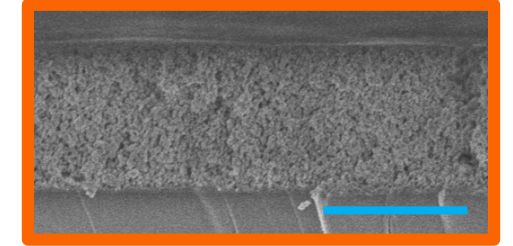
Organic binder  
Viscous solvent



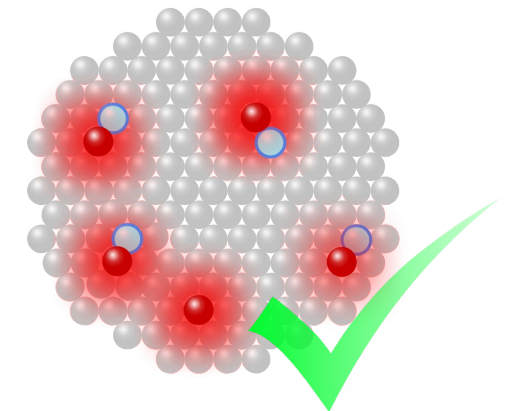
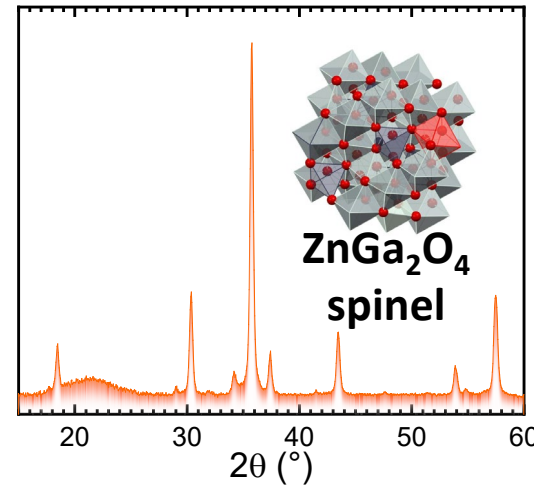
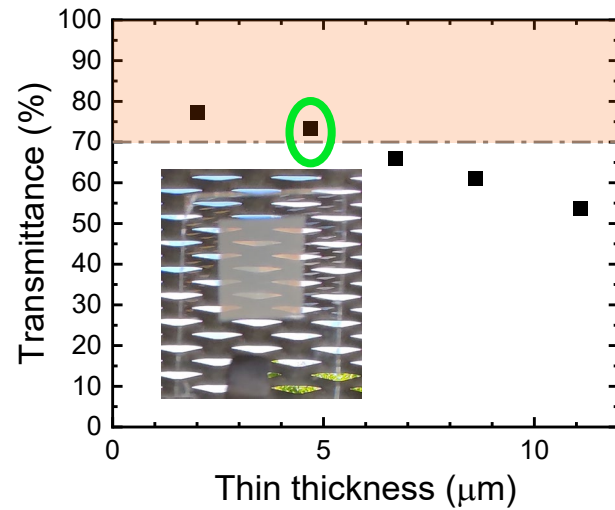
Doctor blade



Annealing  
(900 °C)



2 μm

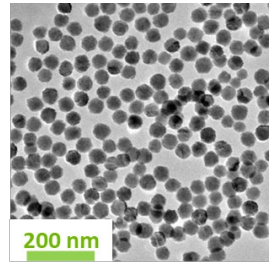


**NONPARTICLE DEPOSITION ↔ TRANSPARENT NANOPHOSPHOR FILM**



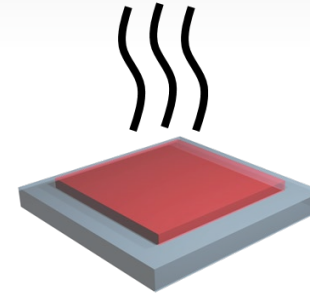
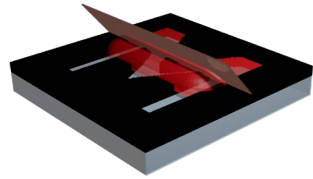
## PERSISTENT NANOPHOSPHOR PREPARATION :

