

5th European Conference on Metal Organic Frameworks and Porous Polymers

EUROMOF

24-27 September

2023

| *Granada*

www.euromof2023.com

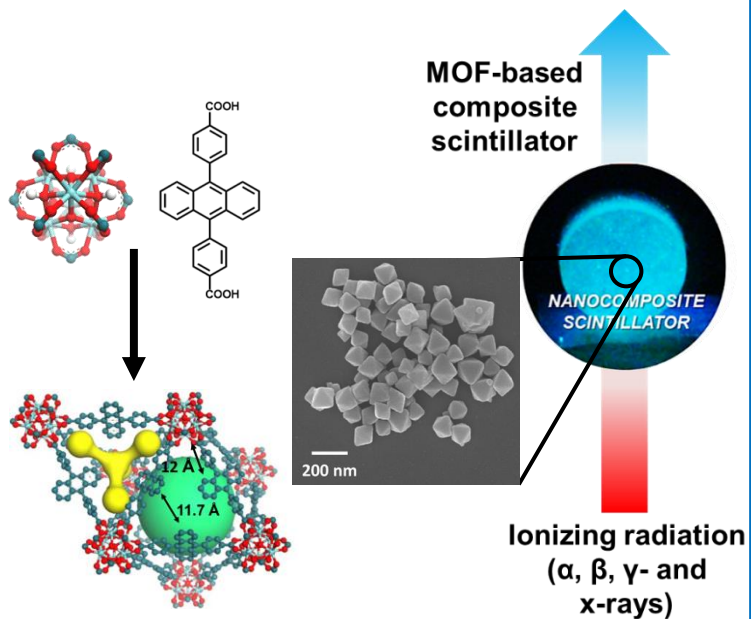




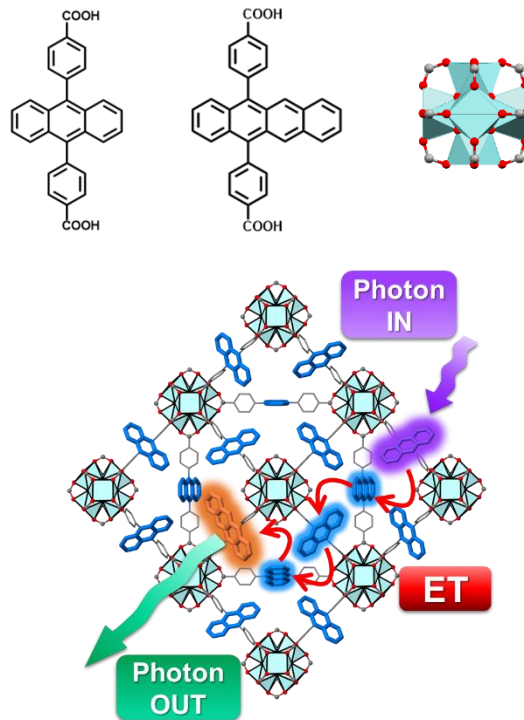
Luminescent MOF Architectures for radioactive gas detection and engineering large Stokes shift

Luminescent and scintillating MOFs

MOFs and MOFs composite for high-energy radiation detection

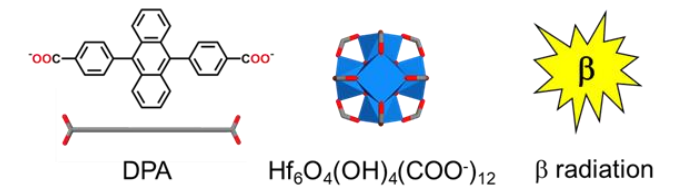


Large Stokes shift heteroligand MOFs

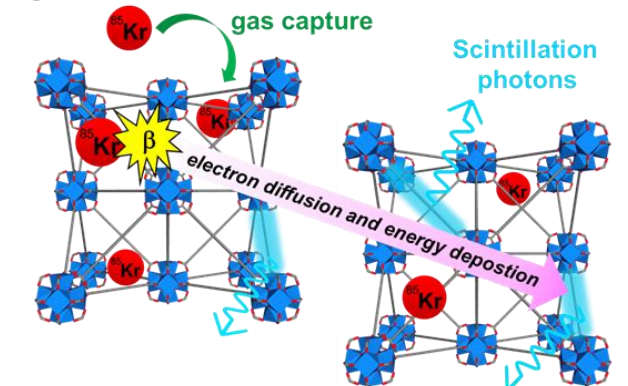


Radioactive gas detection with scintillating MOFs

Scintillating nanosponges concept



gas radionuclide



Nature Photonics, **2021**, 15, 393 - 400.

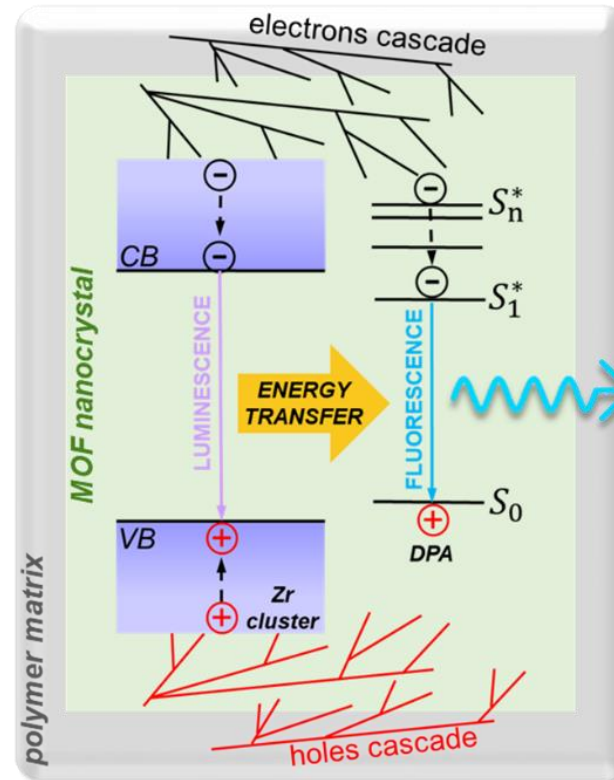
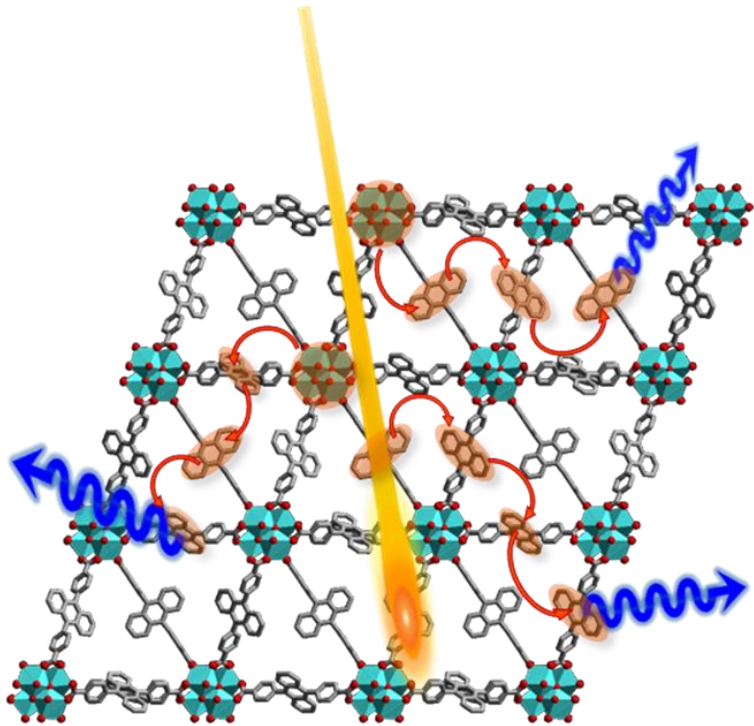
Nature Communications, **2022**, 13, 3504.

Nature Photonics, **2023**, 17, 672 - 678.

