Porous composites based on scintillating metal-organic frameworks nanocrystals for radioactive gas detection.

M. Orfano, J. Perego, F. Cova, Christophe Dujardin, Benoit Sabot, Sylvie Pierre, C. Daniel, S. Bracco, A. Comotti, P. Sozzani, et al.

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16th SCINT conference, Santa Fe, NM, USA 19th – 23th September 2022

Advanced Nanocomposite Materials for Scintillation

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OVERVIEW

1. What is a nanocomposite? And why we need it?
2. Scintillation in nanocomposites.
3. Nanocomposites to tailor emission properties.
4. Nanocomposites to exploit structural properties.
5. Conclusions.

1. WHAT IS A NANOCOMPOSITE?

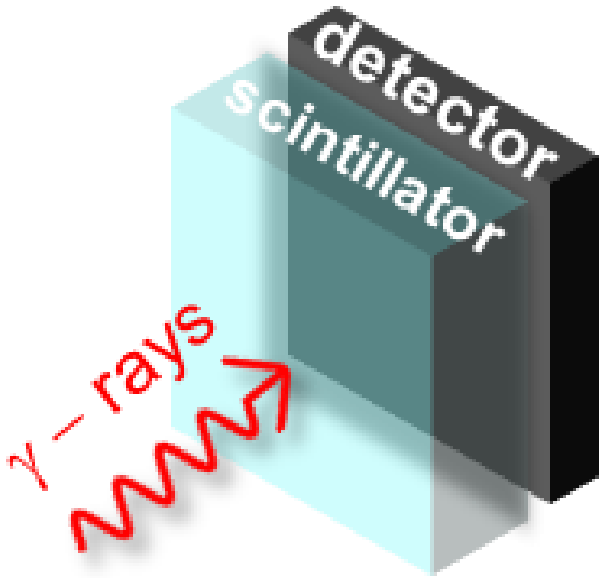
Nanocomposite is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometers (nm) or structures having nano-scale repeat distances between the different phases that make up the material.

The idea behind nanocomposite is to use **building blocks with dimensions in nanometer range** to design and create **new materials with unprecedented physical properties**.

The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nanocomposite will differ markedly from that of the component materials.

1. WHY WE NEED NANCOMPOSITES?

Many detectors of ionizing radiation exploit a **scintillation counter**



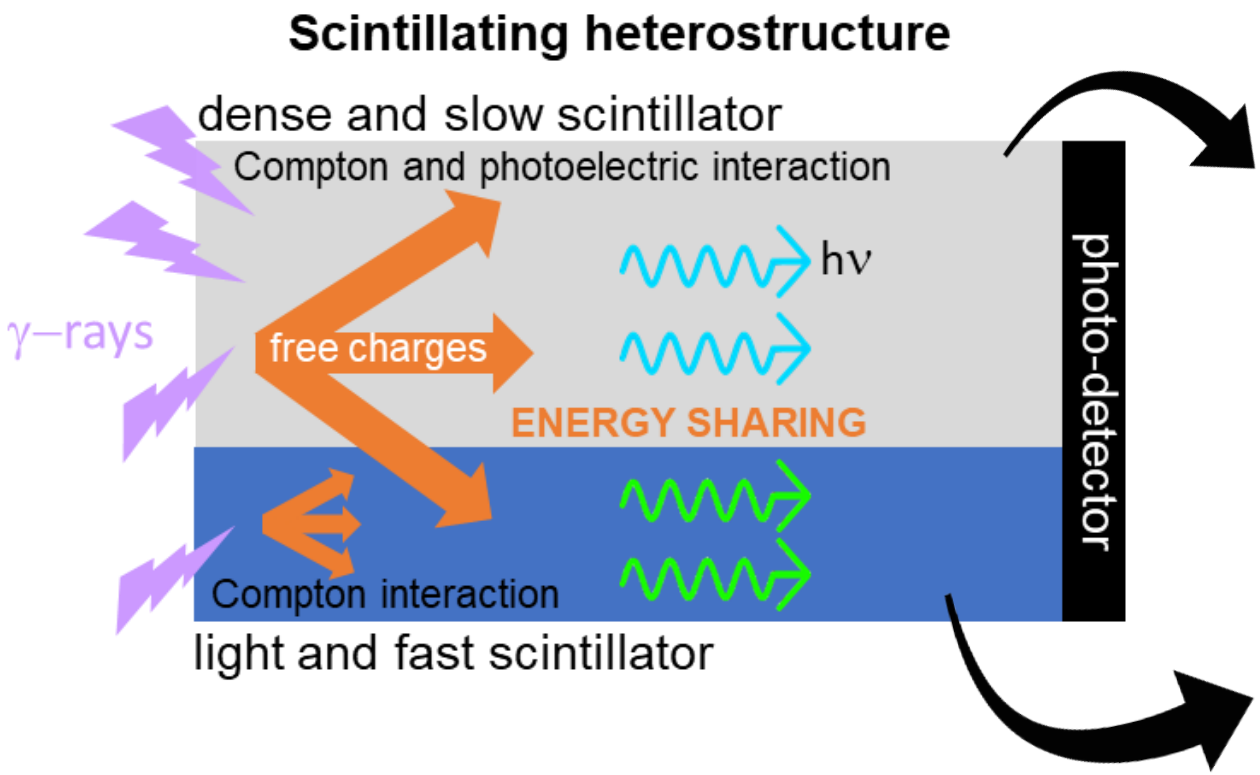
- Healthcare
- Geology
- Safety
- Environmental control
- High energy experiments
- Medical-imaging technologies

Forefront applications requires to surpass the state of the art standard materials

the versatility of scintillating nanocomposites can be a solution

1. WHY WE NEED NANOCOMPOSITES?

EXAMPLE: Medical-imaging technologies, ToF-PET



Dense Scintillator, for stopping power, energy resolution and events selection.

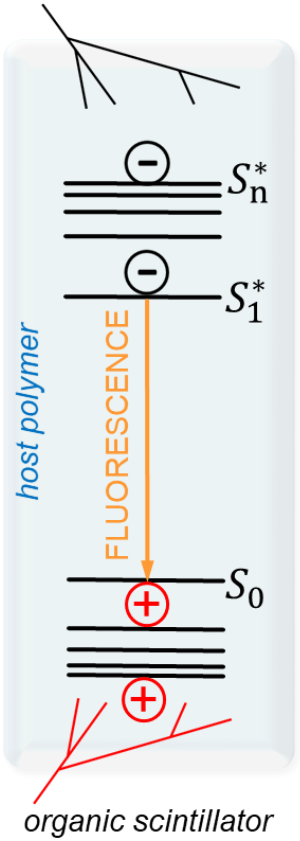
Better ToF-PET sensors

Fast Scintillating Nanocomposite

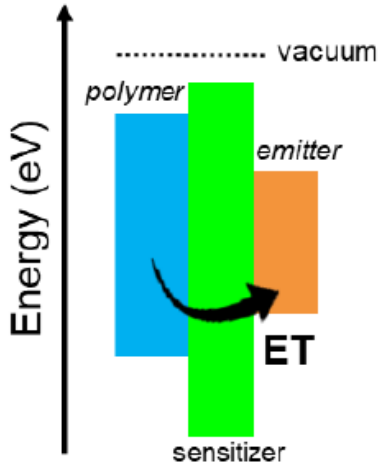
for better fast light output

2. SCINTILLATION IN NANOCOMPOSITES

Plastic Scintillator

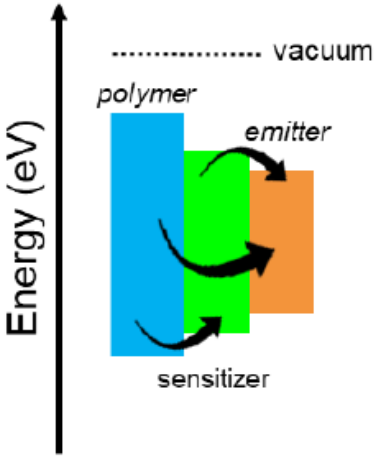


Passive Sensitization

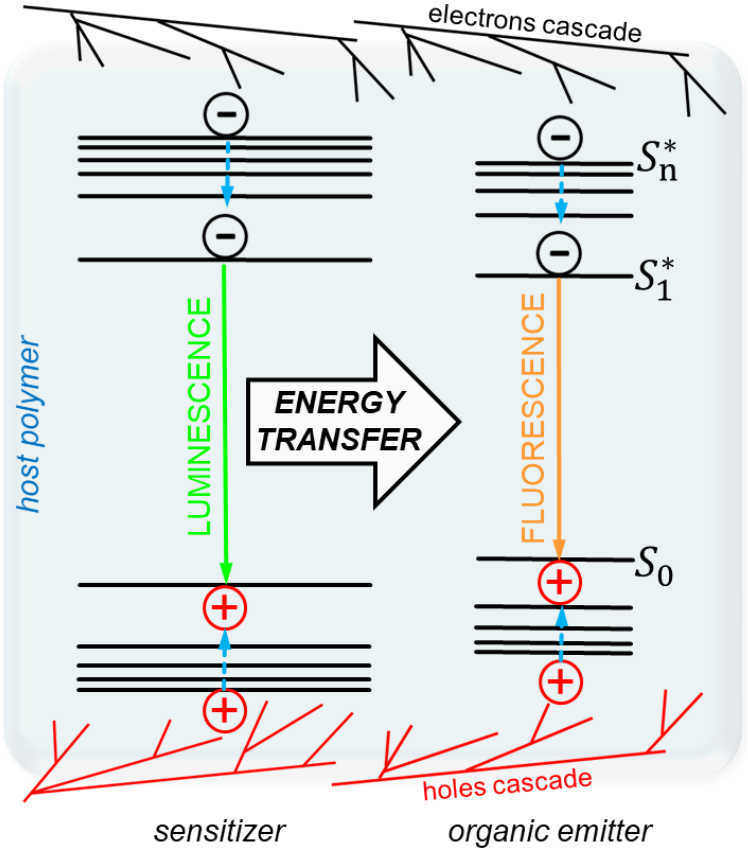


heavy nanoparticle only increase the material density

Active Sensitization



Active Sensitization Photophysics



Villa. I. et al., *Nanomaterials* **2021**, 11, 3387

2. SCINTILLATION IN NANOCOMPOSITES

Rate equations for emitting excited states in a nanocomposite scintillator

(RAPID DIFFUSION LIMIT)

Sensitizer

$$\frac{\partial}{\partial t}[S^*] = (\alpha C_S - \beta C_E - \sigma)N - k_{0,S}[S^*] - k_{ET}\,[S^*]$$

Emitter

$$\frac{\partial}{\partial t}[E^*] = (\beta C_E - \alpha C_S - \sigma)N - k_{0,E}[E^*] + k_{ET}\,[S^*]$$

C_S and C_E: sensitizer and emitter concentration.

α and β : free charges capture rate constants for the sensitizer and emitter

σ is a loss rate constant determined by the matrix characteristics.

$k_{0,S}$ and $k_{0,E}$ are the spontaneous recombination rates of the sensitizer/emitter excited states

N is the total number of electron/hole pairs generated in the material.

k_{ET} interaction rate

Villa. I. et al., *Nanomaterials* **2021**, 11, 3387

2. SCINTILLATION IN NANOCOMPOSITES

Emission Intensity

$$I_{RL}(C_S, C_E) = \chi\phi_E[E^*] = \chi\phi_{pl}(\phi_S\phi_{ET} + \phi_E)N$$

Charge Capture Yields

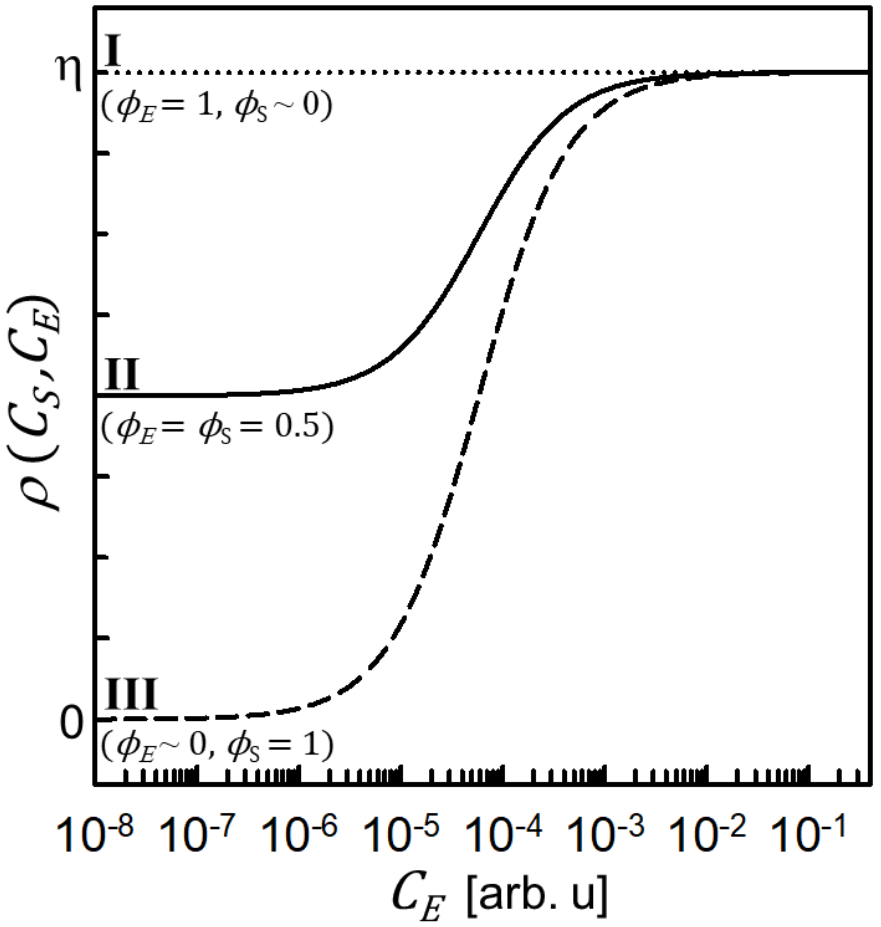
$$\phi_S = \frac{\alpha C_S}{\alpha C_S + \beta C_E + \sigma} \qquad \phi_E = \frac{\beta C_E}{\alpha C_S + \beta C_E + \sigma}$$

Radiosensitization Effect

$$\rho = (\phi_S\phi_{ET} + \phi_E)\eta = \varepsilon(C_S, C_E)\eta \qquad \eta = \frac{N - N_0}{N_0}$$