*Tag design and characterization*



Organic binder

Viscous solvent





## PERSISTENT NANOPHOSPHOR PREPARATION :

*Tag design and characterization*

- Translucent coating

Day light

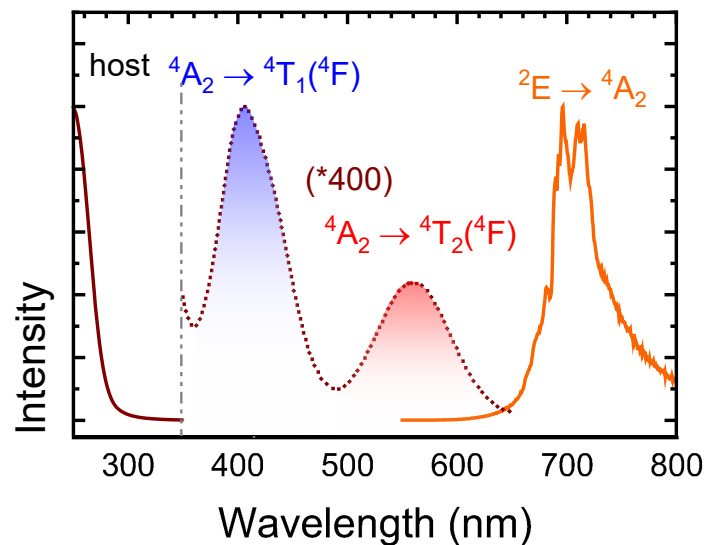




## PERSISTENT NANOPHOSPHOR PREPARATION :

### Tag design and characterization

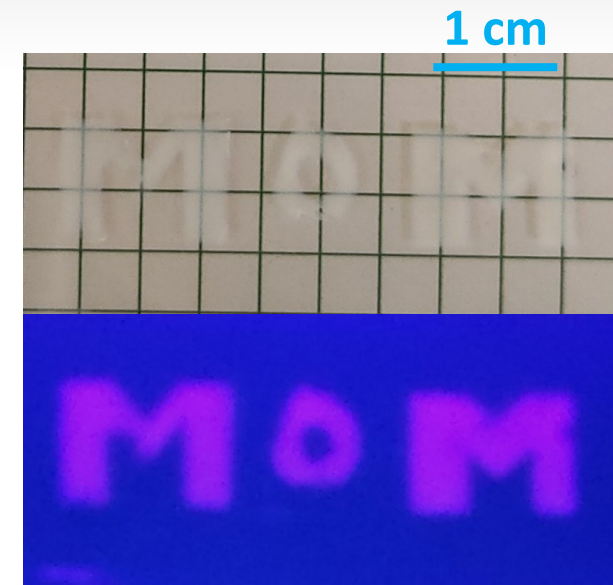
- Translucent coating
- Deep red emission  
PLQY ~ 20 %



Day light



UV on

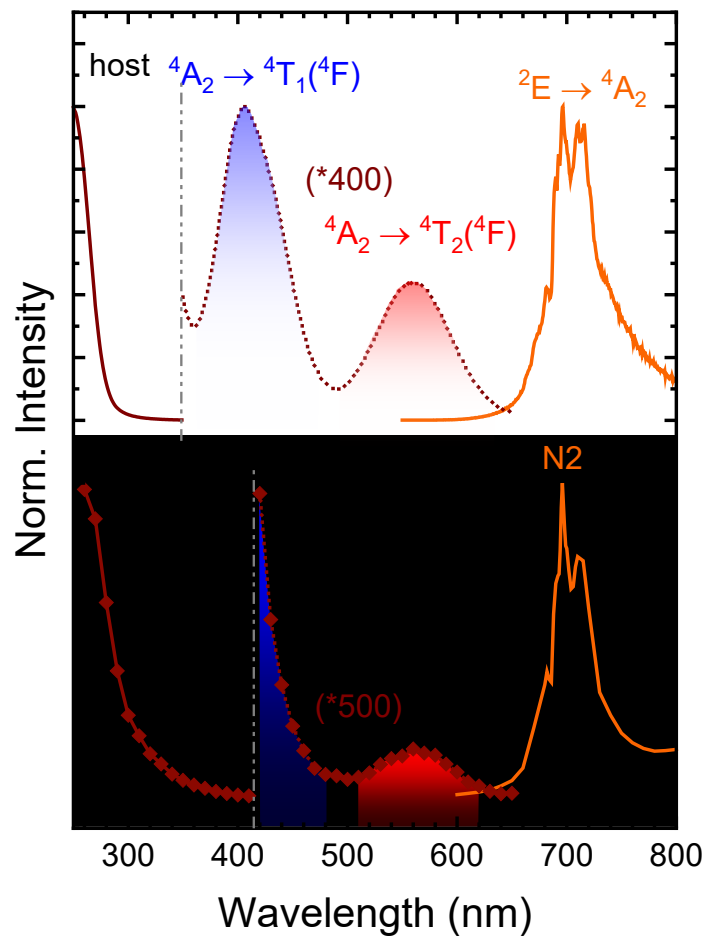




# PERSISTENT NANOPHOSPHOR PREPARATION :

## Tag design and characterization

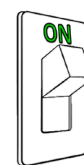
- Translucent coating
- Deep red emission
- Deep red PersL
- Difficult to observe