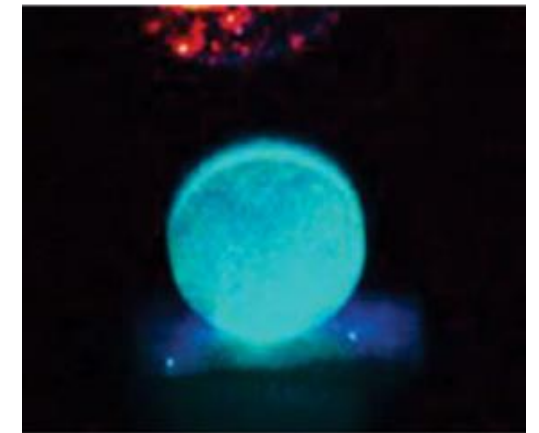
Luminescent and scintillating MOFs

Radioluminescence and scintillating properties of MOFs and MOF composites

Scintillators: materials that produce light pulses upon interaction with ionizing radiation



MOF@polymer based composite scintillator

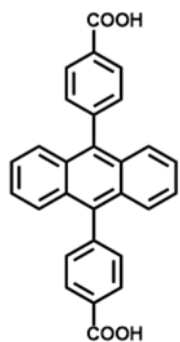
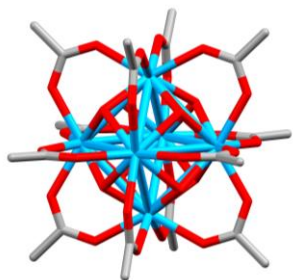


- Fast time response (few ns)
- High light-yield compared to pure organic scintillators

Scintillation process in MOF nanocrystals

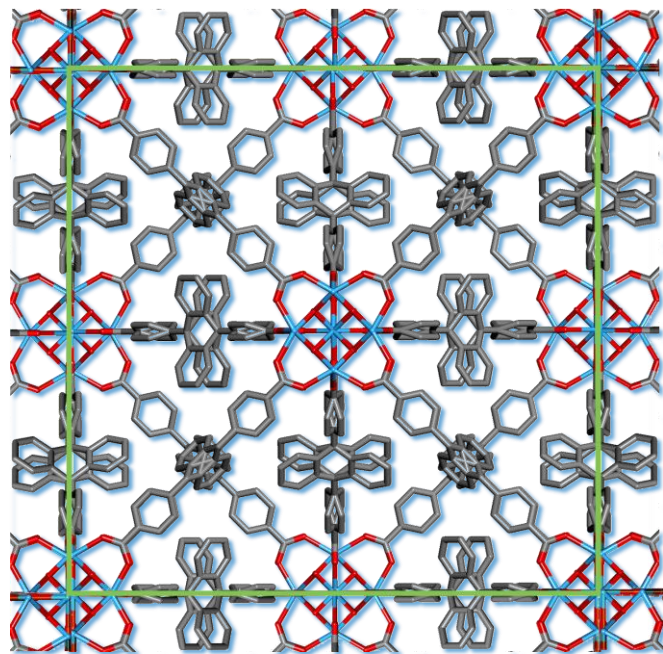
Luminescent and scintillating MOFs

Synthesis and crystal structure

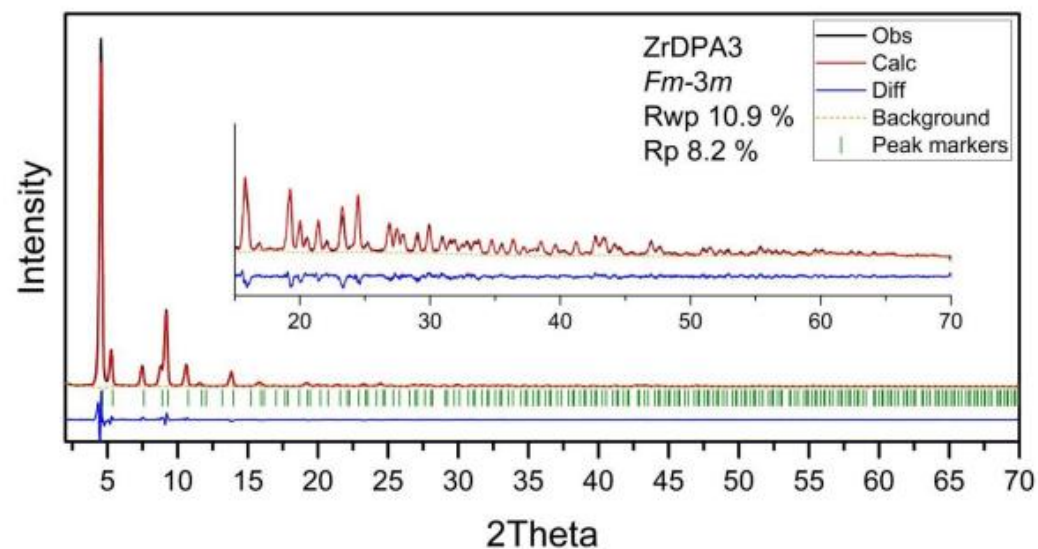


DPA

Diphenylanthracene



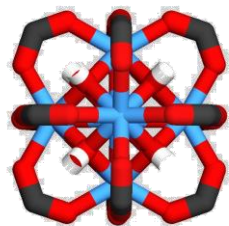
Fcc, face-centered
cubic structure



Luminescent and scintillating MOFs

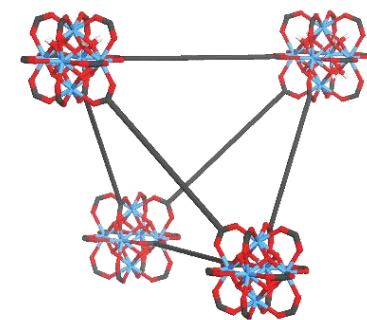
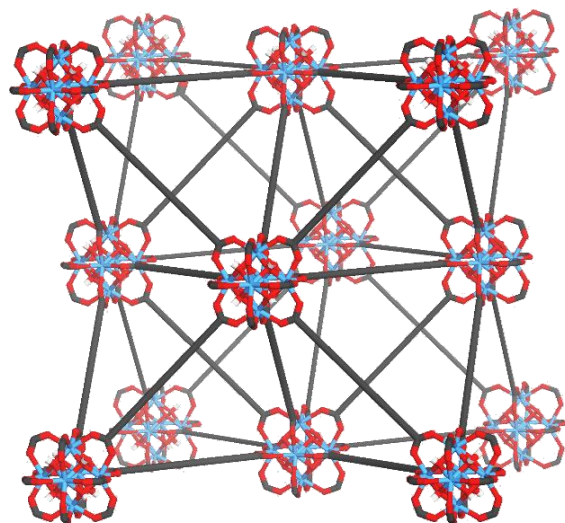
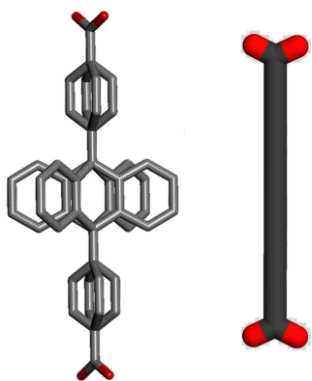
Synthesis and crystal structure

$Zr_6O_4(OH)_4(COO^-)_{12}$
cluster

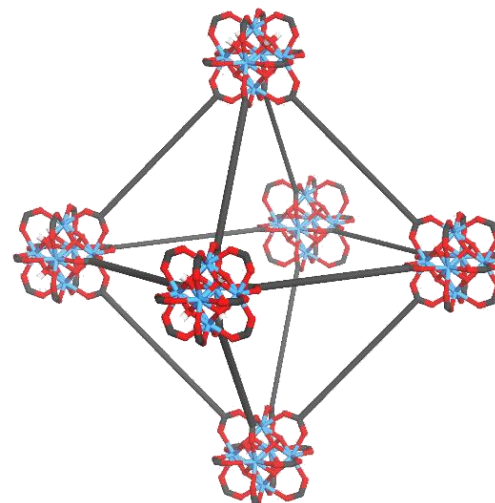


DPA

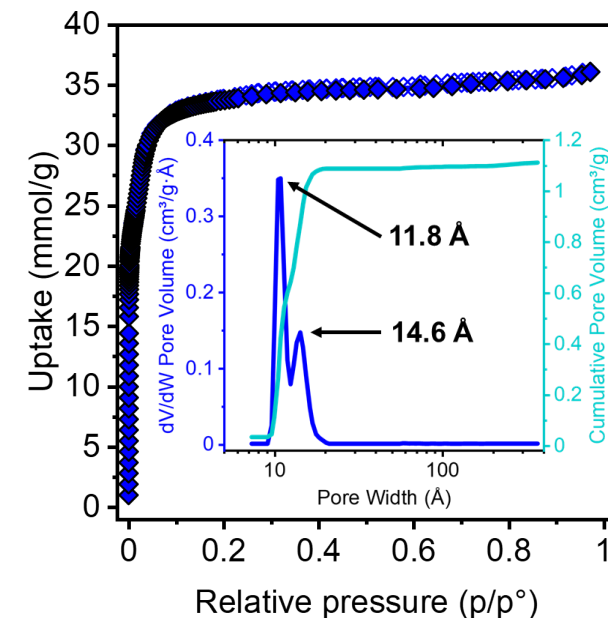
diphenylanthracene



Tetrahedral cavity



Octahedral cavity



Pore volume (cm³/g)

Calculated	Experimental ^a
1.20	1.11

Density (g/cm³)

