



list
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Scintillating MOF, Photophysiques and radiation detection

DE LA RECHERCHE À L'INDUSTRIE



5 septembre 2022

Dr. Guillaume BERTRAND

Context

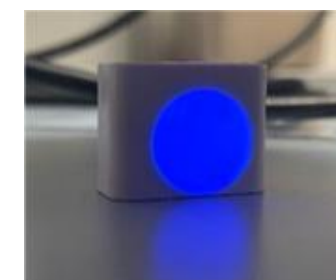
- What is scintillation?
- MOF chemistry: a new playground for scintillator design

Photophysiques of Zinc based MOF

- Synthesis of large crystal
- Unraveling the true luminescence of Zn-MOF

Radiation detection

- MOF as based materials for a novel type of scintillator
- Radioactive gas detection with MOF



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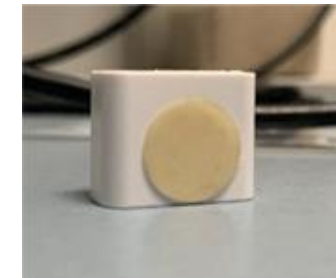
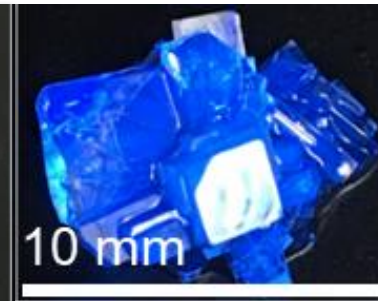
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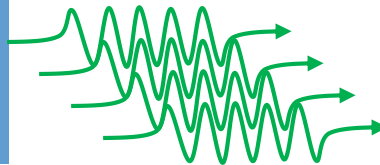
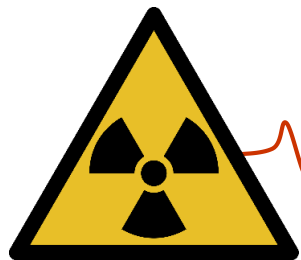
- MOF as based materials for a novel type of scintillator
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- A scintillator is a material that emits visible photons when excited by an ionizing radiation

Ionizing particle or photon
e.g.: 1 photon 1 MeV (gamma)

Visible domain
Ex : 10^4 photons 3 eV (410 nm)



Materials	Examples	Advantages	Defaults	Uses
Plastic scintillator	polystyrene + fluorophores	Cheap Large volume available	Low scintillation yields Low density	Static / hand held devices Research
Liquid scintillator	xylenes + fluorophores	Solubilisation of the radioactivity	Chemical waste Offline detection	Environmental control
Organic monocrystals	Stilbene, anthracene	High scintillation yields	Expensive, < 20g	Research
Inorganic monocrystals	NaI:Tl, LaBr ₃ :Ce, LYSO	High scintillation yields High density Diversity of formulation	Hygroscopic Expensive	Static / hand held devices Research

- So why MOF as a new materials for scintillation ?
- Research interest :
 - Scintillation is a photophysic phenomenon.
 - **Understanding the photophysics of MOFs** is the base of our present and future exploration.
- MOFs are a mixed Organic/Inorganic materials :
 - **Best of both worlds ?**
 - MOFs are not a finality, can be a **precursor for new materials**
- **None of the existing scintillating materials are porous.**
 - Only liquid scintillation see some use as a radioactive gas sensor.
 - High surface area can mimic liquid scintillation
 - **Trapping or concentrating a radioactive gas while detecting it**

Context

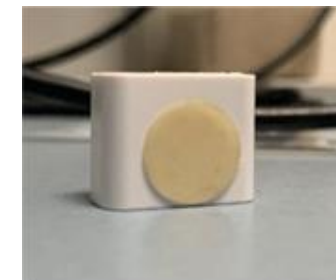
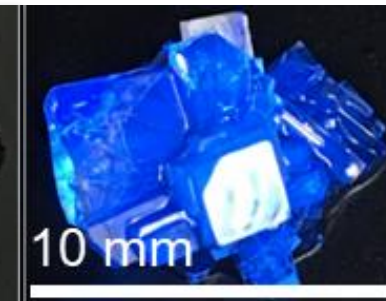
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- MOF-5 : Iconic MOFs

