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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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M. Orfano, J. Perego, F. Cova, Christophe Dujardin, Benoit Sabot, et al.. Porous composites based on scintillating metal-organic frameworks nanocrystals for radioactive gas detection.. SCINT 2022 - 16th SCINT 2022 Scintillating Materials and their Applications, Sep 2022, Santa Fe, United States. cea-03869822

HAL Id: cea-03869822

<https://cea.hal.science/cea-03869822v1>

Submitted on 24 Nov 2022

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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.

I. WHAT IS A NANOCOMPOSITE?

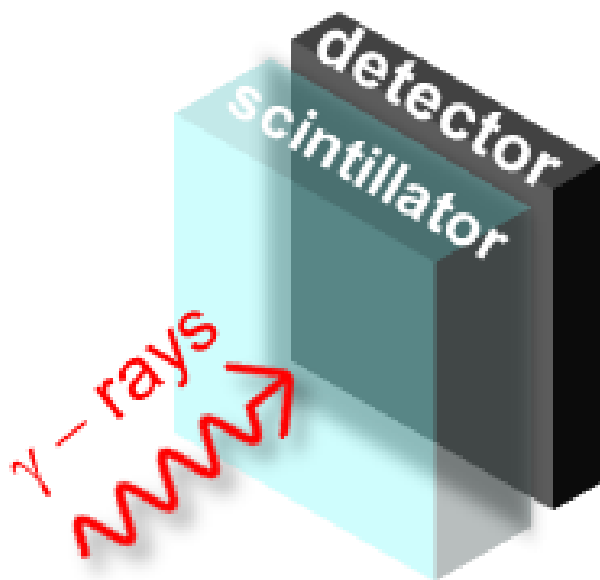
Nanocomposite is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometers (nm) or structures having nano-scale repeat distances between the different phases that make up the material.

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.

I. WHY WE NEED NANCOMPOSITES?

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



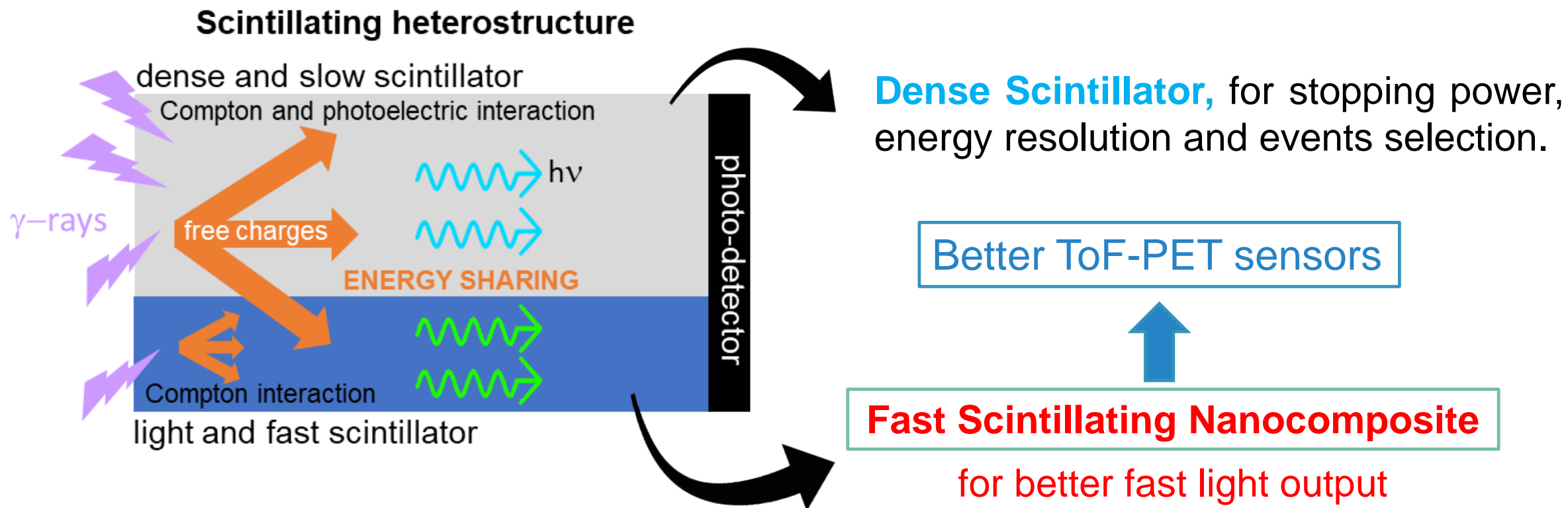
- Healthcare
- Geology
- Safety
- Environmental control
- High energy experiments
- Medical-imaging technologies

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

the versatility of scintillating nanocomposites can be a solution

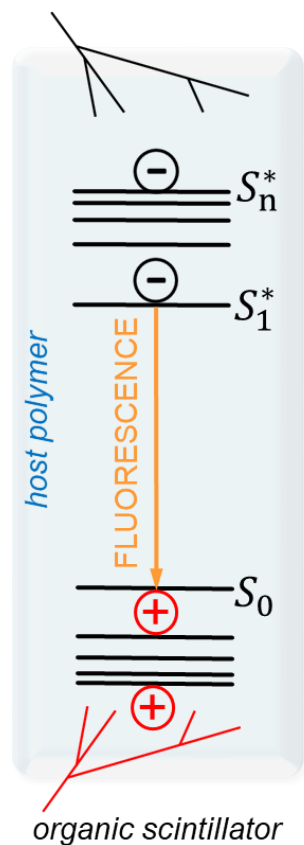
I. WHY WE NEED NANOCOMPOSITES?

EXAMPLE: Medical-imaging technologies, ToF-PET

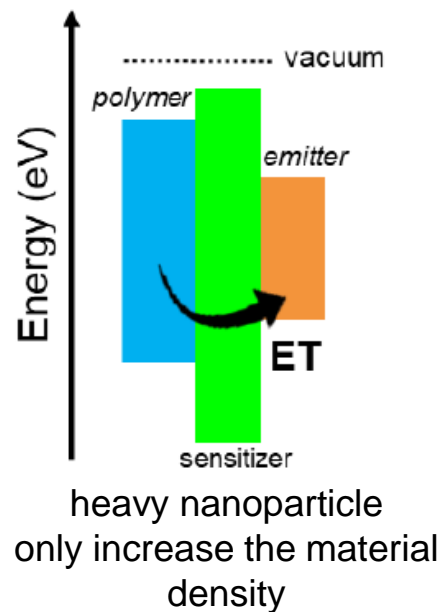


2. SCINTILLATION IN NANOCOMPOSITES

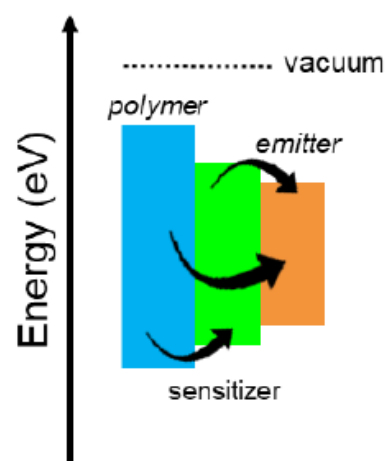
Plastic Scintillator



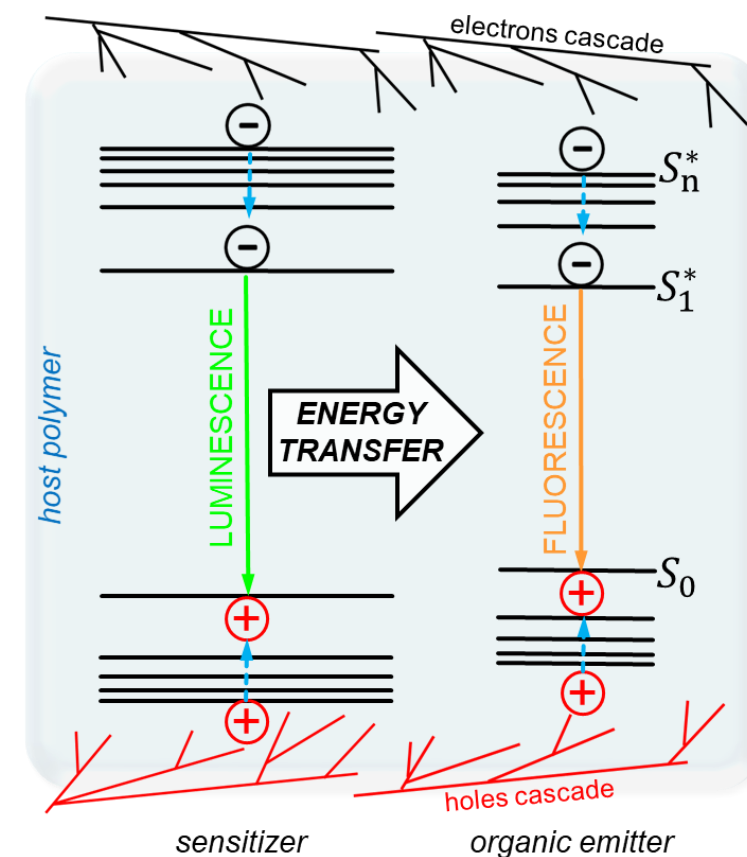
Passive Sensitization



Active Sensitization



Active Sensitization Photophysics



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

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

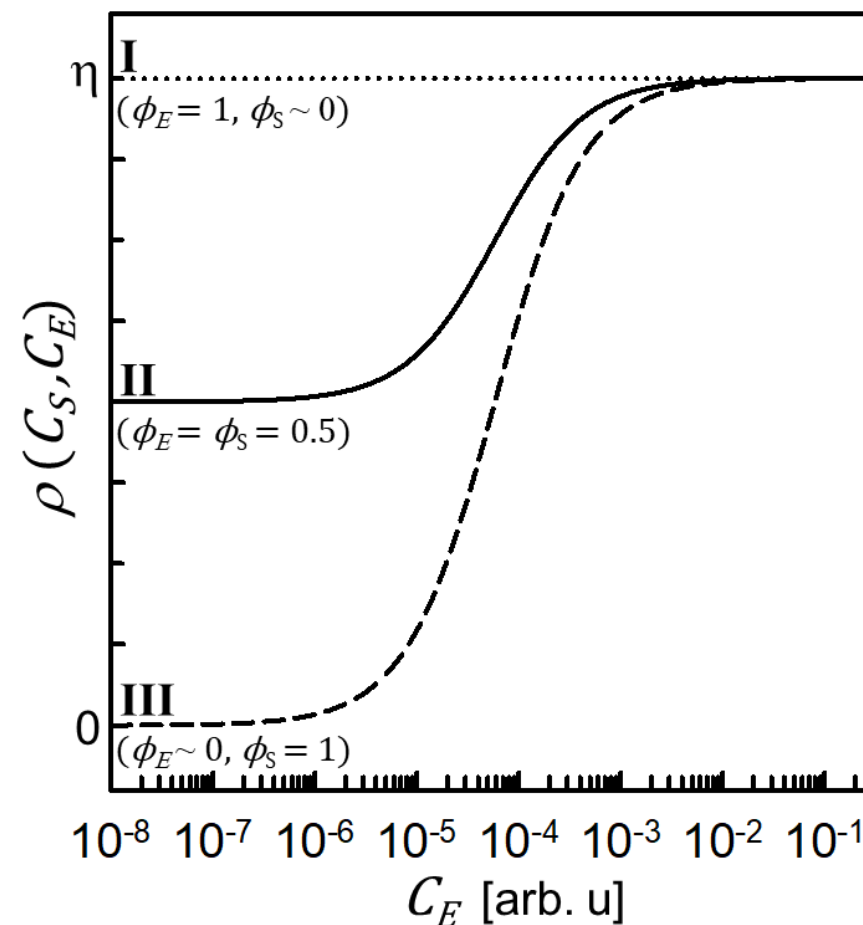
$$\phi_S = \frac{\alpha C_S}{\alpha C_S + \beta C_E + \sigma} \quad \phi_E = \frac{\beta C_E}{\alpha C_S + \beta C_E + \sigma}$$

Radiosensitization Effect

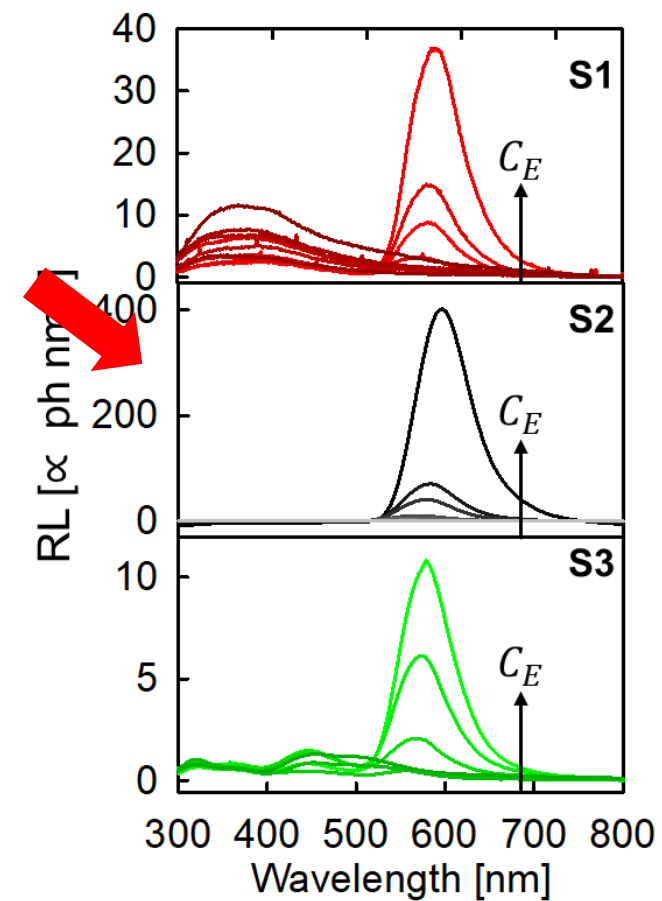
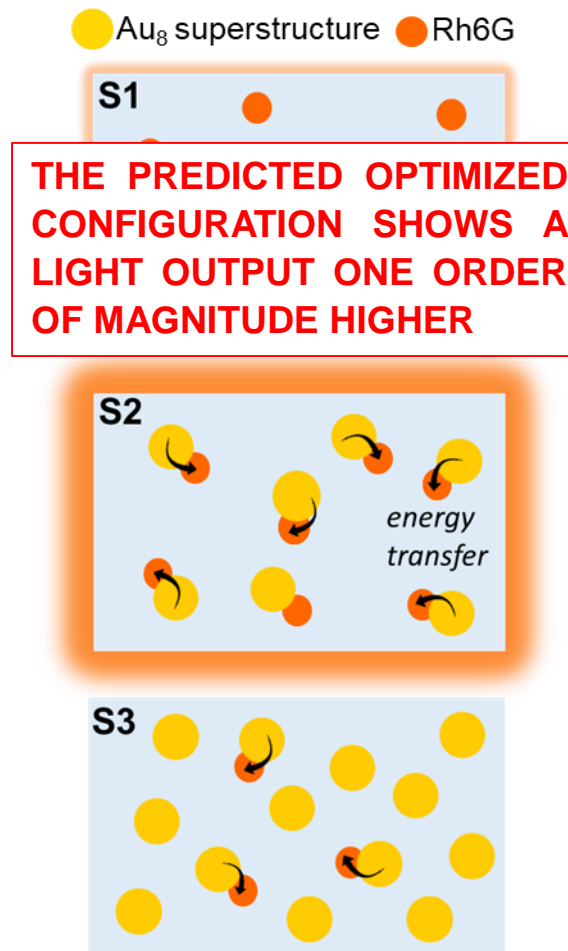
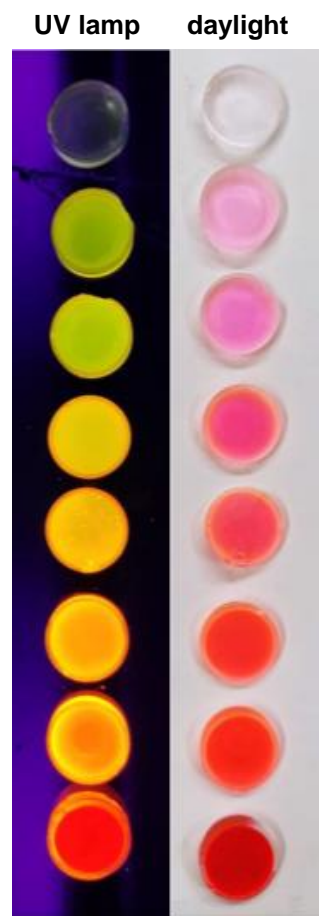
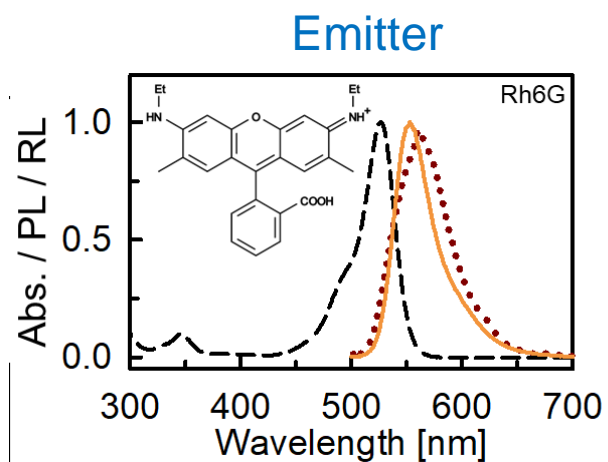
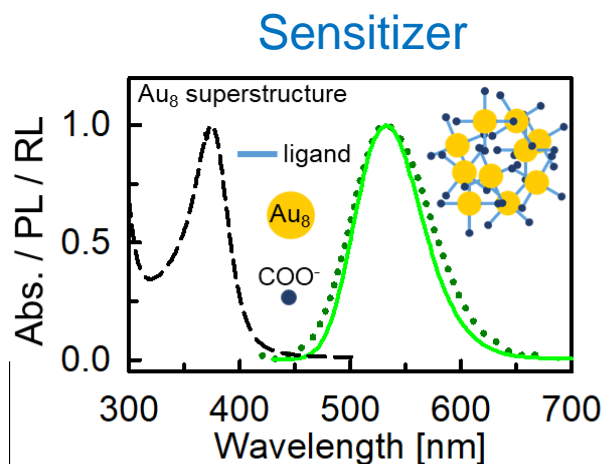
$$\rho = (\phi_S \phi_{ET} + \phi_E) \eta = \varepsilon(C_S, C_E) \eta \quad \eta = \frac{N - N_0}{N_0}$$