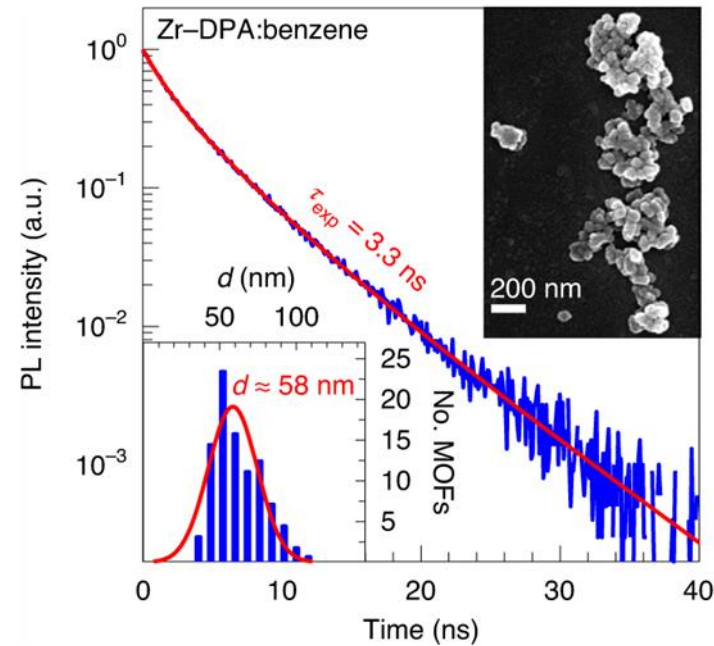
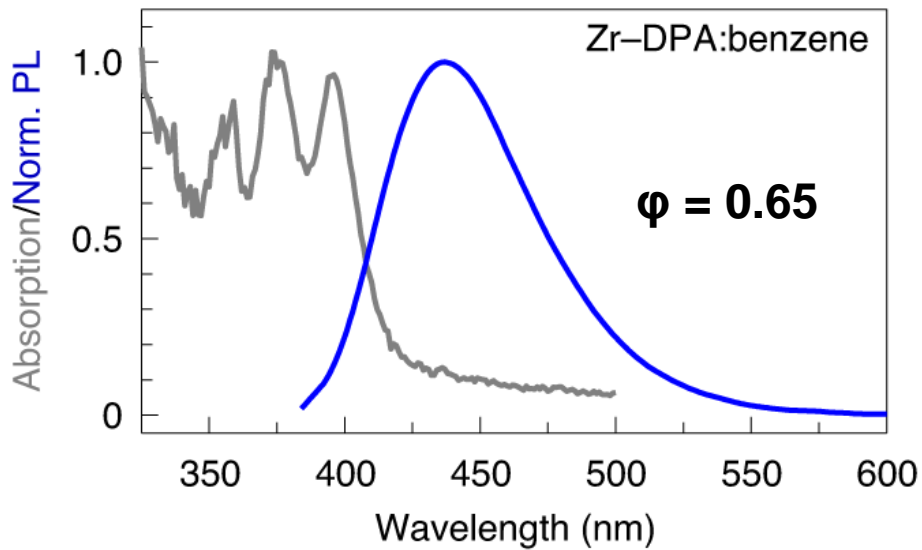
Calculated	Experimental ^b
0.591	0.581

Luminescent and scintillating MOFs

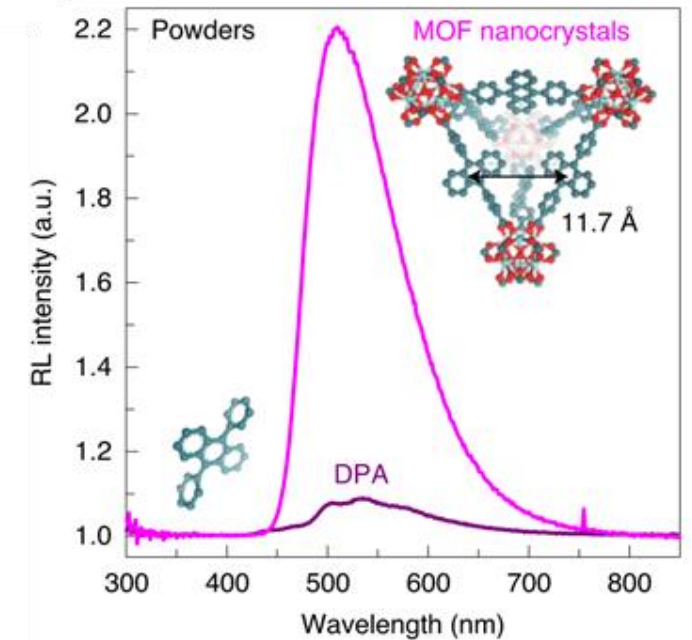
Photophysics and radioluminescence properties

MOF nanocrystals: photo- and radioluminescence

Photophysical properties of ZrDPA nanocrystals



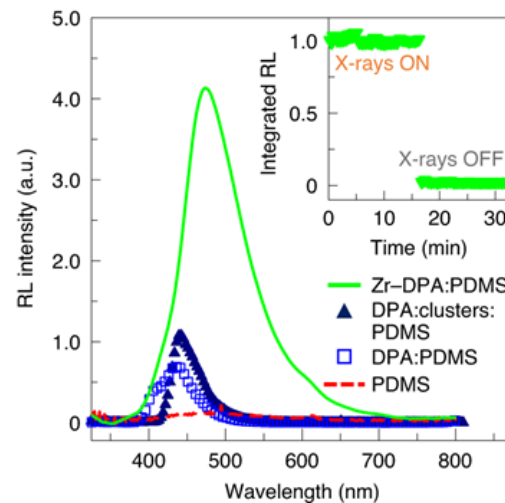
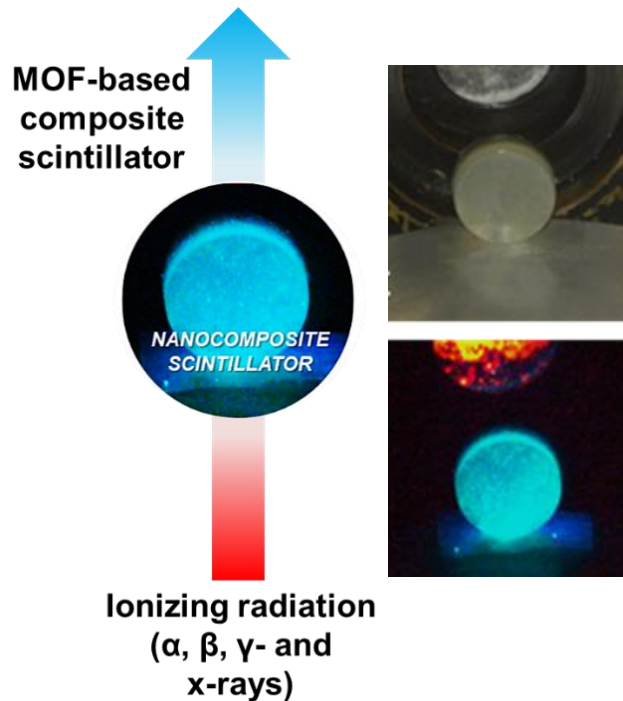
Sensitization effect of the inorganic building blocks



Luminescent and scintillating MOFs

MOFs@polymer nanocomposites for fast scintillation

Synergistic behaviour of inorganic/organic components inside ZrDPA nanostructures



Polymer composites radioluminescence

Ultrafast time-resolved scintillation experiments (x-rays exposure)

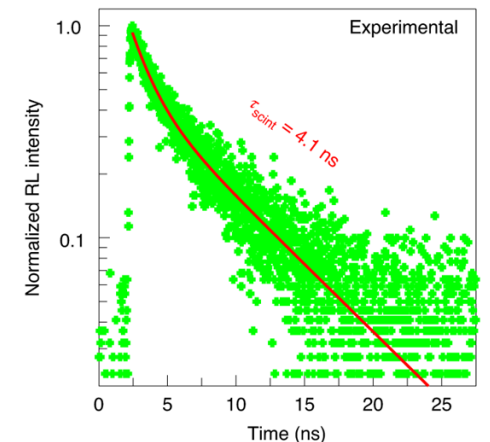
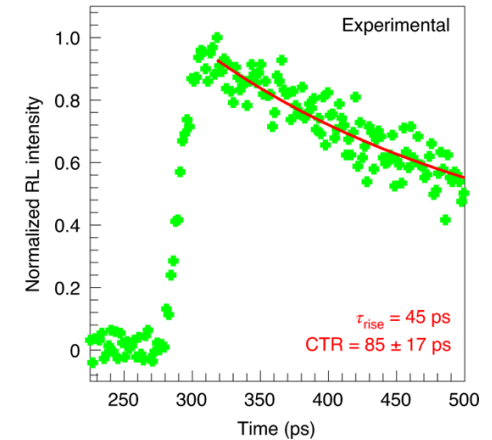
Scintillation rise time

$$\tau_{\text{RISE}} = 45 \text{ ps}$$

Scintillation decay time

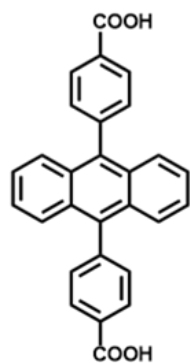
$$\tau_{\text{DECAY}} = 4.1 \text{ ns}$$

