



HAL
open science

Re-absorption free scintillating MOFs crystals activated by ultrafast energy transfer

J. Perego, M. Orfano, C.X. Bezuidenhout, F. Cova, A. Vedda, C. Dujardin,
Benoit Sabot, P. Sozzani, S. Bracco, A. Comotti, et al.

► To cite this version:

J. Perego, M. Orfano, C.X. Bezuidenhout, F. Cova, A. Vedda, et al.. Re-absorption free scintillating MOFs crystals activated by ultrafast energy transfer. SCINT 2024 - 17th International Conference on Scintillating Materials and their Applications, Jul 2024, Milan, Italy. cea-04789669

HAL Id: cea-04789669

<https://cea.hal.science/cea-04789669v1>

Submitted on 18 Nov 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Reabsorption-free scintillating MOFs crystals activated by ultrafast energy transfer

Dr. Jacopo Perego

Dept. of Materials Science, University of Milano-Bicocca

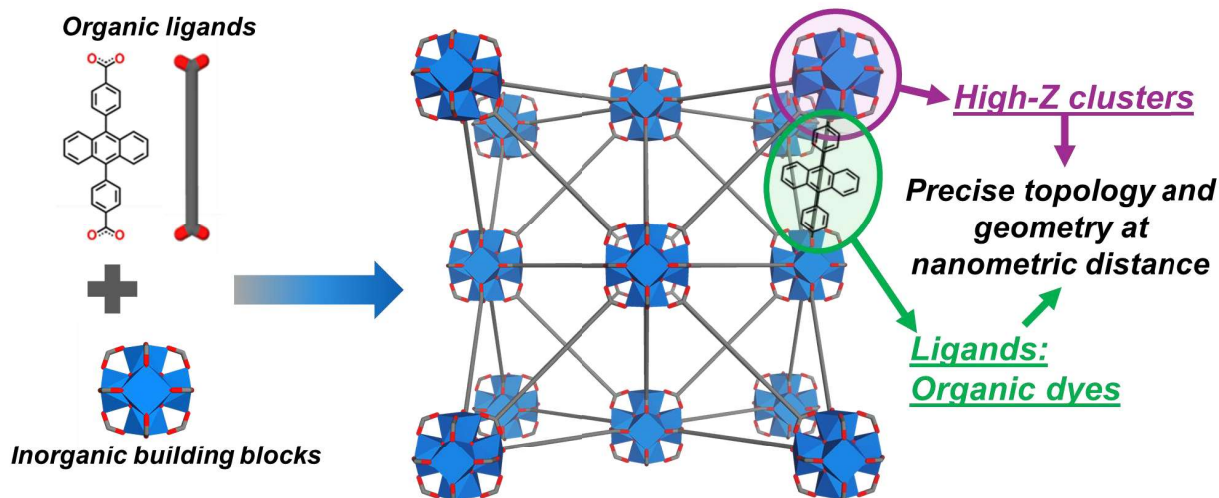


Metal-Organic Frameworks (MOFs)

Hybrid (organic/inorganic) crystalline nano-porous materials

"Targeted three-dimensional networks with unprecedented porosity can be designed from first principles. The diversity of nodes and ligands available allows fine-tuning of the molecular recognition features of these porous solids".
(M. Zaworotko, 2000)

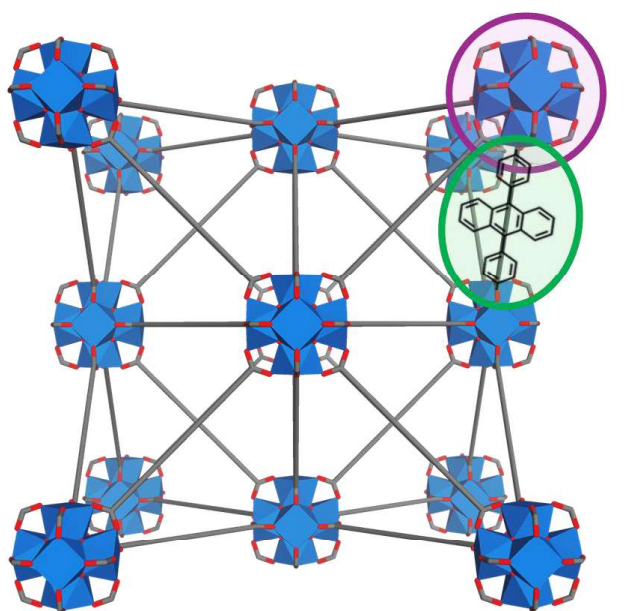
More than 100000 crystal structure of MOF materials (CSD, 2020)



CrystEngComm, 2012, 14 (9), 3001-3004. *J. Am. Chem. Soc.*, 1990, 112, 1546. *Angew. Chem. Int. Ed.*, 2000, 39, 3052 – 3054.

Metal-Organic Frameworks (MOFs)

Engineering hybrid scintillators at the nanoscale



Adv. Mater., 2009, 21, 95–101.