Sens / Emitt.
Interaction

Enhancement of
charges production

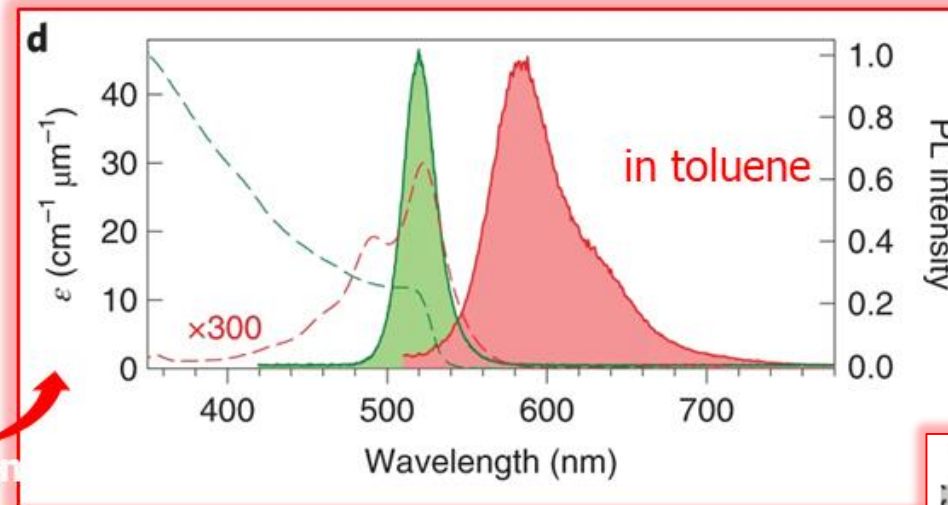
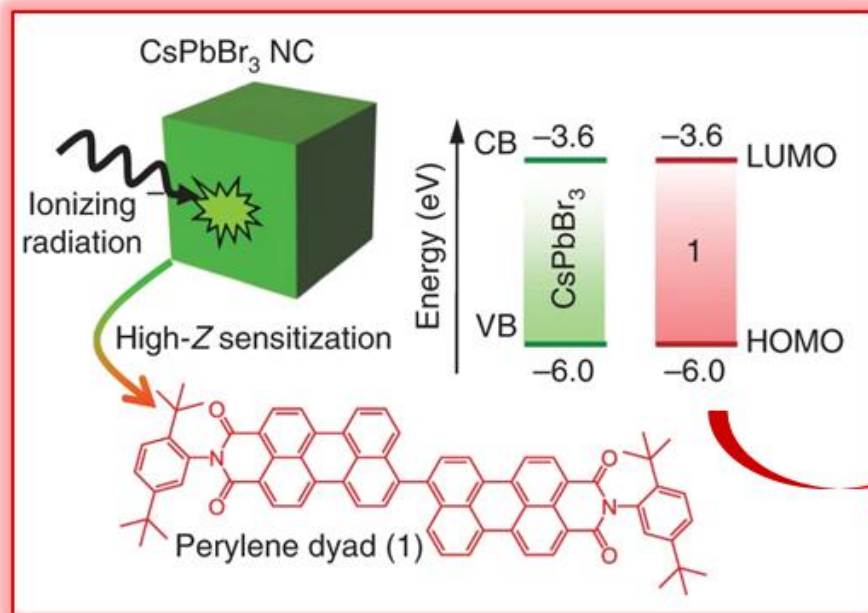


2. SCINTILLATION IN NANOCOMPOSITES



3. NANOCOMPOSITES TO TAILOR EMISSION PROPERTIES.

Perovskite nanocrystals based composite scintillators

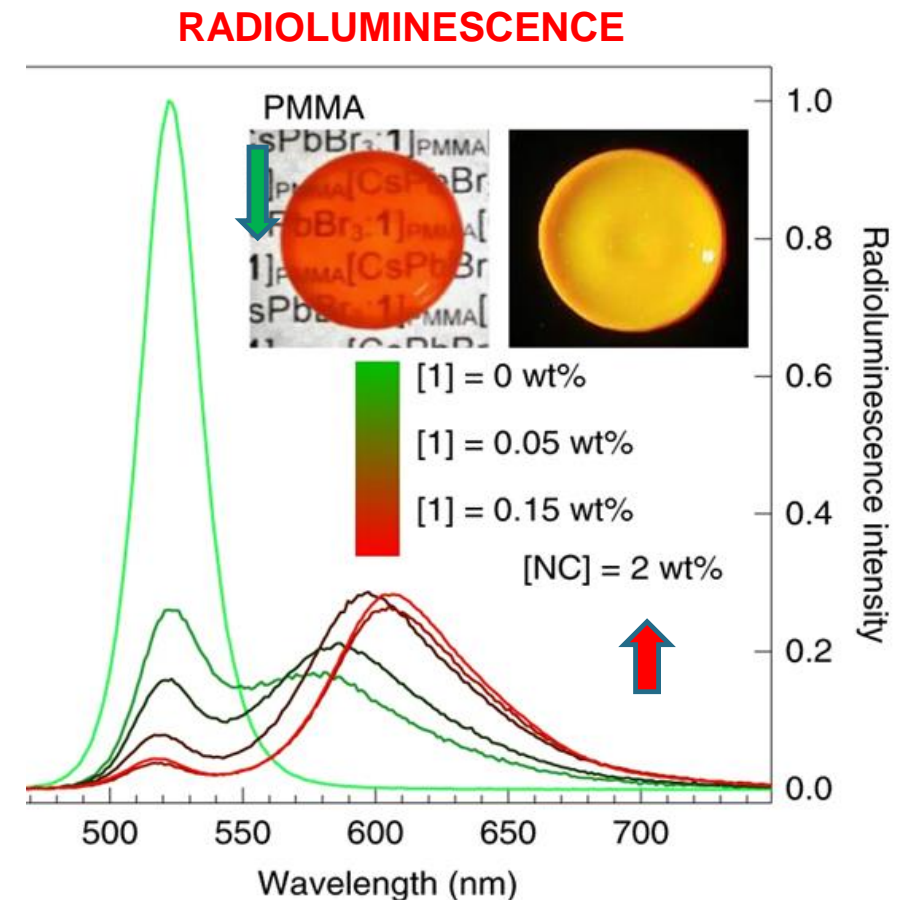


NC 2.0 wt% : Dye 0.15 wt% in PMMA



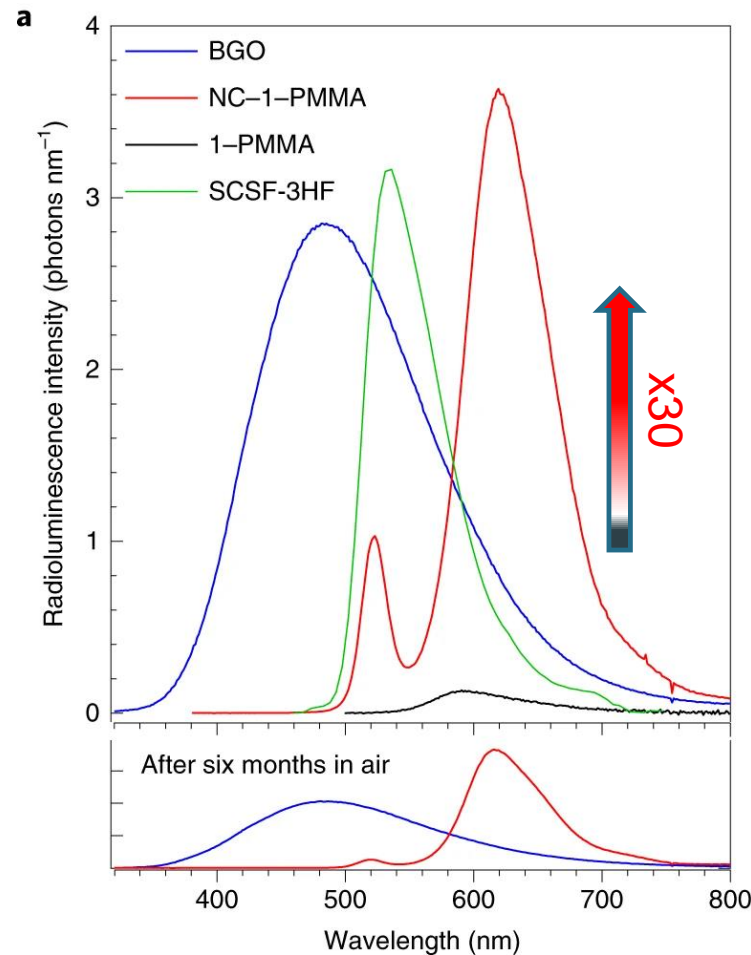
3. NANOCOMPOSITES TO TAILOR EMISSION PROPERTIES.

1. **CsPbBr₃** (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

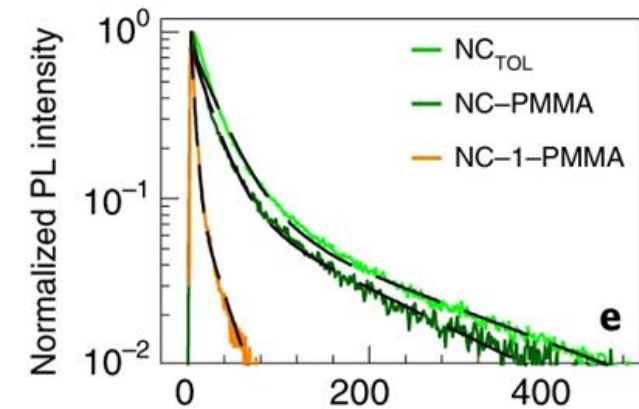


3. NANOCOMPOSITES TO TAILOR EMISSION PROPERTIES.

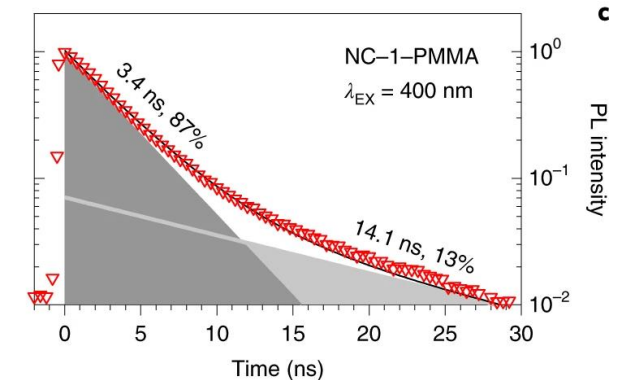
- RL intensity of the nanocomposite is comparable to that of the commercial scintillators
- Estimated LY of NC-1-PMMA nanocomposite comparable to ~9,000 photons/MeV
- **RL of 1 is 30-fold stronger in the nanocomposite → effectiveness of sensitization**
- Considering the fast decay time of the nanocomposite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



Sensitizer to emitter energy transfer OK!

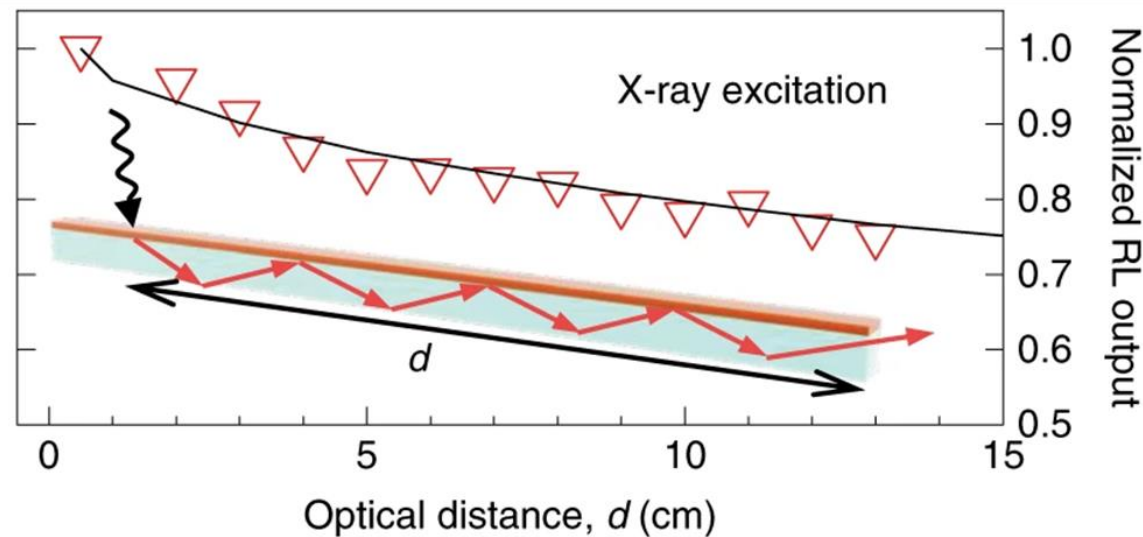


Mostly fast emission from dyes OK!



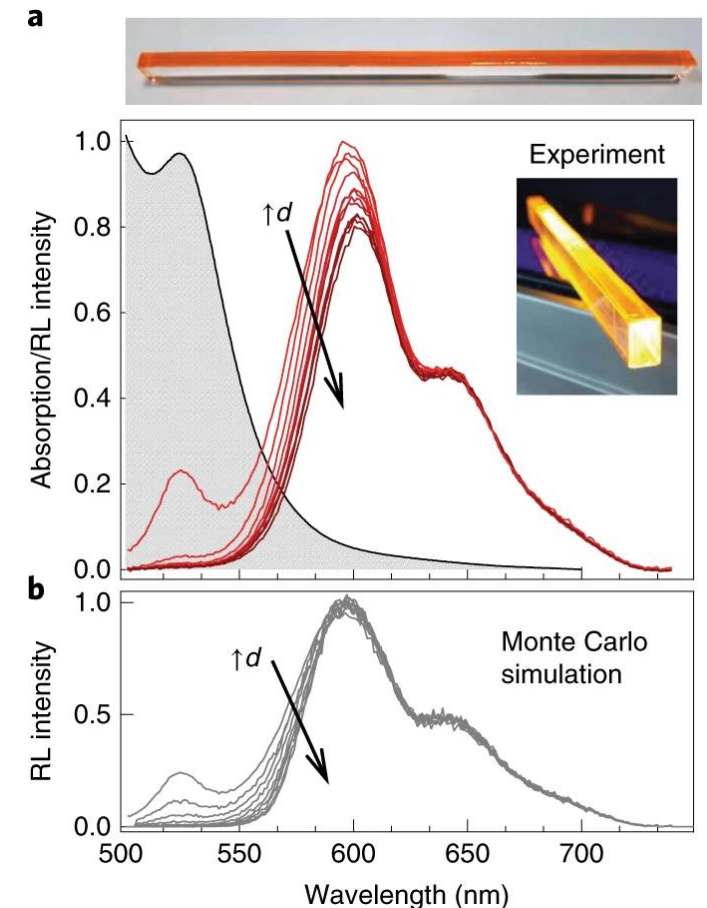
3. NANOCOMPOSITES TO TAILOR EMISSION PROPERTIES.