$$\text{CTR} = 85 \pm 17 \text{ ps}$$

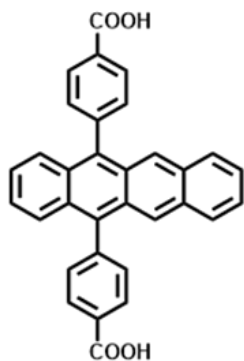


Hetero-ligand MOFs with large Stokes shift

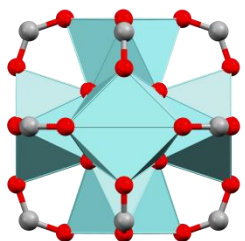
Photon management in co-assembled MOFs



DPA

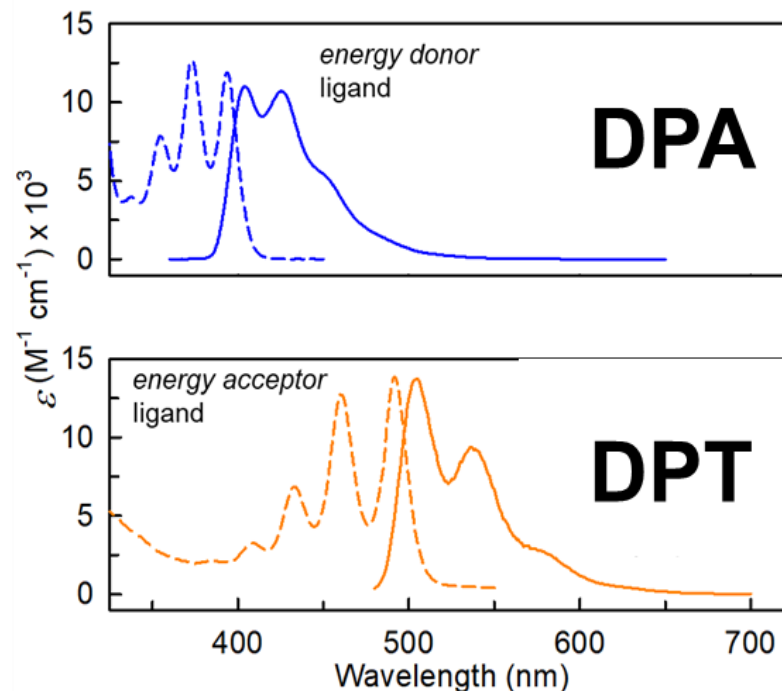


DPT

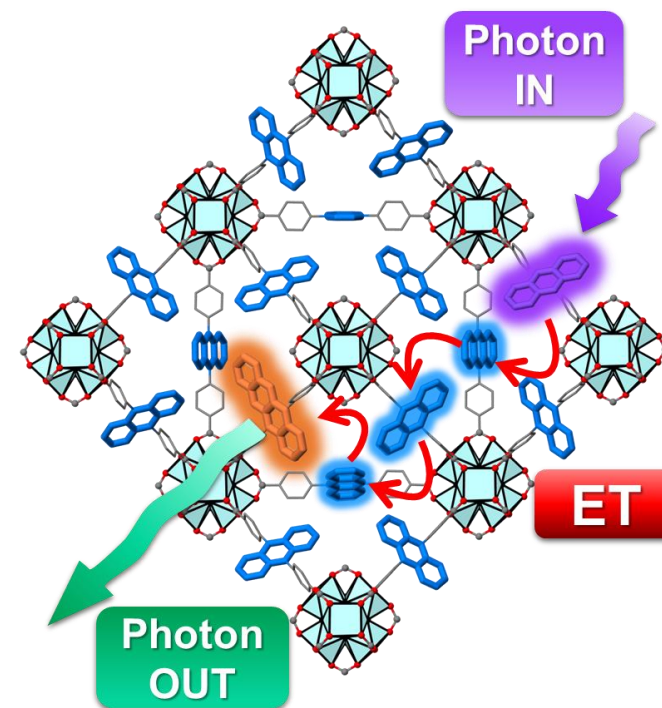


**Zirconium
cluster**

Complementary photophysical properties



Fast emitting reabsorption-free MOF nanocrystals

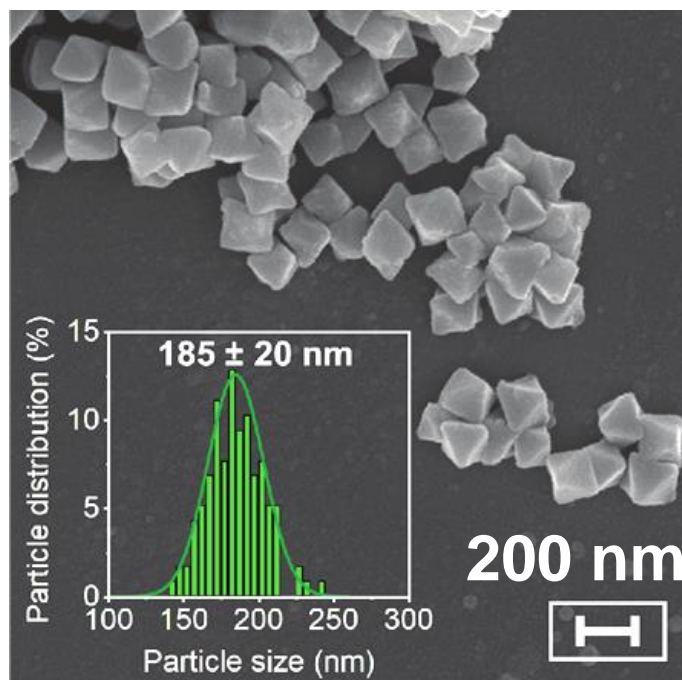
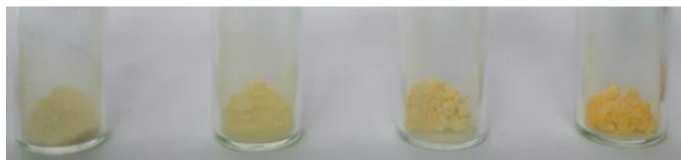


Hetero-ligand MOFs with large Stokes shift

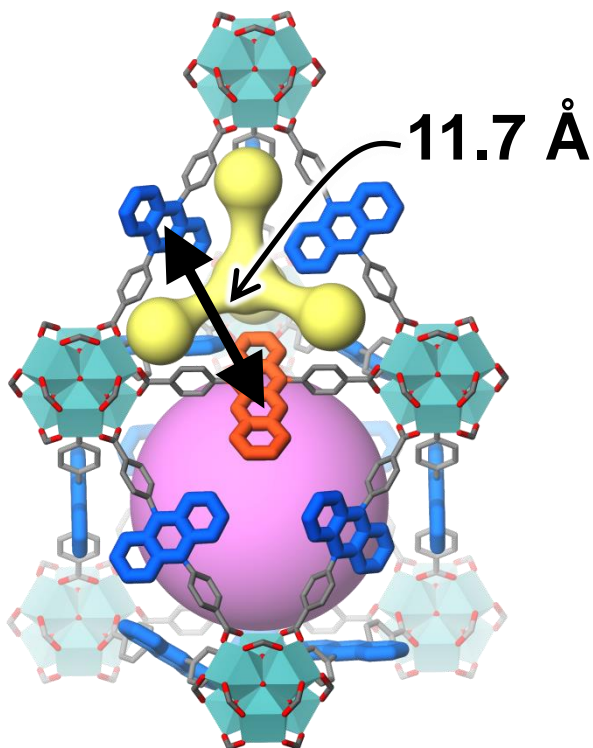
Controlled growth of nanometer-sized Zr-based hetero-ligand MOFs

Co-assembly of the 2 different ligands in various ratio generate a family of hetero-ligand MOFs with different concentration of DPT units.