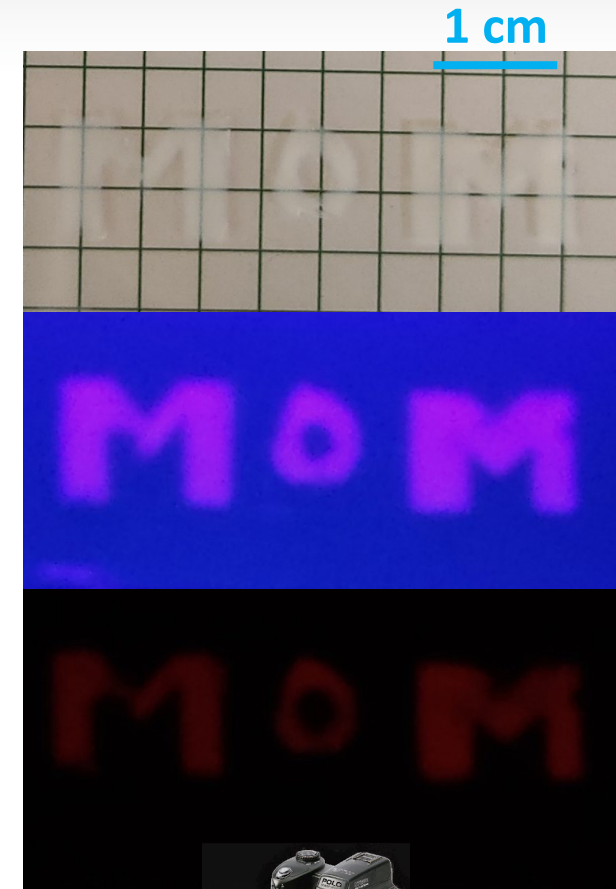
Day light



UV on



UV off

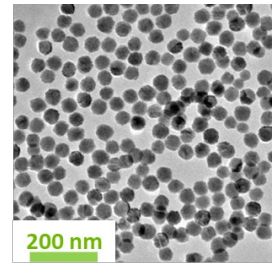




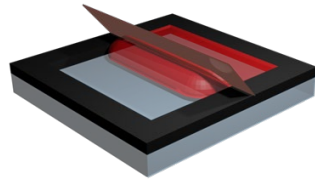


# PERSISTENT NANOPHOSPHOR OPTICAL DESIGN :

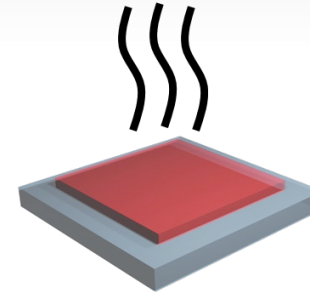
## Preparation



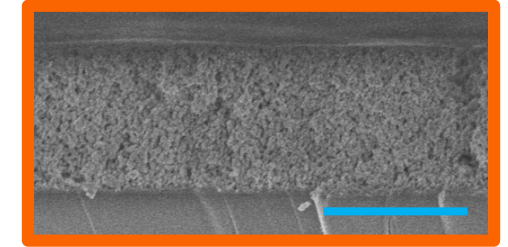
Organic binder  
Viscous solvent



Doctor blade

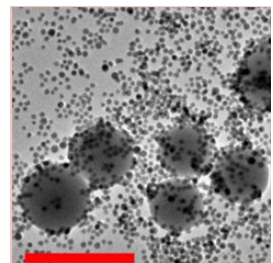


Annealing  
(900 °C)

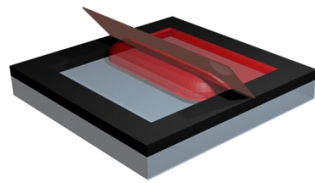


2 μm

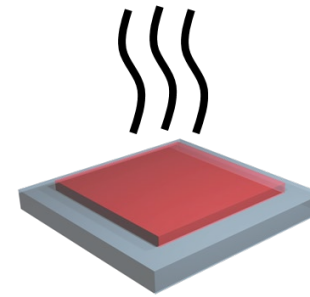
Mix with  
TiO<sub>2</sub> spheres



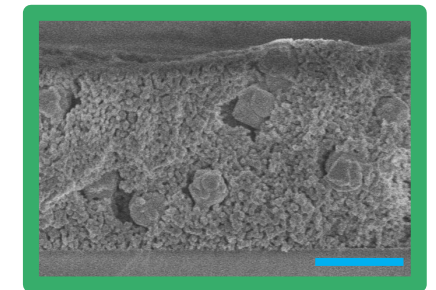
Organic binder  
Viscous solvent



Doctor blade



Annealing  
(900 °C)