Sensitization → low emitters concentration → reabsorption-free scintillator



Intensity small drop ($\sim 25\%$) 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*

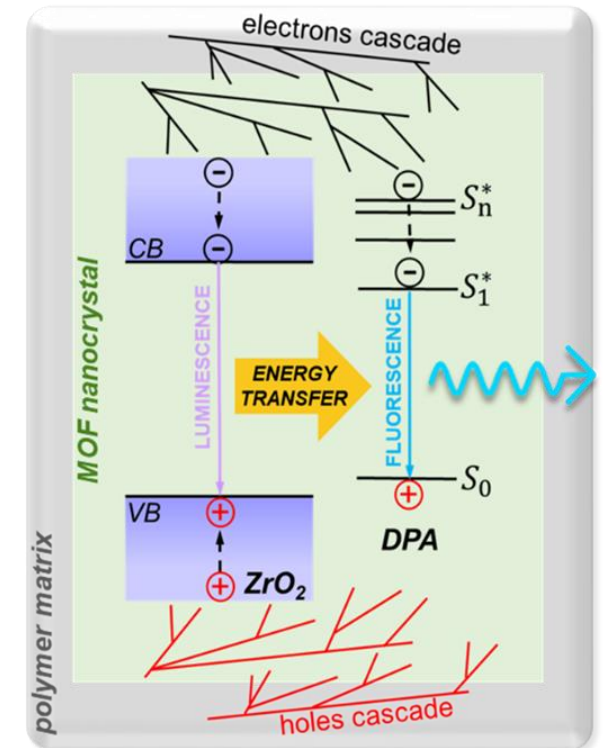
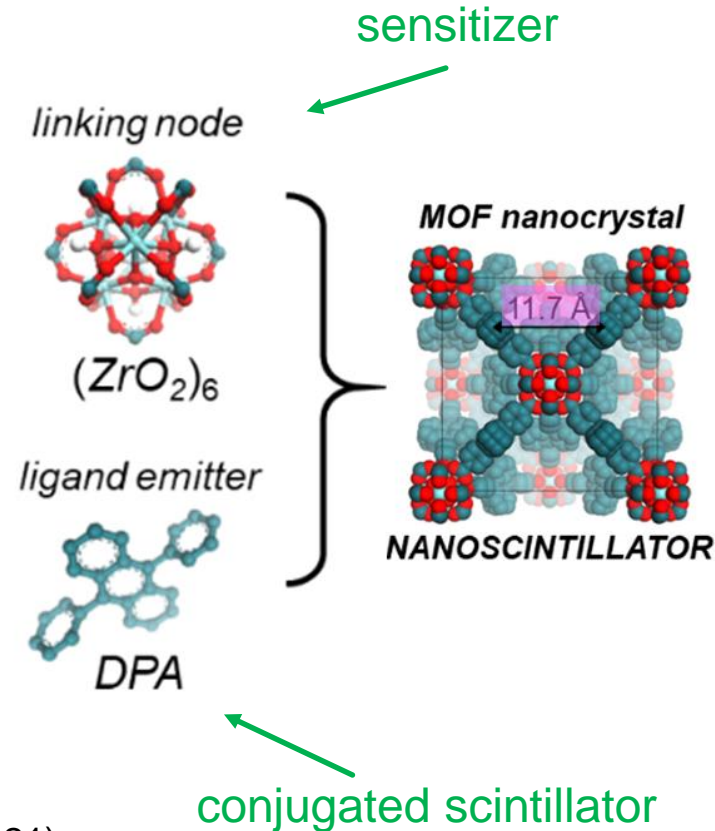


3. NANOCOMPOSITES TO TAILOR EMISSION PROPERTIES.

MOF nanocrystals based composite scintillators

MOF = metal organic framework crystalline systems

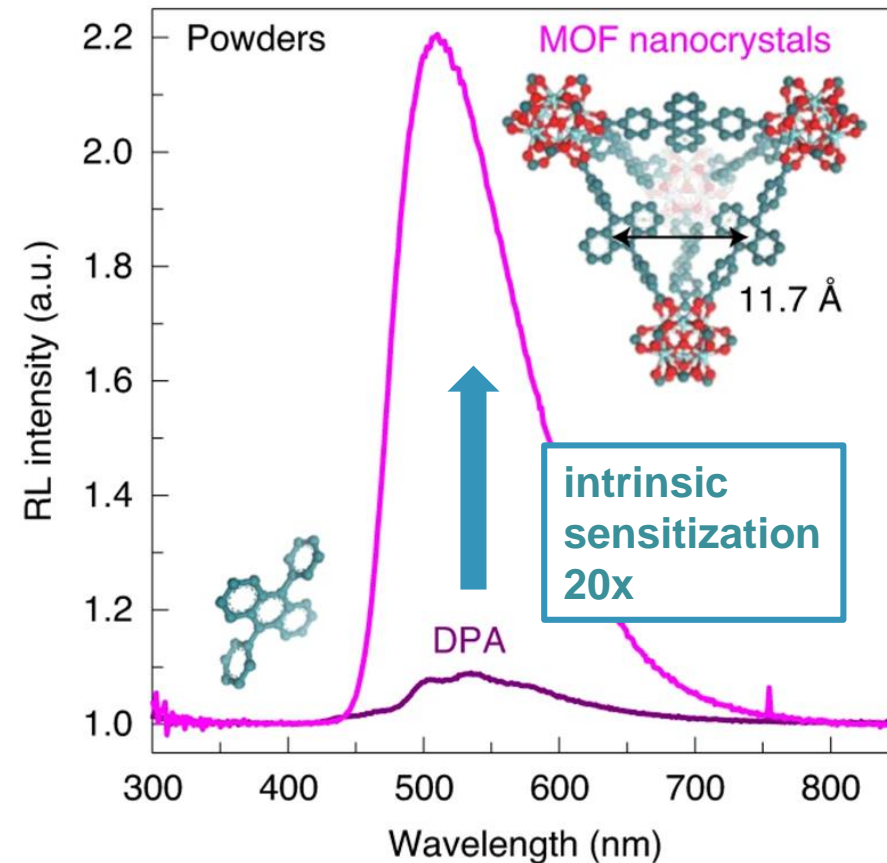
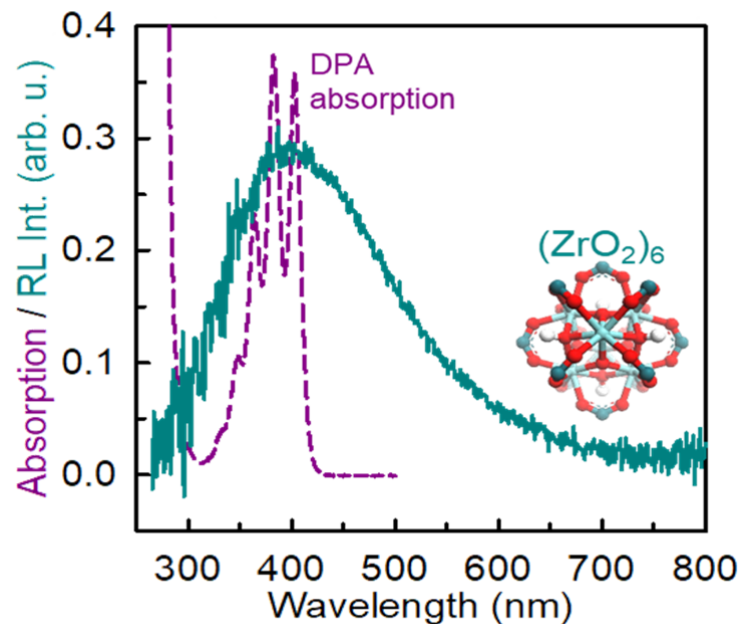
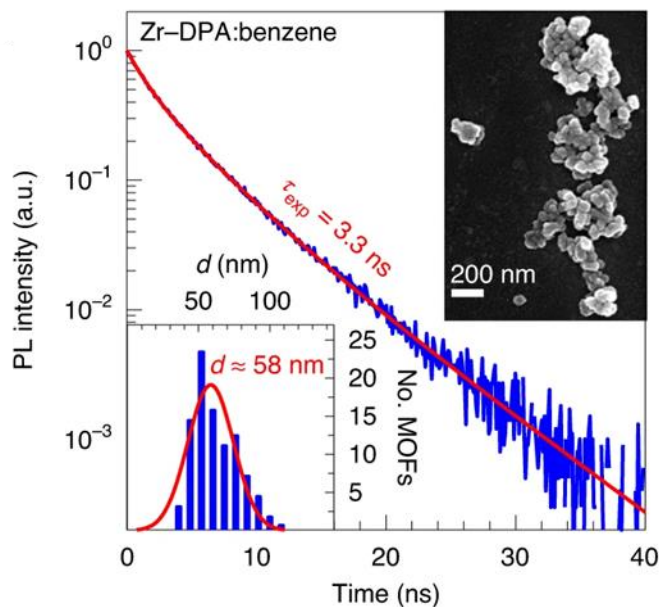
- Tunable structure/composition
- Cost effective synthesis and processing
- MOF architecture preserve the properties of constituent fluorophore



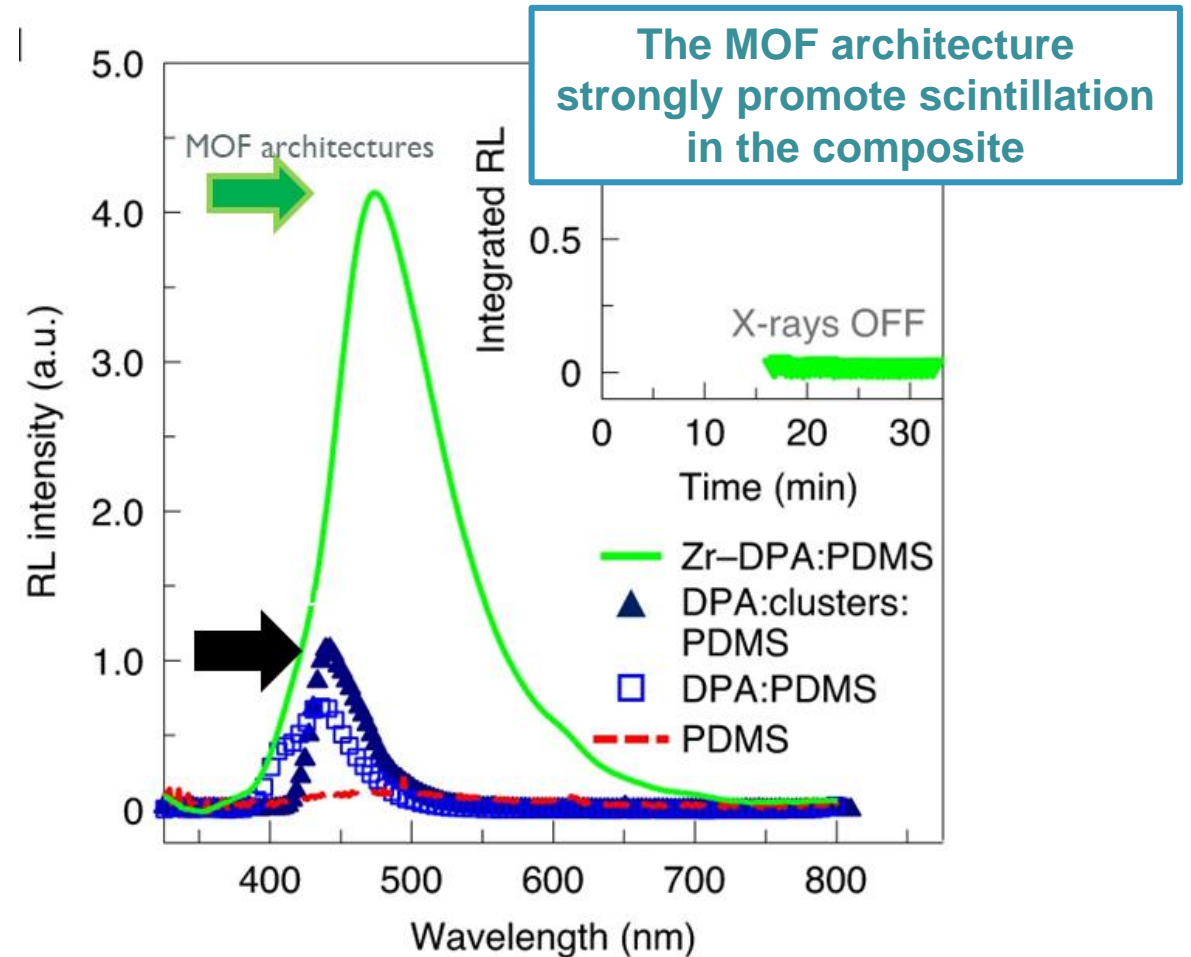
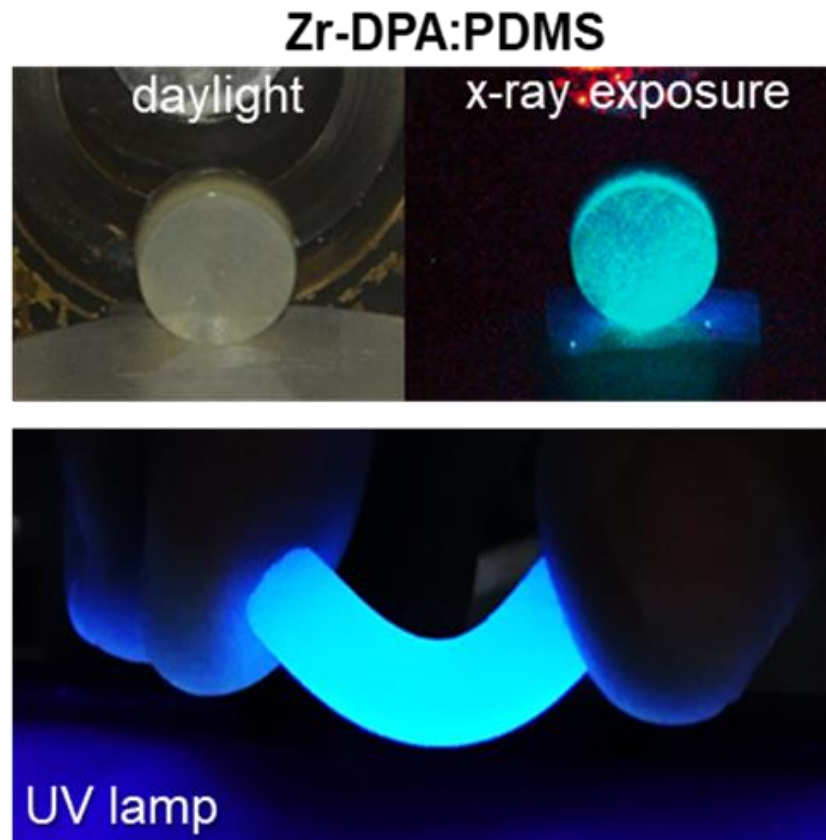
3. NANOCOMPOSITES TO TAILOR EMISSION PROPERTIES.