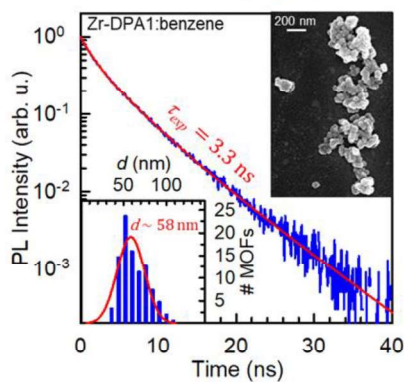
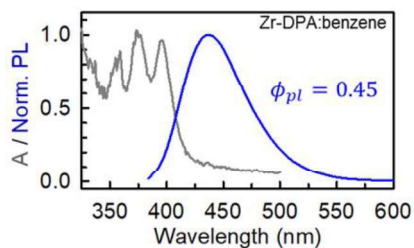
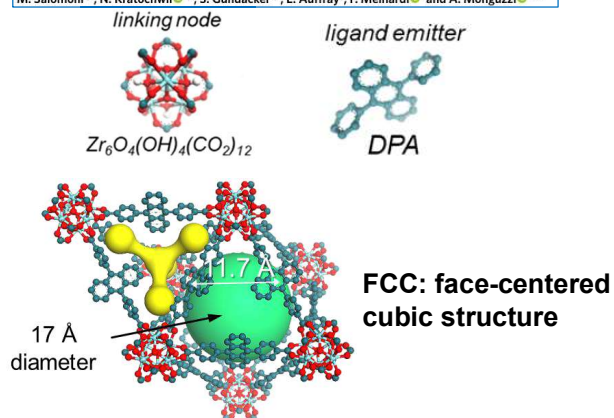
Properties:

- **Hybrid heterostructure** with an intimate interaction between the inorganic and organic components (**at nm scale**).
- Extremely versatile platform: **the metal-based cluster and organic ligand can be fine-tuned**. Engineering of the **spatial arrangement and the intermolecular interactions between nearest neighbours**.
- **High nano-porosity to be exploited**.

Dr. M. Allendorf (SNL, senior scientist)
First proposal of MOF crystals as scintillators

Luminescent and scintillating MOFs

Co-assembly of inorganic and organic building blocks by design



Perego J., Villa, I. *et al.* *Nature Photonics*, **2021**, *15*, 393 - 400.

Luminescent and scintillating MOFs

Co-assembly of inorganic and organic building blocks by design

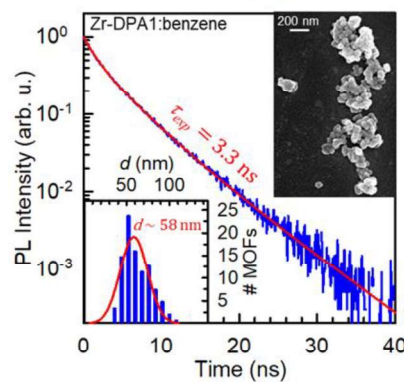
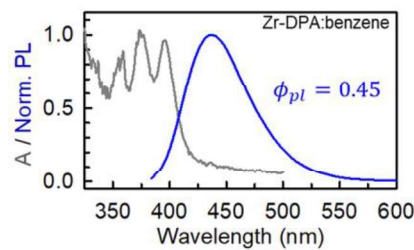
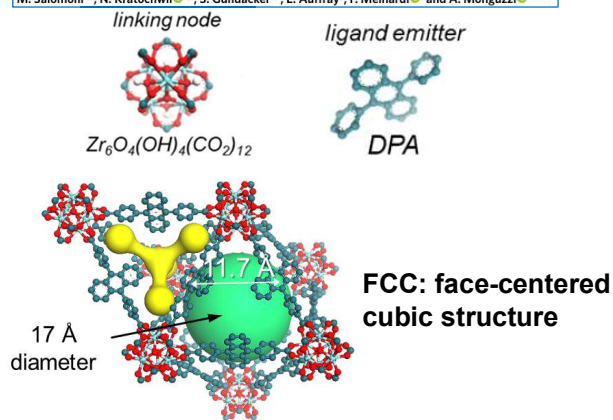
nature
photonics

ARTICLES
https://doi.org/10.1038/s41566-021-00769-2

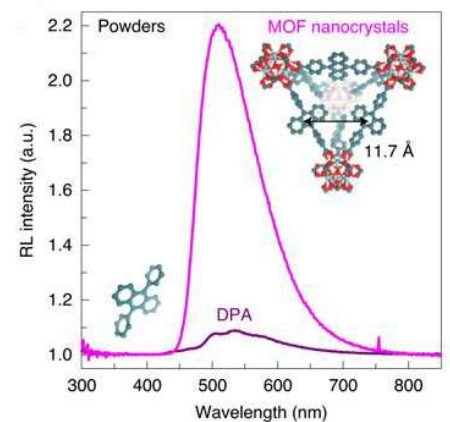
Check for updates

Composite fast scintillators based on high-Z fluorescent metal-organic framework nanocrystals