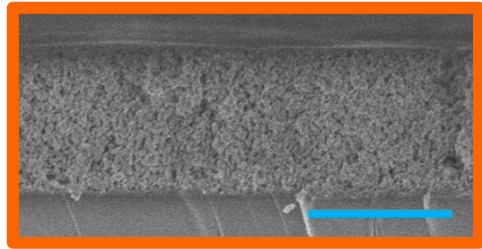


1 μm

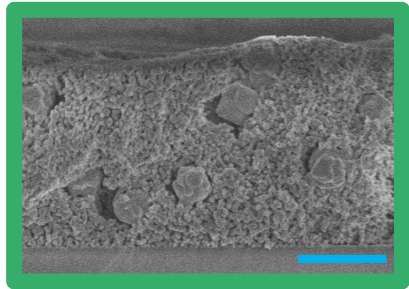


# PERSISTENT NANOPHOSPHOR OPTICAL DESIGN :

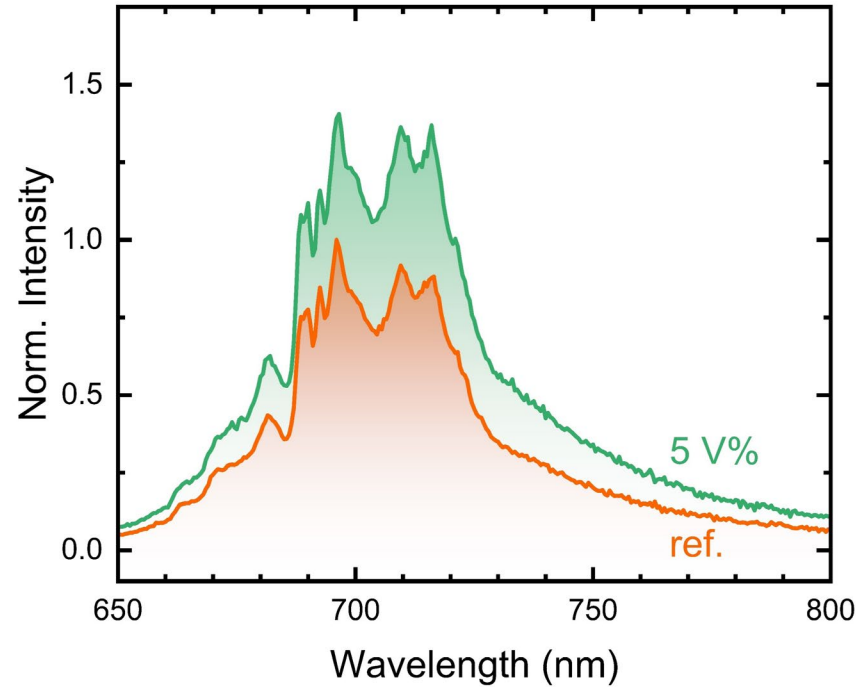
*Property enhancement*



2 μm

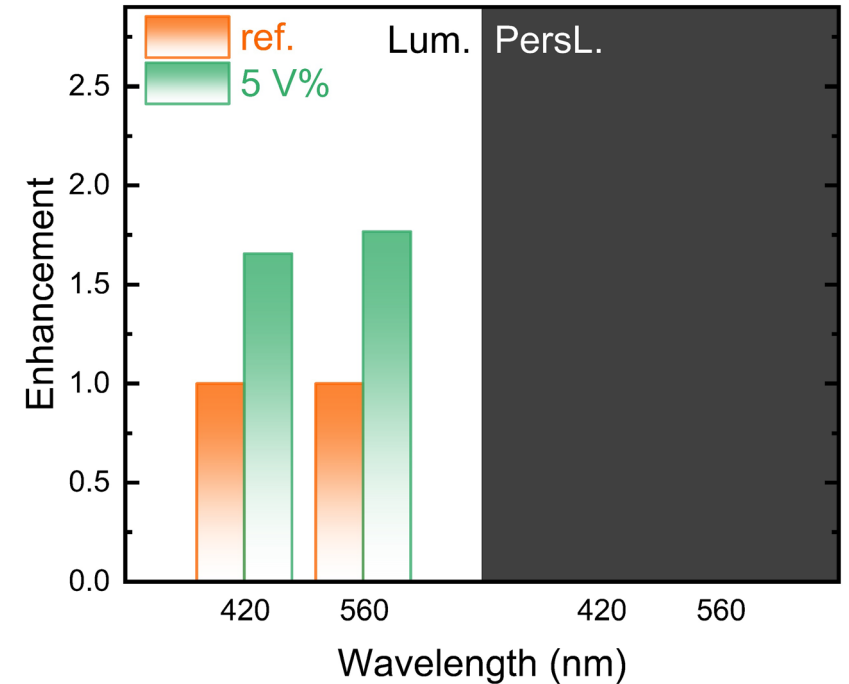


1 μm



**Enhancement :**

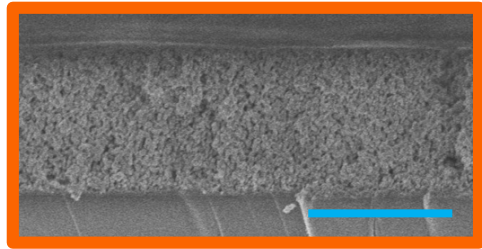
$$\beta_{Lum}(\lambda_{exc}) = \frac{\int_{\lambda_1}^{\lambda_2} Lum_{sample}(\lambda_{exc}, \lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} Lum_{ref}(\lambda_{exc}, \lambda) d\lambda}$$



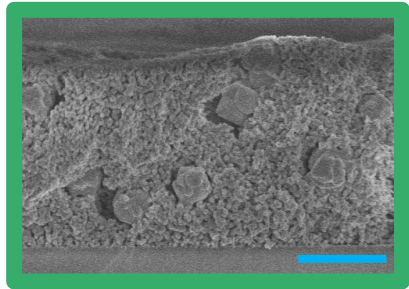


# PERSISTENT NANOPHOSPHOR OPTICAL DESIGN :

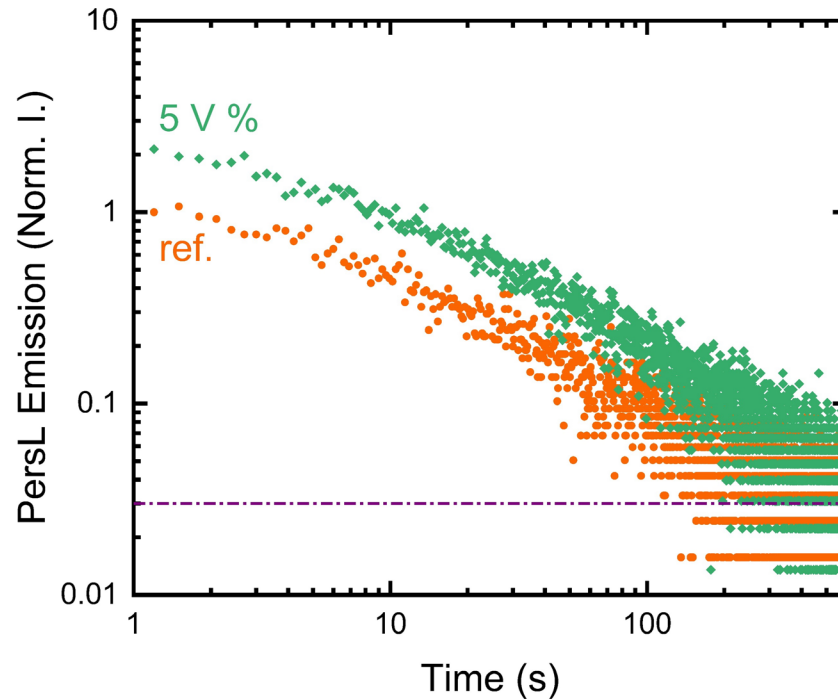
*Property enhancement*



2 μm

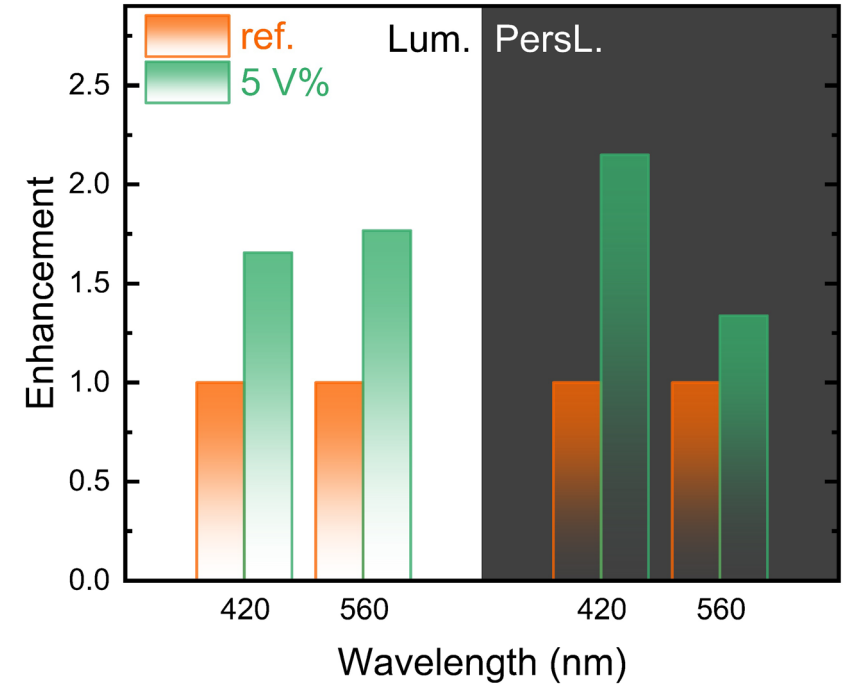


1 μm



**Enhancement :**

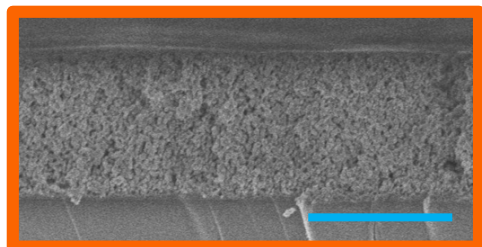
$$\beta_{PersL}(\lambda_{exc}) = \frac{\int_{t_1}^{t_2} \int_{\lambda_1}^{\lambda_2} PersL_{sample}(\lambda_{exc}, \lambda, t) d\lambda dt}{\int_{t_1}^{t_2} \int_{\lambda_1}^{\lambda_2} PersL_{ref}(\lambda_{exc}, \lambda, t) d\lambda dt}$$