- **MOF: zirconium oxo-hydroxy as heavy node + organic scintillator (DPA) as ligand** (QY 96%, $t=6$ ns 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}

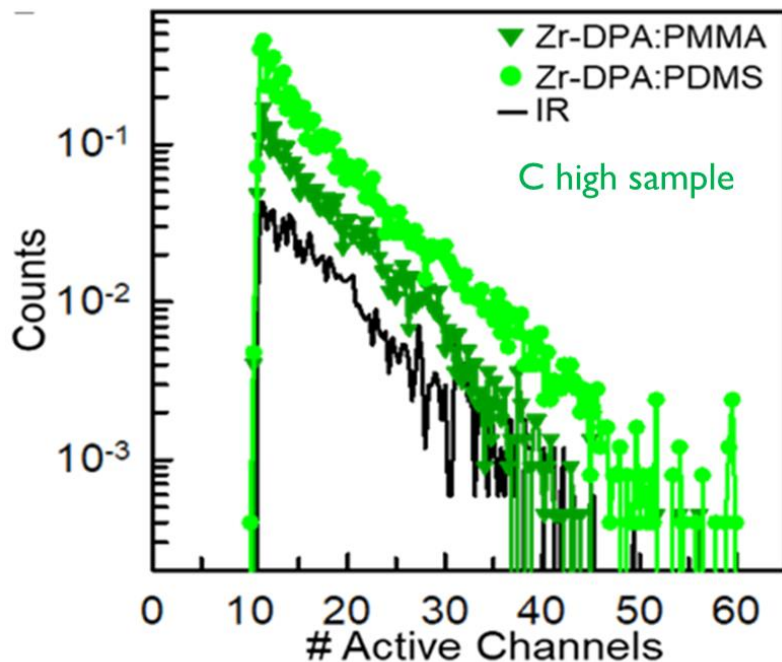


3. NANOCOMPOSITES TO TAILOR EMISSION PROPERTIES.

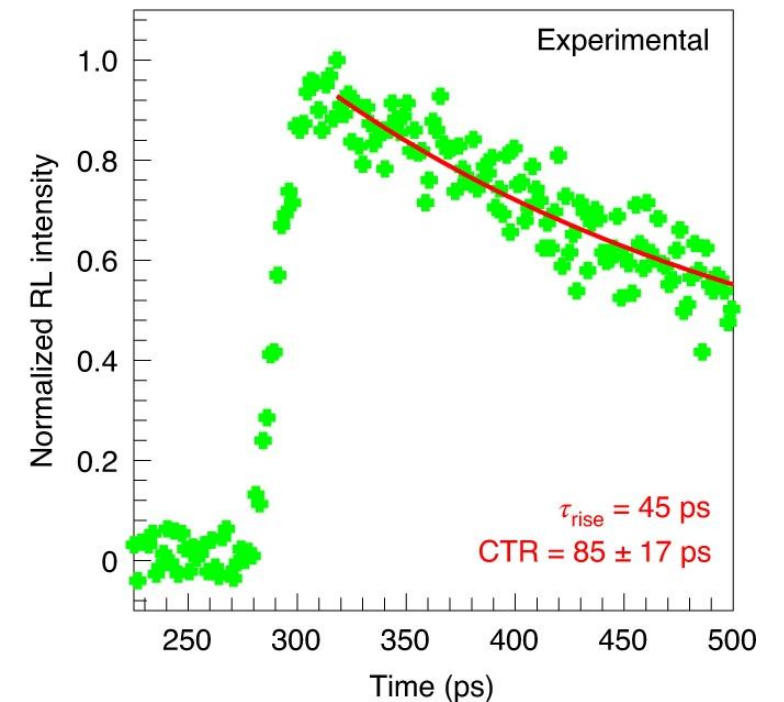
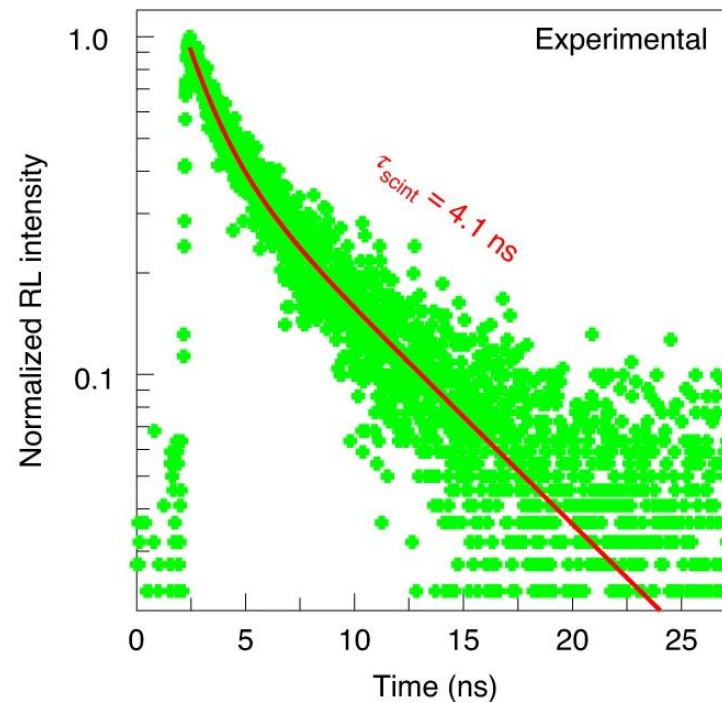


3. NANOCOMPOSITES TO TAILOR EMISSION PROPERTIES.

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



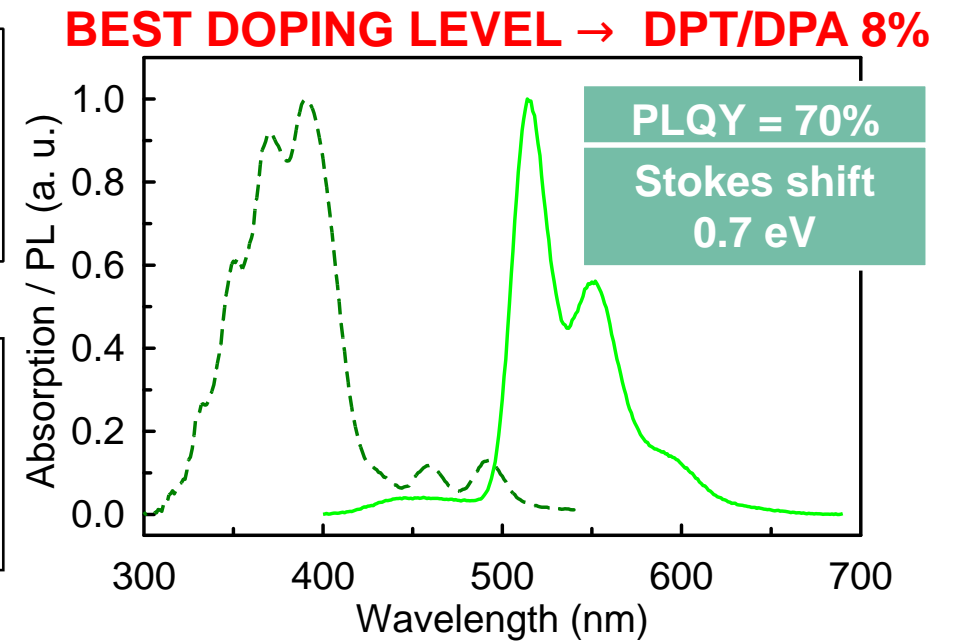
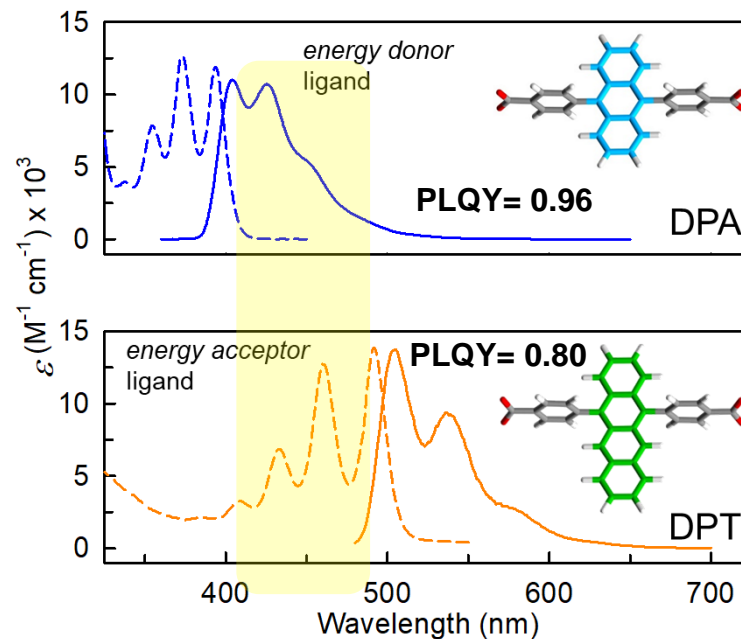
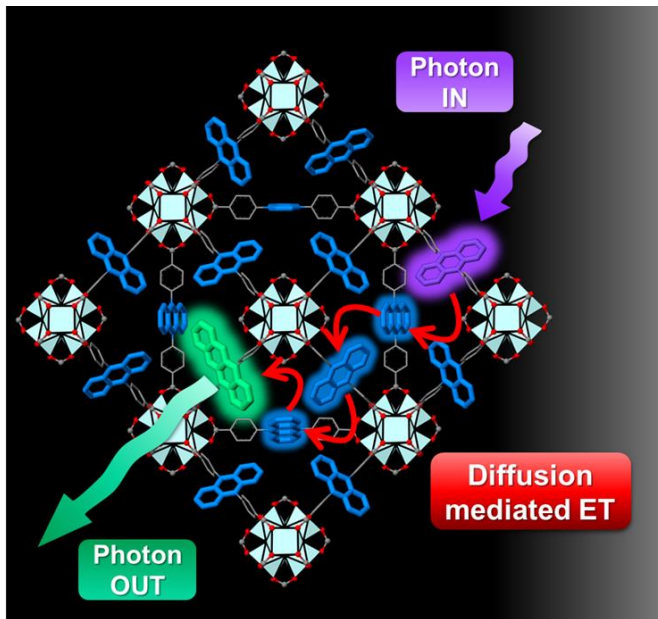
Scintillation dynamics: fast rise, fast decay



3. NANOCOMPOSITES TO TAILOR EMISSION PROPERTIES.

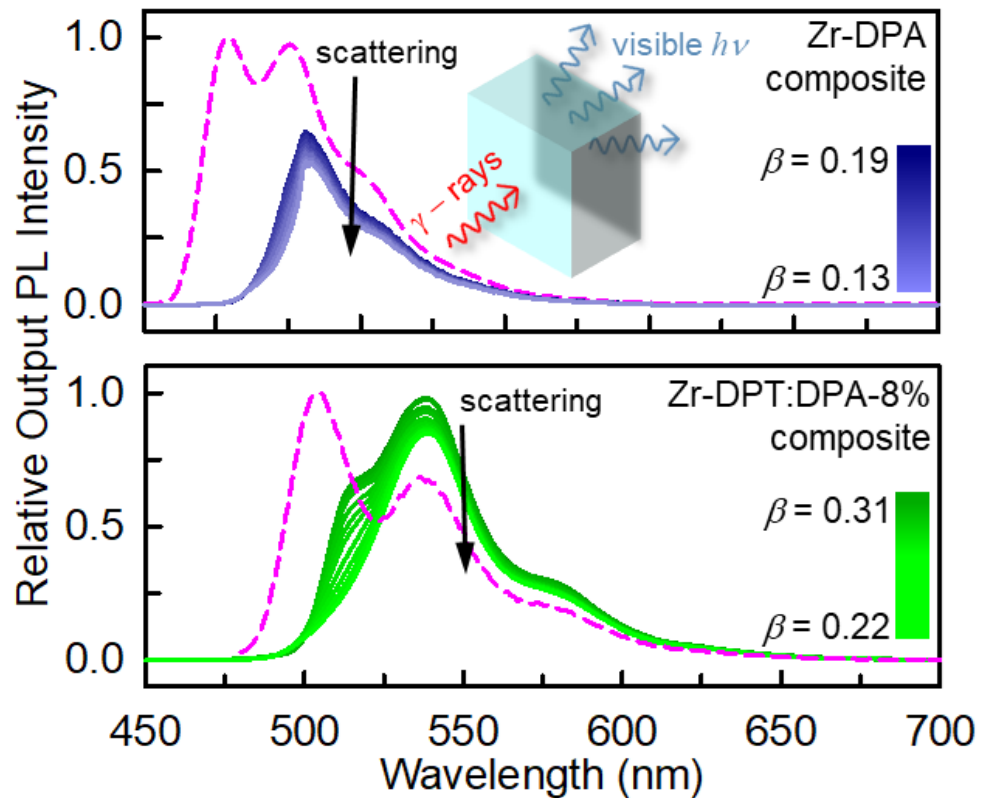
ULTRALARGE STOKES SHIFT SCINTILLATING NANOCOMPOSITES

Heteroligand Fluorescent MOF Nanocrystals

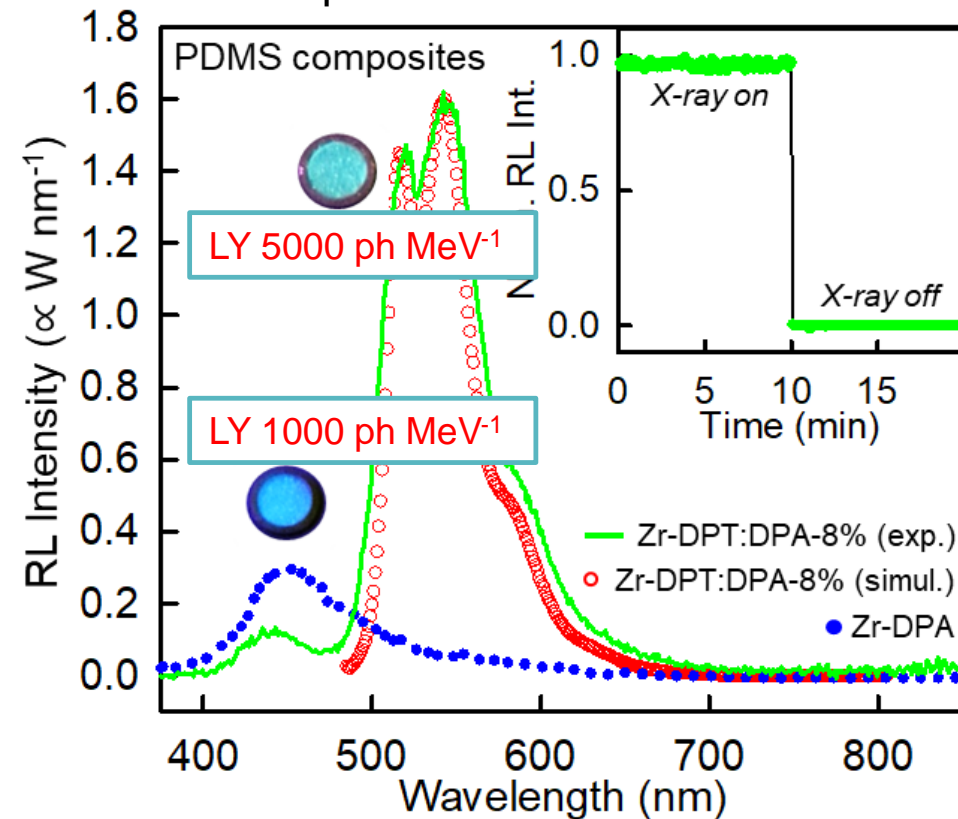


3. NANOCOMPOSITES TO TAILOR EMISSION PROPERTIES.

Theoretical light output (Monte Carlo)



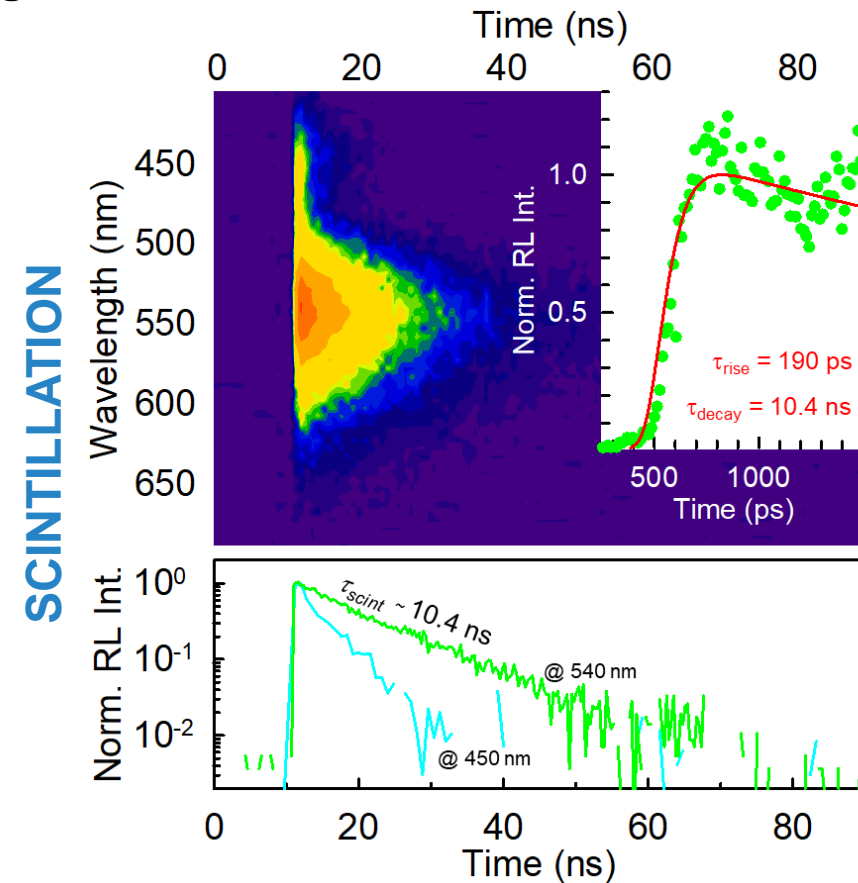
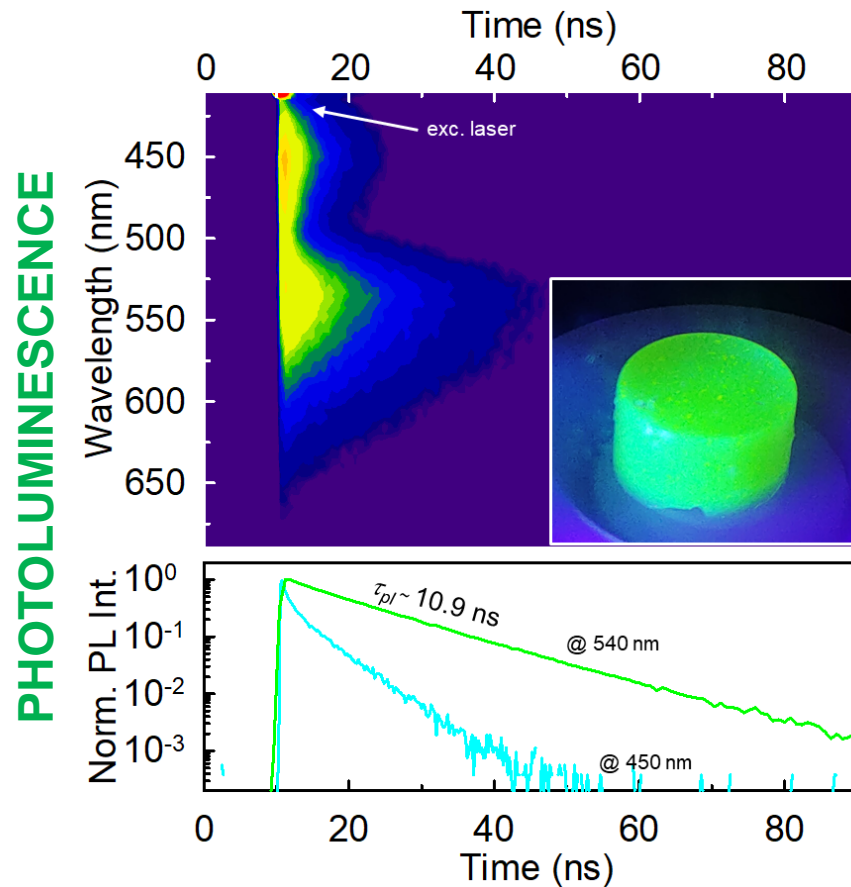
Experimental scintillation LY