Several reports on its fluorescence

	λ_{em} [nm]	Origin
Bordiga et al.	518	LMCT
Tachikawa et al.	525	ZnO Quantum Dots
Allendorf et al.	397	LLCT

Several reports on the theory of it

	Method	λ_{em} [nm] (predicted)	Origin
Qiu et al.	DFT	349	LLCT
Pham et al.	DFT	348	Ligand centered
Starobin et al.	Bloch mode analysis	380	Ligand centered
Poloni et al.	Many-body perturbation theory	350	Ligand centered

- Experimental observation based on powder disperse in solvent
- Our approach : Photophysiques on pristine single crystal
- Objective: millimeter size single crystals

Bordiga, S.; Lamberti, C.; Ricchiardi, G.; Regli, L.; Bonino, F.; Damin, A.; Lillerud, K. P.; Bjorgen, M.; Zecchina, A. *Chem. Commun.* **2004**, 10 (20), 2300–2301.

Tachikawa, T.; Choi, J. R.; Fujitsuka, M.; Majima, T. *J. Phys. Chem. C* **2008**, 112, 14090–14101.

Feng, P. L.; Perry IV, J. J.; Nikodemski, S.; Jacobs, B. W.; Meek, S. T.; Allendorf, M. D. *J. Am. Chem. Soc.* **2010**, 132 (44), 15487–15489.

Ji, M.; Lan, X.; Han, Z.; Hao, C.; Qiu, *J. Inorg. Chem.* **2012**, 51 (22), 12389–12394.

Pham, H. Q.; Mai, T.; Pham-Tran, N. N.; Kawazoe, Y.; Mizuseki, H.; Nguyen-Manh, D. *J. Phys. Chem. C* **2014**, 118 (9), 4567–4577.

Kshirsagar, A. R.; Blase, X.; Attacalite, C.; Poloni, R. *J. Phys. Chem. Lett.* **2021**, 12 (16), 4045–4051.

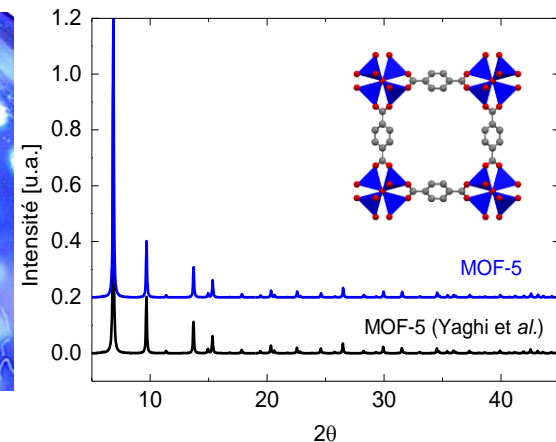
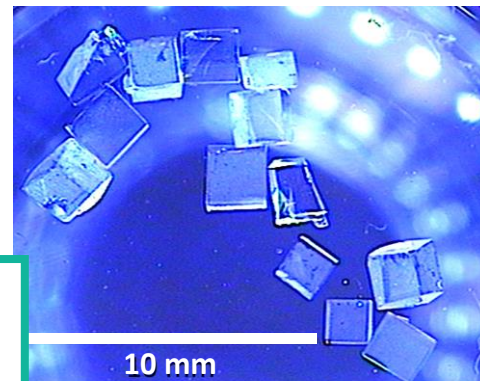
Rathnayake, H.; Saha, S.; Dawood, S.; Loeffler, S.; Starobin, J. *J. Phys. Chem. Lett.* **2021**, 12 (2), 884–891.

- Very consistent synthesis

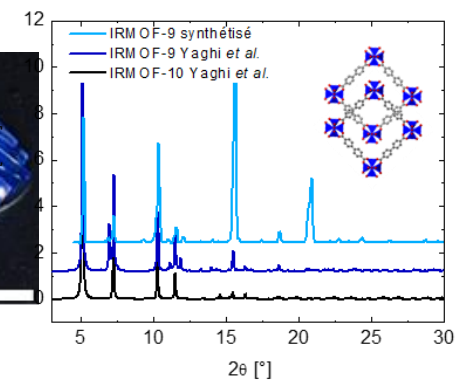
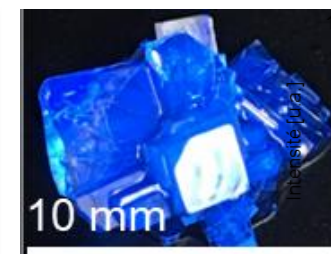
MOF-5