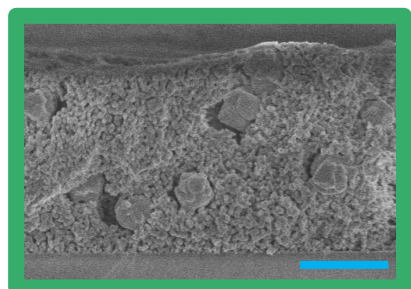


## PERSISTENT NANOPHOSPHOR OPTICAL DESIGN :

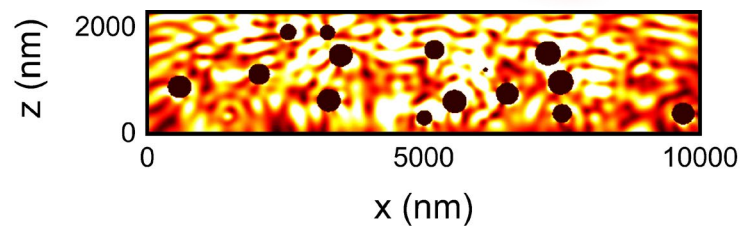
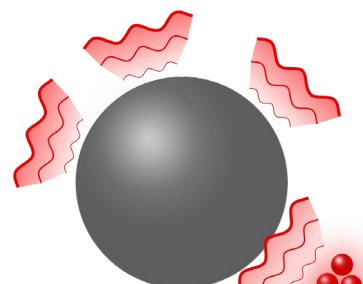
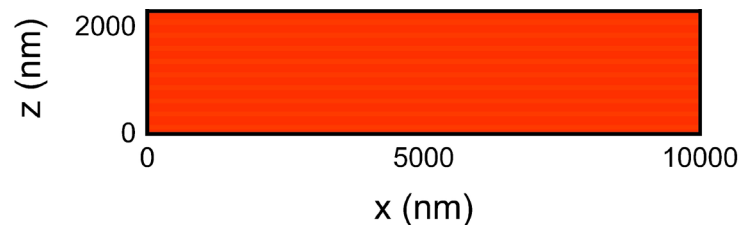
*Property enhancement*