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

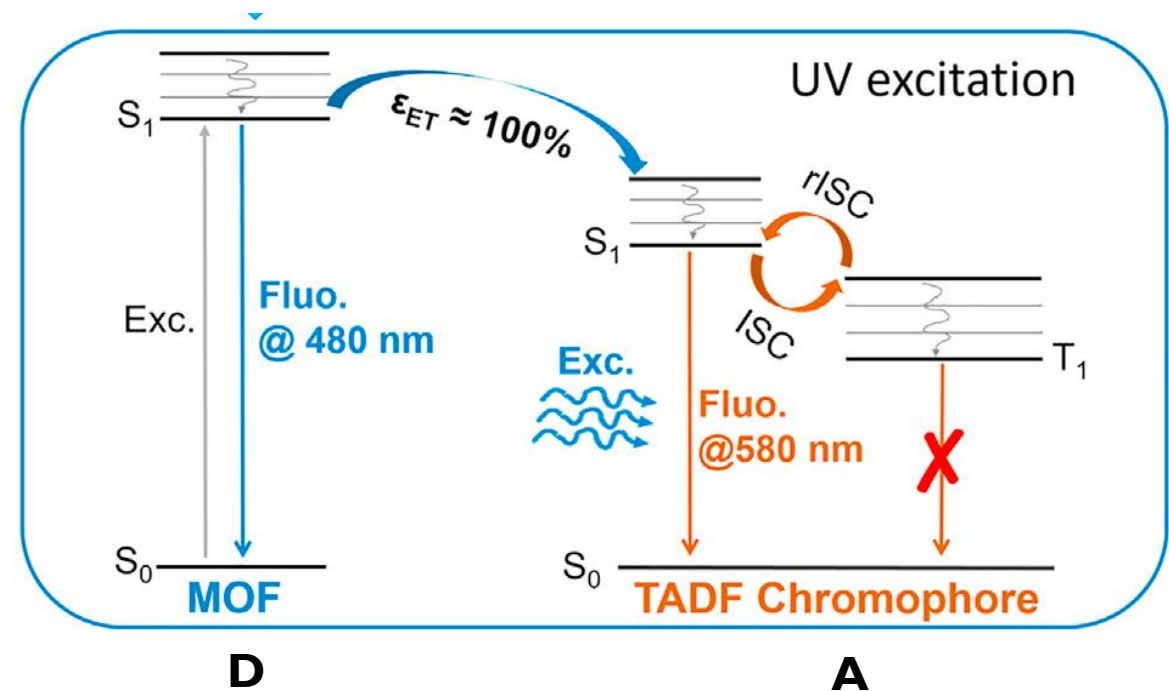
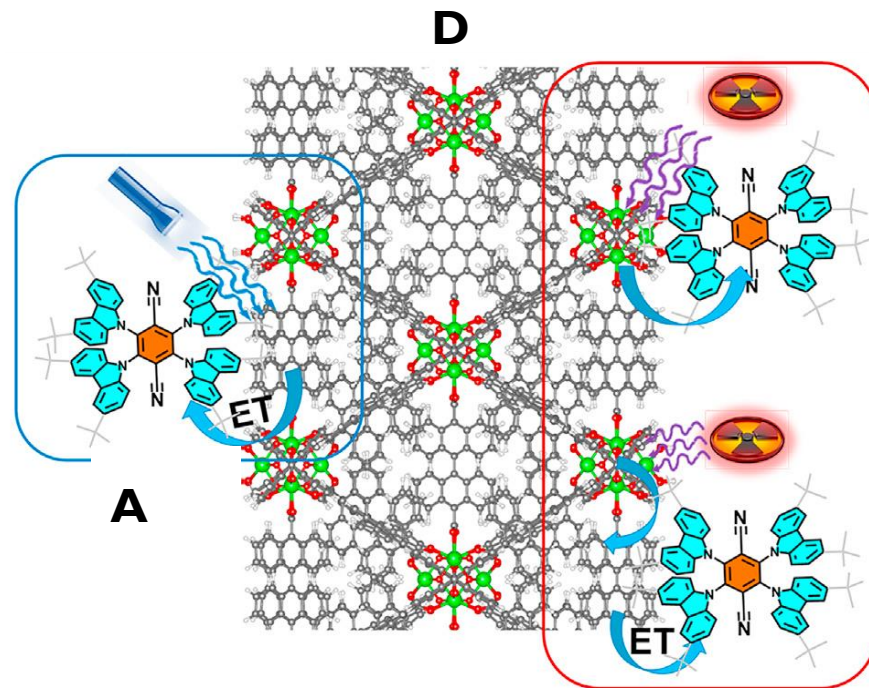


Fast scintillation with negligible reabsorption also in bulk

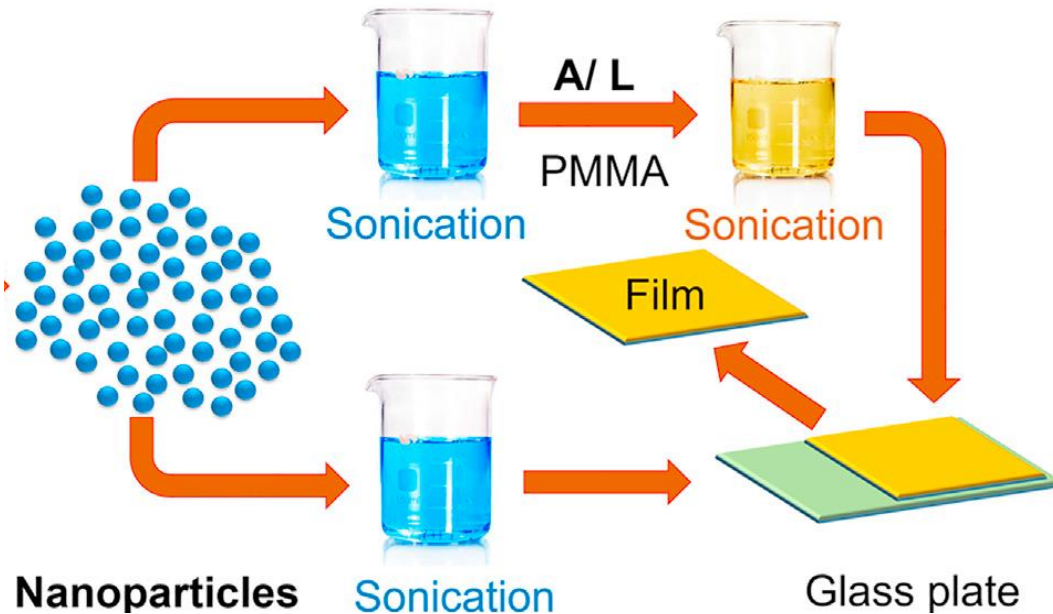
3. NANOCOMPOSITES TO TAILOR EMISSION PROPERTIES.

How to improve the sensitivity of x-ray imaging detectors

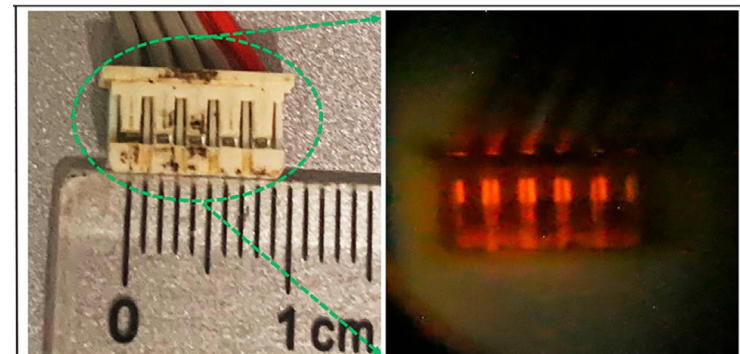
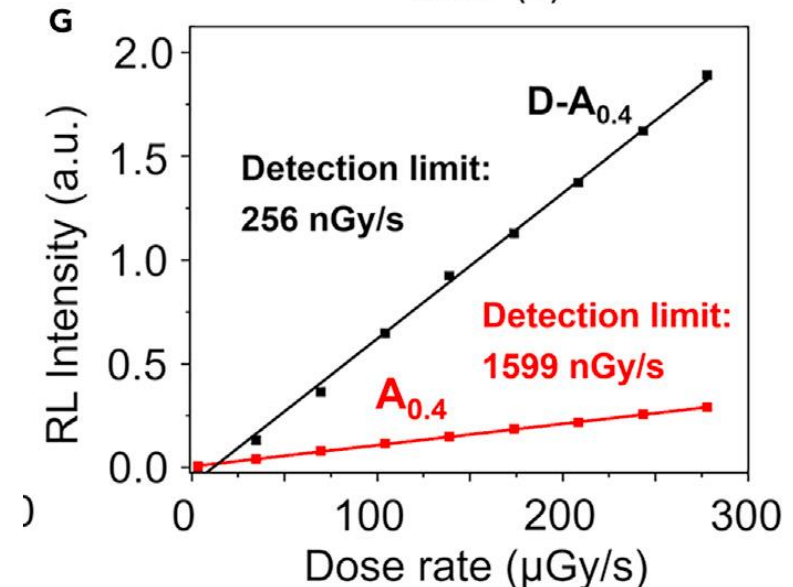
The Zr-MOF (D, donor)-TADF chromophore (A, acceptor) nanocomposite films in poly(methyl methacrylate) (PMMA)



3. NANOCOMPOSITES TO TAILOR EMISSION PROPERTIES.



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



4. NANOCOMPOSITES TO EXPLOIT STRUCTURAL PROPERTIES.

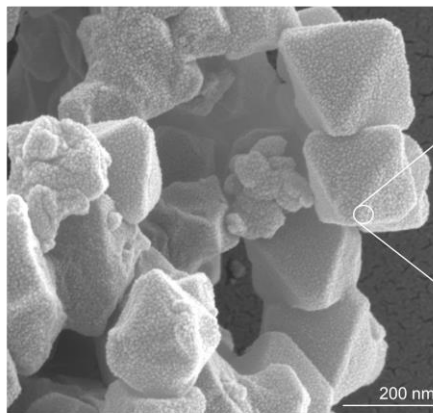


This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 899293

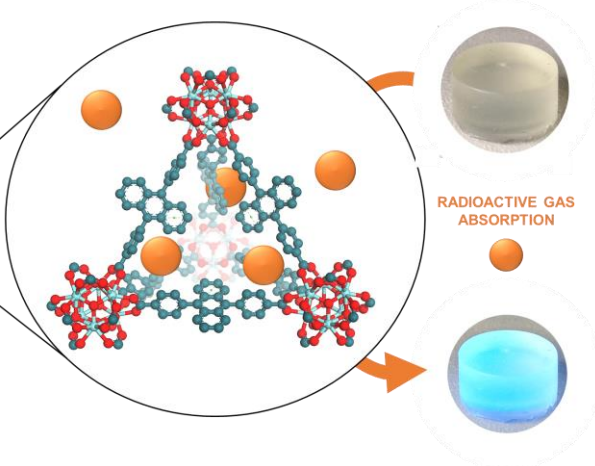
Goal:

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

MOF = POROUS NANOSCINTILLATORS



POROUS HOST



The scintillating composite sponge

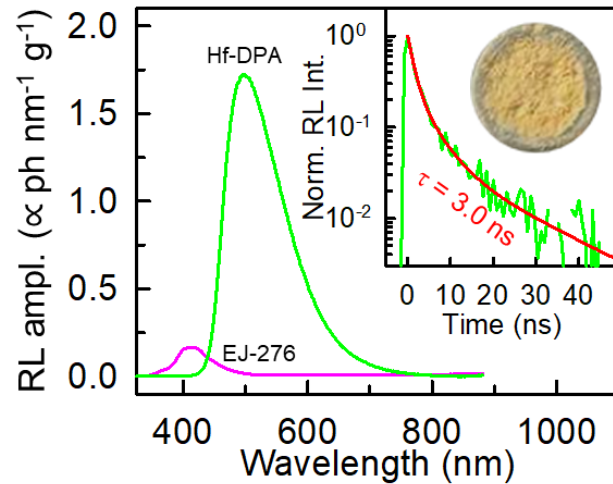
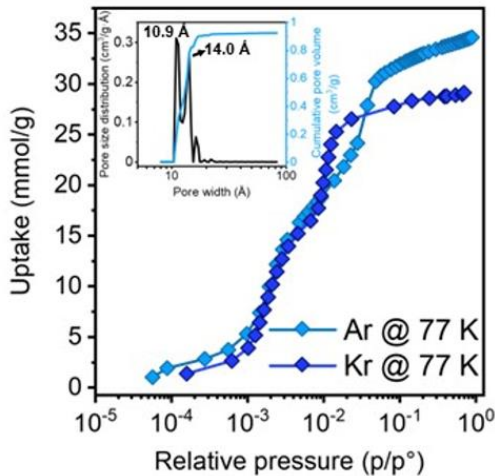
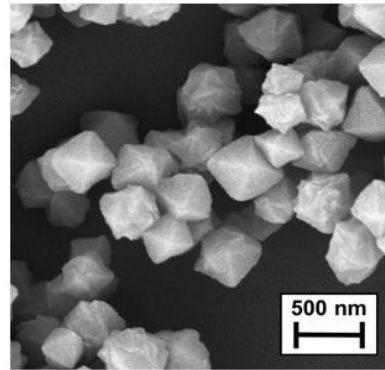


porous scintillators to capture and concentrate β radionuclides

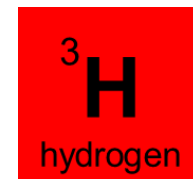
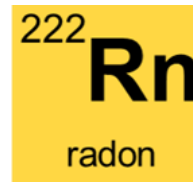
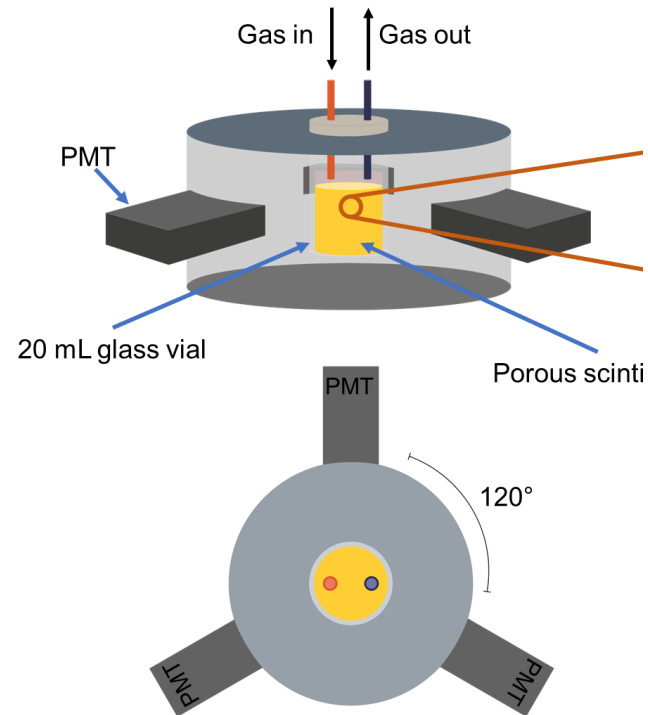
4. NANOCOMPOSITES TO EXPLOIT STRUCTURAL PROPERTIES.