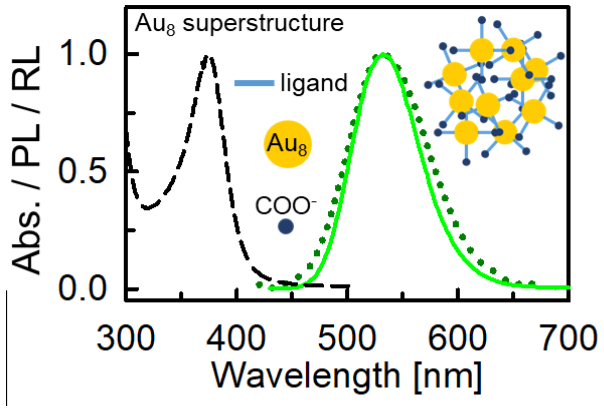
Sens / Emitt. Interaction

Enhancement of charges production

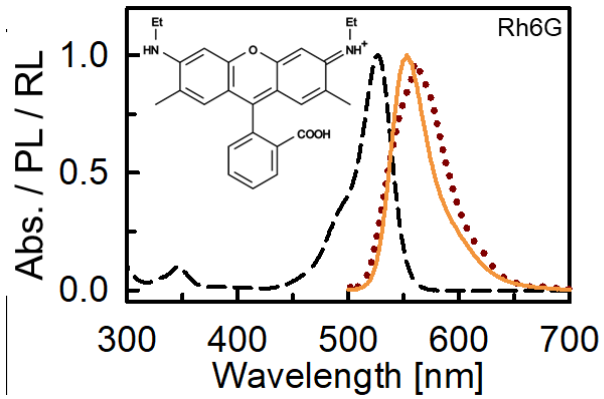


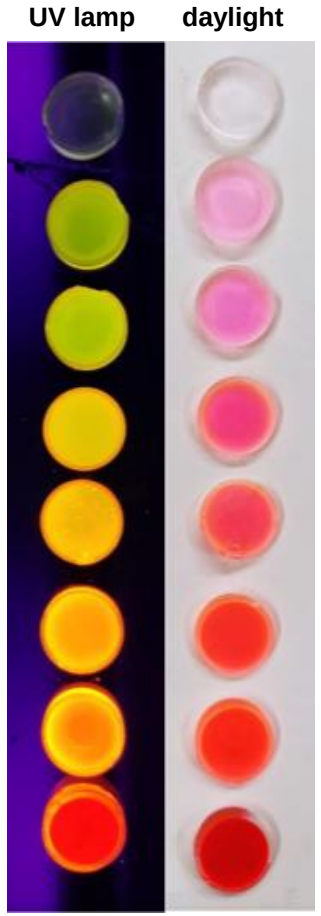
2. SCINTILLATION IN NANOCOMPOSITES

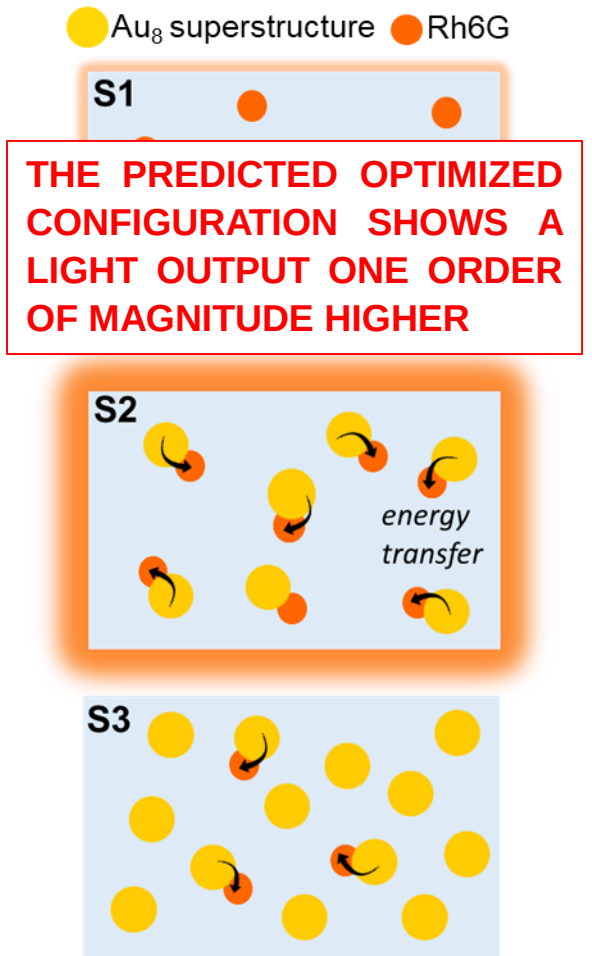
Sensitizer



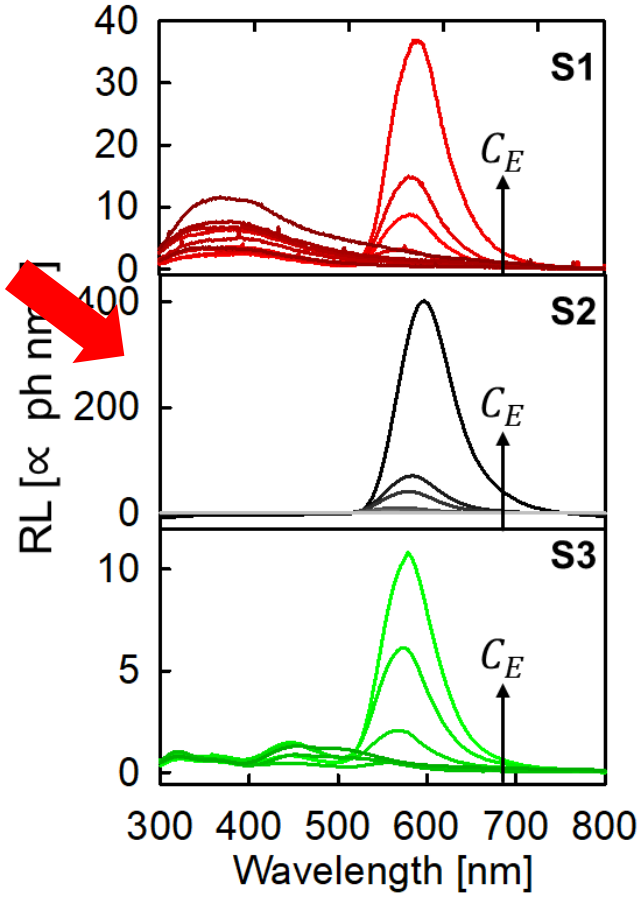
Emitter







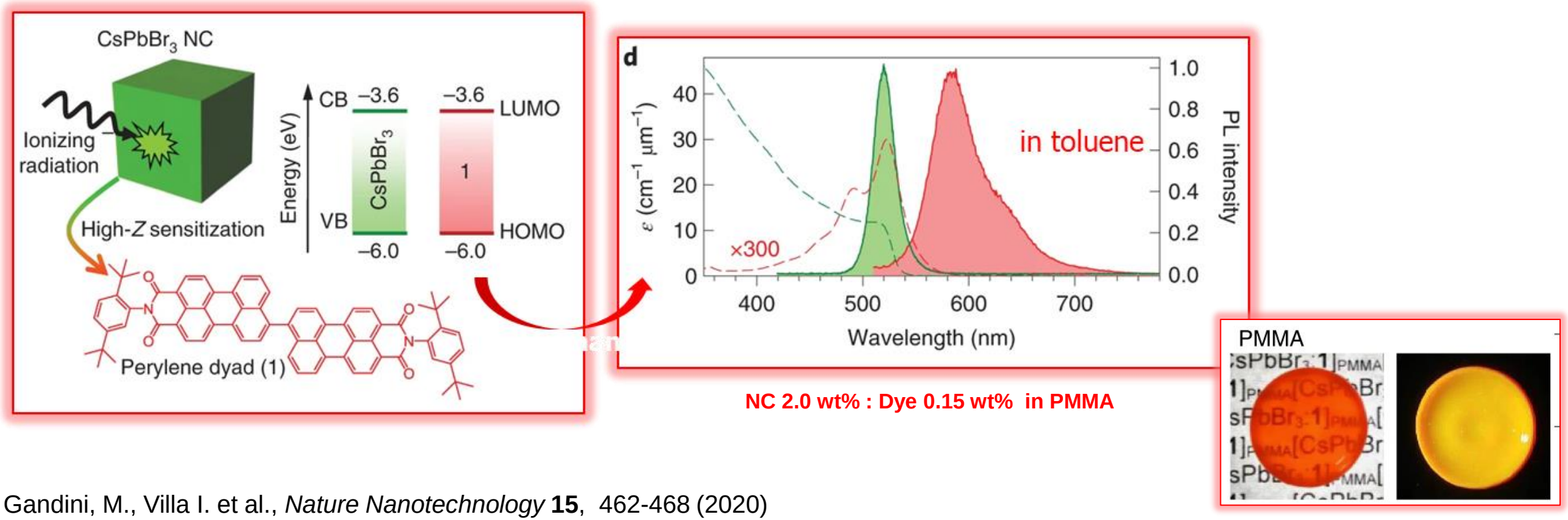
THE PREDICTED OPTIMIZED CONFIGURATION SHOWS A LIGHT OUTPUT ONE ORDER OF MAGNITUDE HIGHER



Nanomaterials **2021**, 11, 3387

3. NANOCOMPOSITES TO TAILOR EMISSION PROPERTIES.

Perovskite nanocrystals based composite scintillators



Gandini, M., Villa I. et al., *Nature Nanotechnology* **15**, 462-468 (2020)

3. NANOCOMPOSITES TO TAILOR EMISSION PROPERTIES.

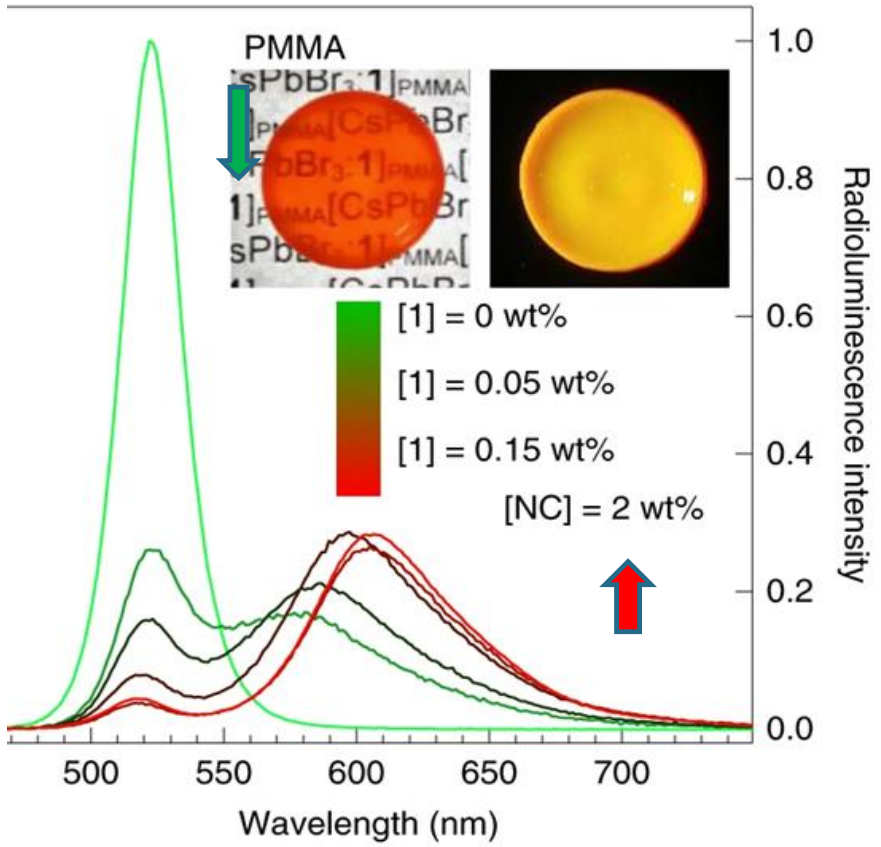
1. **$CsPbBr_3$** (NCs) defects tolerance, tuneable properties , QY 75%

2. High Z NCs to stop the ionizing radiation

3. Conjugated **red organic emitter**(**1**) with QY 60%, 60 nm Stokes shift between absorption and emission spectra and fast lifetime (4 ns in PMMA)
   Large stokes shift→ **suppression of reabsorption**

4. PMMA: radiation hardness, optical quality, low absorption in VIS

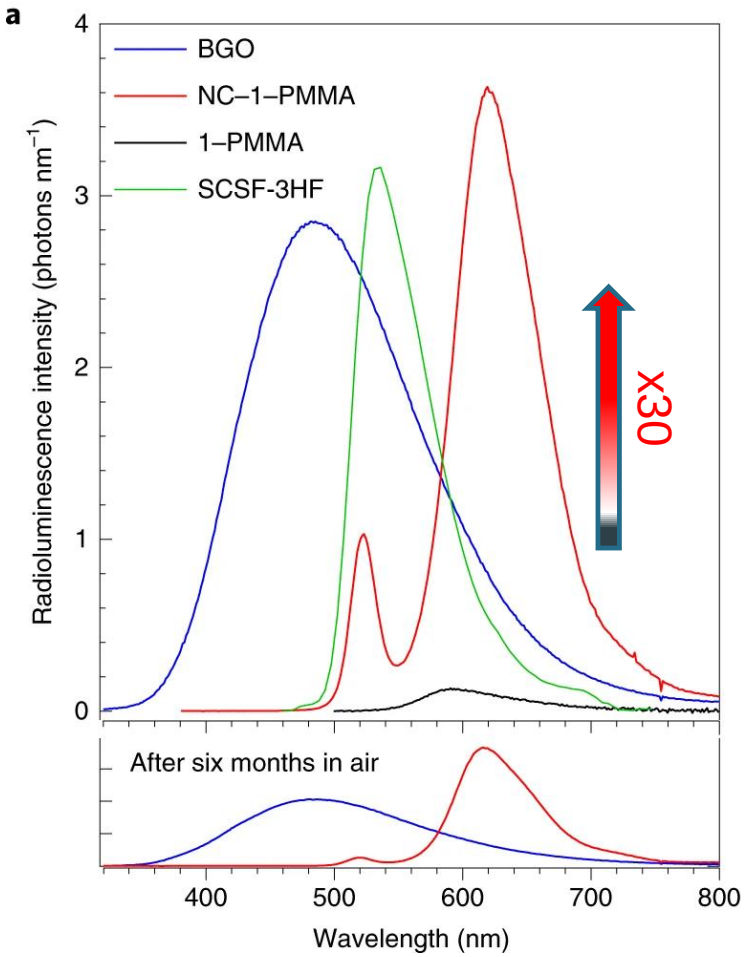
RADIOLUMINESCENCE



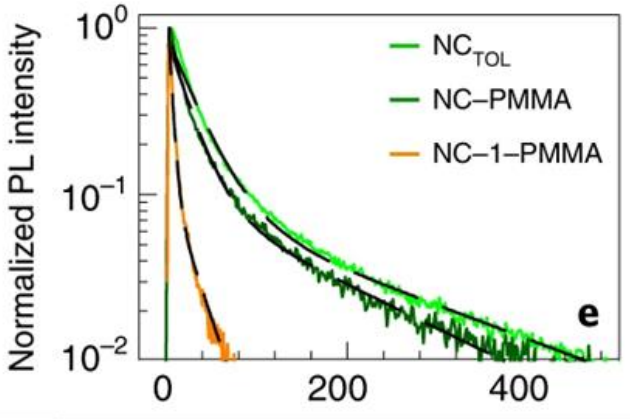
Nature Nanotechnology **15**, 462-468 (2020)

3. NANOCOMPOSITES TO TAILOR EMISSION PROPERTIES.

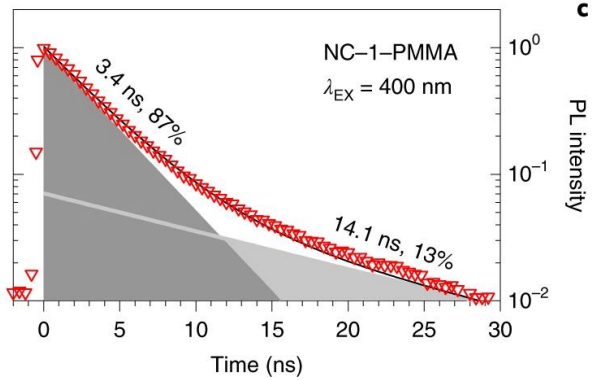
- RL intensity of the nanocomposite is comparable to that of the commercial scintillators
- Estimated LY of NC–1–PMMA nanocomposite comparable to ~9,000 photons/MeV
- **RL of 1 is 30-fold stronger in the nanocomposite→ effectiveness of sensitization**
- Considering the fast decay time of the nanocomposite emission with no slow scintillation tails



Sensitizer to emitter energy transfer OK!



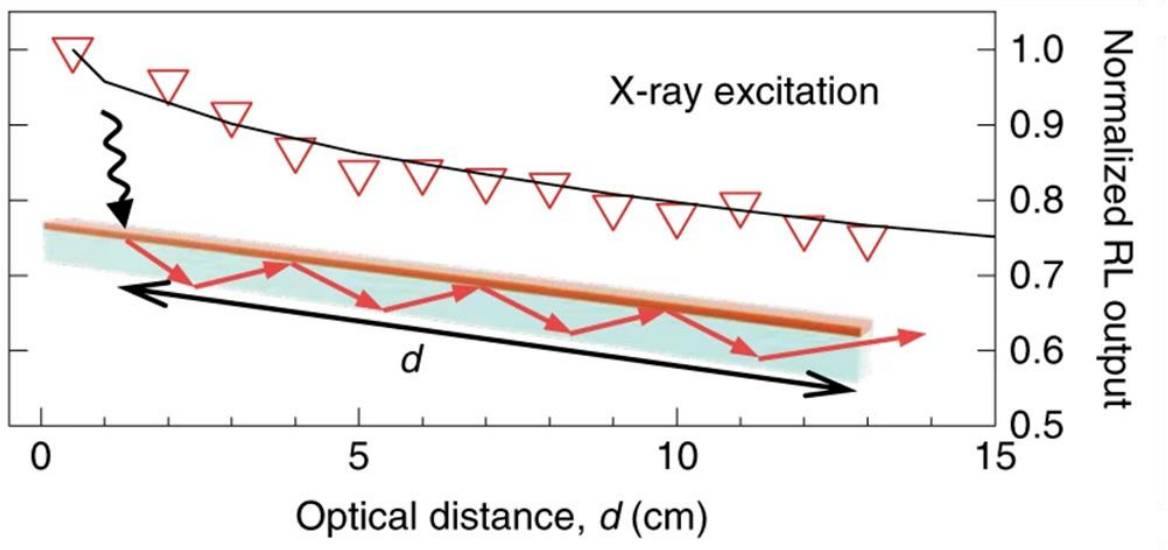
Mostly fast emission from dyes OK!



Nature Nanotechnology **15**, 462-468 (2020)

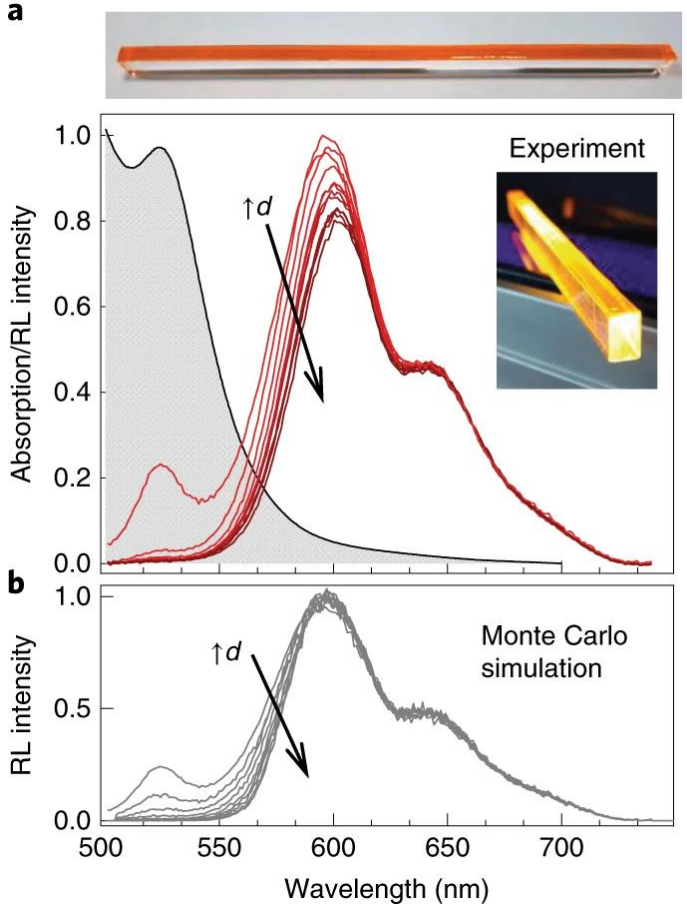
3. NANOCOMPOSITES TO TAILOR EMISSION PROPERTIES.