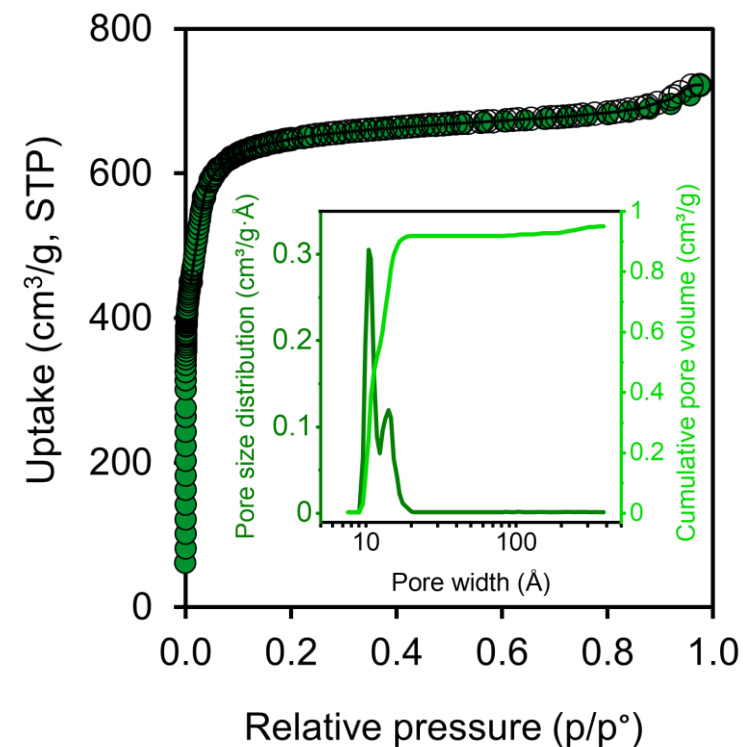
0.1 % DPT 0.5 % DPT 1 % DPT 8 % DPT



Zr-DPT:DPA-X%
0.1 % < X < 8 %

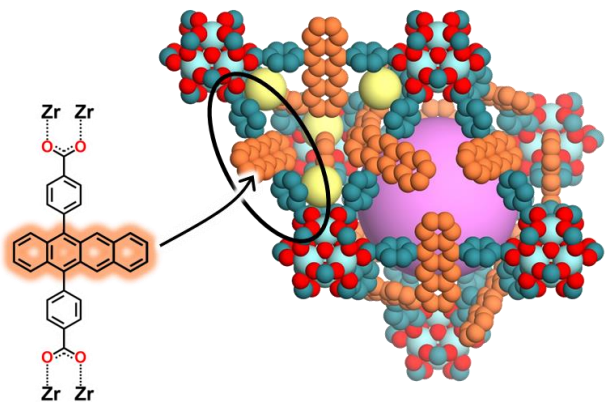


$S_{\text{langmuir}} = 2930 \text{ m}^2/\text{g}$

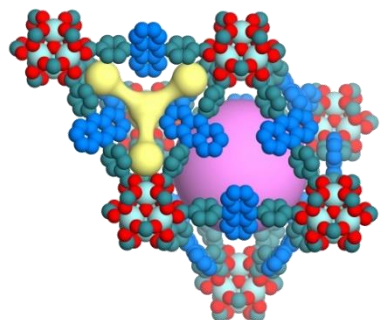


Hetero-ligand MOFs with large Stokes shift

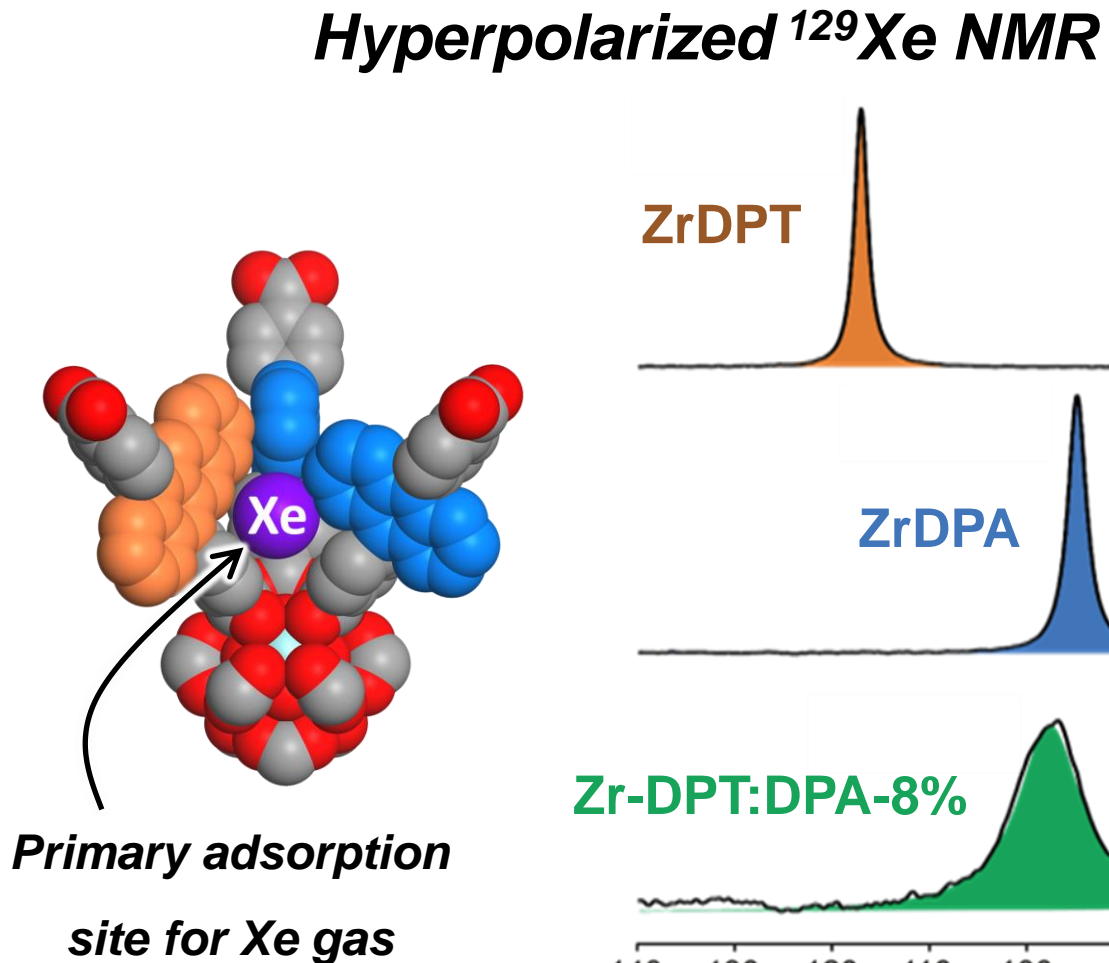
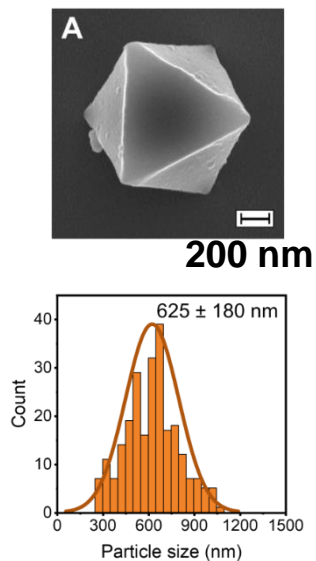
Homogeneous distribution of ligands: HP ^{129}Xe NMR



Zr-DPT



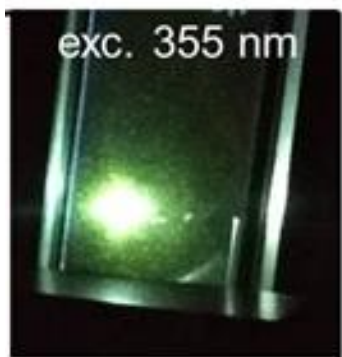
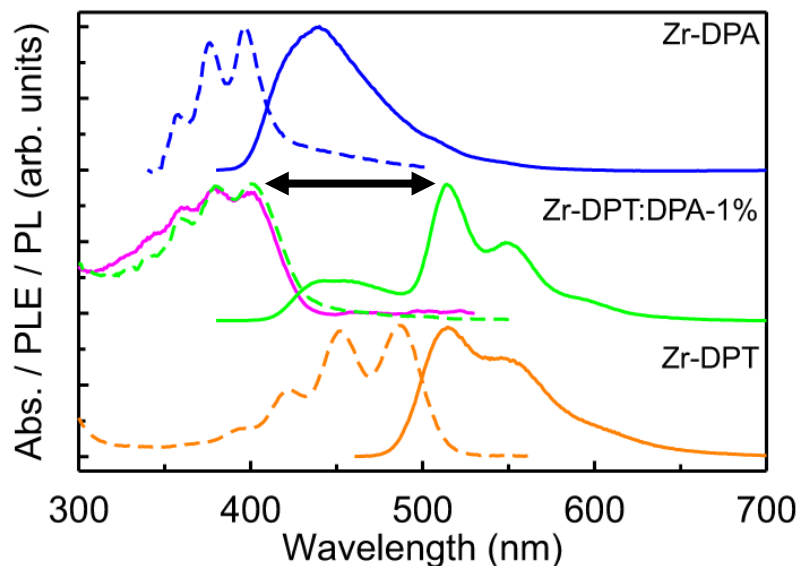
Zr-DPA