n_{Zn} [mmol]	n_{BDC} [mmol]	DEF [mL]	Temp [°C]	Time [h]
5,9	1,9	50	75	192

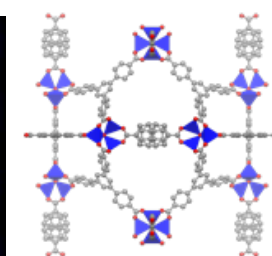
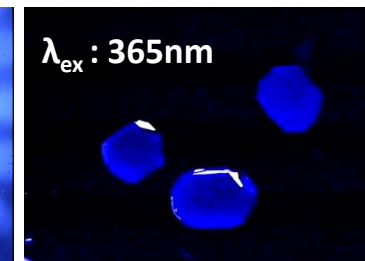
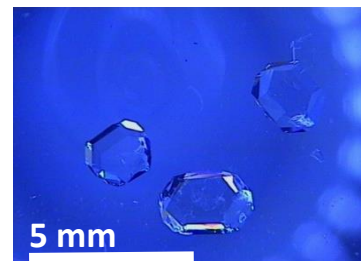
Quartz capillary + MOF sealed in glove box



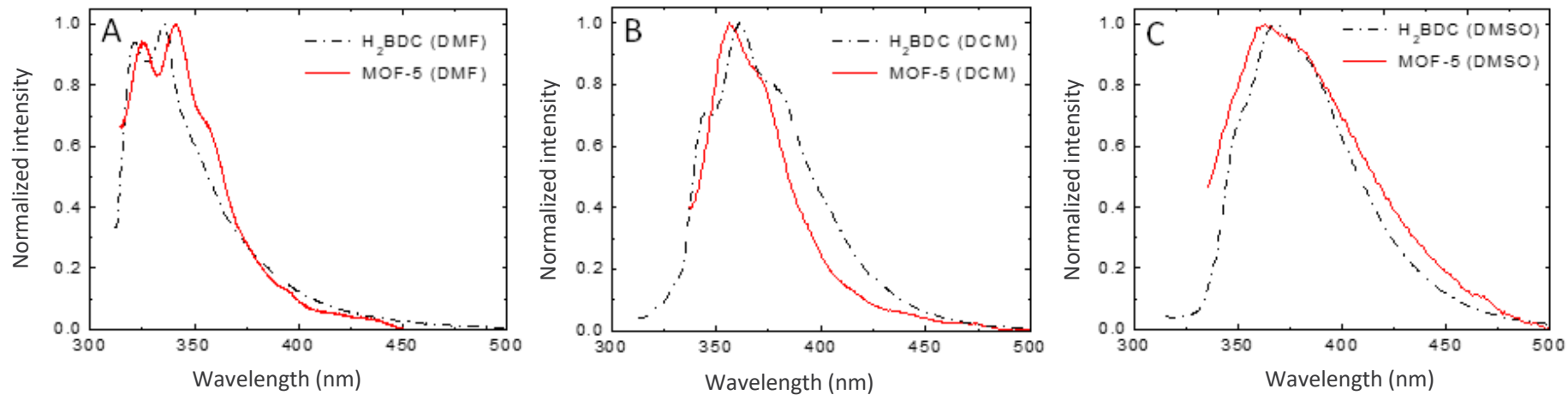
MOF-9



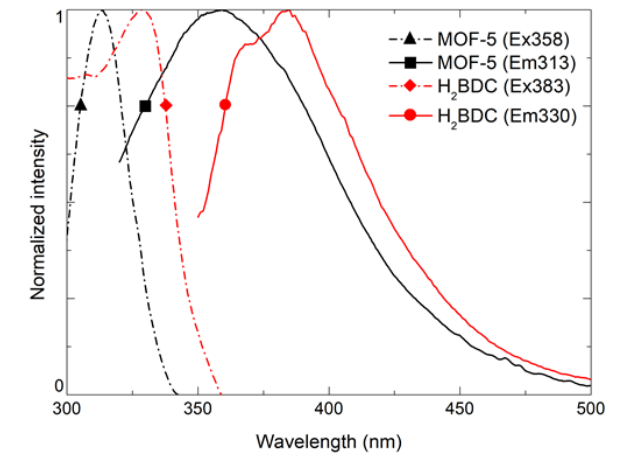