Sensitization → low emitters concentration → reabsorption-free scintillator



Intensity small drop (~25%) in ~12 cm (see also MonteCarlo simulation).

→ ***Reabsorption is negligible***
→ *QY of dye is preserved, and light waveguided across the scintillator length*
→ *Red emission suitable for scintillating heterostructure*

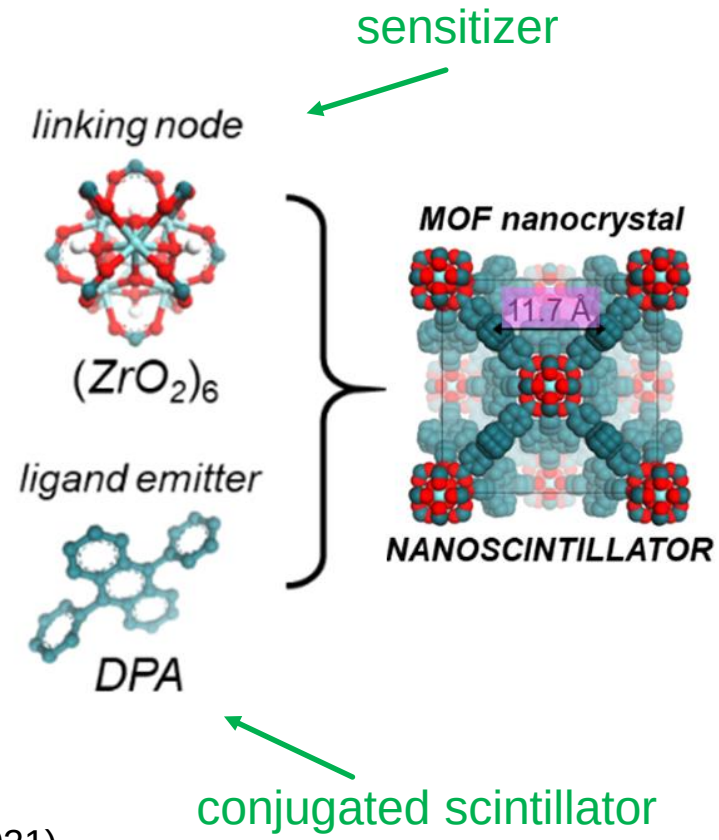


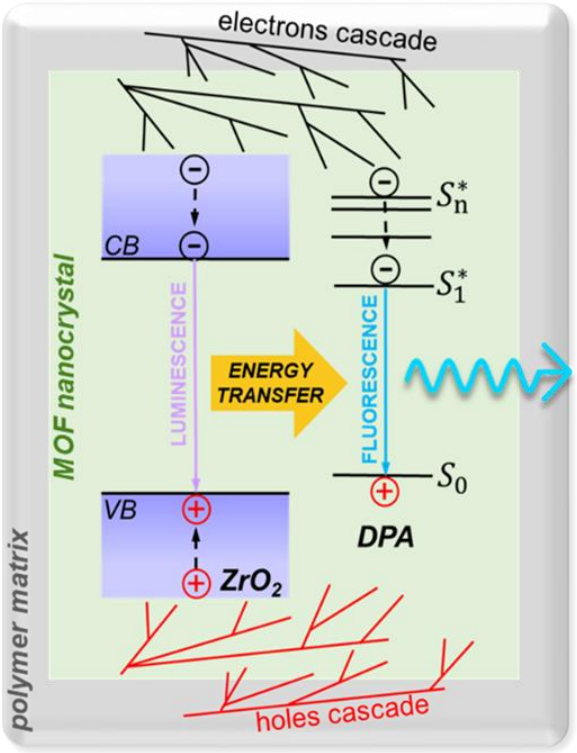
3. NANOCOMPOSITES TO TAILOR EMISSION PROPERTIES.

MOF nanocrystals based composite scintillators

MOF = metal organic framework crystalline systems

- Tunable structure/composition
- Cost effective synthesis and processing
- MOF architecture preserve the properties of constituent fluorophore



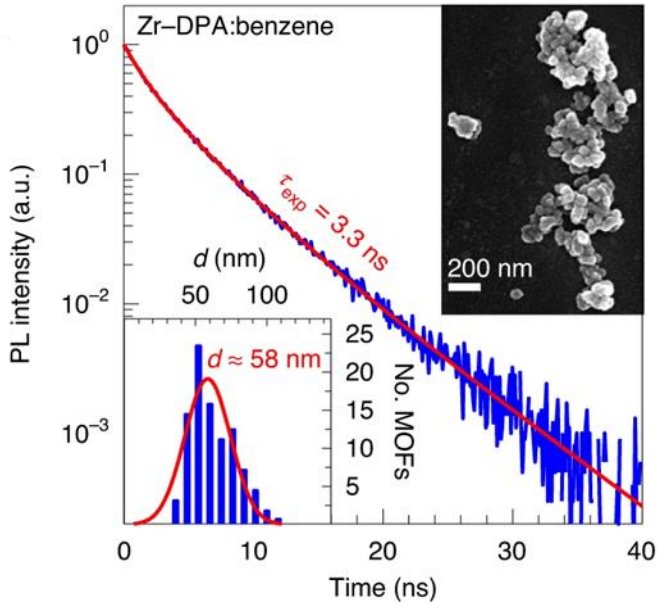


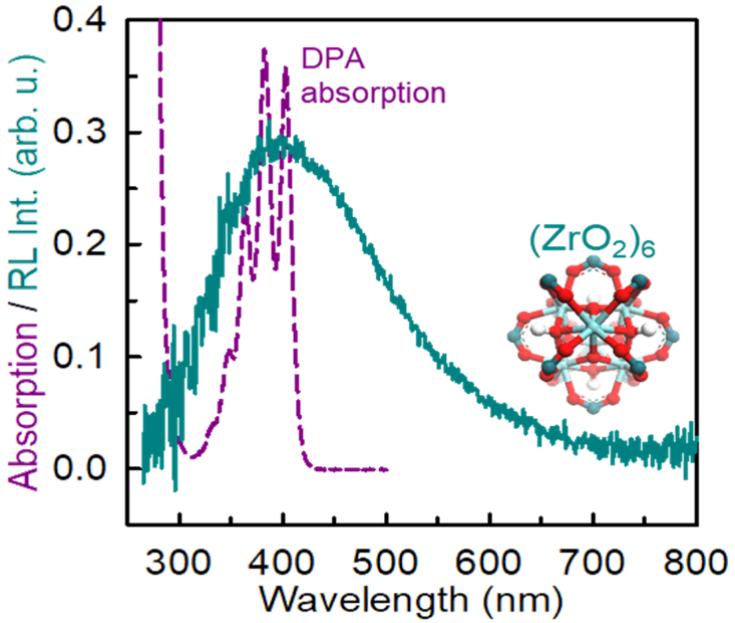
J. Perego, I. Villa, et al. *Nature Photonics* **15**, 393–400 (2021)

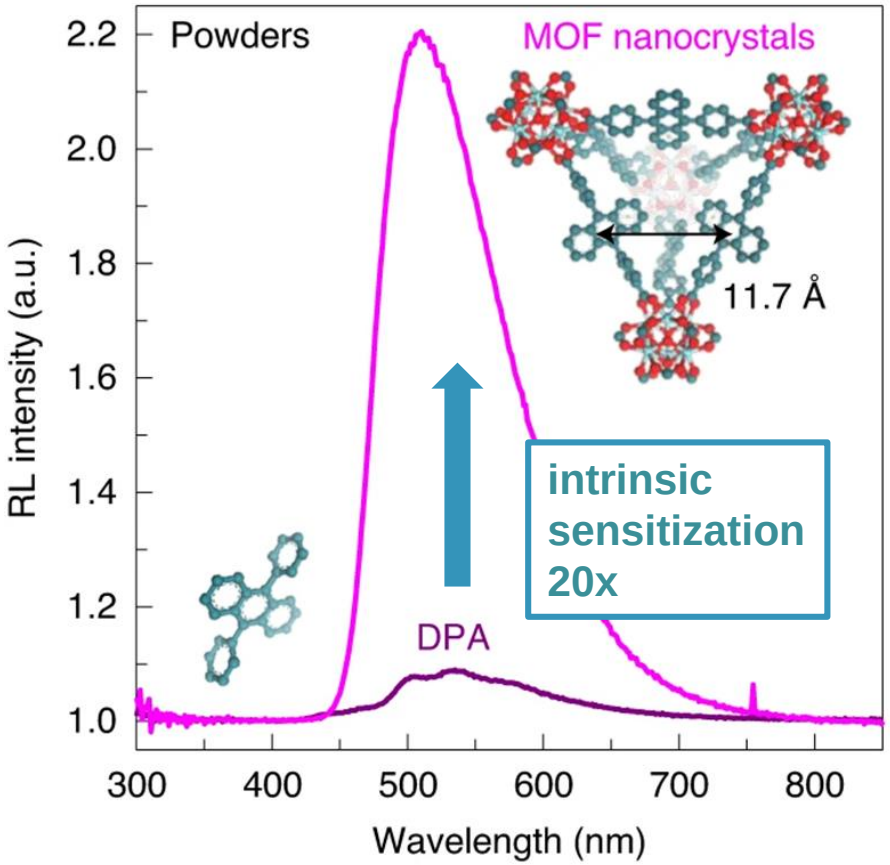
3. NANOCOMPOSITES TO TAILOR EMISSION PROPERTIES.

- **MOF: zirconium oxo-hydroxy as heavy node + organic scintillator (DPA)** as ligand (QY 96%, t=6ns ns)
- High Z elements
- Close packed sensitizers/ligands to have ultrafast non-radiative ET

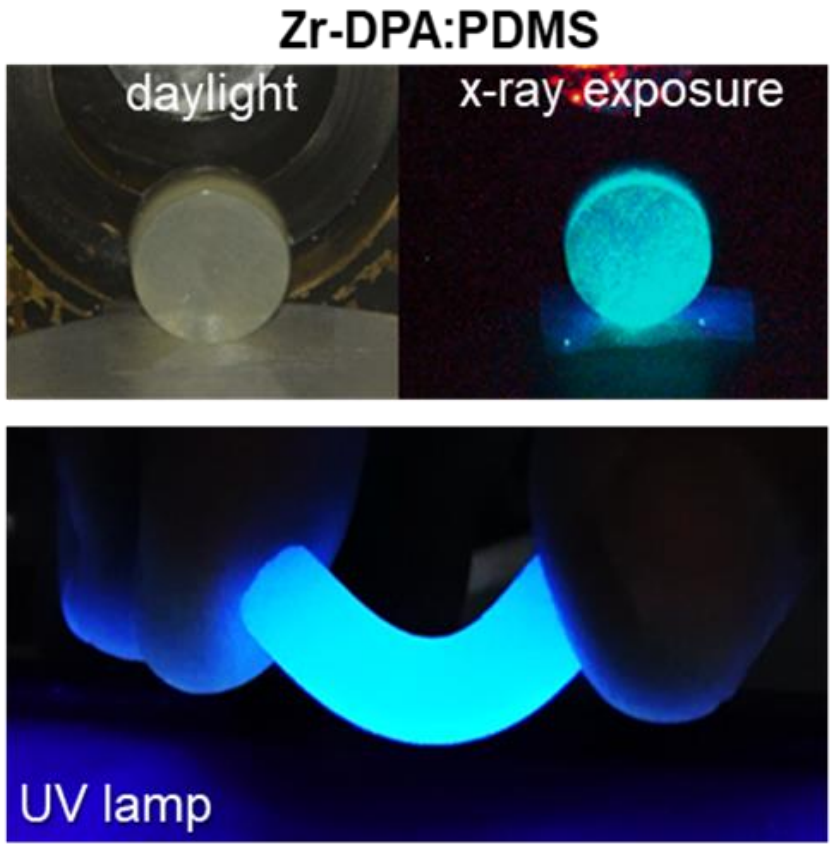
DPA density = 1.10 g cm^{-3}
MOF density = 0.7 g cm^{-3}

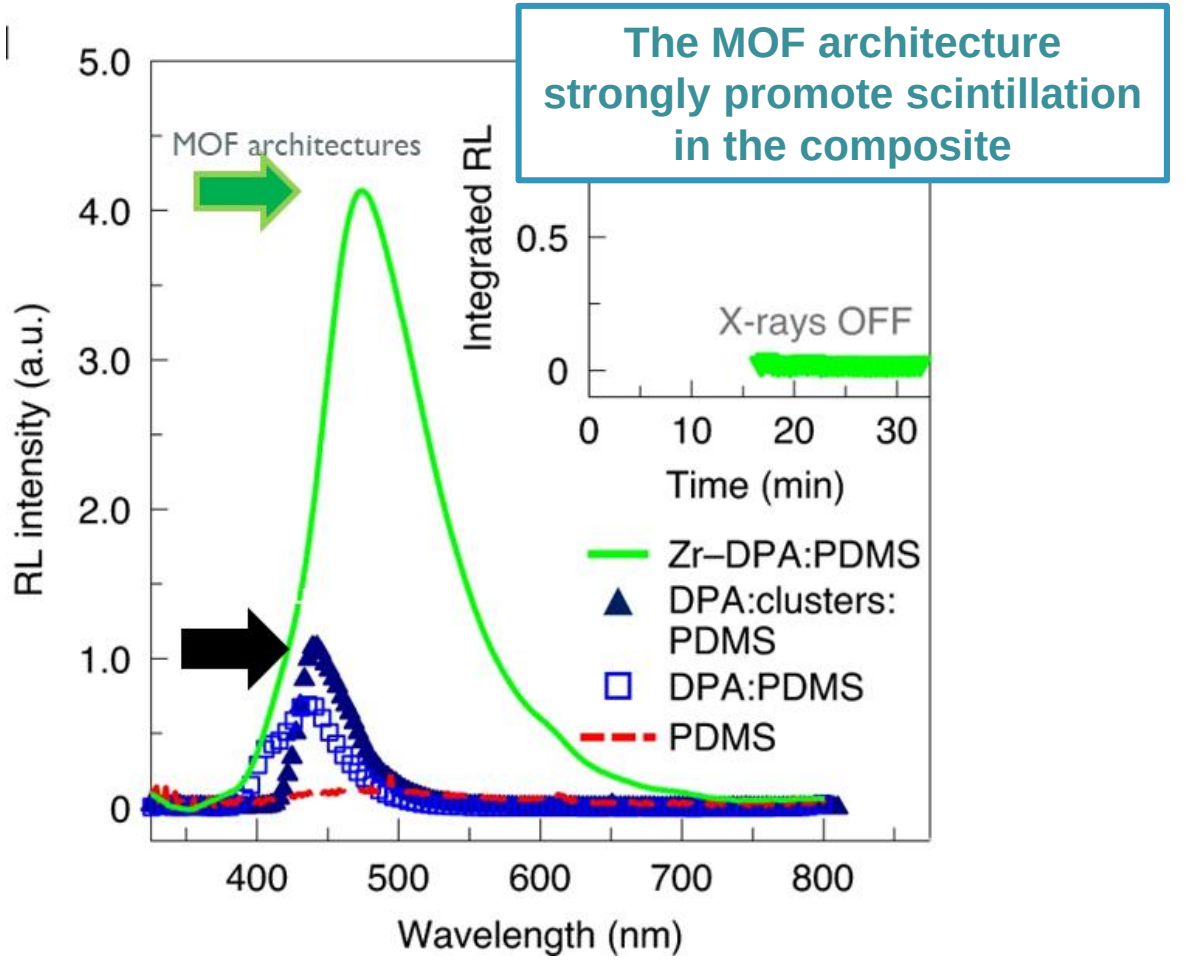






3. NANOCOMPOSITES TO TAILOR EMISSION PROPERTIES.



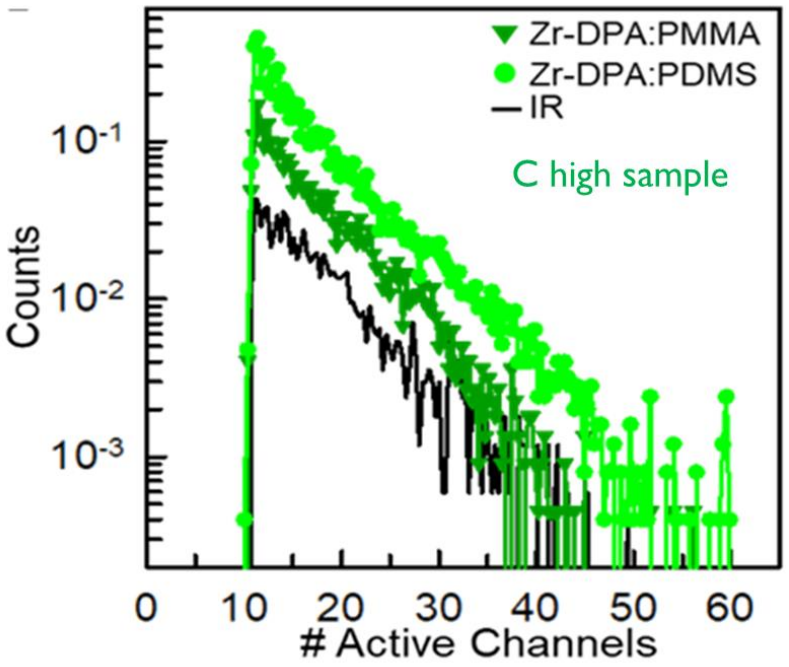


The MOF architecture strongly promote scintillation in the composite

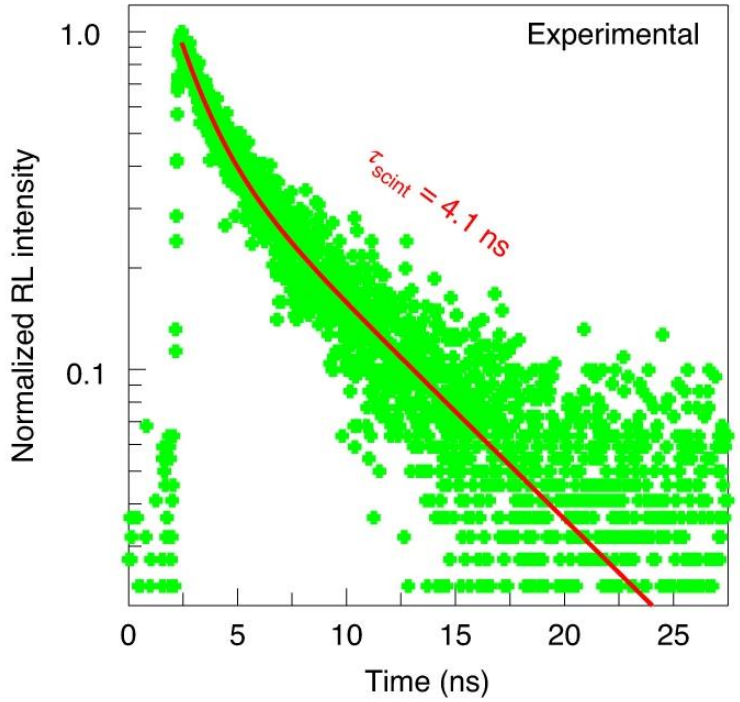
Nature Photonics **15**, 393–400 (2021)