J. Perego^{1,2}, I. Villa^{1,2}, A. Pedrini¹, E. C. Padovani¹, R. Crapanzano¹, A. Vedda^{1,3,4}, C. Dujardin⁵, Charl X. Bezuidenhout⁶, S. Bracco¹, P. E. Sozzani¹, A. Comotti^{1,3,5}, L. Gironi^{1,3,5}, M. Beretta¹, M. Salomoni^{1,4}, N. Kratochwil^{1,4}, S. Gundacker^{1,4}, E. Auffray¹, F. Meinardi¹ and A. Monguzzi^{1,3,5}



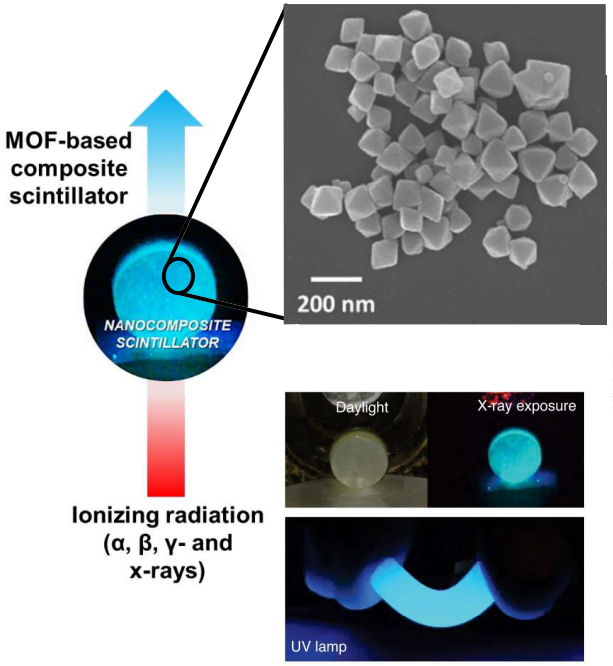
Sensitization effect of the inorganic building blocks – synergy between the organic and inorganic building blocks



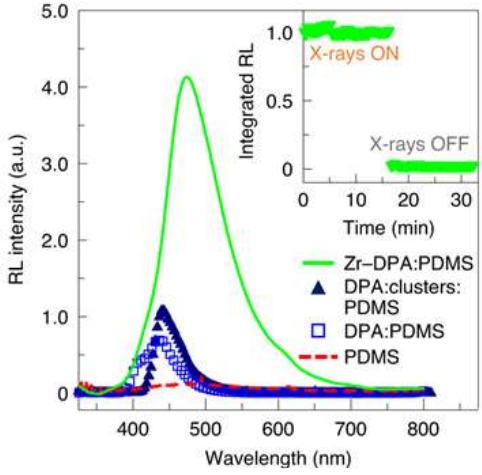
Perego J., Villa, I. *et al.* *Nature Photonics*, **2021**, *15*, 393 - 400.

Luminescent and scintillating MOFs

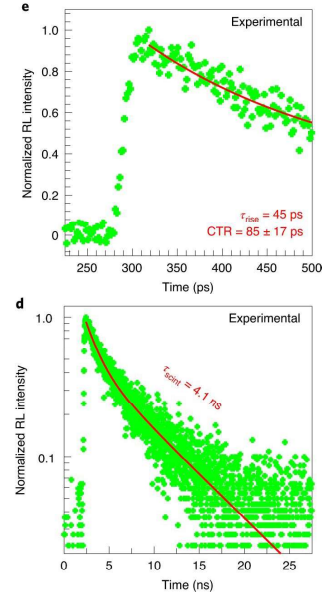
Polymer nanocomposite scintillators based on luminescent MOFs



Polymer composite radioluminescence under soft X-ray excitation



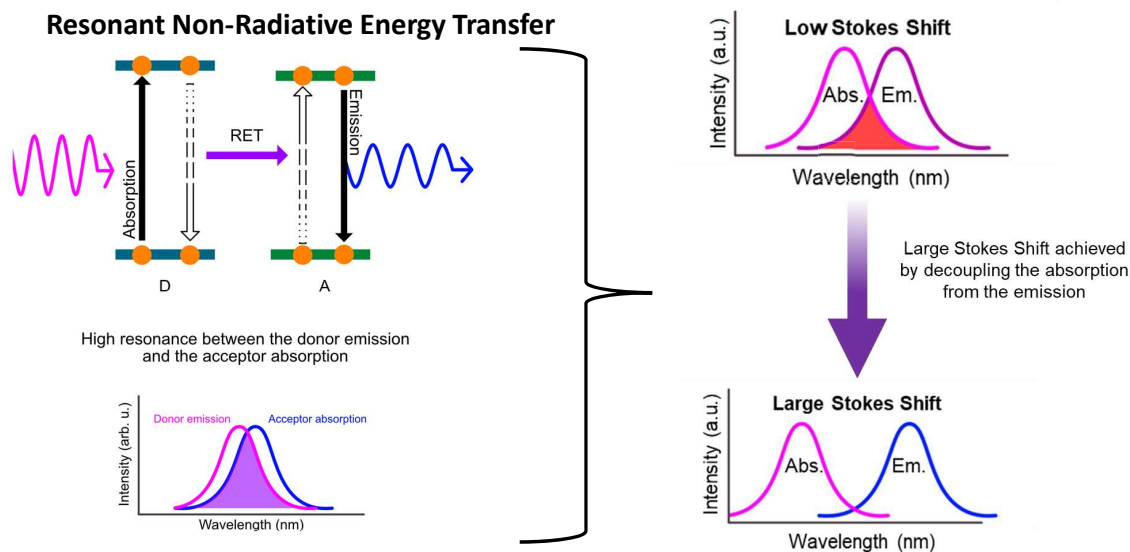
ultrafast time-resolved scintillation experiments (X-ray excitation)