Hafnium-based DPA MOFs

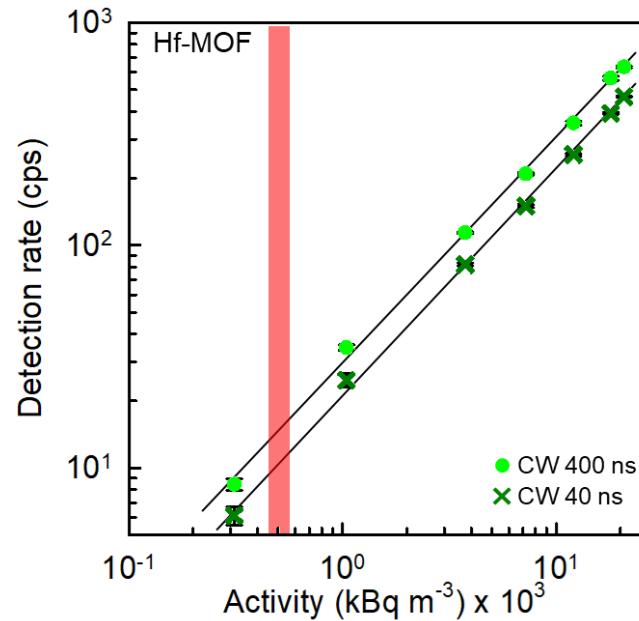
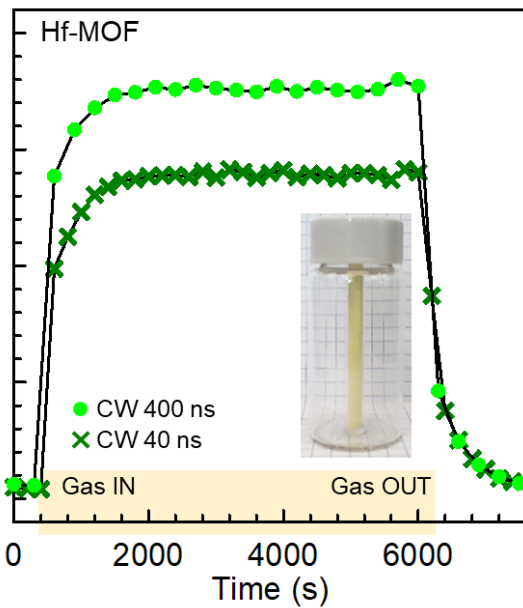
- **Higher Z**
- **Ideal pores size**
- **Fast emission TCR**



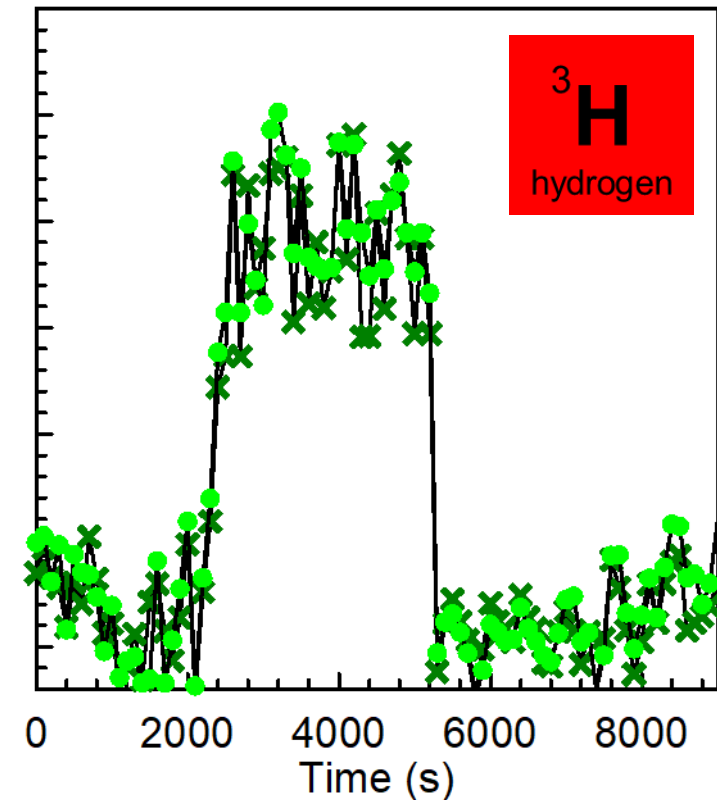
Time Coincidence Detection



4. NANOCOMPOSITES TO EXPLOIT STRUCTURAL PROPERTIES.



3x signal than reference



⁸⁵Kr
krypton

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

4. NANOCOMPOSITES TO EXPLOIT STRUCTURAL PROPERTIES.

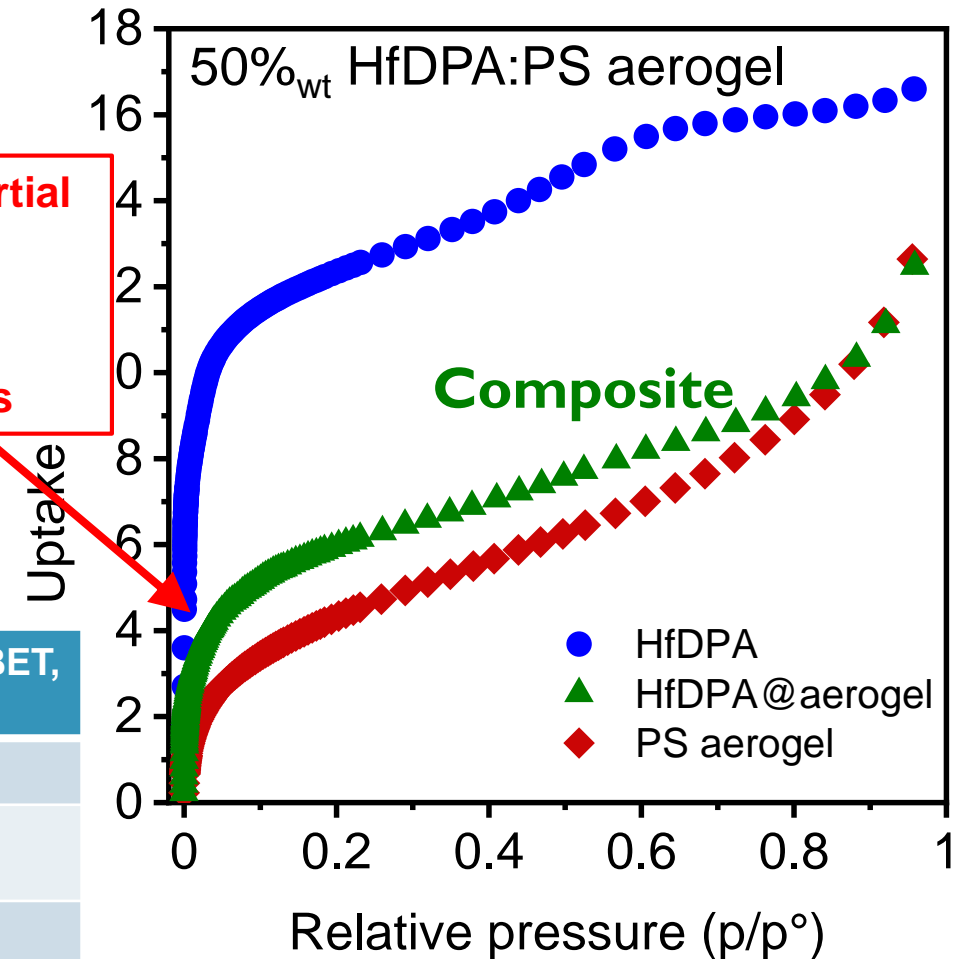
COMPOSITE: composite **POLYSTYRENE AEROGEL+ MOF**
(produced by Nano Active Film srl)



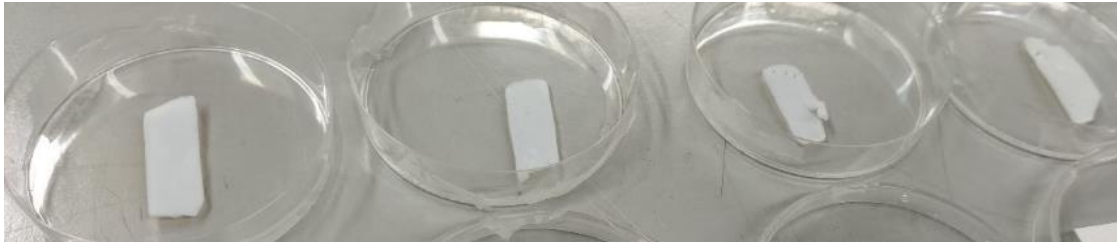
Increased uptake at low partial pressure

Higher microporosity: adsorption in MOF pores

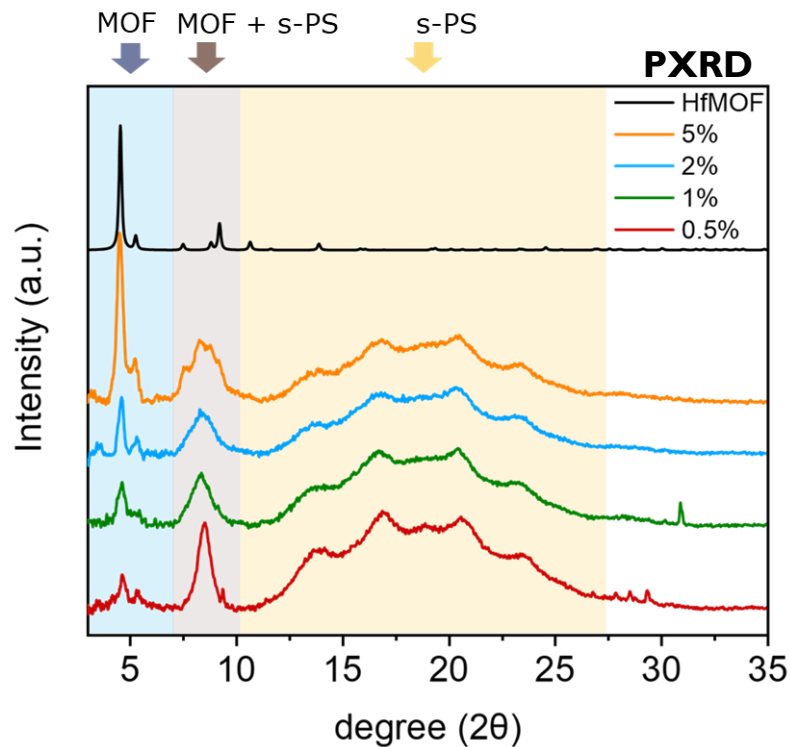
Sample	Surface area (BET, m ² /g)
s-PS aerogel	340
HfDPA@aerogel	500
HfDPA 4.1	1050



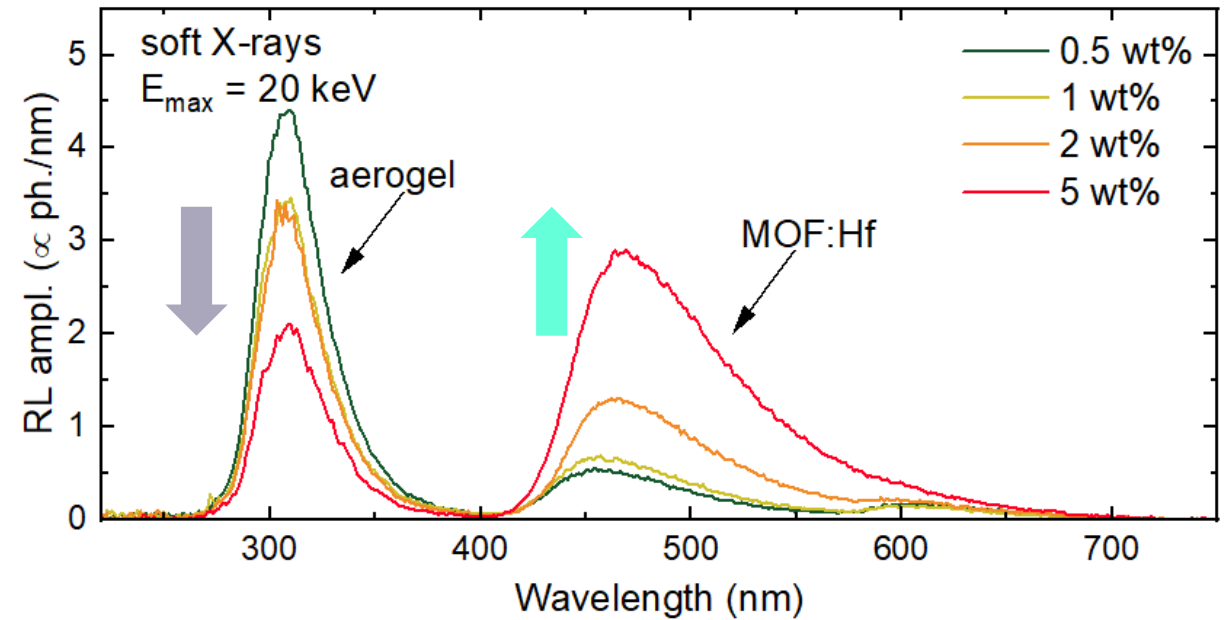
4. NANOCOMPOSITES TO EXPLOIT STRUCTURAL PROPERTIES.



Increase MOF loading



POROUS COMPOSITES RADIOLUMINESCENCE



Gas detection: *WORK IN PROGRESS*

5. CONCLUSIONS

- ❑ The scintillation in composite materials can be achieved 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 heterostructures and porous systems are ongoing**

1° WARNING: the composite development 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



Mr. M. Orfano
Dr. J. Perego
Dr. F. Cova
Dr. C. X. Bezuidenhout
Dr. L. Gironi
Prof. S. Bracco
Prof. P. E. Sozzani
Prof. A. Comotti
Prof. Meinardi
Prof. A. Vedda



Dr. I. Villa
Prof. M. Nikl



Mr. P. Mai
Prof. C. Dujardin



Dr. B. Sabot
Dr. P. Sylvie



Dr. F. Pagano
Dr. M. Salomoni
Dr. I. Franck
Dr. N. Kratochwil
Dr. S. Gundacker
Dr. E. Auffray



Dr. M. Antico
Prof. C. Daniel



ACKNOWLEDGMENTS: FUNDING

FROM EUROPE



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



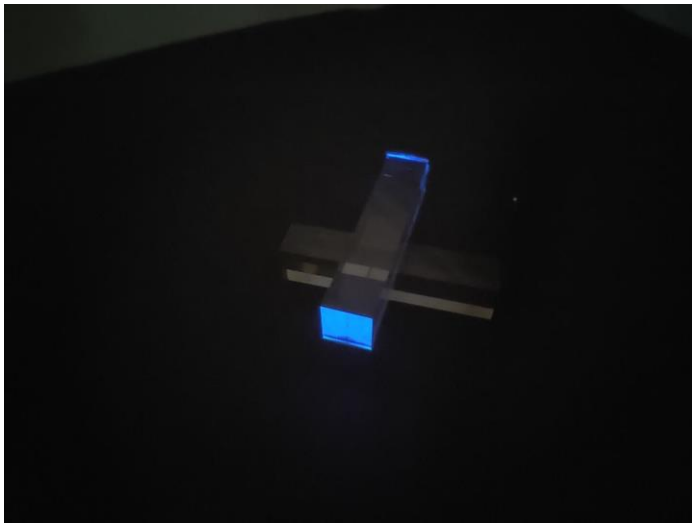
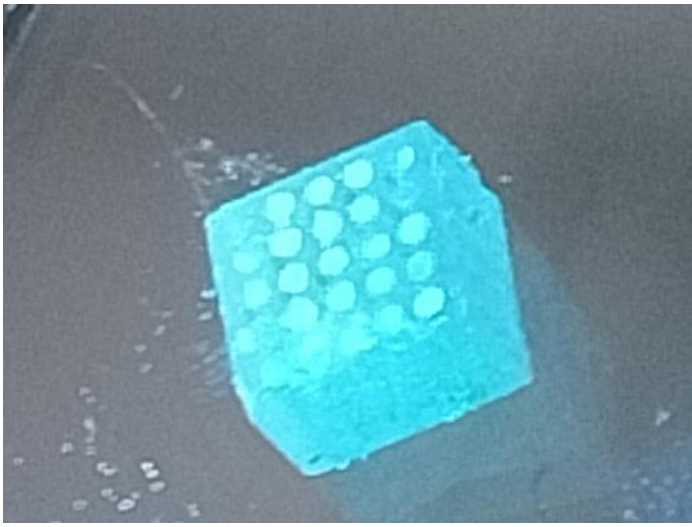
FROM ITALY