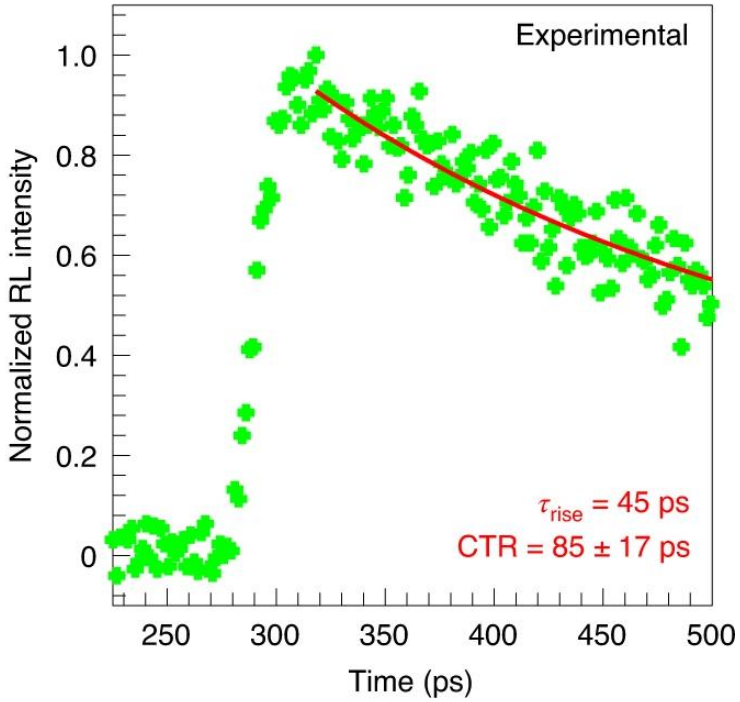
3. NANOCOMPOSITES TO TAILOR EMISSION PROPERTIES.

Detection test: ^{60}Co γ-ray source (1,173.2 and1,332.5 keV)



Scintillation dynamics: fast rise, fast decay





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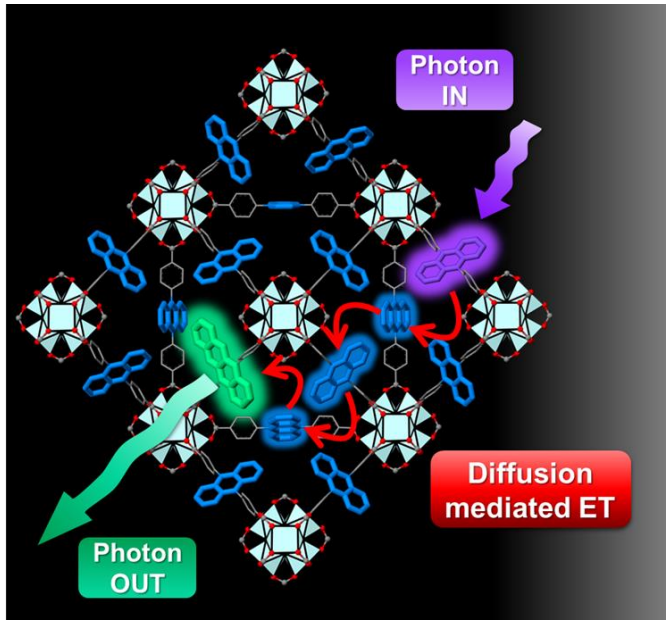
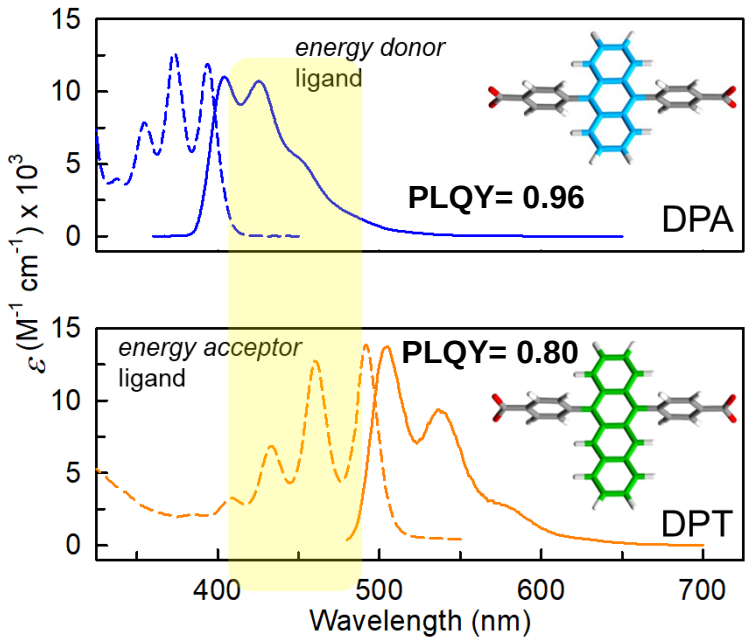
3. NANOCOMPOSITES TO TAILOR EMISSION PROPERTIES.

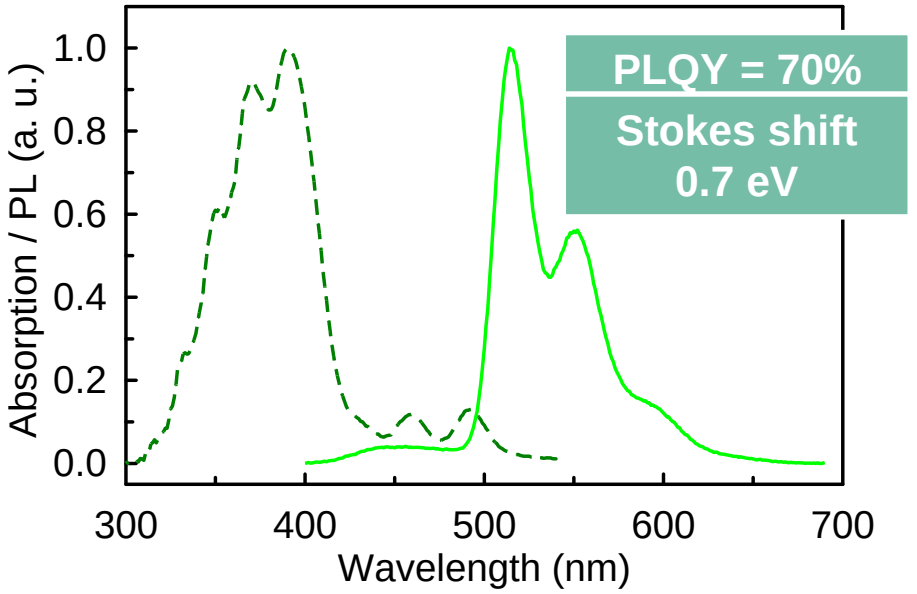
ULTRALARGE STOKES SHIFT SCINTILLATING NANOCOMPOSITES

Heteroligand Fluorescent MOF Nanocrystals





BEST DOPING LEVEL → DPT/DPA 8%

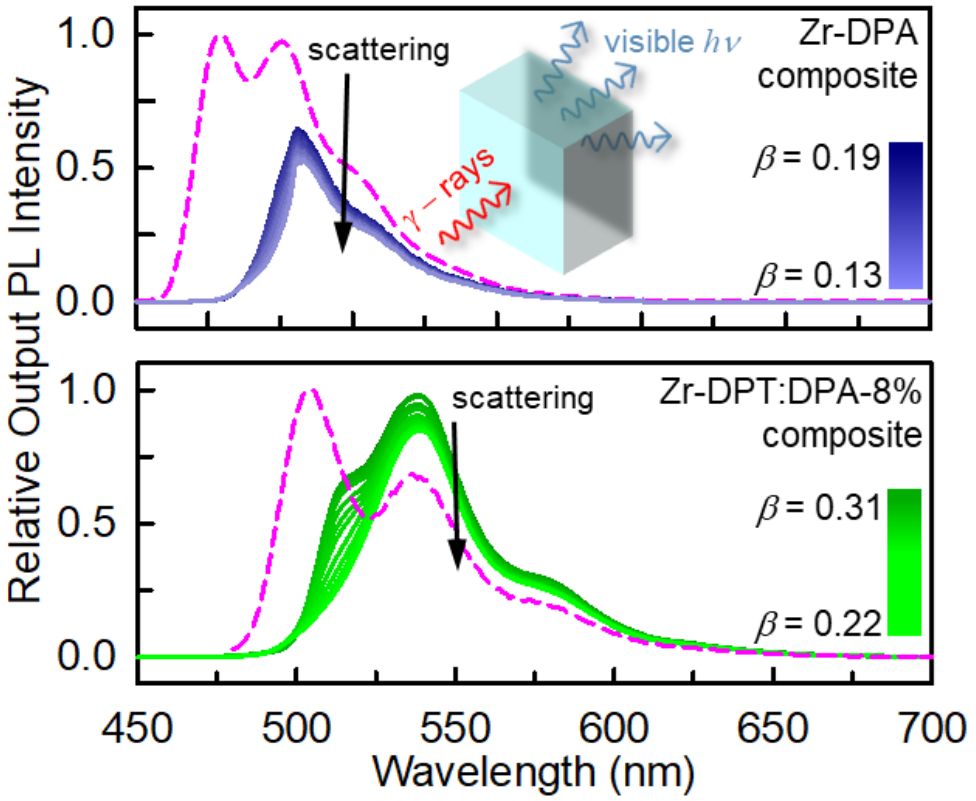


Perego, J., Bezuidenhout, C.X. *et al. Nature Commun.* **13**, 3504 (2022)

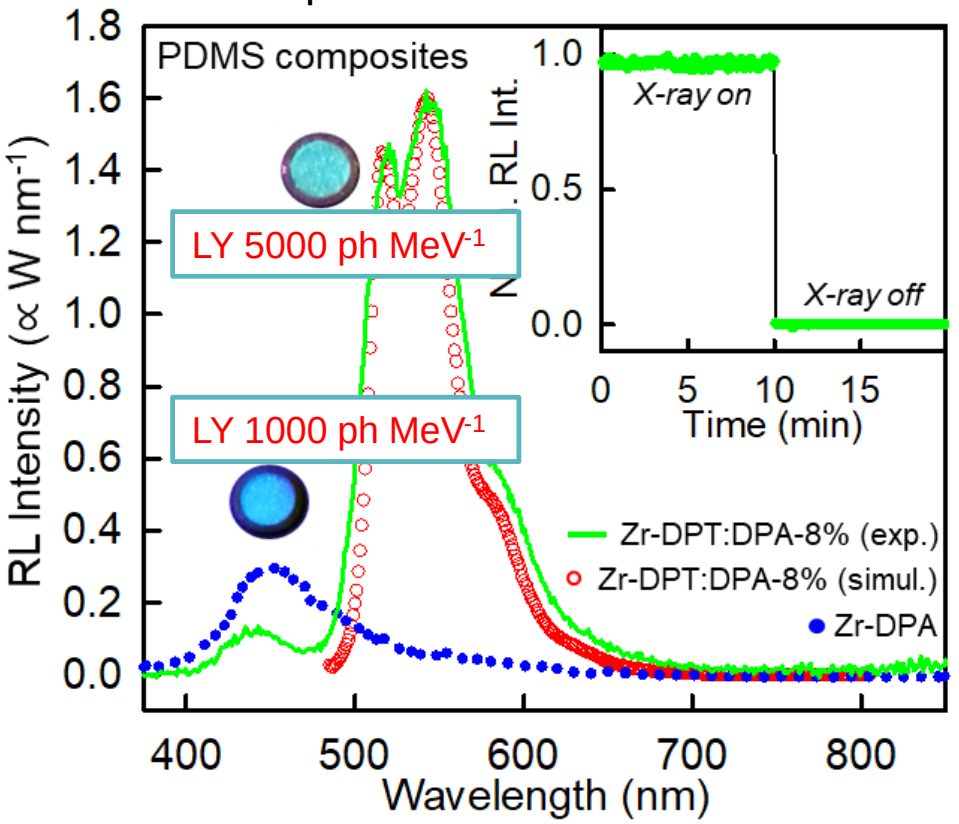
PCT/IB2022/054391 patent

3. NANOCOMPOSITES TO TAILOR EMISSION PROPERTIES.

Theoretical light output (Monte Carlo)



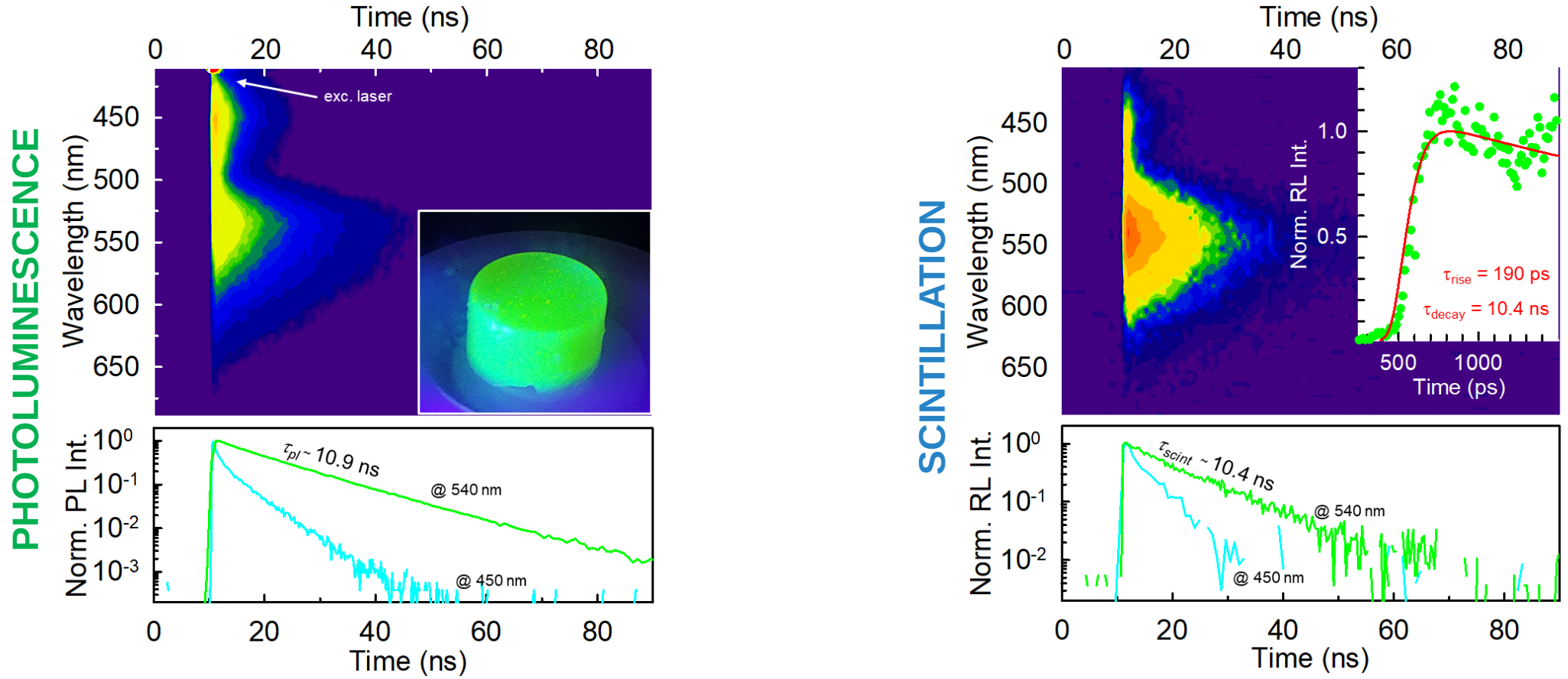
Experimental scintillation LY



Hetero-ligand MOFs shows large scintillation yield than homo-ligand MOFs thanks to the Stokes shift