Hetero-ligand MOFs with large Stokes shift

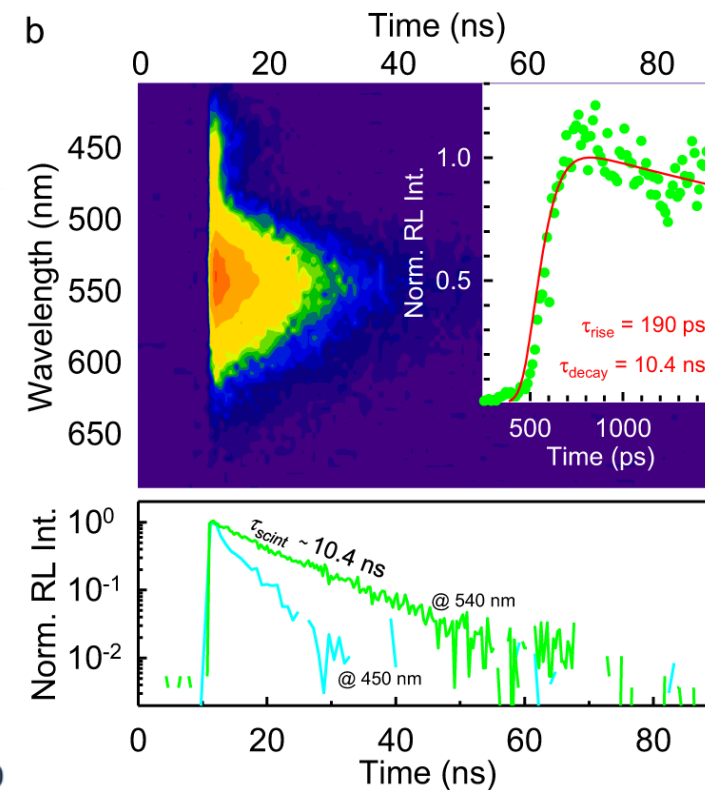
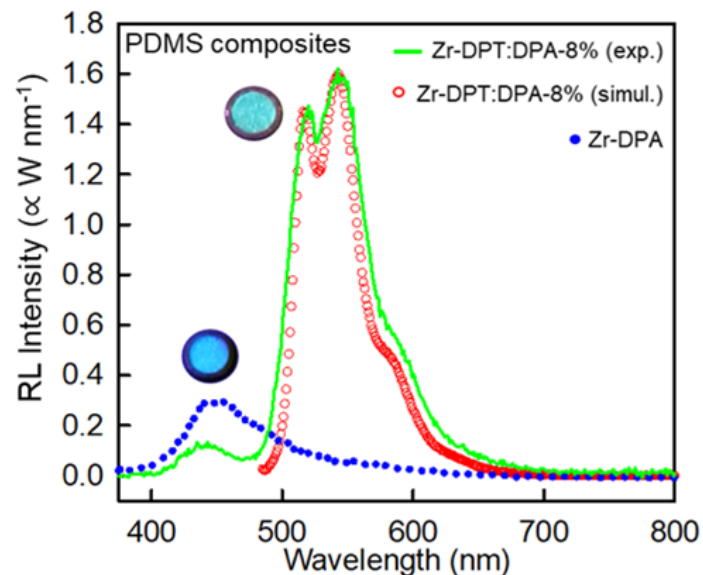
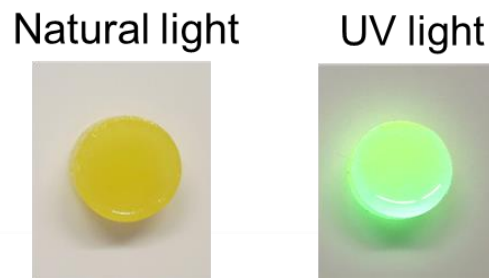
Photoluminescence and scintillation properties

Large Stokes Shift emission



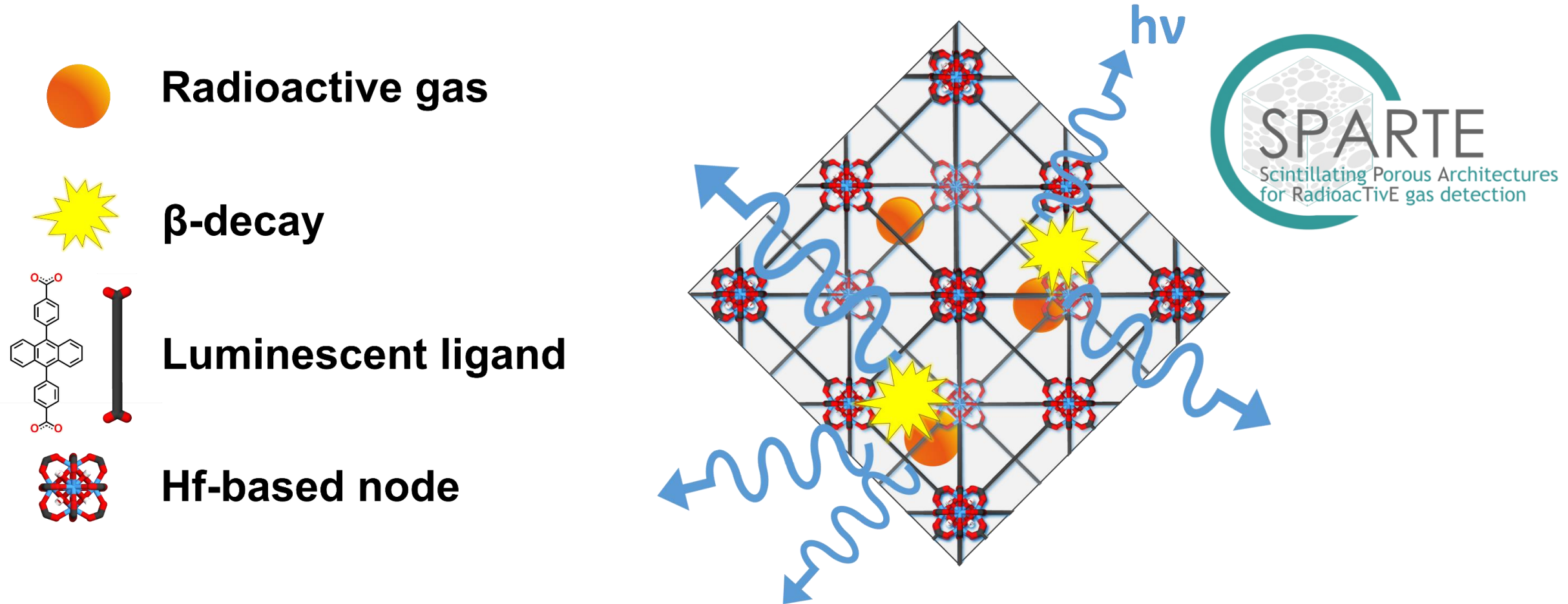
Zr-DPT:DPA-8%
Dispersion in THF

Scintillation of mixed-linker MOFs



Scintillating sponges concept

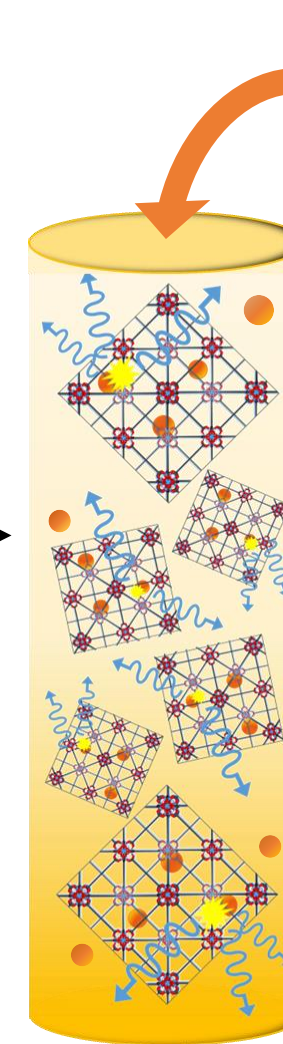
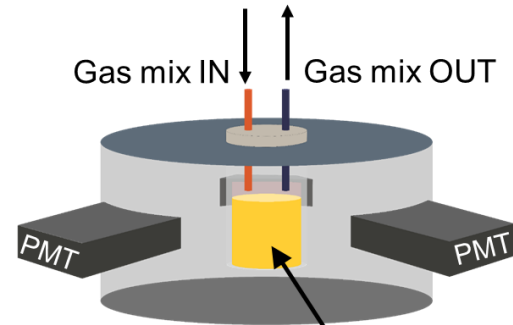
SPARTE project: nanoporous scintillator for radioactive gas detection



Scintillating sponges concept

Prototype device for radioactive gas detection

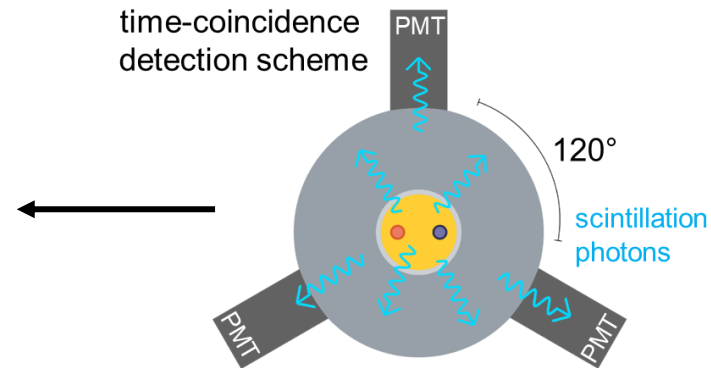
Radioactive gas detection with porous scintillators



Air contaminated with radionuclides (^3H , ^{85}Kr and ^{222}Rn).