2022-2025 project SHERPA

Scintillating HEterostructures for High Resolution PET imaging





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 τ_{rise}

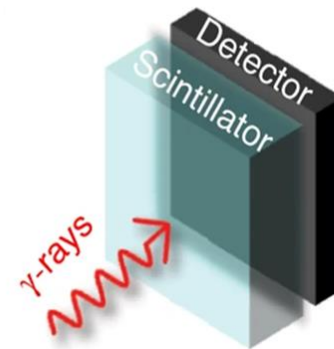
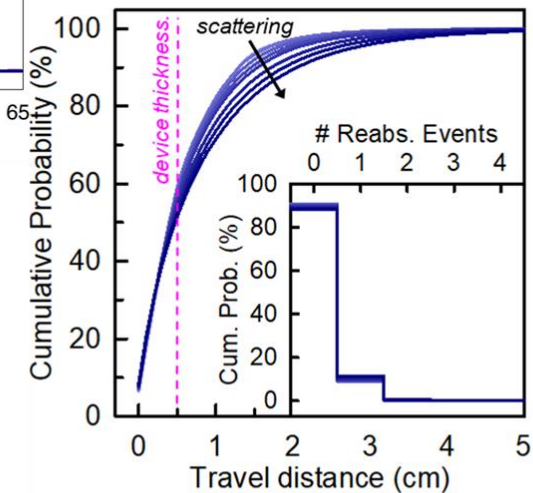
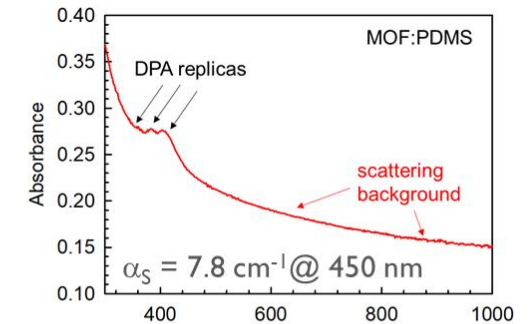
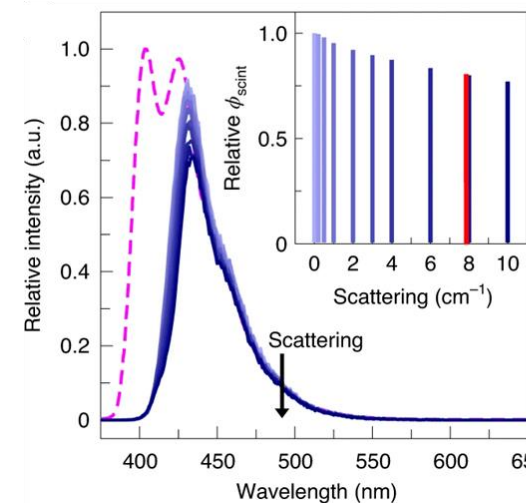
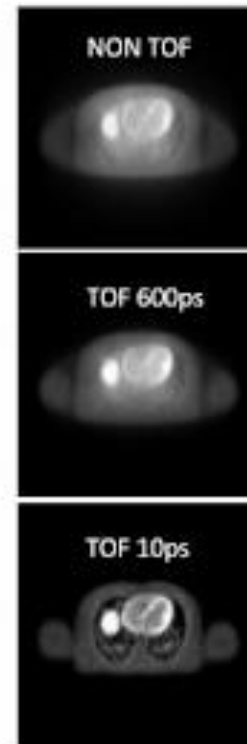
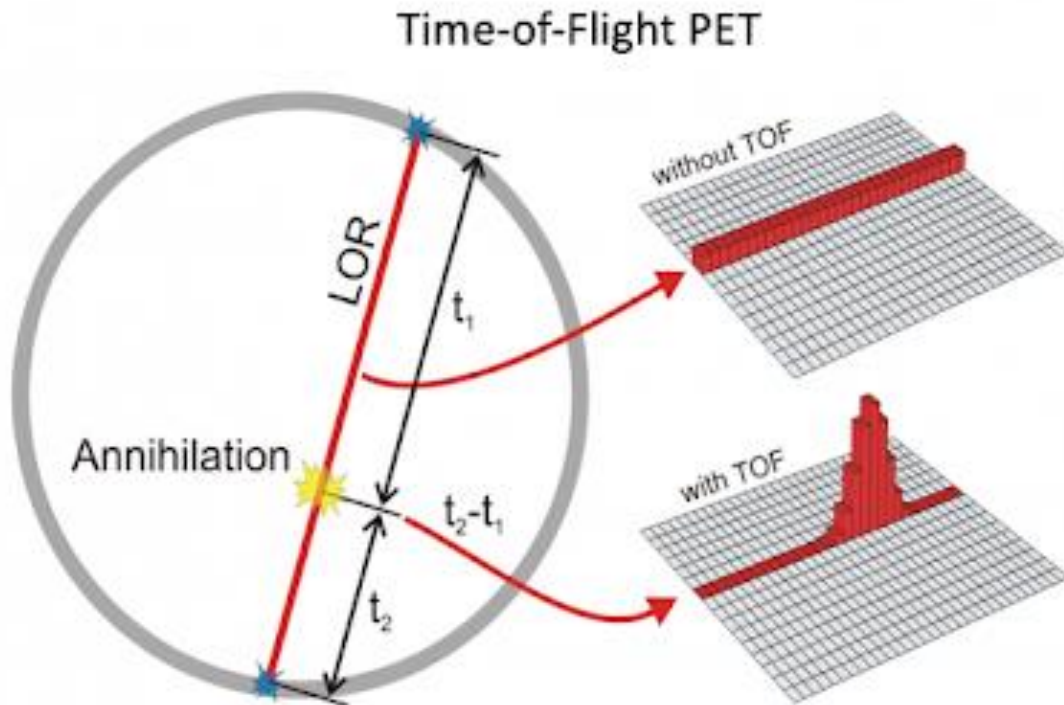


Photo-detector coupled by an index-matching material to the irradiated nanocomposite

ULTRAFAST TOF-PET REQUIRES NEW SCINTILLATORS



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

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

τ_{rise} = scintillation rise time

τ_{decay} = scintillation decay time

LY = light yield [ph/MeV] @ 511 keV

η = photo-detection efficiency

Commercial CTR = 200 ps

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)

Potentially lower PLQY
slow emission

For conjugated systems:

Phosphorescence
Charge transfer states

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

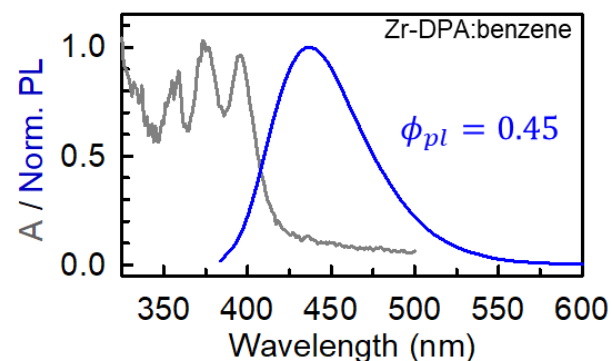
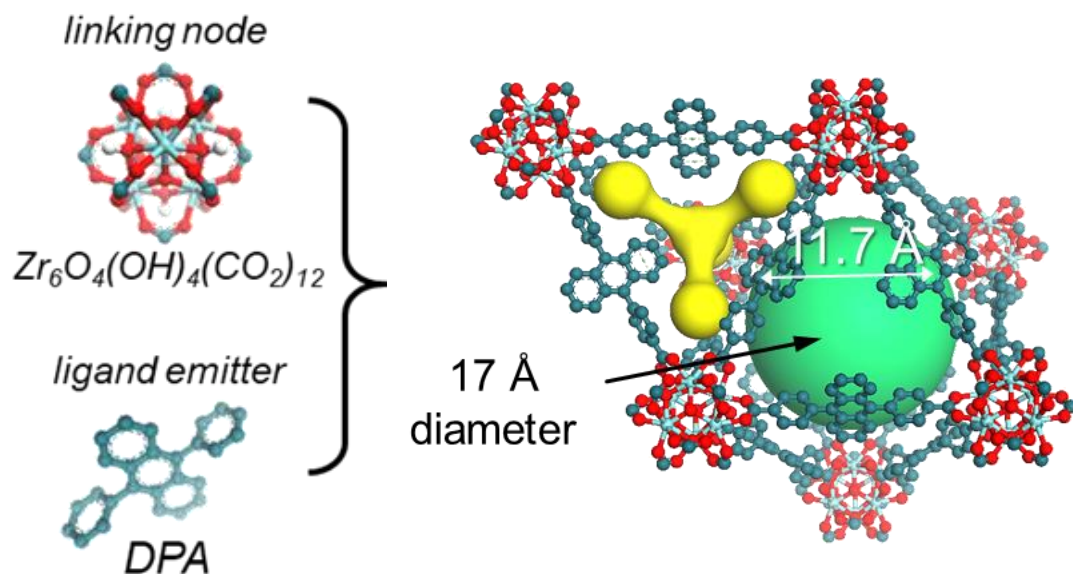
Nature Photonics **15**, 187 (2021)

~~Radiative Energy Transfer?~~

LARGE STOKES SHIFT IN MOF NANOCRYSTALS

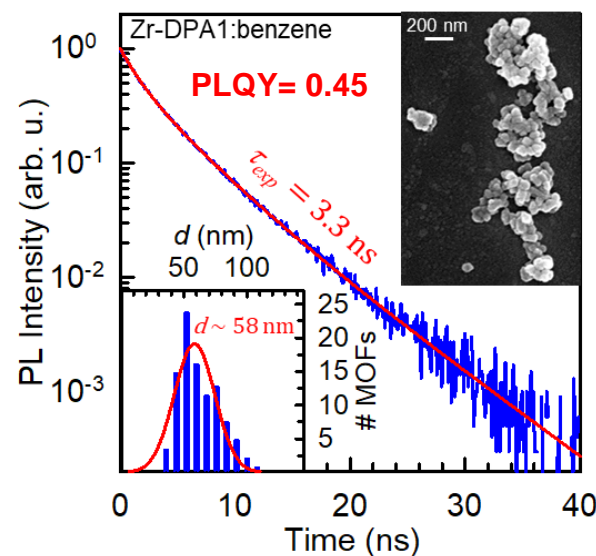
Metal-organic Frameworks

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



Scintillating MOF Nanocrystals

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



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

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

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

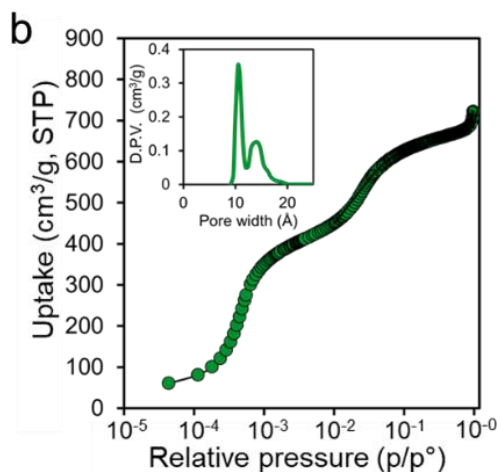
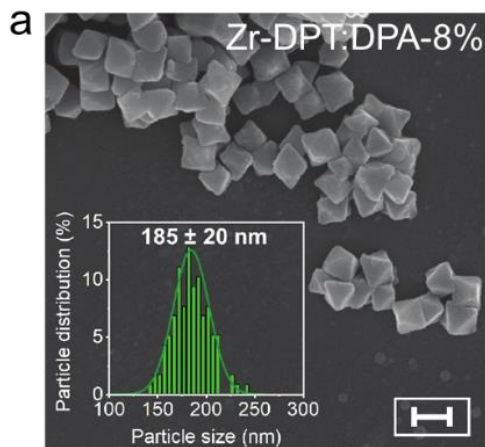
Singlet hopping rate >> Rapid diffusion limit model for ET

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

DPA-DPT energy transfer rate and yield

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

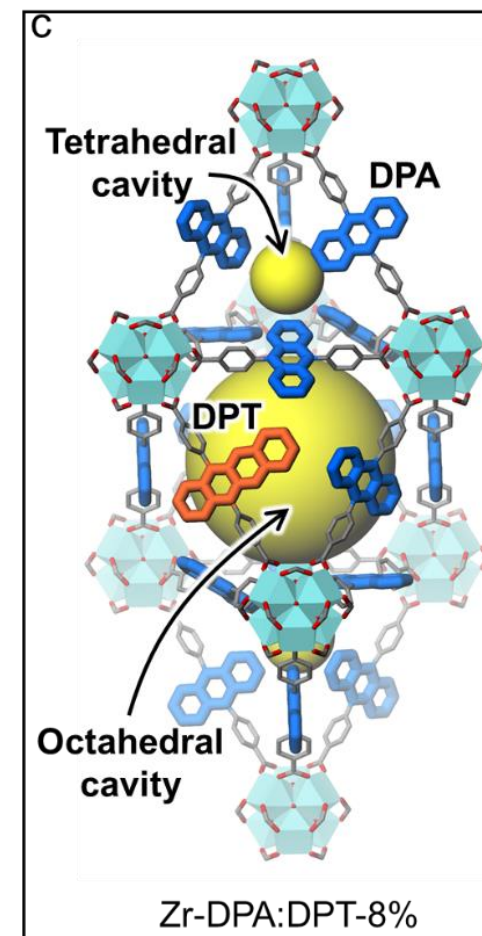
SYNTHESIS OF HETERO-LIGAND NANO-MOFs



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

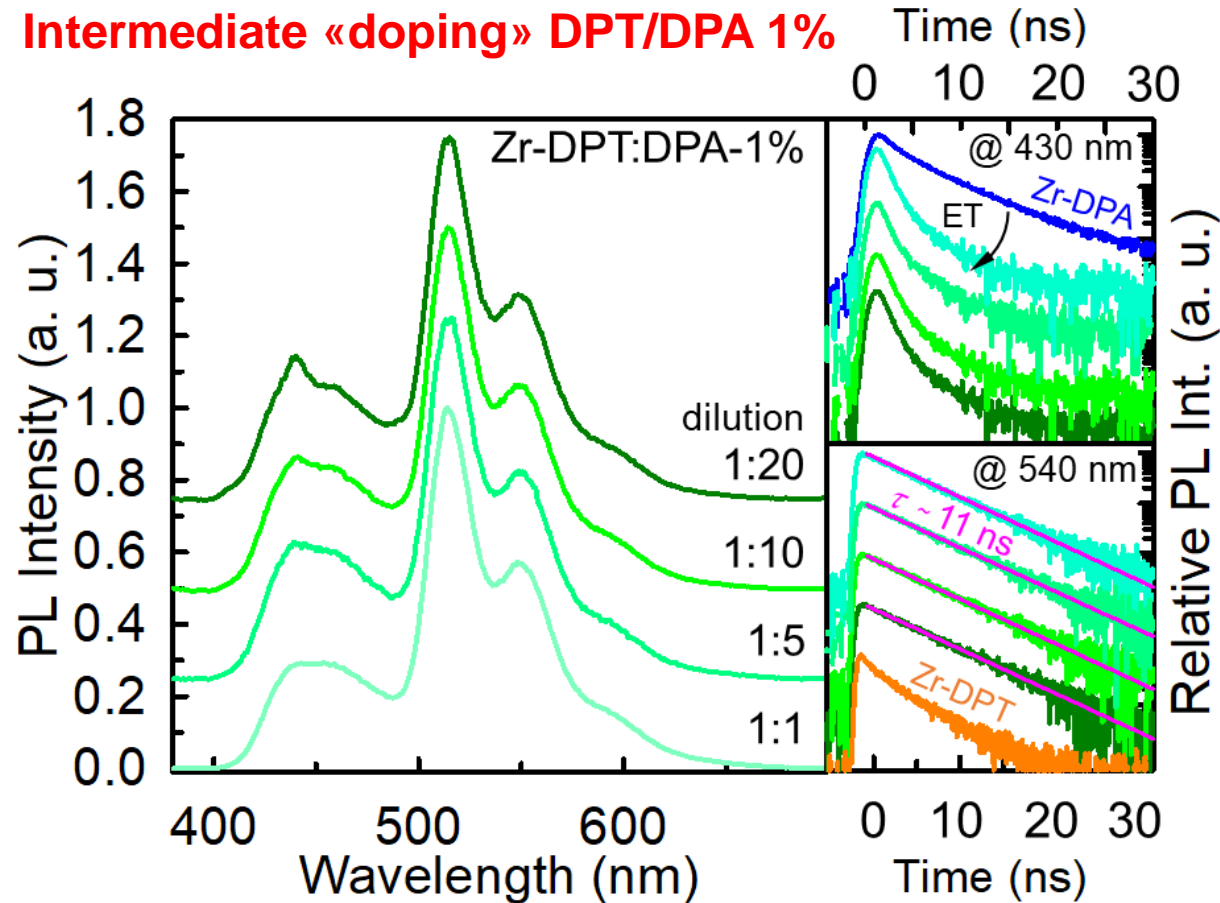


cubic crystal structure (space group *Fm-3m*). The Zr-based nodes ($Zr_6(m_3-O)_4(m_3-OH)_4(CO_2)_{12}$ clusters) have 12-coordinated ligands which connect the nodes in the 3D framework while the DPA units are disordered over three positions