3. NANOCOMPOSITES TO TAILOR EMISSION PROPERTIES.

PDMS, 0.5% wt MOF loading, 5 mm thickness



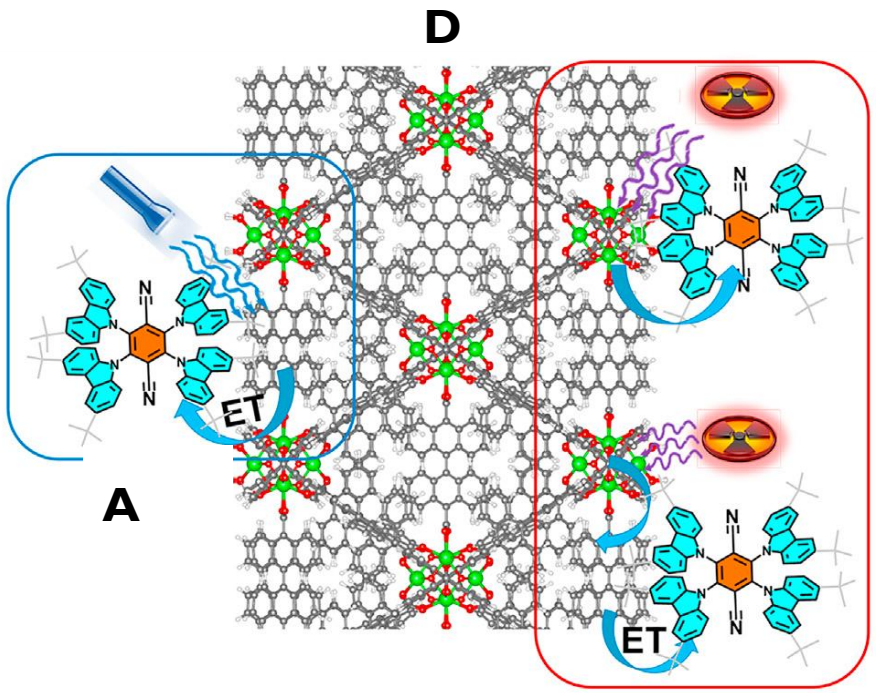
Fast scintillation with negligible reabsorption also in bulk

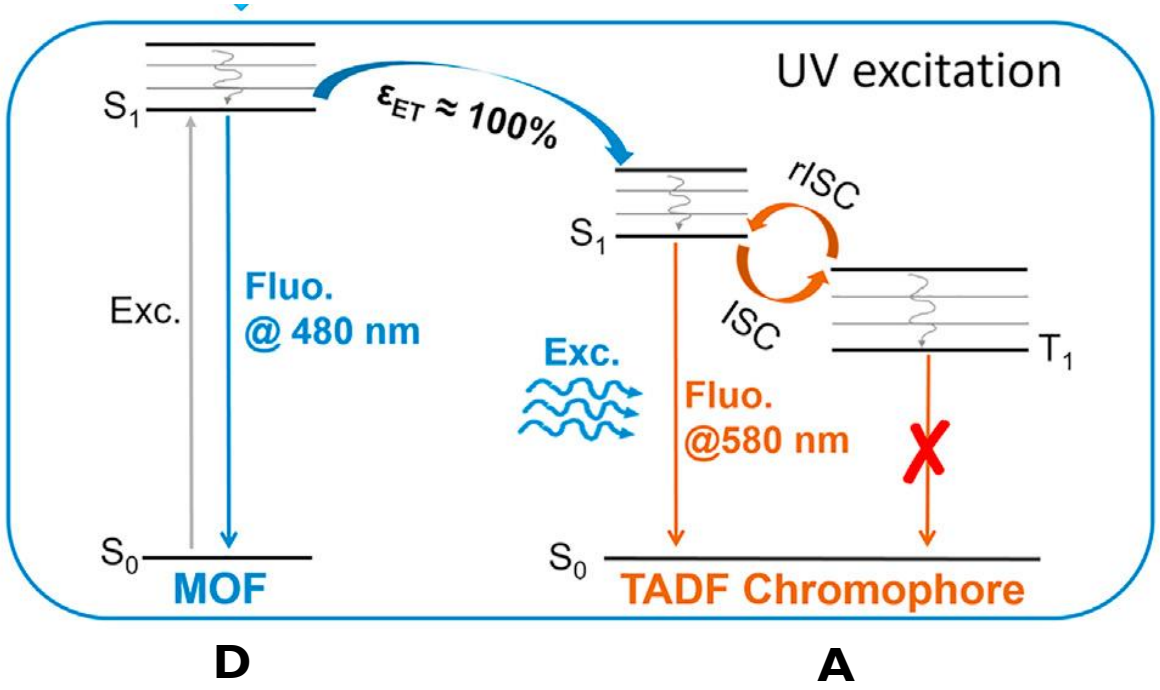
Nature Commun. **13**, 3504 (2022)

3. NANOCOMPOSITES TO TAILOR EMISSION PROPERTIES.

How to improve the sensitivity of x-ray imaging detectors

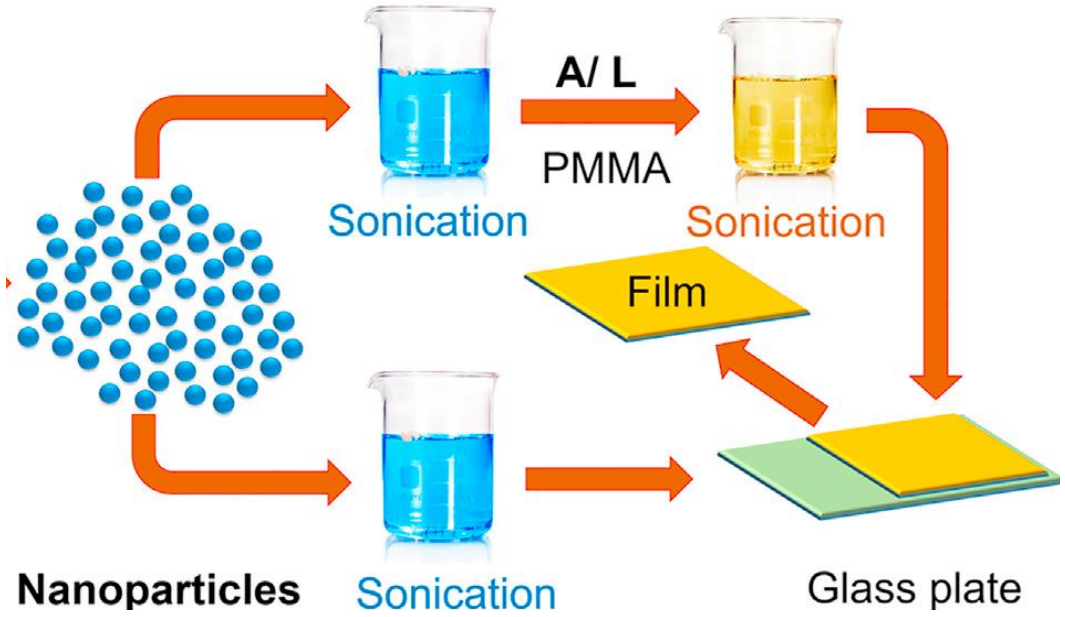
The Zr-MOF (**D, donor**)-TADF chromophore (**A, acceptor**) nanocomposite films in poly(methyl methacrylate) (PMMA)

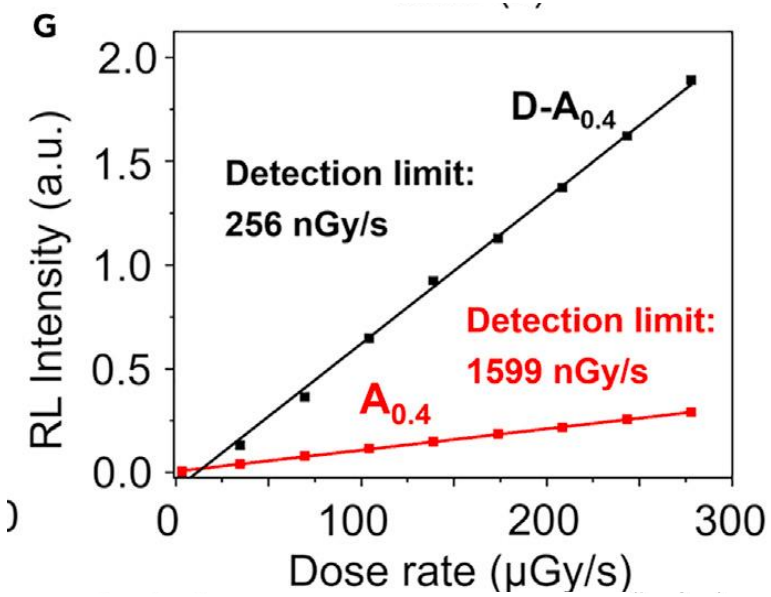


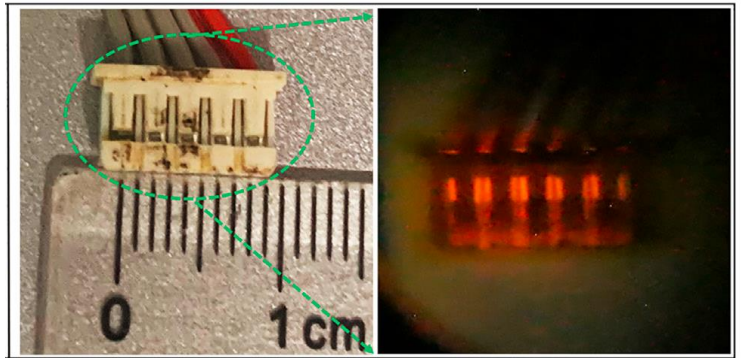


Wang J-X, et al. *Matter* **5**, 253-265 (2022)

3. NANOCOMPOSITES TO TAILOR EMISSION PROPERTIES.







X-ray imaging scintillator based on the D-A nanocomposite film exhibits a 400 um resolution and a detection limit of 256 nGy/s

Wang J-X, et al. *Matter* **5**, 253-265 (2022)

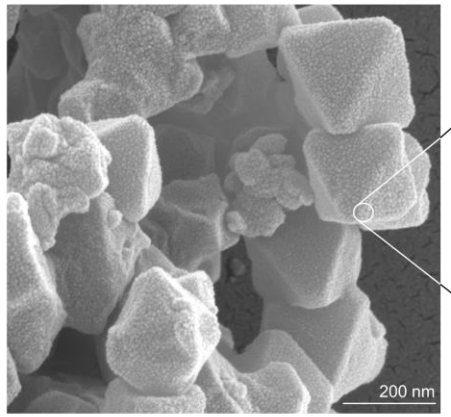
4. NANOCOMPOSITES TO EXPLOIT STRUCTURAL PROPERTIES.

SPARTE
Scintillating Porous Architectures for RadioacTivE gas detection

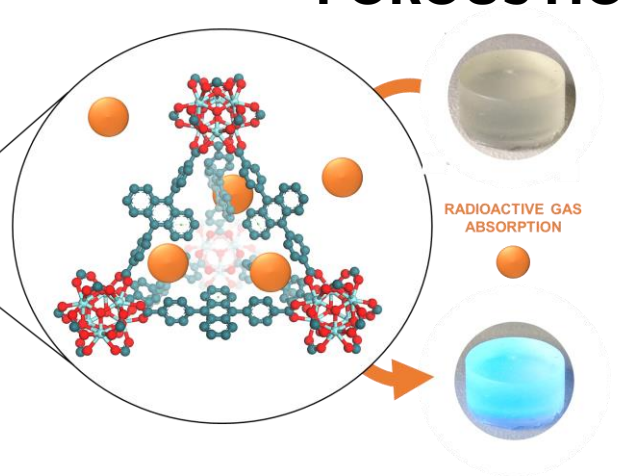
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 899293

Goal:
detecting low activities of radioactive gas containing β emitters and doing metrology using porous materials

MOF = POROUS NANOSCINTILLATORS



POROUS HOST



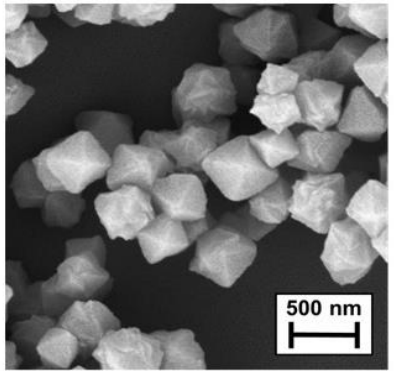
porous scintillators to capture and concentrate β radionuclides

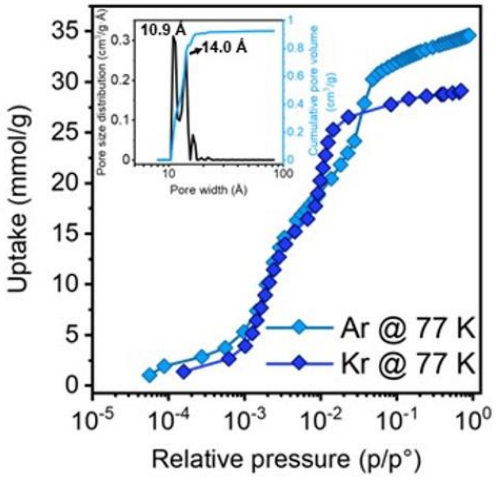
The scintillating composite sponge

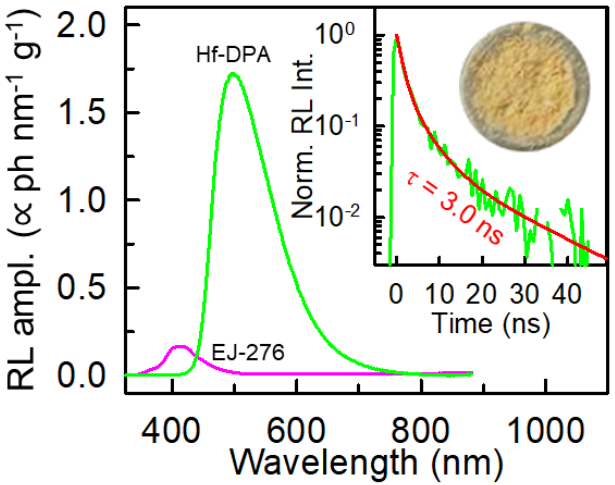
4. NANOCOMPOSITES TO EXPLOIT STRUCTURAL PROPERTIES.