MOF-205



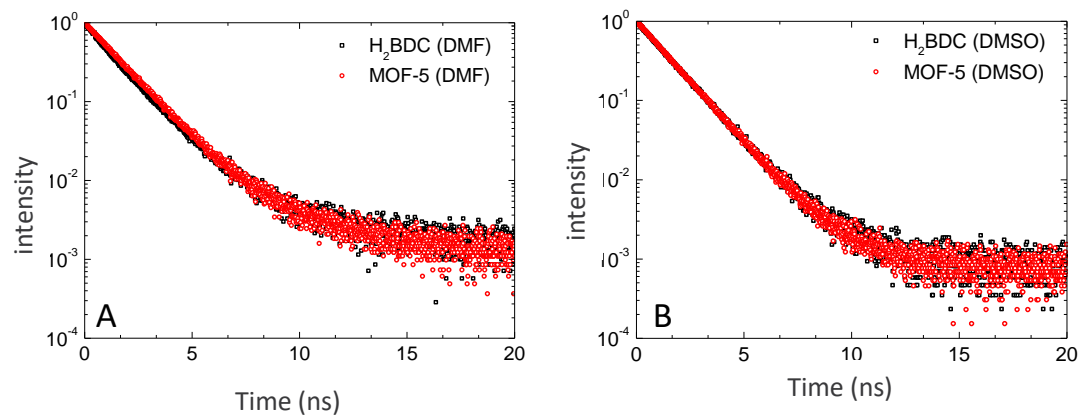
In different solvent : MOF-5 emission close to the ligand emission : support a Ligand centered origin of the fluorescence and closer to the theoretical value



Activated MOF

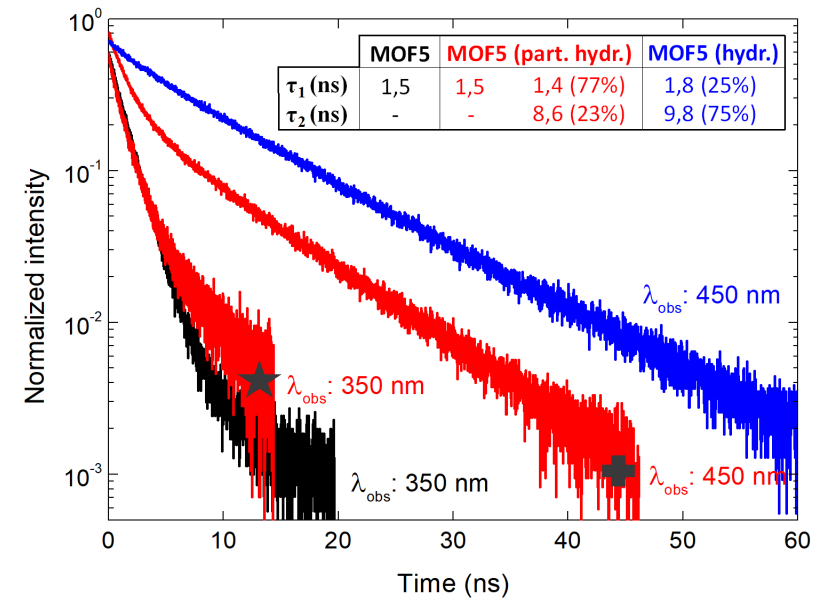
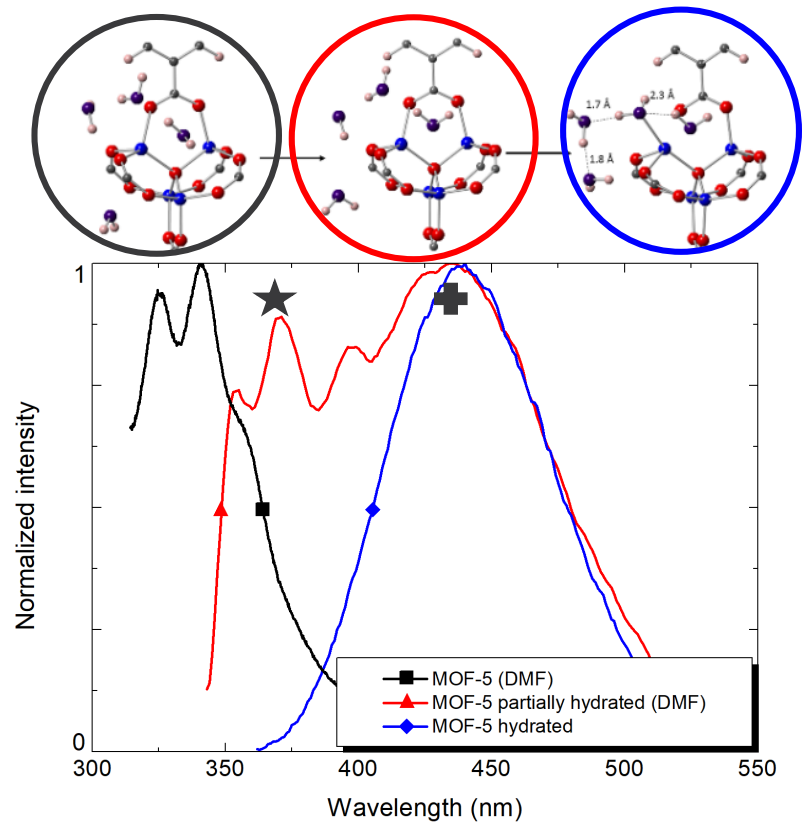