2 μm

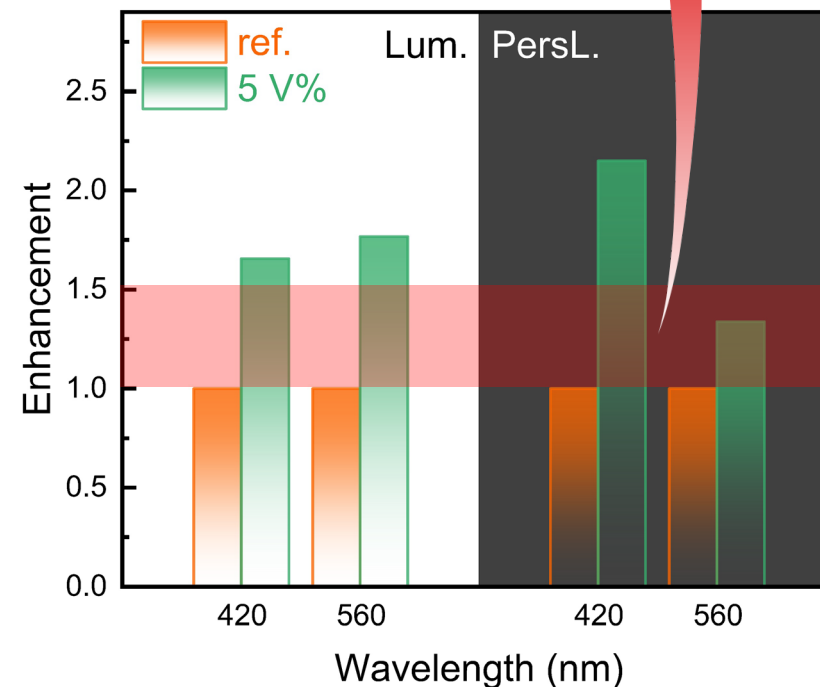


1 μm



**Enhancement :**

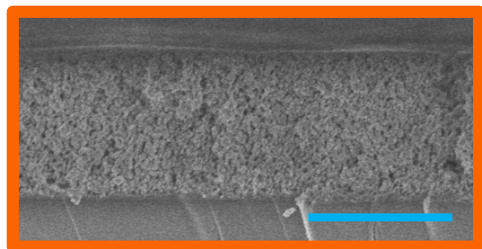
- **outcoupling ( $\approx 1.5$ )**



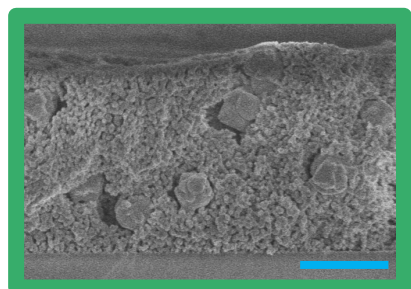


# PERSISTENT NANOPHOSPHOR OPTICAL DESIGN :

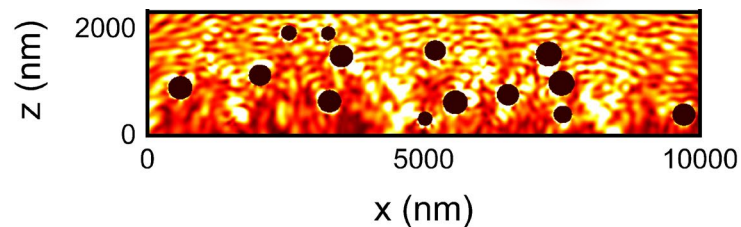
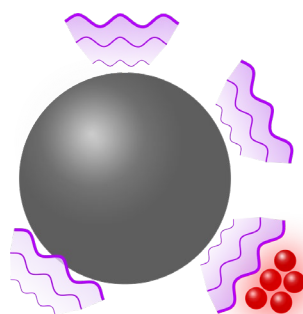
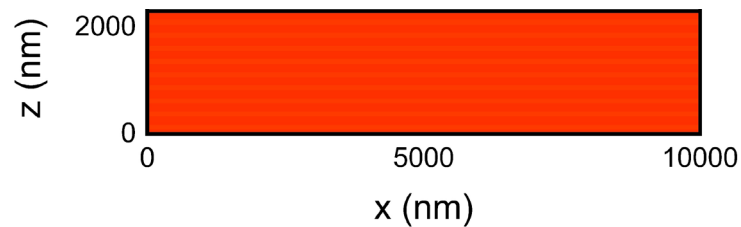
*Property enhancement*



2 μm

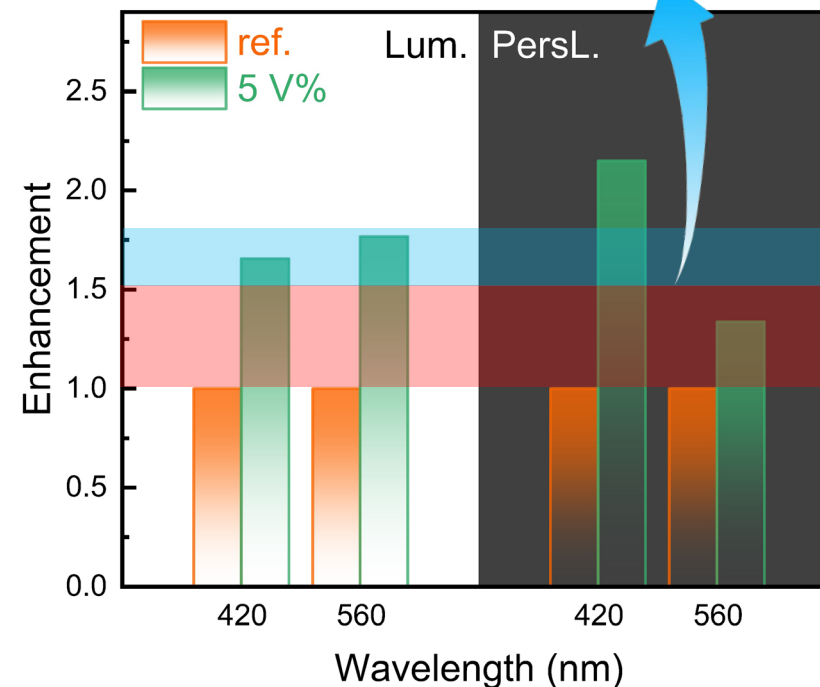


1 μm



**Enhancement :**

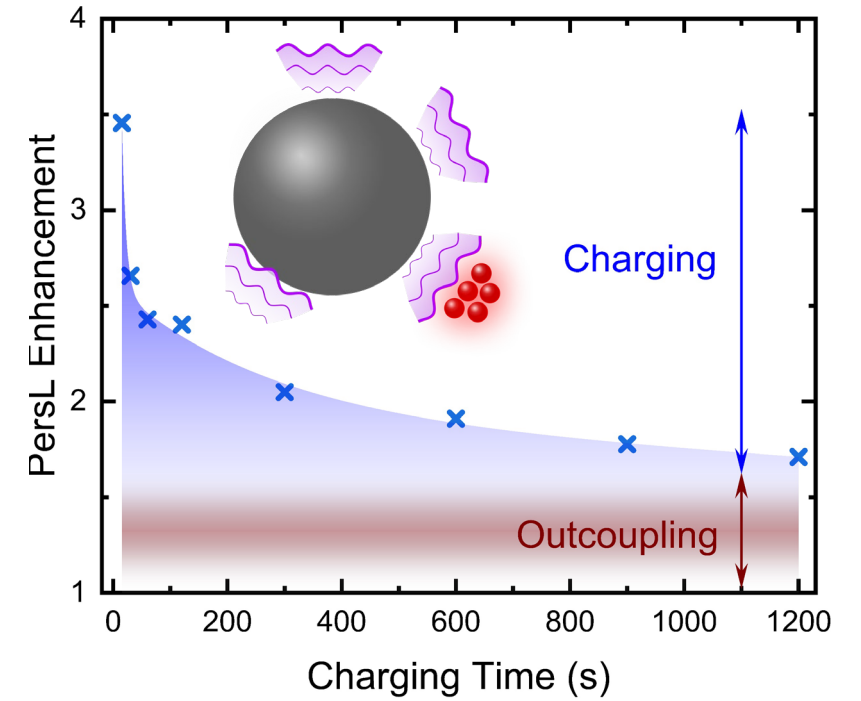
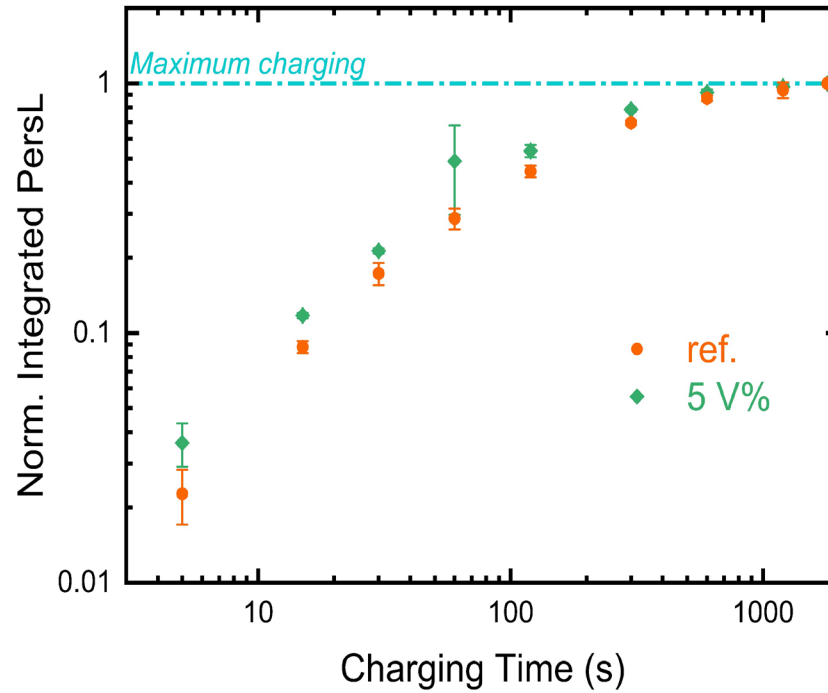
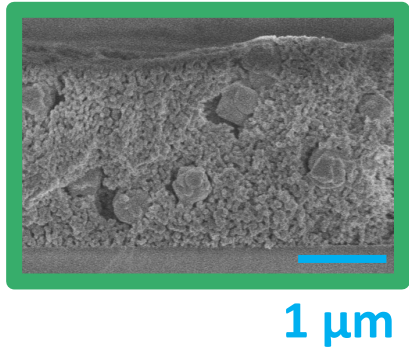
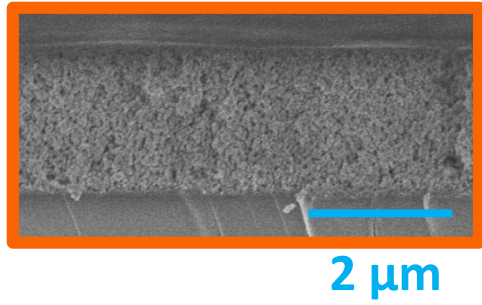
- outcoupling ( $\approx 1.5$ )
- absorption ( $\approx 1.3$ )