Large Stokes shift engineering in MOFs

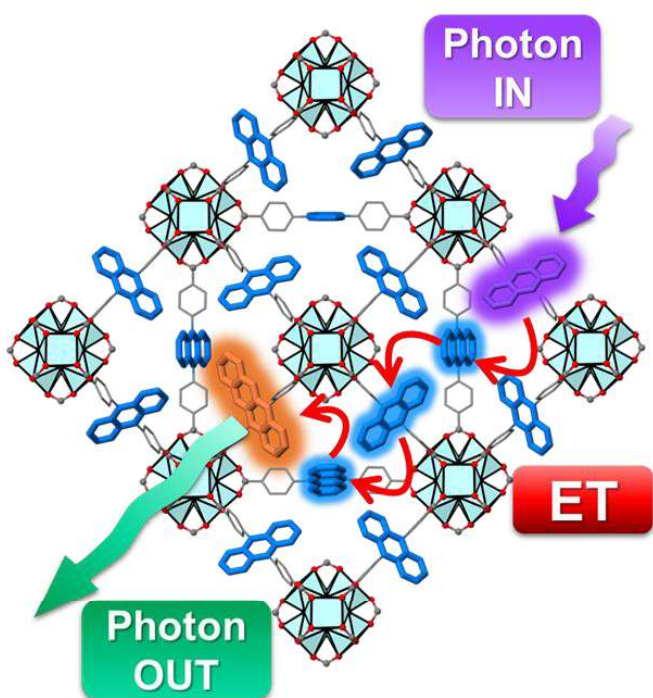
How do we deal with the reabsorption issue?

In MOF architectures, large Stokes shift can be engineered exploiting the **fast diffusion of singlet excitons within the framework** and the ultra-fast **non-radiative energy transfer between donor and acceptor molecules**.



Large Stokes shift engineering in MOFs

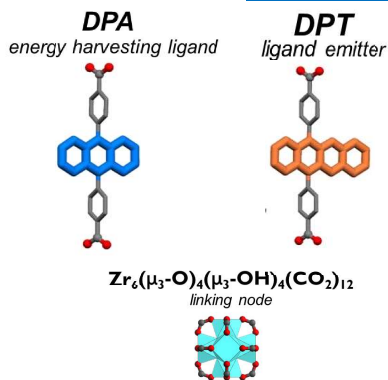
Large Stokes shift exploiting NON-Radiative energy transfer



- In MOF architectures, large Stokes shift can be engineered exploiting the **fast diffusion of singlet excitons within the framework** and the ultra-fast **non-radiative energy transfer between donor and acceptor molecules**.
- Inserting organic dyes with complementary electronic properties controls the **kinetics of the emission activation** and the **Stokes shift emission** → **Hetero-ligand MOFs**

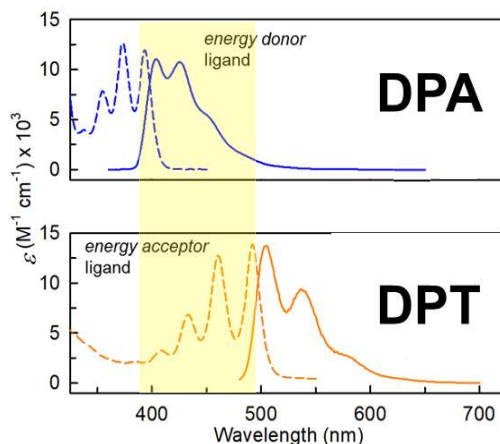
Large Stokes shift engineering in MOFs

Preparation of hetero-ligand MOFs

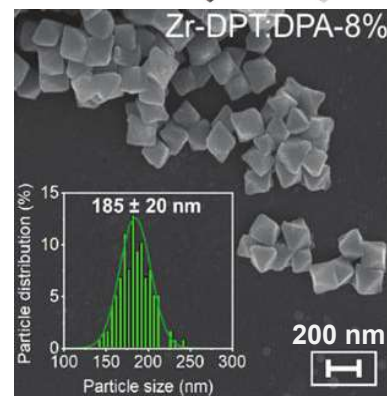
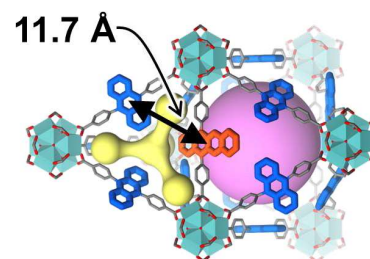


Perego, J. et al., *Nature Communications*, 2022, 13, 3504.