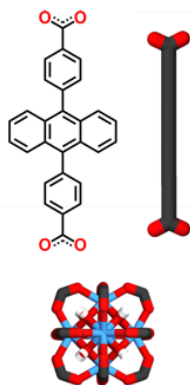
**Scintillating
Nanosponge**

**Fast and effective
radioactive gas
detection in a solid
state detector**



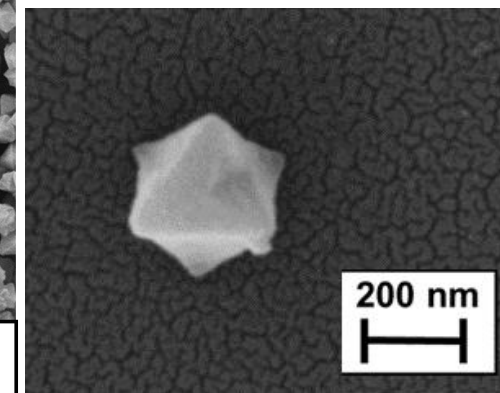
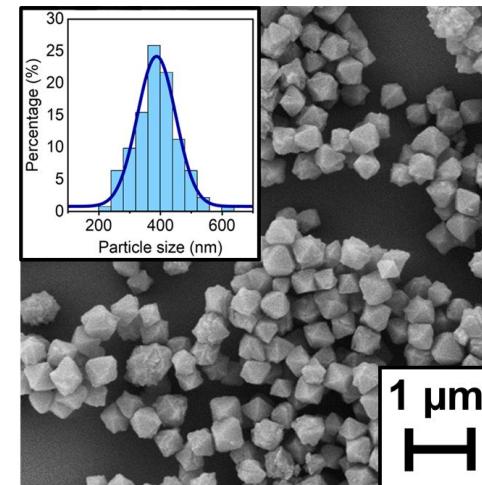
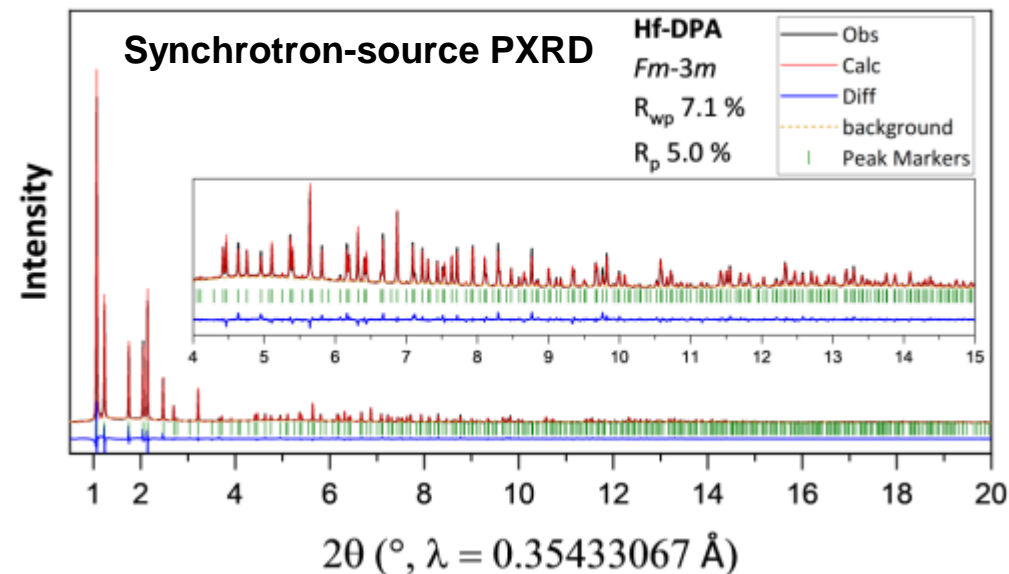
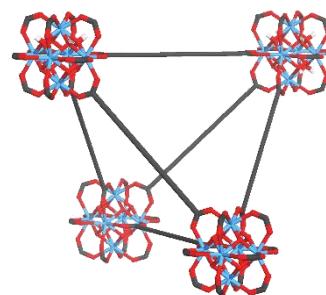
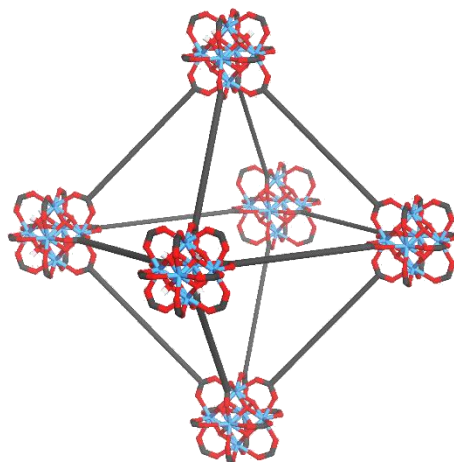
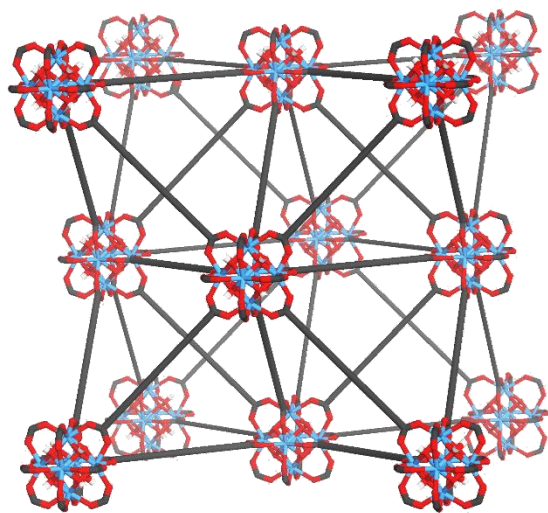
Scintillating Hf-based MOFs