# PERSISTENT NANOPHOSPHOR OPTICAL DESIGN :

*Unique charging speed-up*



• charging acceleration

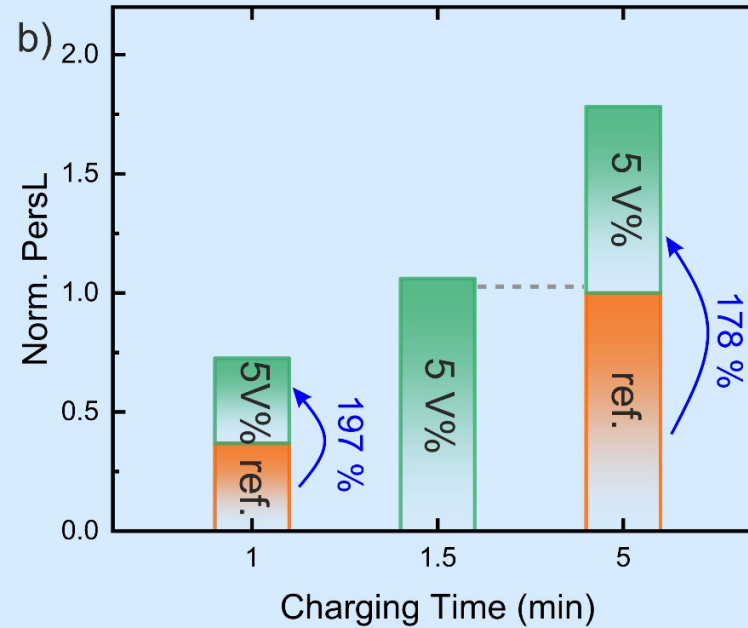
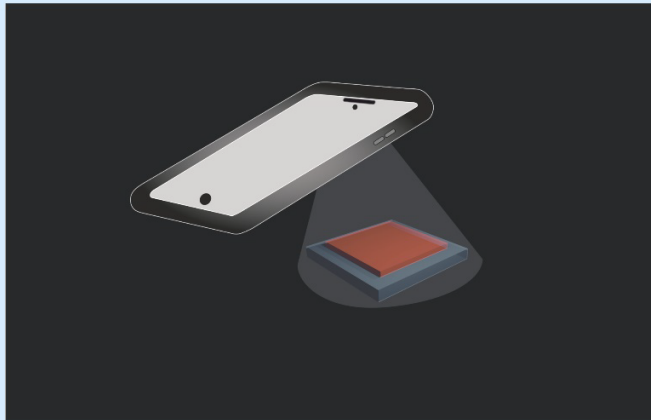
• high PersL enhancements



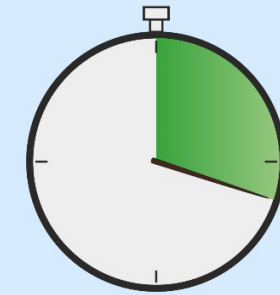
## OPPORTUNITIES FOR ANTICOUNTERFEITING APPLICATIONS :

### (i) Smartphone write-in

a)