Hafnium-based DPA MOFs

- ***Higher Z***
- ***Ideadl pores size***
- ***Fast emission TCR***

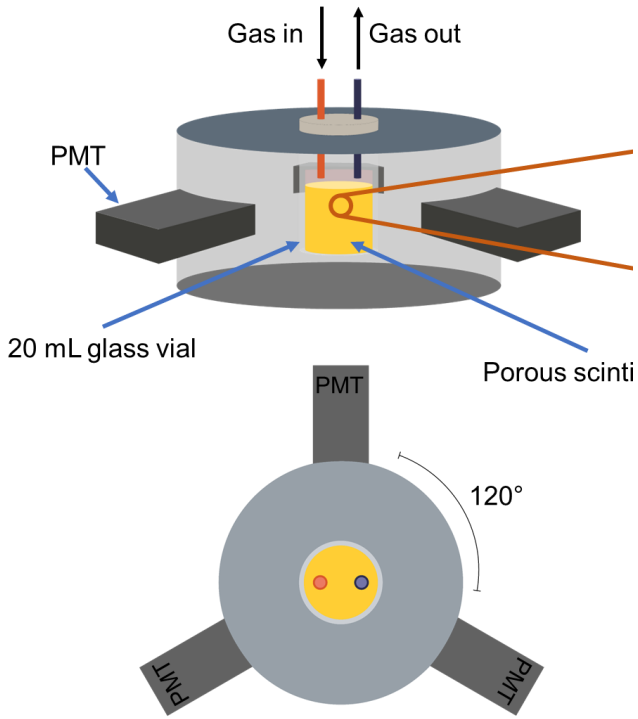






M. Orfano et al. in preparation

Time Coincidence Detection

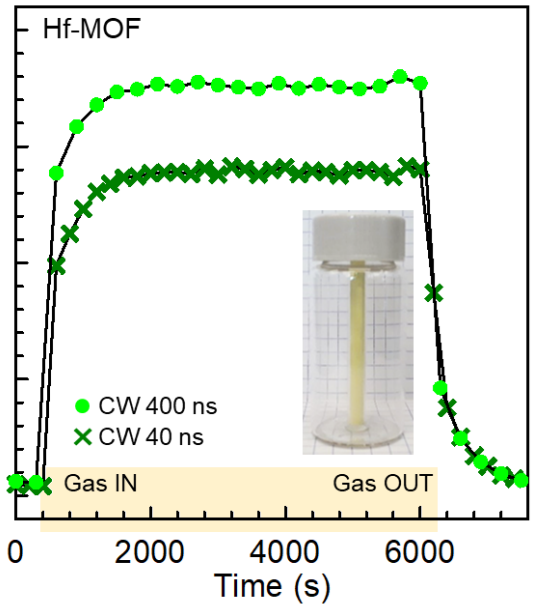


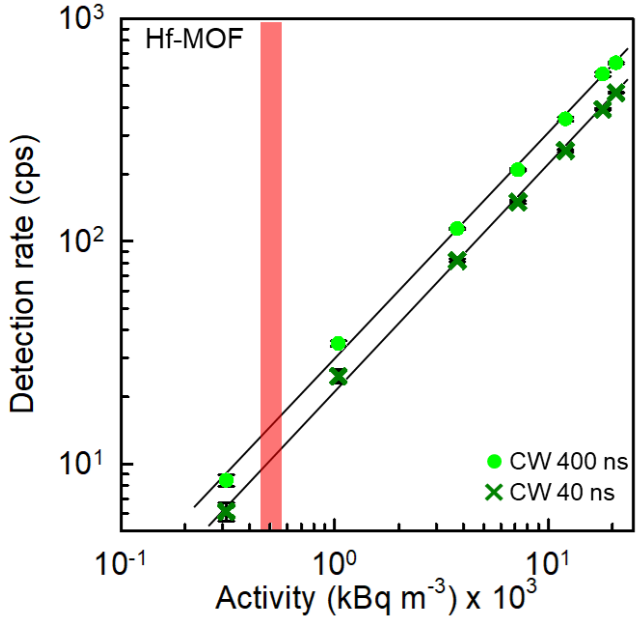
^{85}Kr krypton

^{222}Rn radon

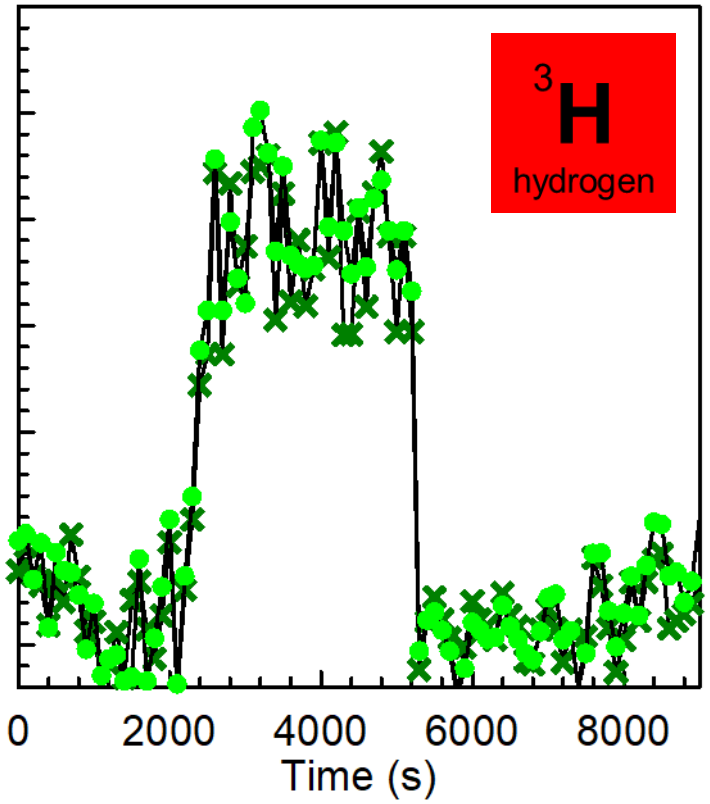
^{3}H hydrogen

4. NANOCOMPOSITES TO EXPLOIT STRUCTURAL PROPERTIES.





3x signal than reference



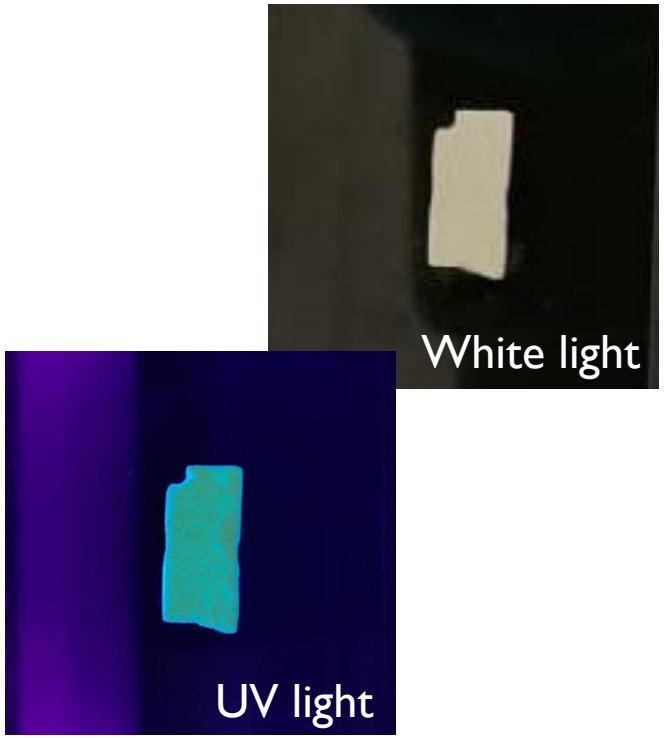
^{85}Kr
krypton

- Gas adsorption kinetic is observed
- 5x signal than reference
- Better sensitivity than commercial devices

M. Orfano et al. in preparation

4. NANOCOMPOSITES TO EXPLOIT STRUCTURAL PROPERTIES.

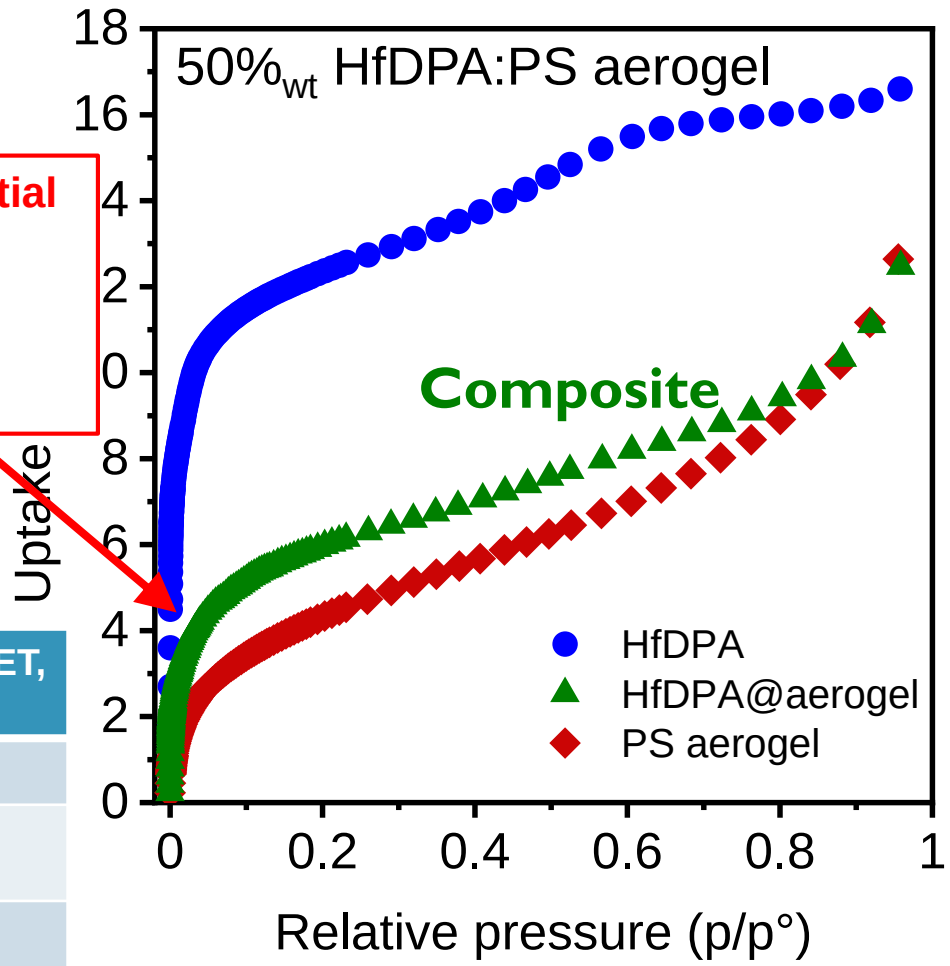
COMPOSITE: composite **POLYSTYRENE AEROGEL+ MOF**
(produced by **Nano Active Film srl)**



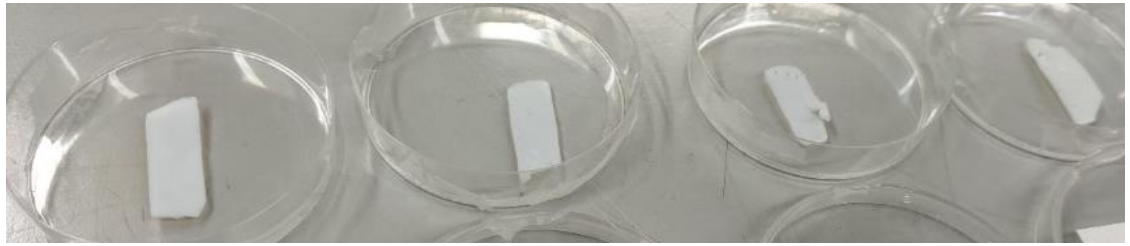
Increased uptake at low partial pressure

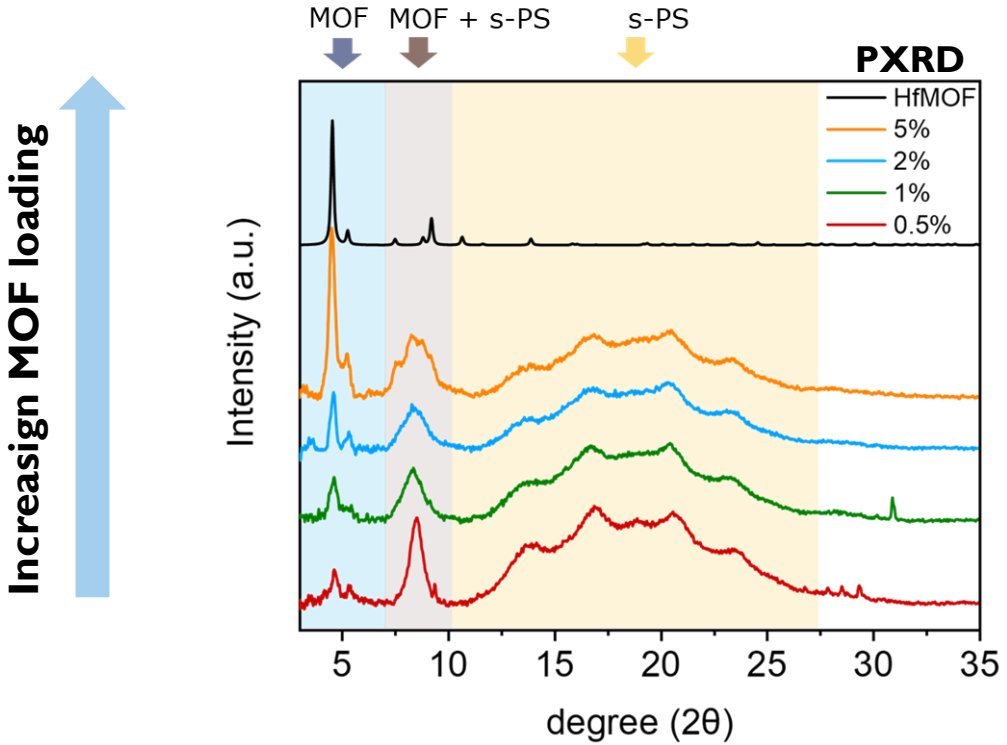
Higher microporosity: adsorption in MOF pores

Sample	Surface area (BET, m^2/g)
s-PS aerogel	340
HfDPA@aerogel	500
HfDPA 4.1	1050

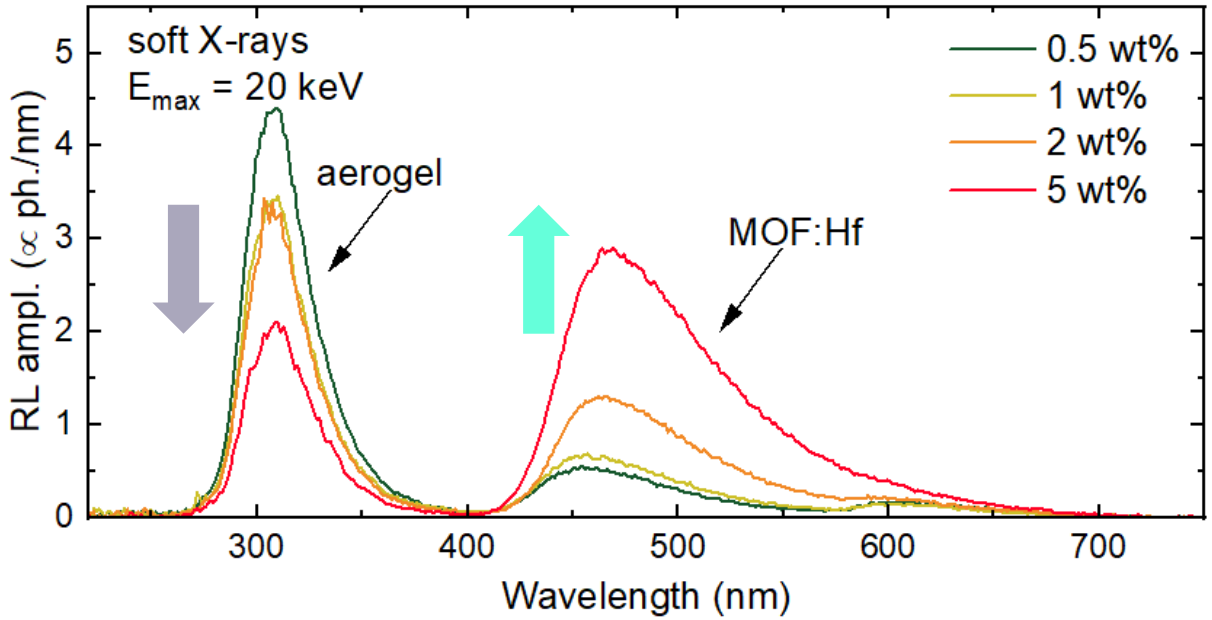


4. NANOCOMPOSITES TO EXPLOIT STRUCTURAL PROPERTIES.





POROUS COMPOSITES RADIOLUMINESCENCE



Gas detection: *WORK IN PROGRESS*

5. CONCLUSIONS

- The scintillation in composite materials can be achived and tuned, to be exploited to obtain better scintillators with tailored emission properties.

- The nanocomposite concept opens to way to different strategies to surpass classical scintillators by realizing new design concepts devices or materials with better engineered composition.

  → **Test on heterostrucures and porous systems are ongoing**

1° WARNING: the composite developement is strictly related to the application.

2° WARNING: The problem of the low density of classical composites based on polymers is not yet completely solved.

ACKNOWLEDGMENTS: PEOPLE

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Mr. P. Mai
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FROM EUROPE

SPARTE
Scintillating Porous Architectures for RadioacTivE gas detection

SPARTE (2020-2024)
https://www.sparte-project.eu/

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 899293

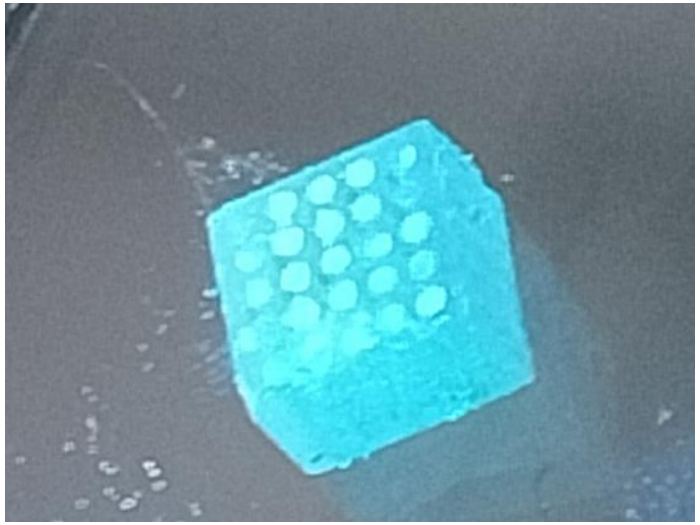
FROM ITALY

MUR
Ministero dell'Università e della Ricerca

2022-2025 project SHERPA

Scintillating **HE**terostructures for High **R**esolution **P**ET ima**g**ing

Consiglio Nazionale delle Ricerche



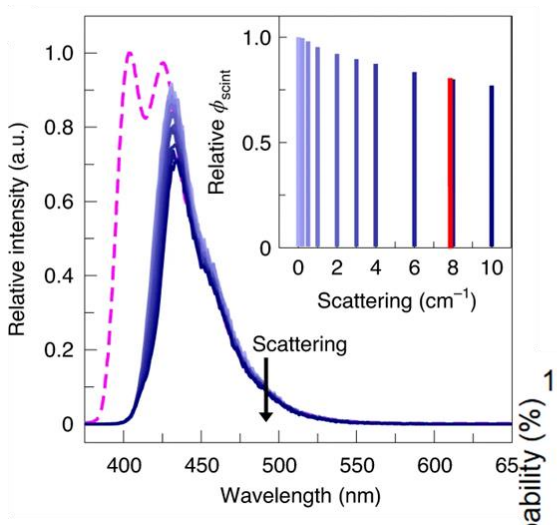
MODELING THE LIGHT PROPAGATION IN SMALL NANOCOMPOSITES

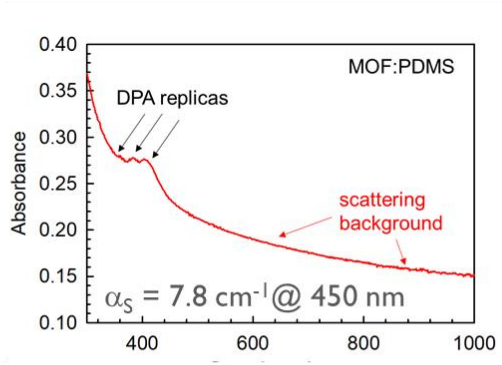
- **For small size scintillator**

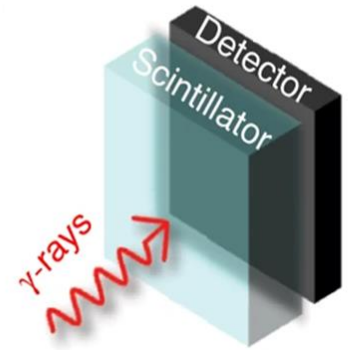
The number of re-absorption/emission events of the light entrapped in the scintillators is small