Complementary photophysical properties

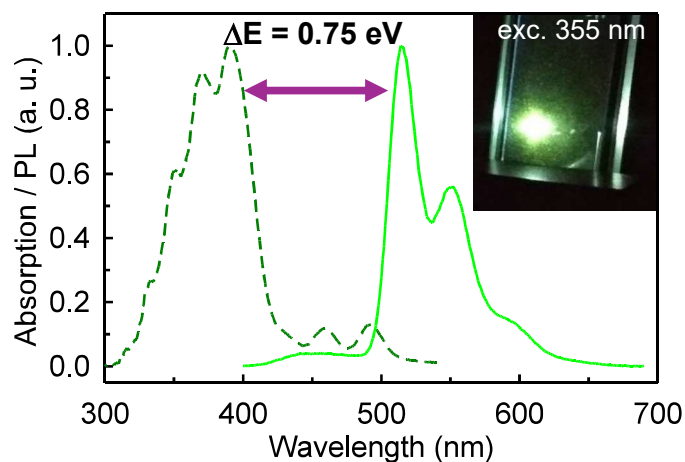
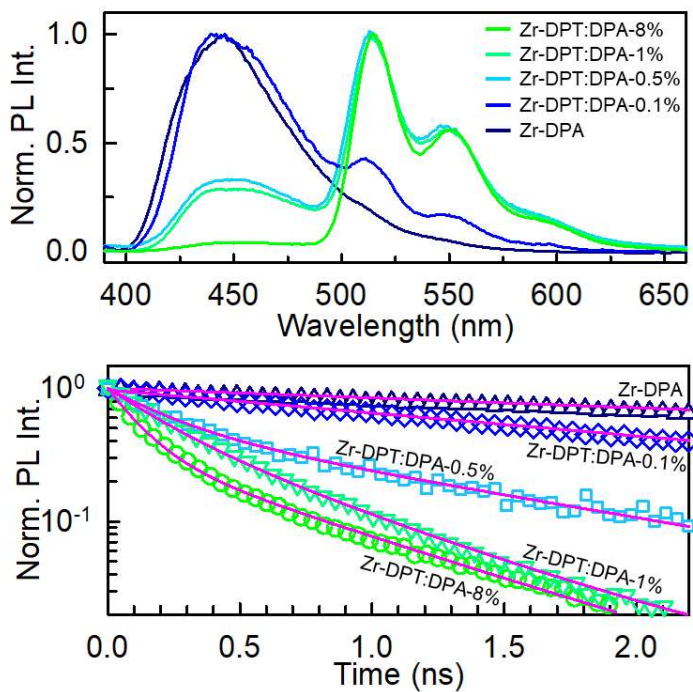


Zr-DPT:DPA-x%
0.1 < DPT(%) < 8



Large Stokes shift engineering in MOFs

Energy transfer and large Stokes shift emission of hetero-ligand MOFs

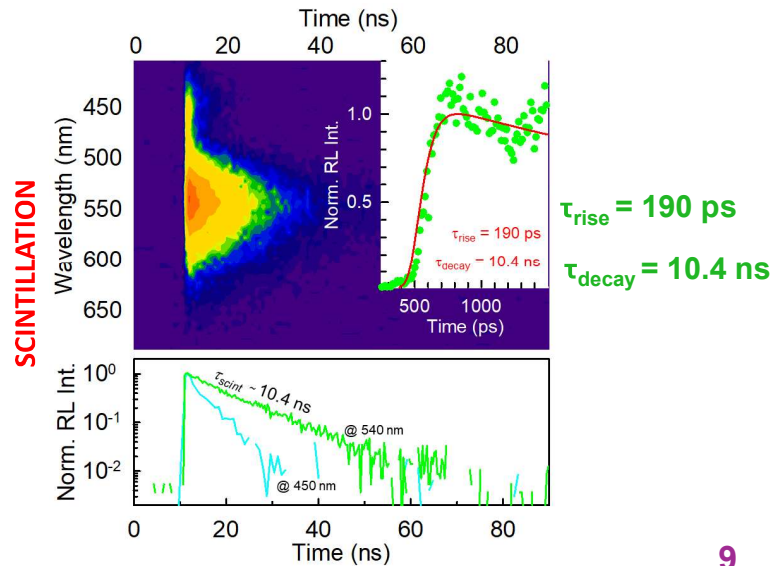
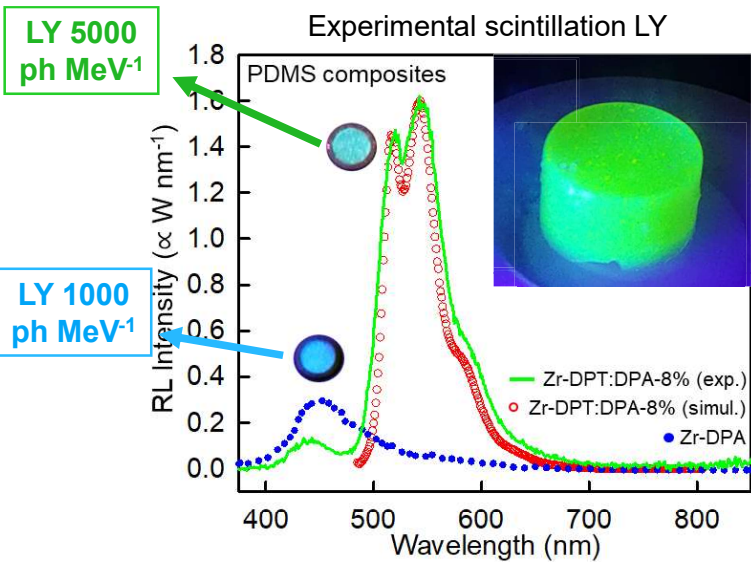