Reduced charging time to obtain similar number of PersL photons



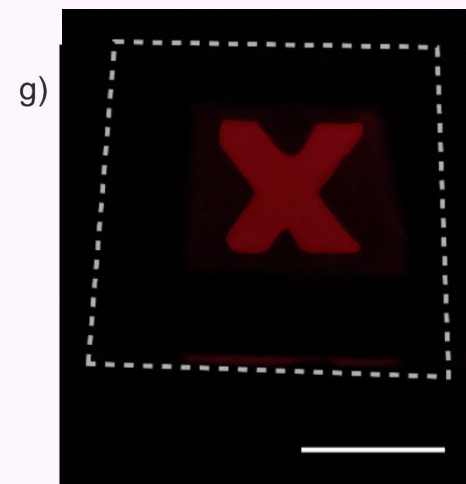
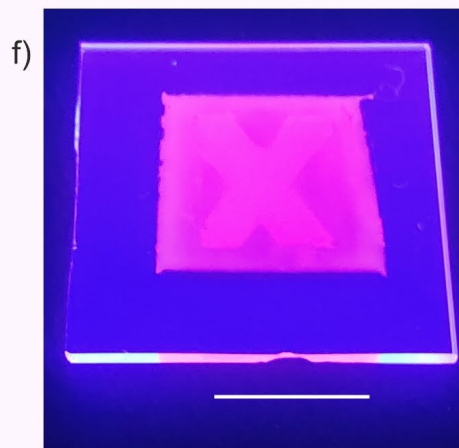
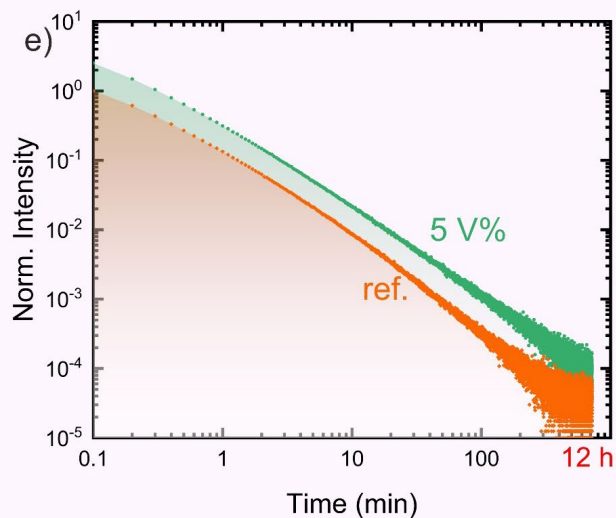
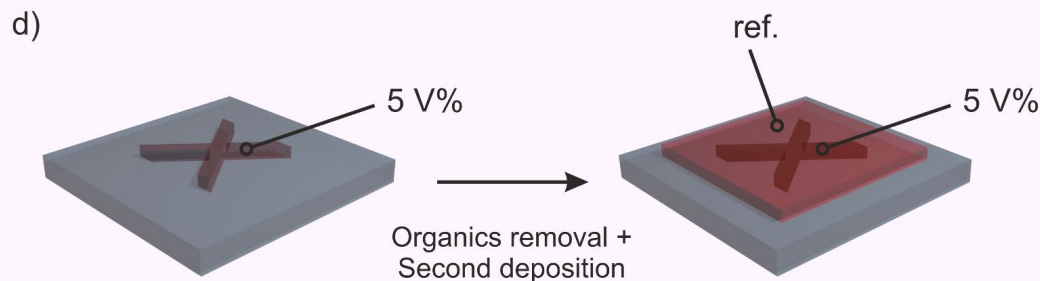
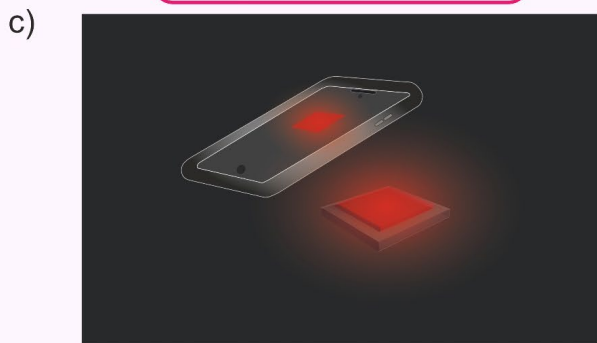
**70%  
Energy saved**

**SCATTERING EASES W-LED CHARGING  
70 % ENERGY SAVE**



# OPPORTUNITIES FOR ANTICOUNTERFEITING APPLICATIONS :

(ii) Smartphone read-out

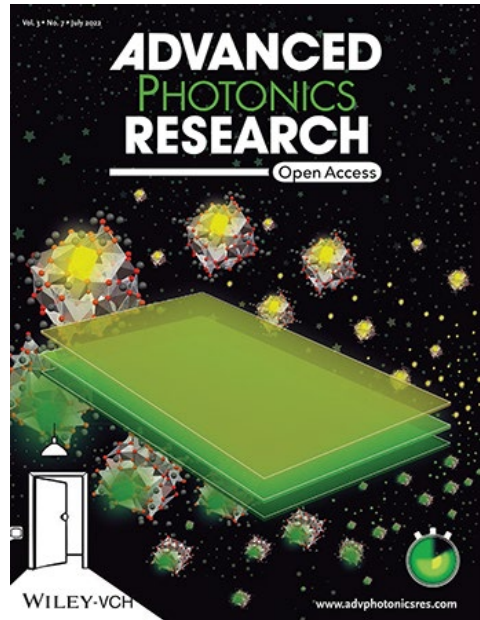


**SCATTERING ALLOWS  
SMARTPHONE READ-OUT  
NEW MEMORY  
DIMENSION**





● CONCLUSION AND OUTLOOKS



Translucent PersL films were elaborated using nanoparticles and their optical environment was modified.

→ Optical design allows :

- brightness enhancement, without compromising phosphors composition.
- to tailor PersL properties, difficult via composition engineering
- smartphone-driven labelling technologies

*J. Appl. Phys.* **2021**, 130, 080902  
*J. Mater. Chem. C* **2021**, 9, 4474-4485  
*Adv. Photonics Res.* **2022**, 2100367  
*Adv. Opt. Mater.* **2023**, 2301565



## ● ACKNOWLEDGMENTS

Prof. Hernán Míguez

Dr. Gabriel Lozano

Dr. Mauricio Calvo

Dr. Juan Galisteo

Dr. Laura Calìò

Dr. Thi Tuyen Ngo

M. Carmen Gutiérrez

Lucía Castillo

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FPU19/00346



## ● ACKNOWLEDGMENTS