PHOTOLUMINESCENCE OF HETERO-LIGANDS MOF NANOCRYSTALS

PL shape insensitive to dilution: MOFs are an independent emitter

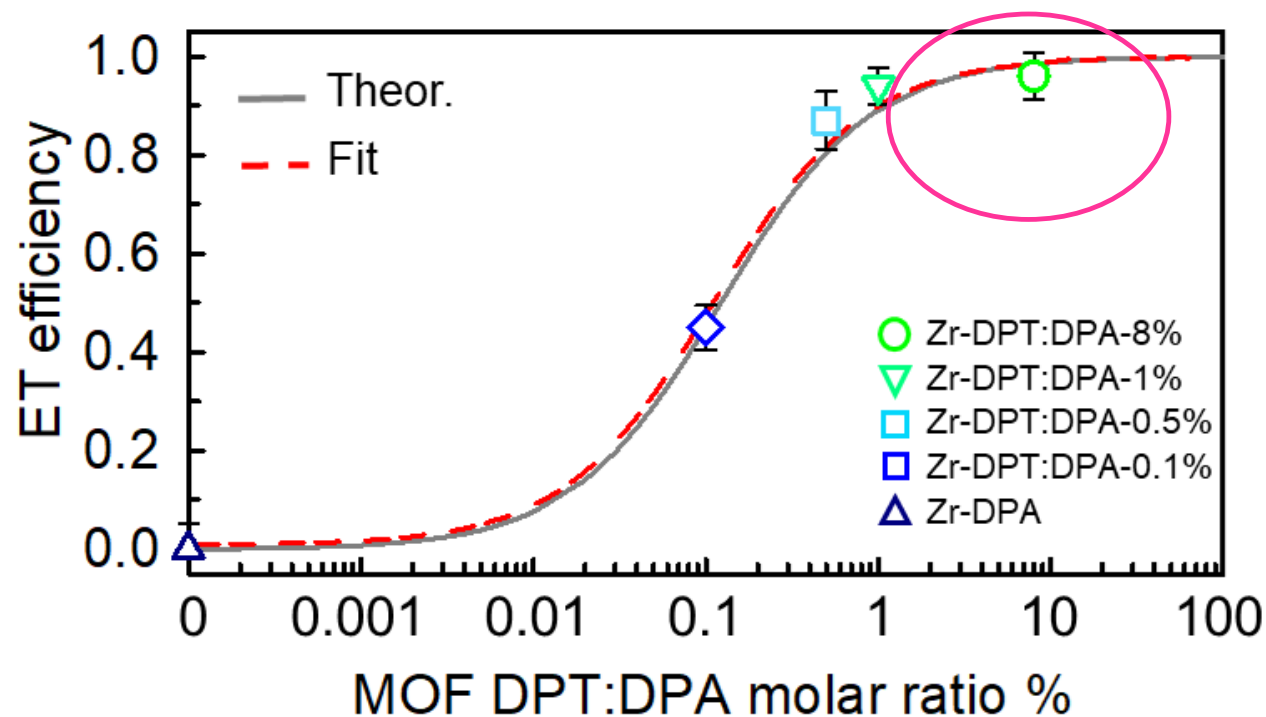
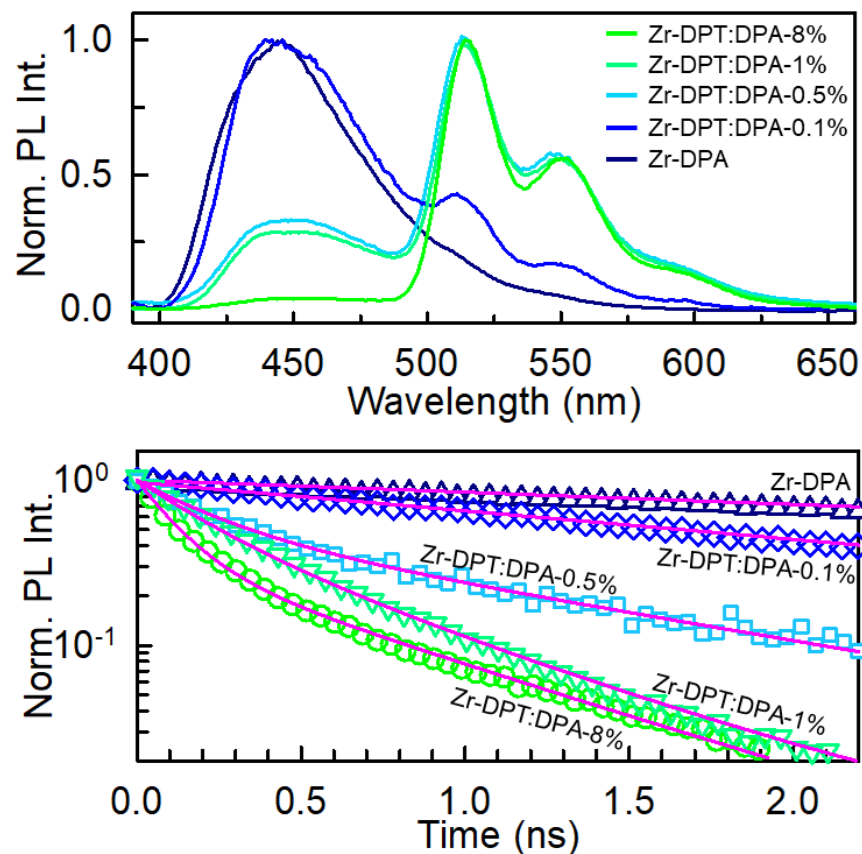


The DPA residual emission lifetime is shortened and constant upon dilution: ET is an intracrystal process.

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

The dopants are not on surfaces, OK!!!

ENERGY TRANSFER KINETICS IN HETERO-LIGANDS MOF NANOCRYSTALS

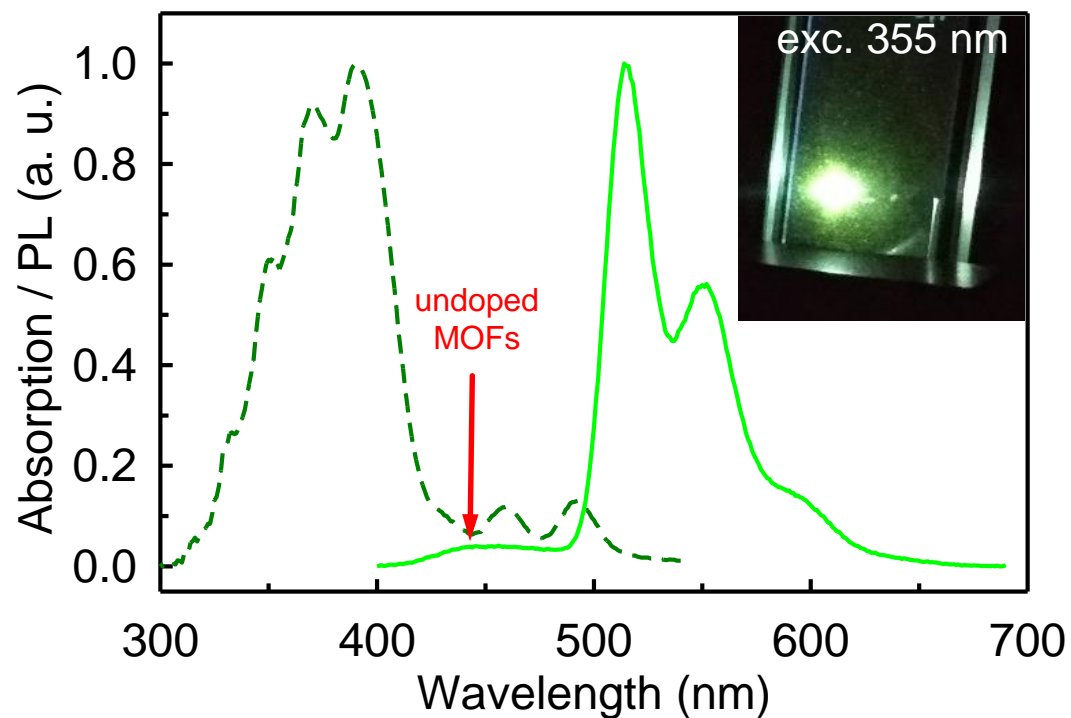


NO DOPING INDUCED QUENCHING

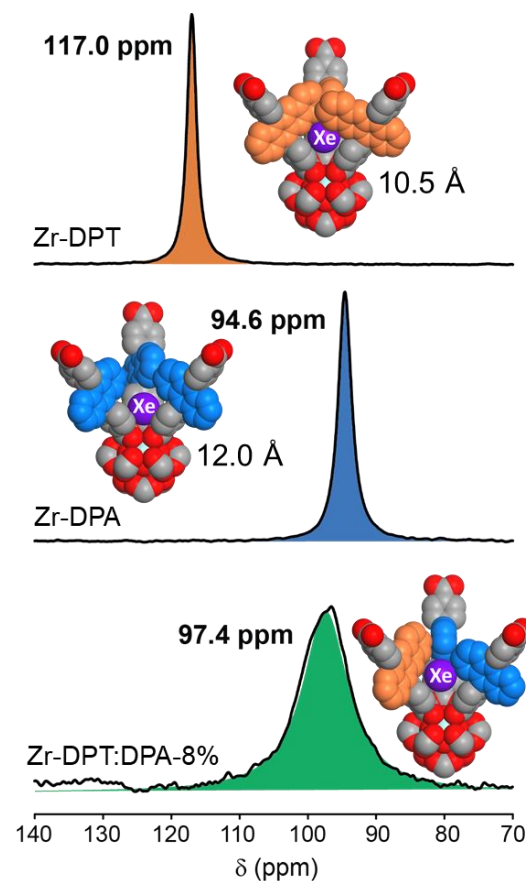
The PL changes by incremental «doping» is perfectly described by diffusion-mediated Foerster ET

HETERO-LIGANDS MOF NANOCRYSTALS

BEST DOPING LEVEL → DPT/DPA 8%



Hyperpolarized Xe NMR:
average doping 6%

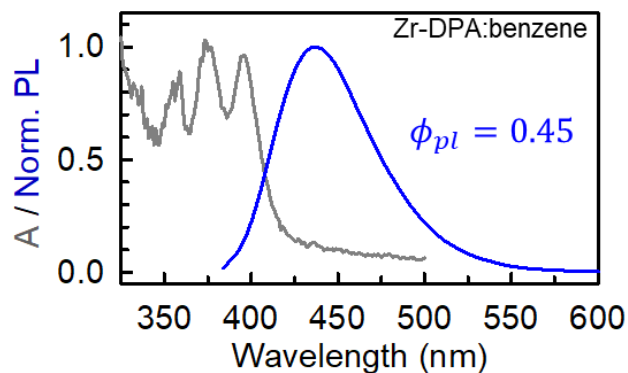


PLQY_{MOF} = 60%
VS.
PLQY_{DPT} = 80%

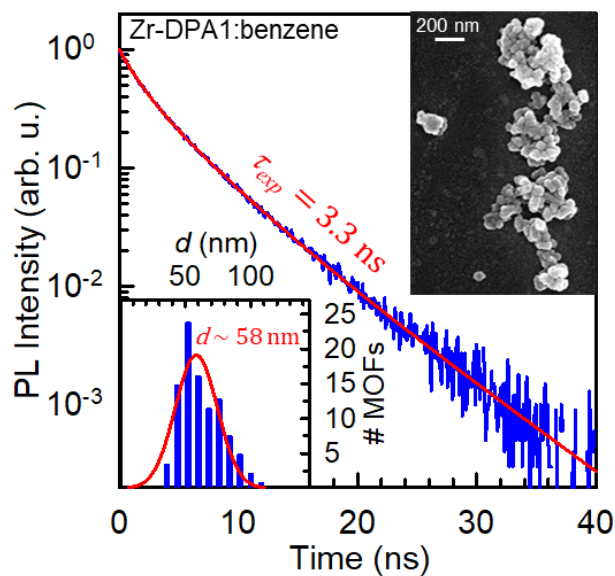
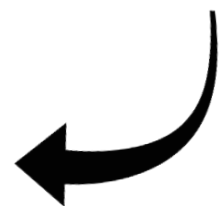


Goal achieved!
PLQY limited only by
distribution of doping with
partially doped
nanocrystals

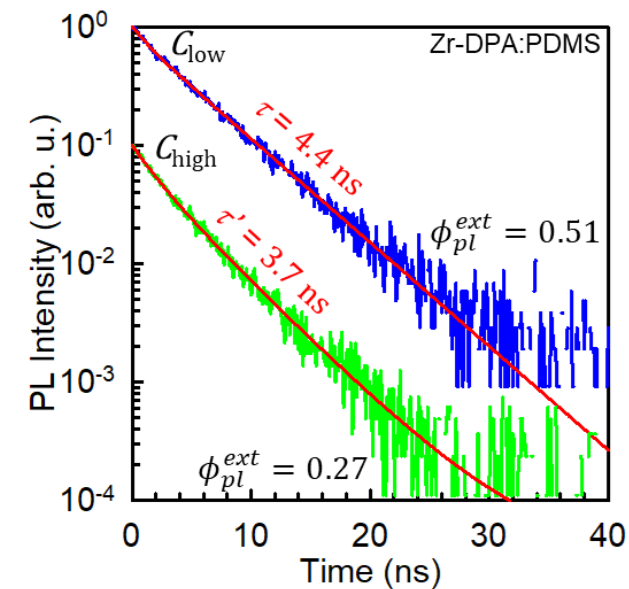
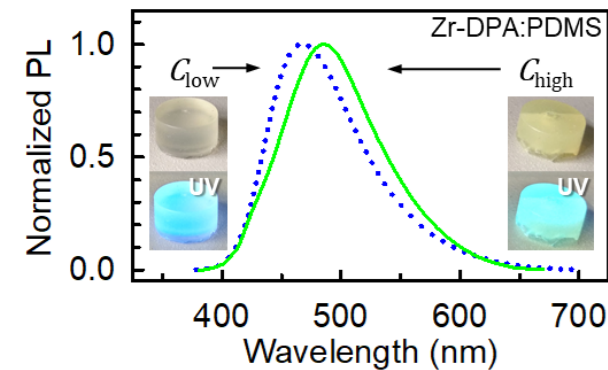
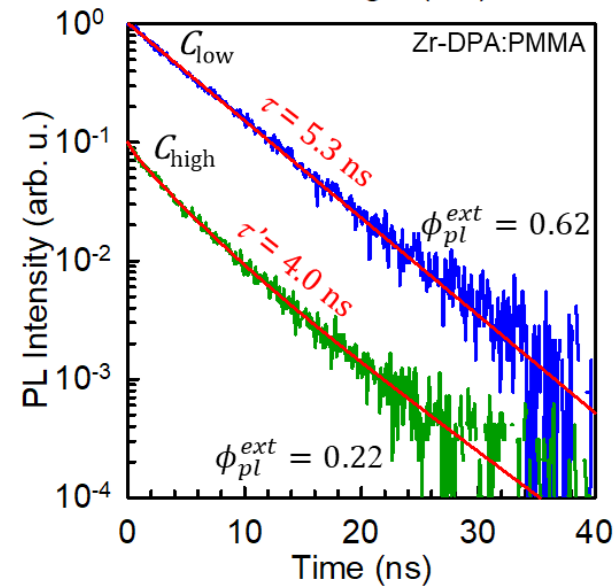
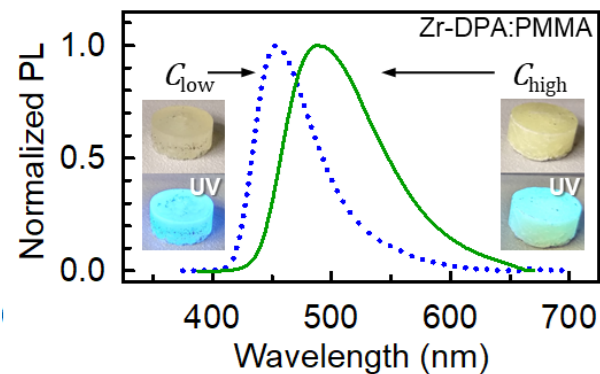
NANO-MOF AND NANOCOMPOSITES PHOTOLUMINESCENCE



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 and 1,332.5 keV).

PHOTOELECTRIC PEAK IS DIFFICULT TO OBSERVE IN LOW DENSITY AND INHOMOGENEOUS 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, $\rho = 0.78$ 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

- **$n_{em} = 821 \pm 82$ photons/MeV**

confirmed by independent relative measurement made with ^{22}Na and a SiPM using BGO as a reference

$\phi_{scint} = 1,160 \pm 350$ photons per MeV