Hf-DPA MOFs as effective solid state nanoporous scintillator



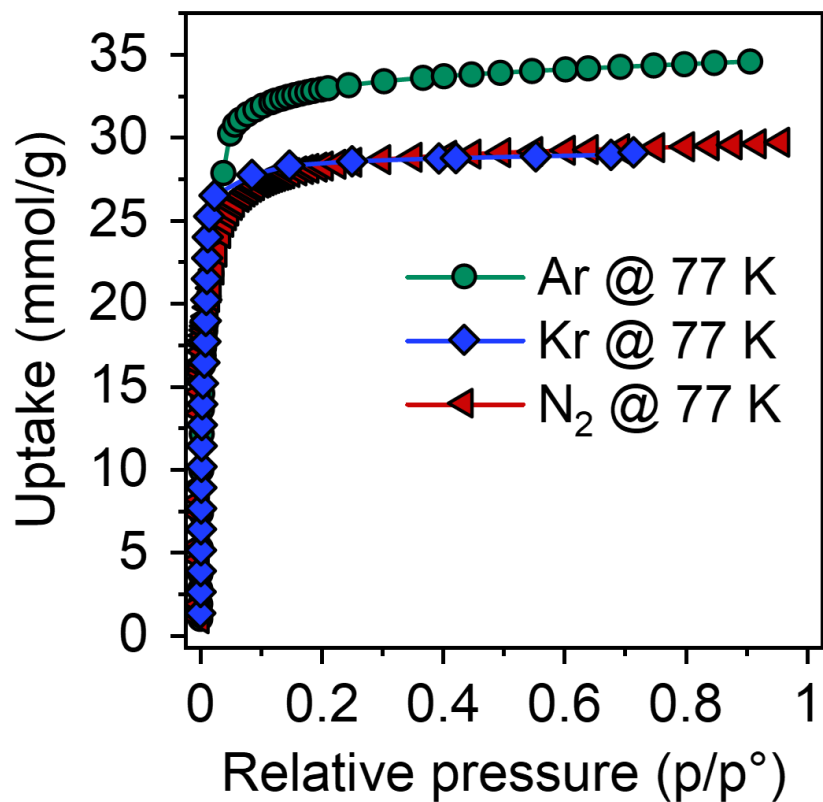
Luminescent ligand

Hf-based node

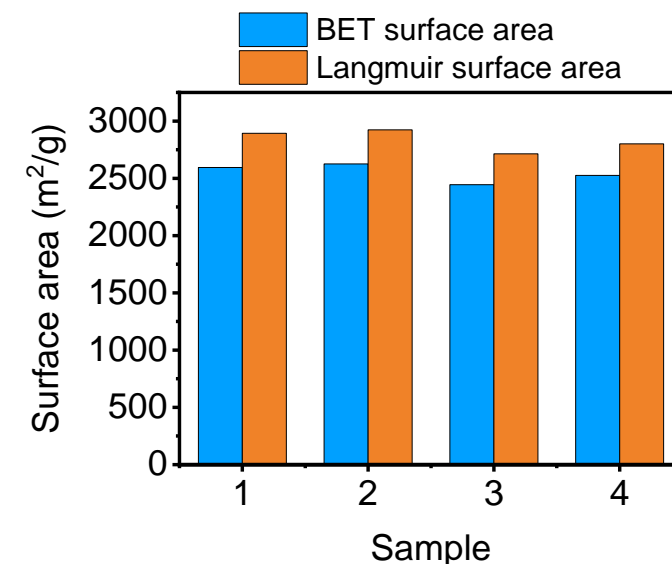
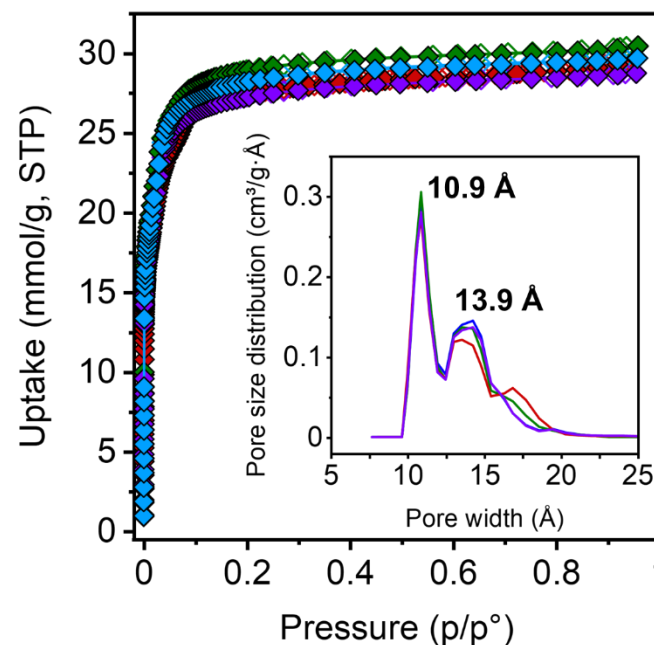


Scintillating Hf-based MOFs

Ultra-high surface area nanoporous scintillators



Nitrogen adsorption isotherms @ 77 K

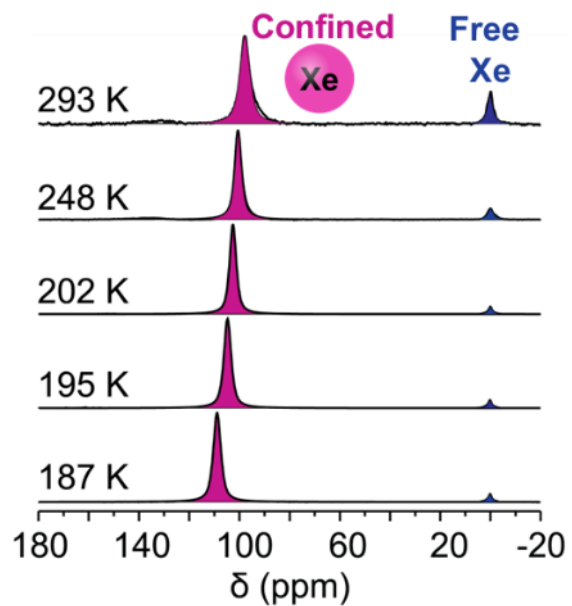


$$S_{\text{BET}} = 2550 \pm 70 \text{ m}^2 \text{ g}^{-1}$$

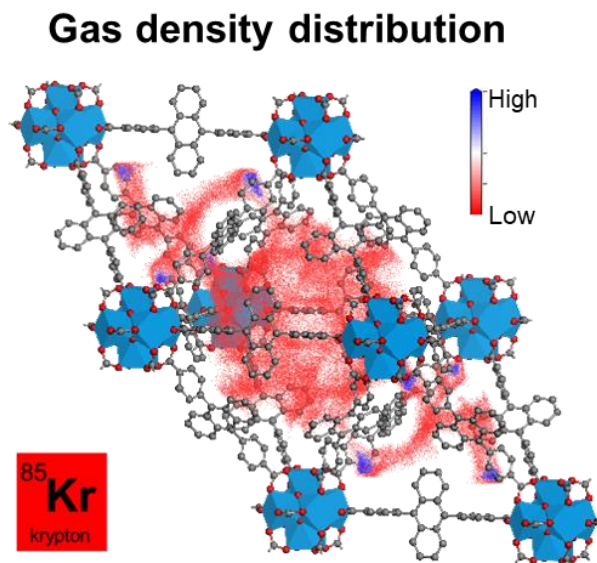
$$S_{\text{langmuir}} = 2830 \pm 82 \text{ m}^2 \text{ g}^{-1}$$

Radioactive gas detection with MOFs

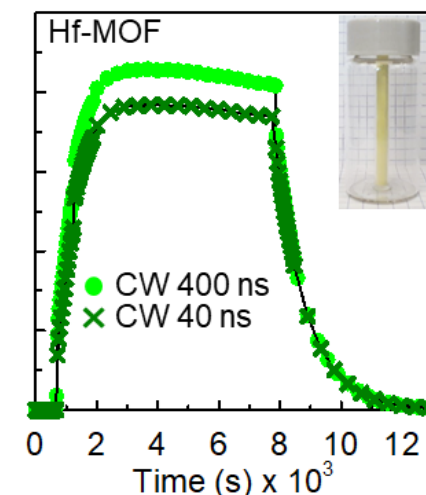
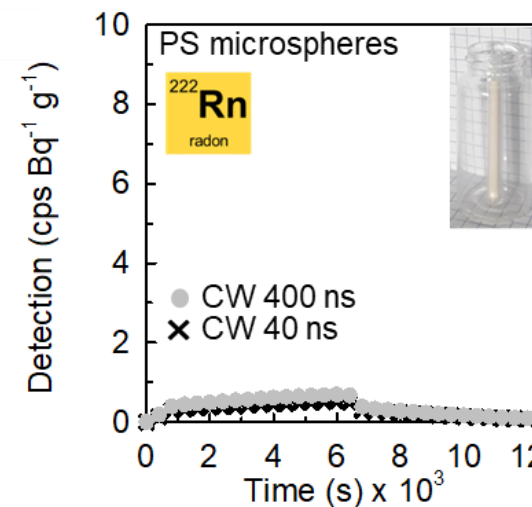
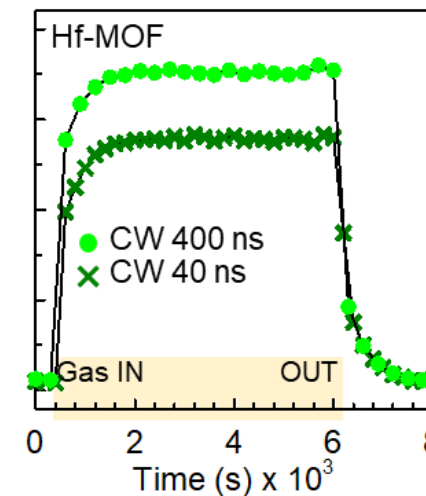
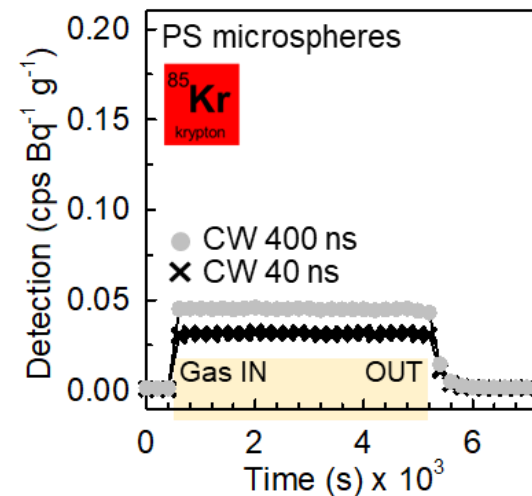
Fast and effective gas diffusion and radioactive gas detection



^{129}Xe hyperpolarized NMR
2% ^{129}Xe in a He/ N_2 mixture at 298 K



GCMC simulation





Nanoporous Materials Research Group

**NMR
Group**

<https://nanoporous.mater.unimib.it/>

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Prof. Angiolina Comotti

Prof. Silvia Bracco

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Prof. Christophe Dujardin

Dr. Benoit Sabot

European Community through the grant n° 899293, HORIZON 2020 – SPARTE



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Please, visit SPARTE website @ <https://www.sparte-project.eu/>

I acknowledge University of Milano-Bicocca for the “**Young talent award 2020**” first prize.

Financial support from the Italian Ministry of University (MUR) through grant no. PRIN 2020—SHERPA no. H45F2100343000

Thank you!

Luminescent and scintillating MOFs

Synthesis and crystal structure

	Pore volume (cm ³ /g)		Density (g/cm ³)	
	Calculated	Experimental ^a	Calculated	Experimental ^b
Zr-DPA	1.20	1.11	0.591	0.581

a. Calculated from N₂ adsorption at 77 K according to NLDFT theory. b. Calculated from He picnometry and N₂ adsorption at 77 K measurements.