ϕ_{scint} determined by self-absorption, scattering effects are negligible (Intensity of light reaching the detector decreases of 0.25 even at the max α)

Light scattering induces a pulse broadening of 50 ps, relevant for τrise







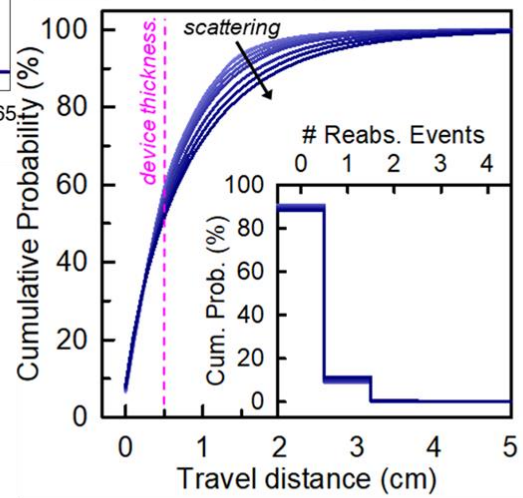
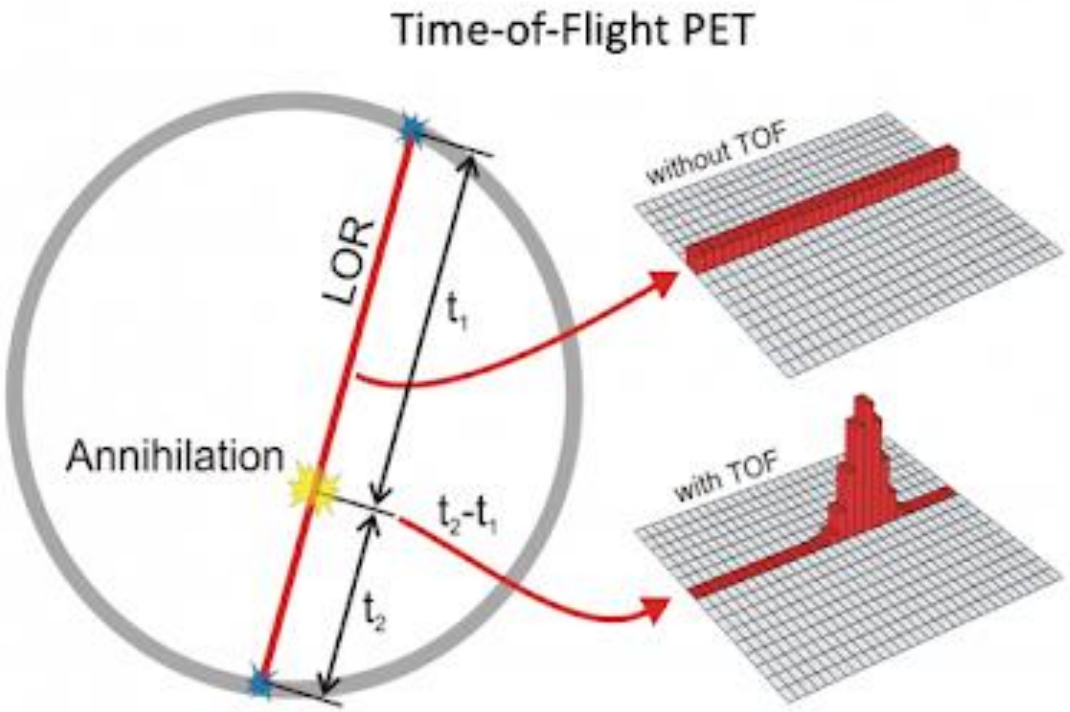
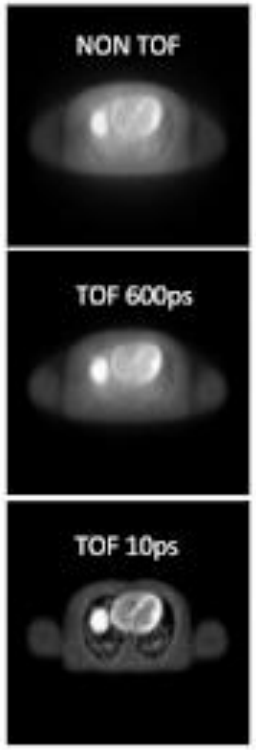


Photo-detector coupled by an index-matching material to the irradiated nanocomposite

ULTRAFAST TOF-PET REQUIRES NEW SCINTILLATORS





$$CTR[\text{ns}] = 2.18\sqrt{\delta^{-1}}$$

$$\delta\ [\text{ph ns}^{-2}] = \frac{\eta LY}{\tau_{rise}\tau_{decay}}$$

τ_{rise} = scintillation rise time
τ_{rise} = scintillation decay time
LY = light yield [ph/MeV] @ 511 keV
η = photo-detection efficiency

Commercial CTR = 200 ps

Conti, M. & Bendriem, B. *Clin. Transl. Imaging* **7**, 139–147 (2019).

LARGE STOKES SHIFT EMITTERS

How to increase the Stokes shift keeping high yield of fast emission?

For inorganic semiconductors:

Electronic Doping

Chemistry of Materials **31**, 1450-1459 (2019)

J. Phys. Chem. Lett. **11**, 5367-5372 (2020)

For conjugated systems:

Phosphorescence
Charge transfer states

Scientific Reports **8**, 6359 (2018)

Nature Photonics **15**, 187 (2021)

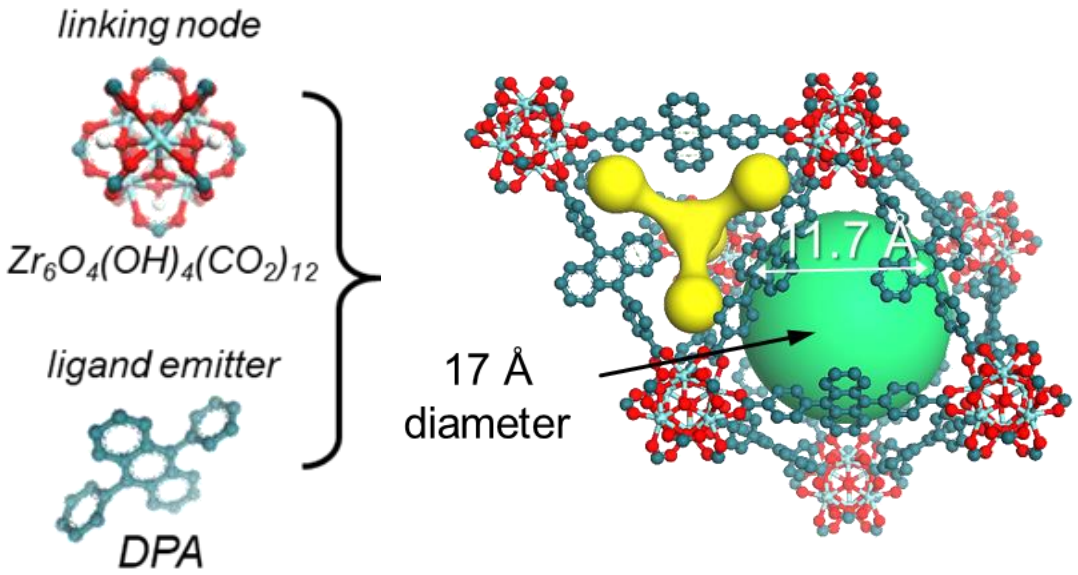
Potentially lower PLQY
slow emission

~~Radiative Energy Transfer?~~

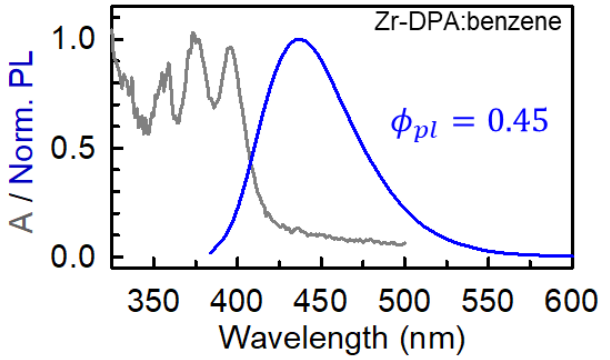
LARGE STOKES SHIFT IN MOF NANOCRYSTALS

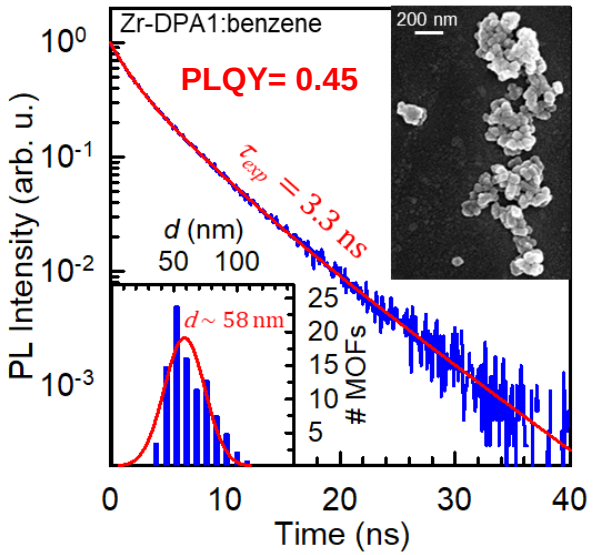
Metal-organic Frameworks

O.M. Yaghi, H.L. Li, *J. Am. Chem. Soc.* 1995, **117**, 10401



Metal–organic frameworks: functional luminescent and photonic materials for sensing applications. *Chemical Society Reviews* **46**, 3242-3285 (2017)





Scintillating MOF Nanocrystals

- **Unaltered ground state properties of conjugated ligands**
- **Tailored structure and porosity**
- **PLQY partially limited by surface quenching of diffusing excitons.**

F. Meinardi et al. *Nano Lett.* **18**, 528−534 (2018)
J. Perego, I. Villa, et al. *Nature Photonics* **15**, 393–400 (2021)

EXCITON DIFFUSION IN HETERO-LIGANDS MOFS

Foerster Radius $R_{fs} = 0.211[J(\lambda)\theta^2 n^{-4}\mathrm{QY_{DPA}}]^{1/6}$

Overlap Integral $J(\lambda) = \dfrac{\int PL(\lambda)\varepsilon(\lambda)\lambda^4 d\lambda}{\int PL(\lambda)d\lambda}$

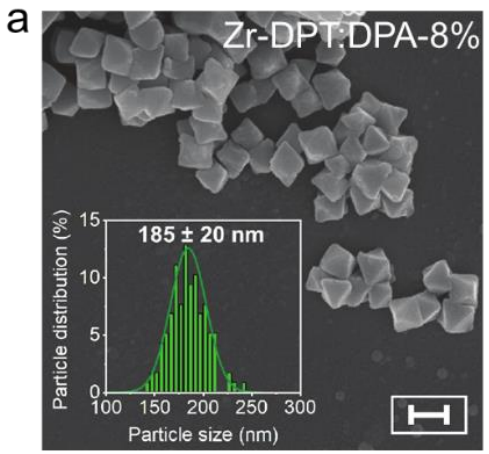
Singlet hopping rate >> Rapid diffusion limit model for ET

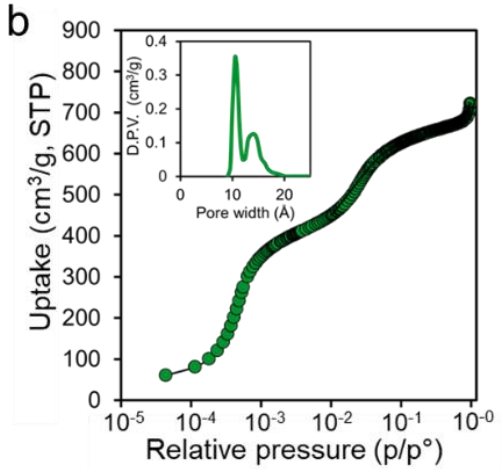
$$k_{hop}^{DPA-DPA} = 6k_{ET}^{DPA-DPA} = 6\frac{1}{\tau_{DPA}}\left(\frac{a}{R_{fs}^{DPA-DPA}}\right)^{-6} = 49\ GHz$$

DPA-DPT energy transfer rate an yield

$$k_{ET} = \frac{4\pi C_{DPT} R_{fs}^6}{3\tau_{DPA} a^3} \qquad \phi_{ET} = \frac{k_{ET}}{k_{ET} + k_{DPA}},$$

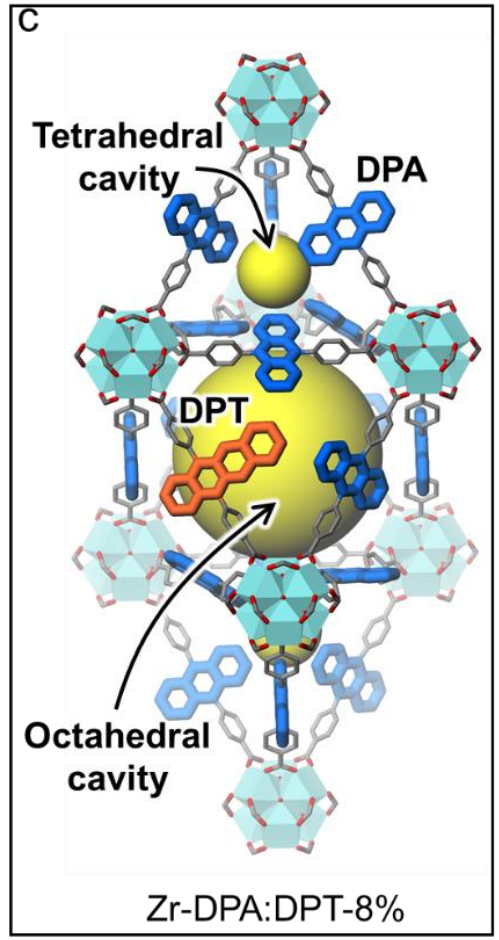
SYNTHESYS OF HETERO-LIGAND NANO-MOFS





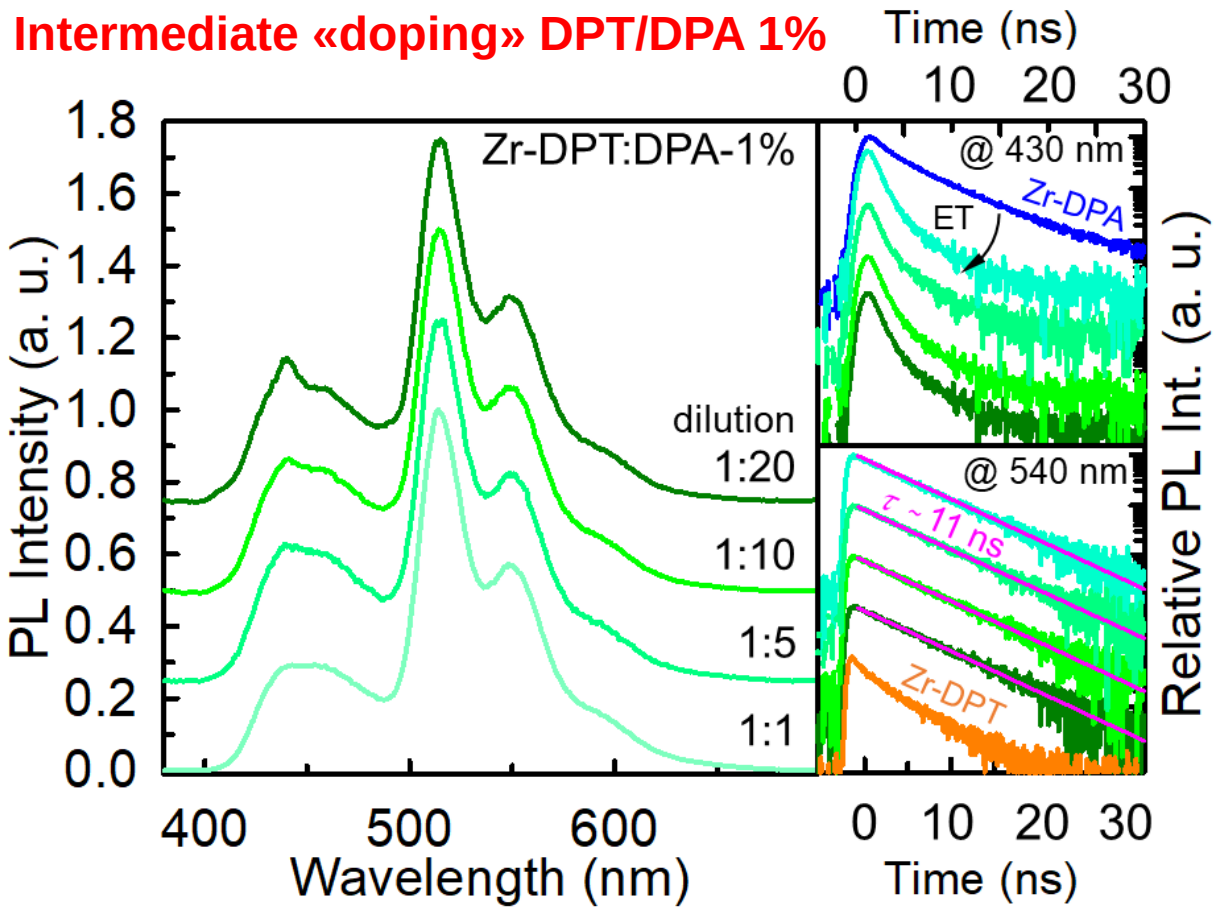
modulated solvothermal process of Zr-ion oxy-hydroxy clusters and the ligands

cubic crystal structure (space group *Fm-3m*). The Zr-based nodes ($Zr_6(m_3\text{-}O)_4(m_3\text{-}OH)_4(CO_2)_{12}$ clusters) have 12-coordinated ligands which connect the nodes in the 3D framework while the DPA units are disordered over three positions