TCSPC (decay time of fluorescence) : same behavior as the ligand in solution



	$\lambda_{\max}(\text{Abso})$	$\lambda_{\max}(\text{Fluo})$
Activated MOF-5	313 nm	358 nm
H ₂ BDC solid	330 nm	383 nm
H ₂ BDC in DCM	314 nm	361 nm

- By unsealing our set-up we were able to follow MOF-5 water hydration by Fluorescence and TSCPC
- Observation of a two step process : in accord with Siegel *et al.*



Same behavior for MOF-9

MOF 205 less water sensitive

Context

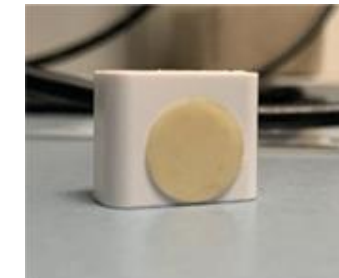
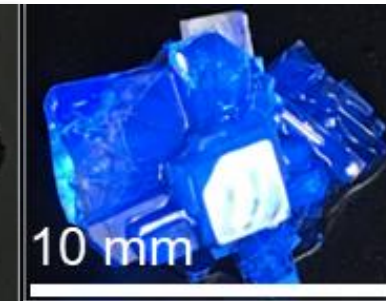
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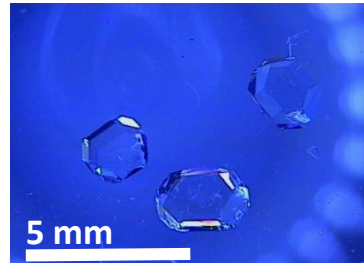
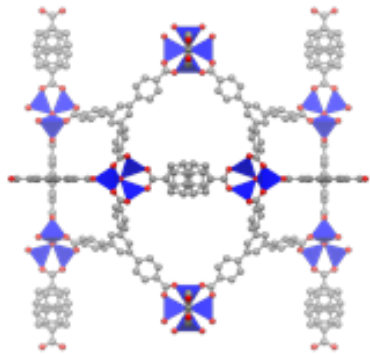
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Radiation detection