Hetero-ligand MOFs with a minimal emitter concentration (8%) display **reabsorption-free, large Stokes shift emission!** DPT acts as an **ultra-fast wavelength shifter** activated by energy transfer!

Large Stokes shift engineering in MOFs

Large Stokes shift emission composites

Hetero-ligand MOFs shows **+500% light yield** compared to the homo-ligand MOFs thanks to the large Stokes shift emission



Large Stokes shift engineering in MOFs

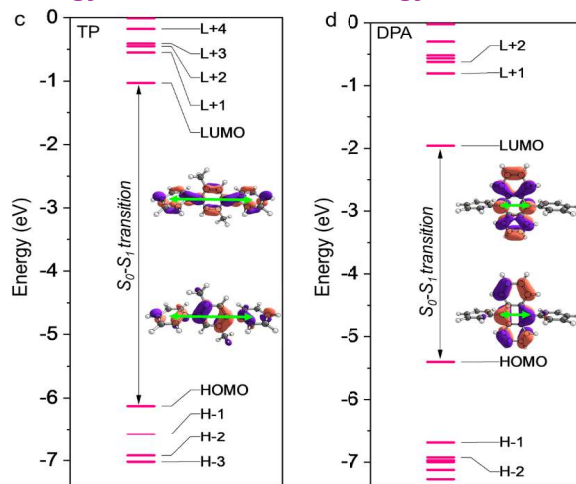
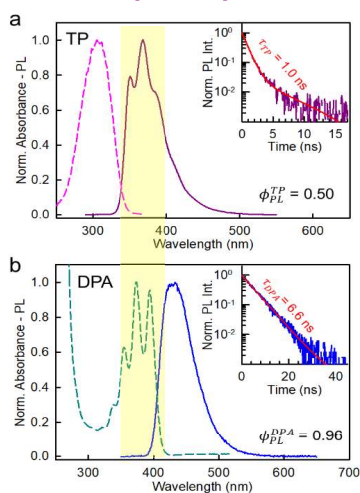
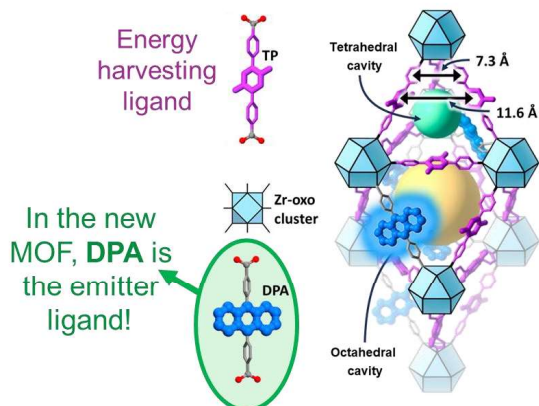
Tuning the emission wavelength and the emission kinetics

The versatile chemistry of MOFs allows for **tuning the emission wavelengths** and the **emission lifetime**.

The TP ligands MO overlap enables exchange interaction between ligands that **promote and speed up the homo-energy transfer and thus energy diffusion**.

Zr-DPA:TP-x%

0.05 < DPA(%) < 22.9

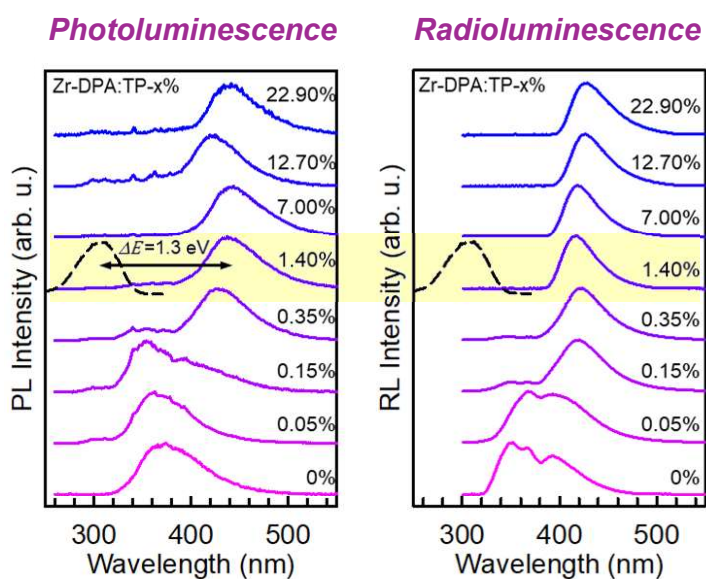


Orfano, M., Perego, J., et al., *Adv. Funct. Mater.* **2024**, 2404480.