PHOTOLUMINESCENCE OF HETERO-LIGANDS MOF NANOCRYSTALS

Intermediate «doping» DPT/DPA 1%



PL shape insensitive to diluton: MOFs are is an independent emitter

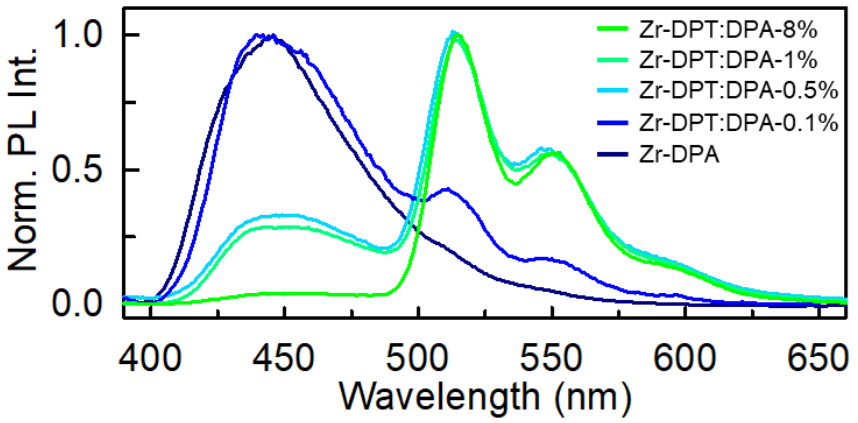
The DPA residual emission lifetime is shortened and constant upon dilution: **ET is an intracrystal process.**

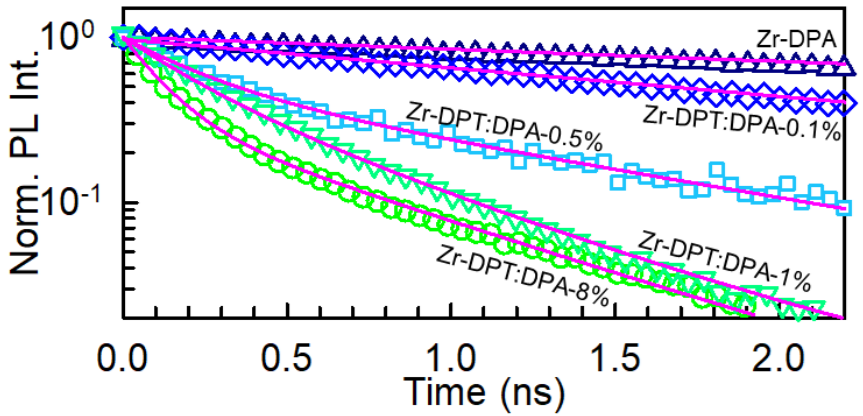
The DPT emission lifetime matches the single molecule: **FULL PROTECTION** from quenching

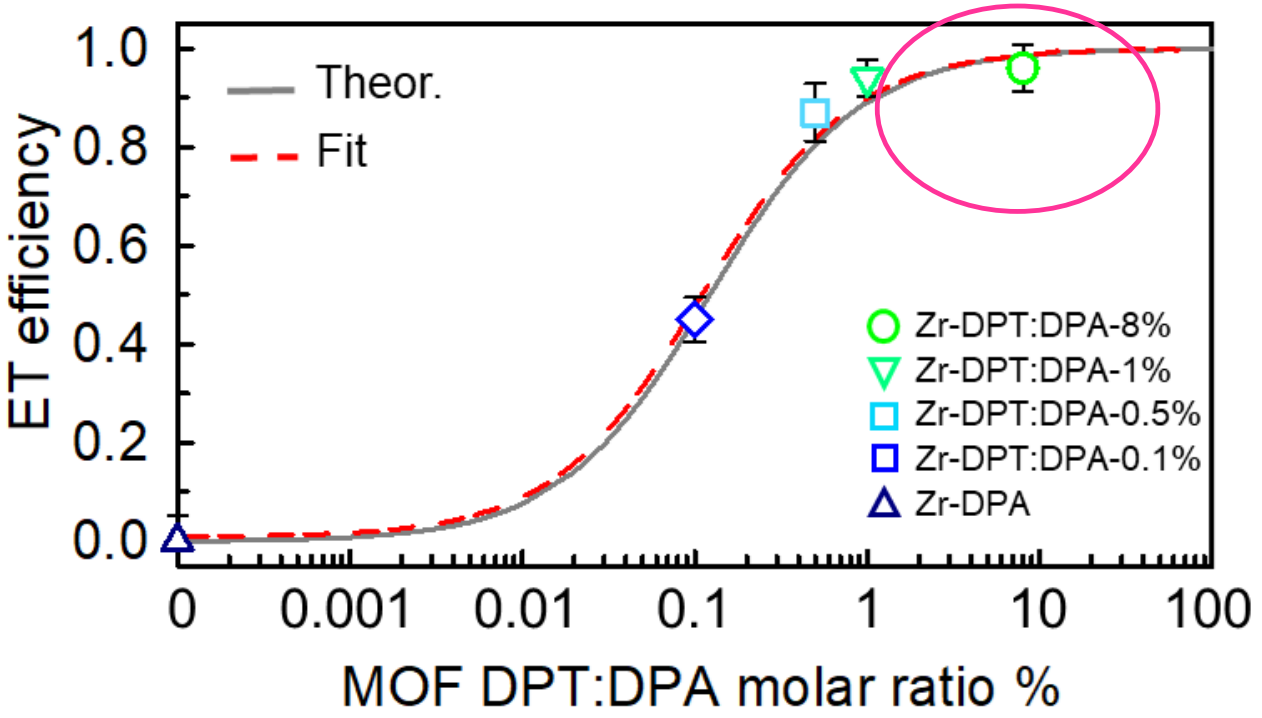
The dopants are not on surfaces, OK!!!

J. Perego, et al. *Nature Commun.*, accepted

ENERGY TRANSFER KINETICS IN HETERO-LIGANDS MOF NANOCRYSTALS







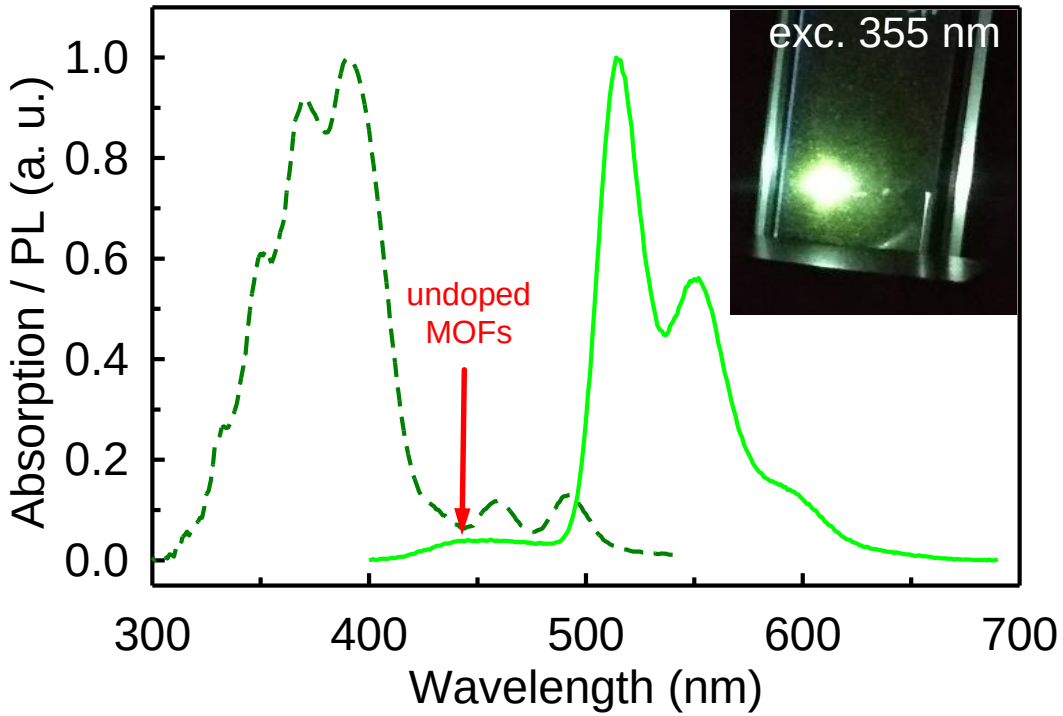
NO DOPING INDUCED QUENCHING

The PL changes by incremental «doping» is perfectly described by diffusion-mediated Foerster ET

J. Perego, et al. *Nature Commun.*, accepted

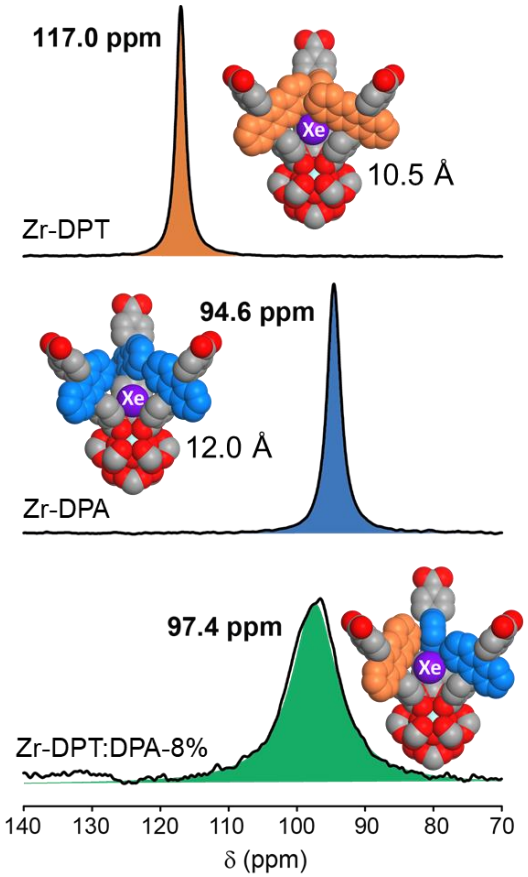
HETERO-LIGANDS MOF NANOCRYSTALS

BEST DOPING LEVEL → DPT/DPA 8%



J. Perego, et al. *Nature Commun.*, accepted

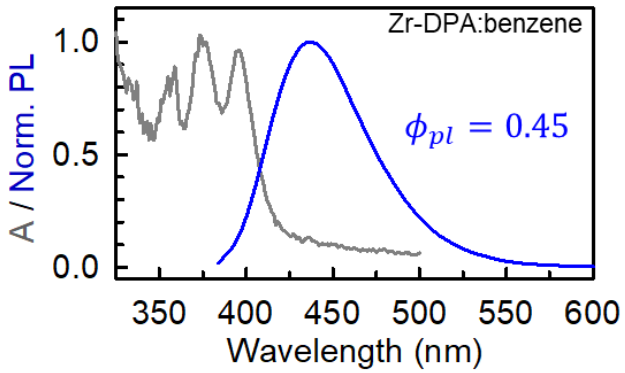
Hyperpolarized Xe NMR:
average doping 6%

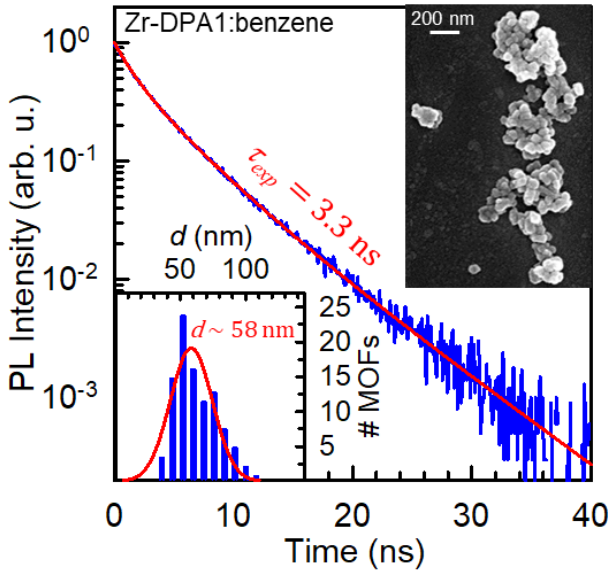


$PLQY_{MOF}$ = 60%
vs.
$PLQY_{DPT}$ = 80%

Goal achieved!
PLQY limited only by distribution of doping with partially doped nanocrystals

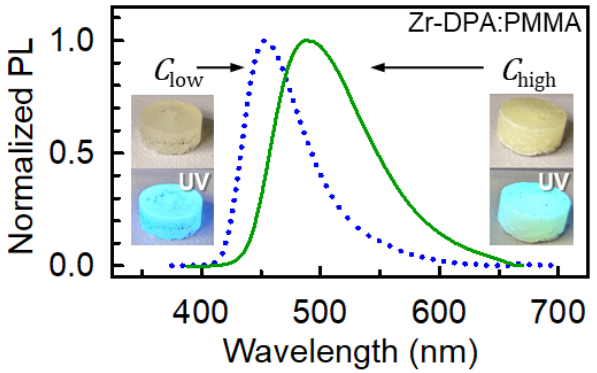
NANO-MOF AND NANOCOMPOSITES PHOTOLUMINESCENCE

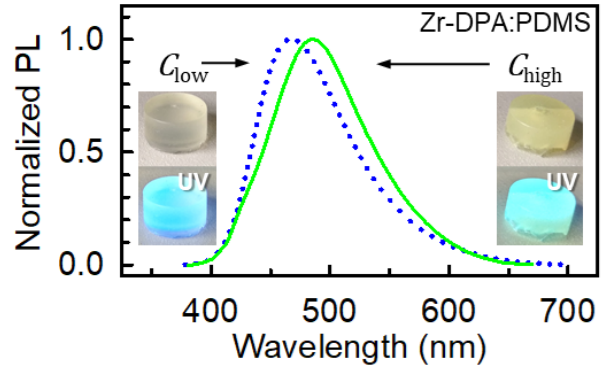


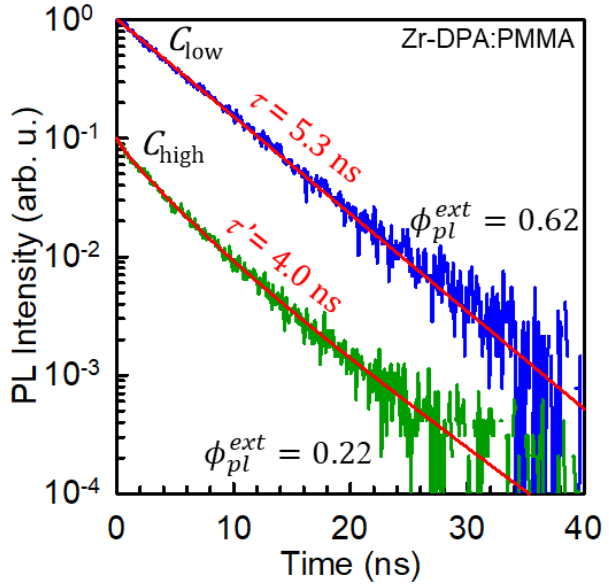


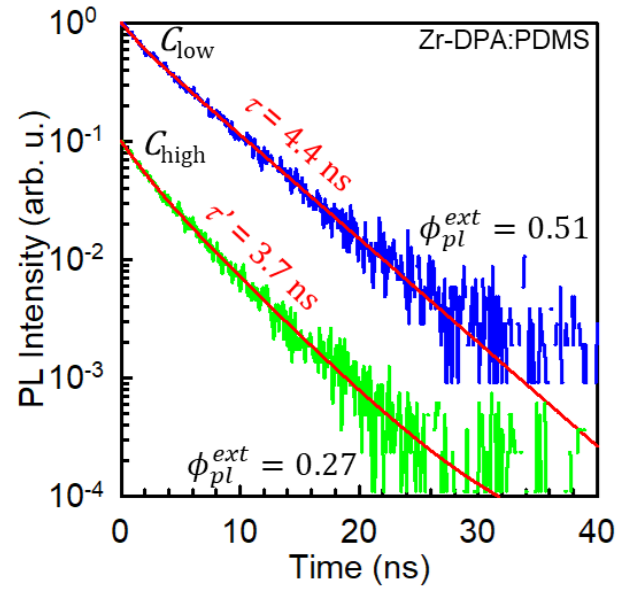
Single crystals

Composites









Measurements and estimation of the parameters: LY

Pulse height spectrum recorded by a SiPM photo-detector coupled to the nanocomposites
^{60}Co γ-ray source (1,173.2 and1,332.5 keV).

PHOTOELECTRIC PEAK IS DIFFUCULT TO OBSERVE IN LOW DENSITY AND INHOMOGEONEUS MATERIALS

Estimation of the intrinsic scintillation yield ϕ_{scint} is 821 ± 82 photons per MeV

- Total number of emitted photon n_{em}
- Detected photons $n_{exp} = \beta\rho\chi n_{em}$,

where $\beta = 0.26$ is the geometrical detection efficiency * and $\chi = 0.3$ is the quantum efficiency of the photo-detector, ρ = 0.78 is an empirical correction factor from comparison with a certified plastic scintillator EJ-276 as the reference.

n_{exp} = maximum number of active cells = 56 photons = max E deposited by Compton = 1,12 MeV from the ^{60}Co γ-rays

- **n_{em} =821±82 photons/MeV**

confirmed by independent relative measurement made with ^{22}Na and a SiPM using BGO as a reference
ϕ_{scint} = 1,160 ± 350 photons per MeV