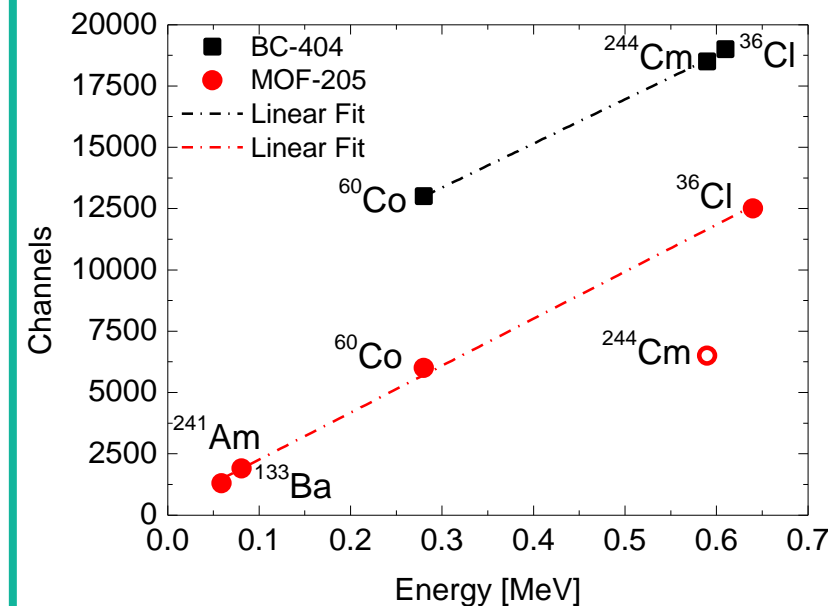
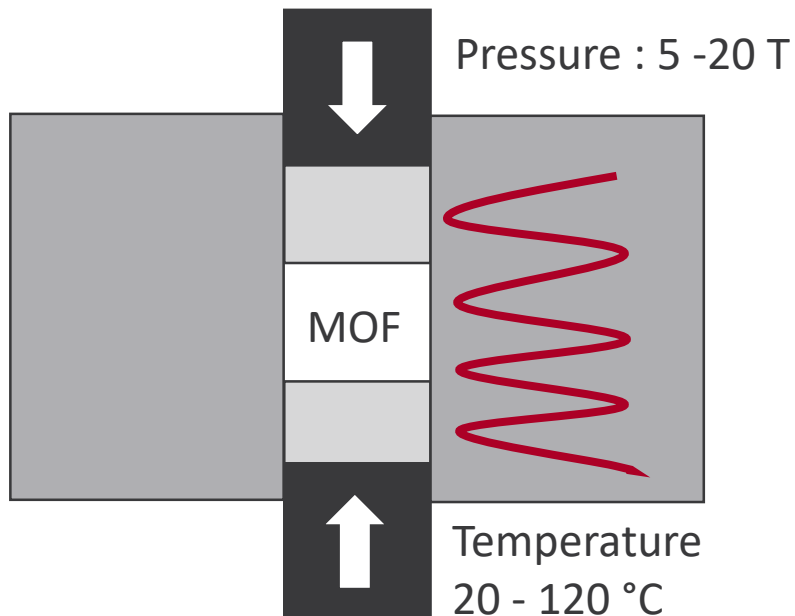
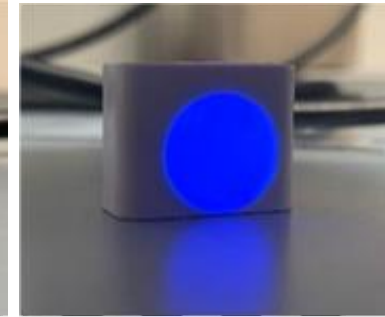
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MOF as starting material for new materials.