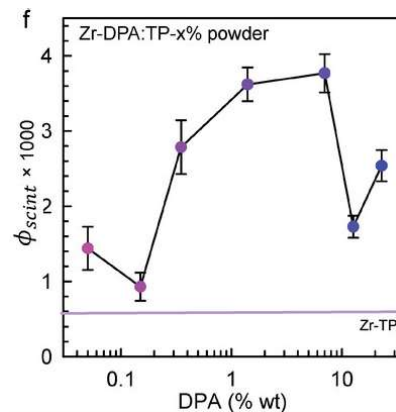
Large Stokes shift engineering in MOFs

Large Stokes shift exploiting NON-Radiative energy transfer

The physical overlap between molecular orbitals of the TP molecules promotes and speeds up the energy diffusion, determining **larger Stokes shift with lower doping ($\Delta E = 1.3$ eV)** with blue emission at **430 nm**.

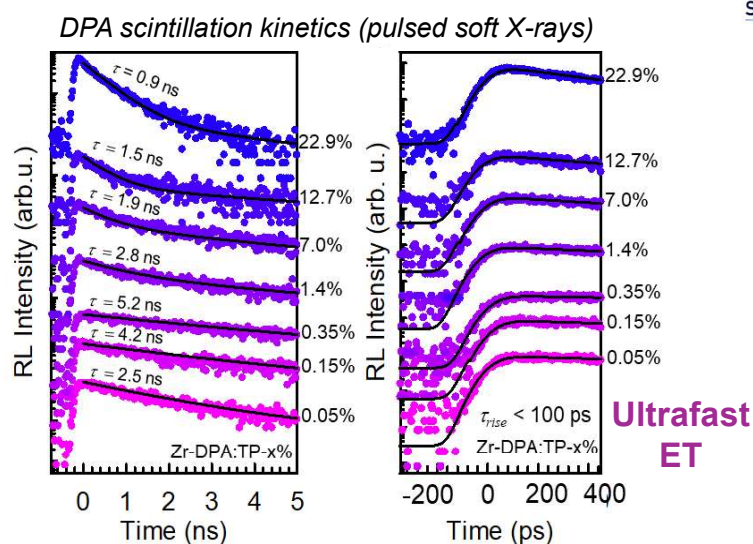
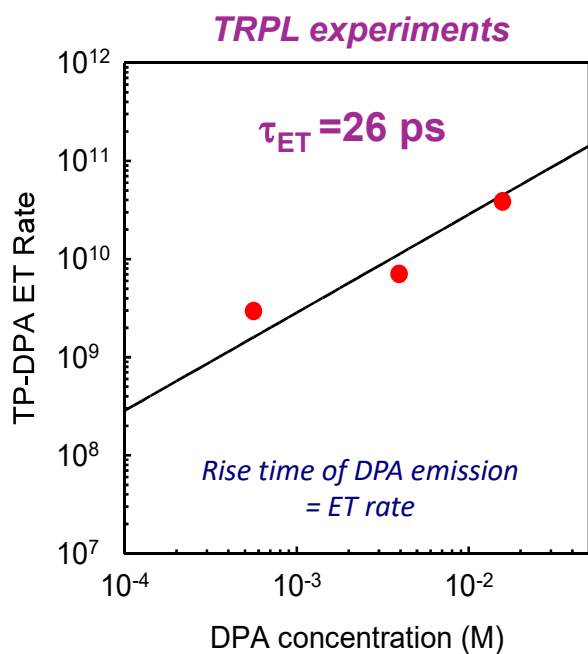