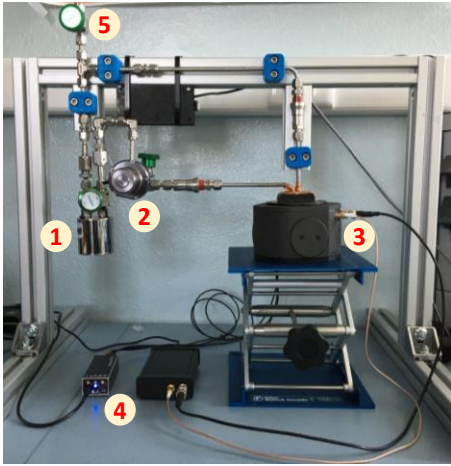


Sintering

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compression

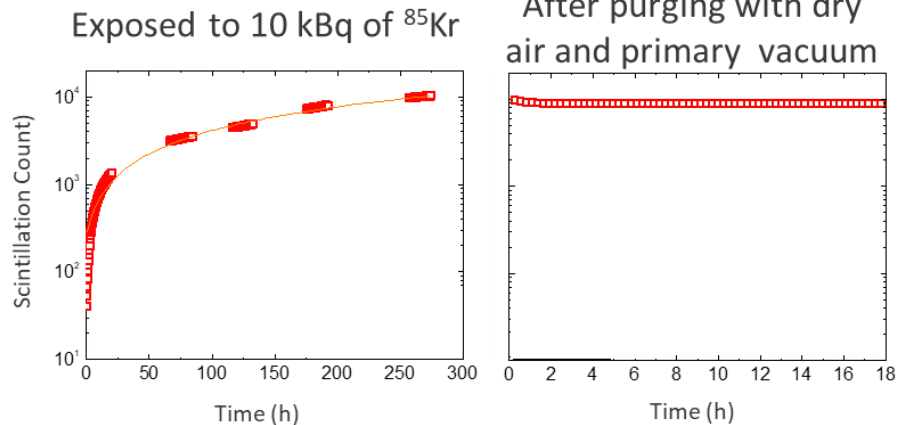
- Calibration curves
- Issue with alpha emitter
- Linearity with beta and gamma emitter.
- Low scintillation yields
- Better total absorption and higher counting rate

Radioactive gas trapping and detection



- Unique in the world radioactive gas Test bench
- Metrological instruments
- All radio-isotopes available

Hydrated MOF-9 (collapsed structure) exposed to ^{85}Kr



Solid radioactive sources of a noble gas isotopes ^{85}Kr

Hamel, M. ; Bertrand, G. ; Sabot, B. ; Villemot, V. French Patent Application FR2008120.

Reversible radioactive gas detection

European project Sparte :



Sharvane Mauree

Exciting results for ^{85}Kr ^{222}Rn and ^3H

Poster : B4.21

list **cea tech** **SPARTE** Scintillating Porous Architectures for Radioactive gas detection

METAL ORGANIC FRAMEWORK SCINTILLATOR FOR RADIOACTIVE GAS DETECTION

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Université Paris-Saclay, CEA, List, Samens and Electronique Architectures Laboratory, F-91191, Palaiseau, France

Context

- ^{85}Kr , ^{222}Rn and ^3H - decay emitting low energy ionizing radiation - online detection required - radioprotection
- ^{222}Rn - 2nd cause of lung cancer, ^{222}Rn - most produced radioactive gas in nuclear fuel cycle, indicator of core's health [1]
- ^3H production predicted to increase with implementation of fusion reactors - ITER, 1st primary fuel for tokamak
- No one-size-fits-all online detection system exists for all of these gases

Our approach

Scintillation

- Definition : a scintillator is a material which emits photons when excited by ionizing radiation
- Plastic/organic scintillators - reflector detection with low penetrating radiation -> surface penetration, low detector production
- Valence/Porous scintillators - Digital detection with low penetrating radiation -> surface penetration, radiation -> bulk penetration, low detector production

Scintillating MOF

- Combines porosity and fluorescence/scintillation
- Pure millimetric single crystals [2]
- Explore well known MOFs
- Doping Strategy

Results with ^{85}Kr

- Blank - No scintillator -> Chemisorption radiolator
- MOFs performance better/comparable to reference material (capsules of polystyrene)
- MOF-5 doped with ADC - improved performance with respect to MOF-5

Radioactive Gas Bench

- Miniature and portable online detection system
- These photo-multiplier tubes (PMTs) - Detection of photons in coincidence - Triple to Double Coincidence Rate (TDCR) [3]

Results at different activities

- Proof of concept that MOF can be used as porous scintillating materials for ^{222}Rn detection
- Similar results with ^{222}Rn in bubble measurement
- Explore other MOFs and doping strategy
- Improving gas bench configuration

Conclusion and Perspectives

- Present
- Future

References

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The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101019719

LCAE



PhD. Guillaume Bertrand



PhD. Matthieu Hamel
Best scintillation
chemist in the world

Left for private sector



Sharvane Mauree
PhD candidate

Synthesis and radioactive
gas detection



Vincent Villemot
PhD obtained 11/2021

Photophysiques and
MOF pellets



Alix Desjonquères
Undergrad intern 04-09/2022

HKUST growth on gold

LNHB



PhD. Benoît Sabot

Radioactive gas test bench



Thank you !