ϕ_{scint} is the highest for Zr-DPA:TP-1.4% and Zr-DPA:TP-7.0%, ≈ 3800 ph MeV⁻¹



Large Stokes shift engineering in MOFs

Large Stokes shift exploiting NON-Radiative energy transfer

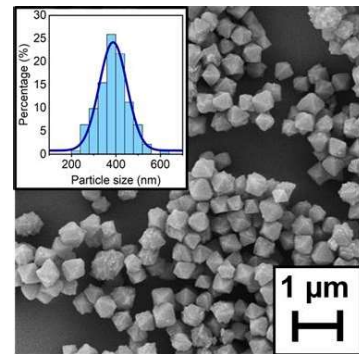
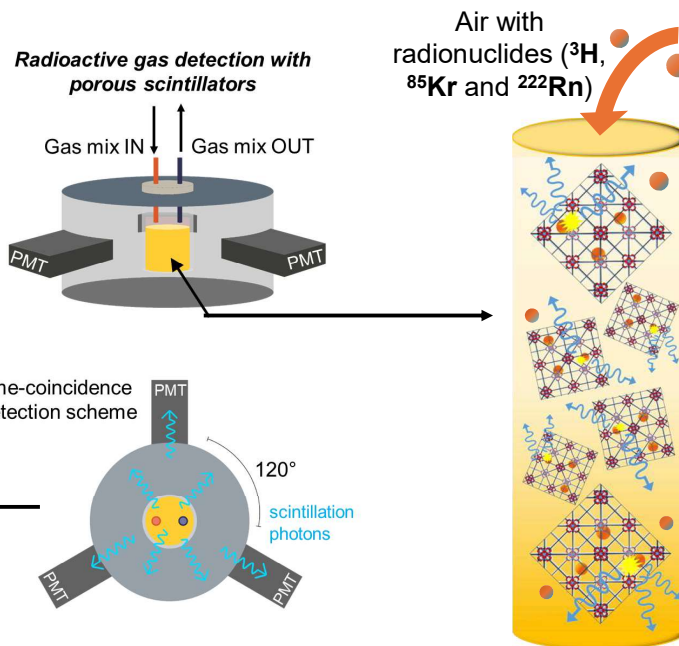
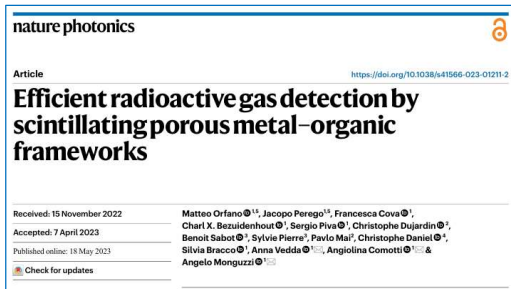


$\tau_{rise} < 100 \text{ ps}$ (26 ps from TRPL experiment)

$\tau_{decay} = 1 - 3 \text{ ns}$

Scintillating MOFs for radioactive gas detection

SPARTE: Scintillating Porous Architectures for RadioacTivE gas detection



cea Dr. B. Sabot
 Dr. S. Pyerre



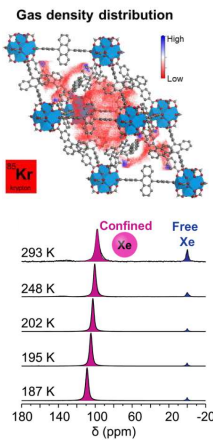
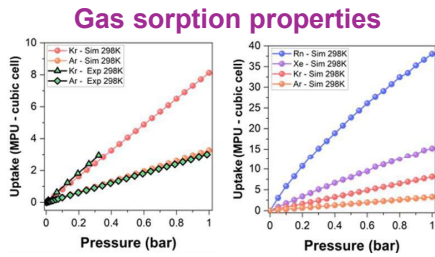
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 899293

Orfano M., Perego, J. *et al.* *Nature Photonics*, **2023**, 17, 672 - 678.



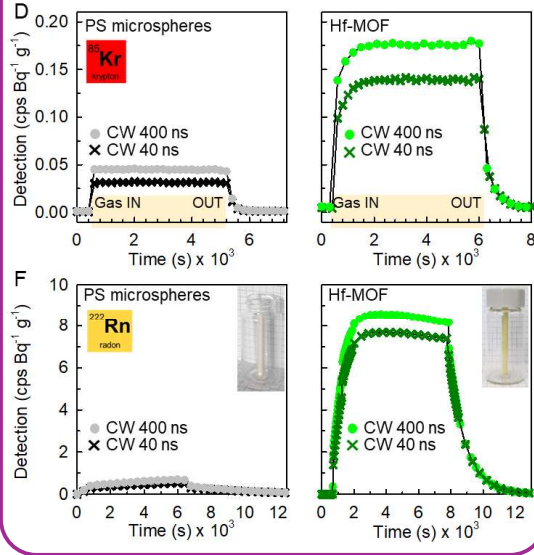
Radioactive gas detection with MOFs

Effective radioactive gas detection with scintillating nanosponges

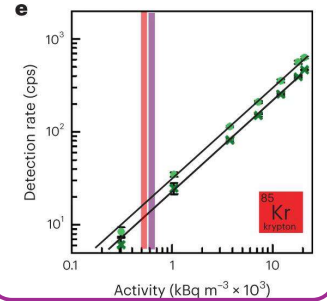


GCMC simulation

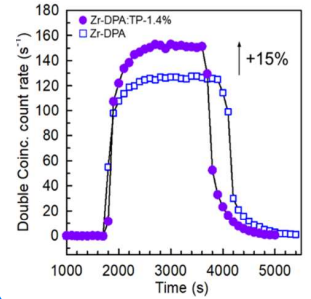
Radioactive gas detection



Ultralow concentration detection and linear response



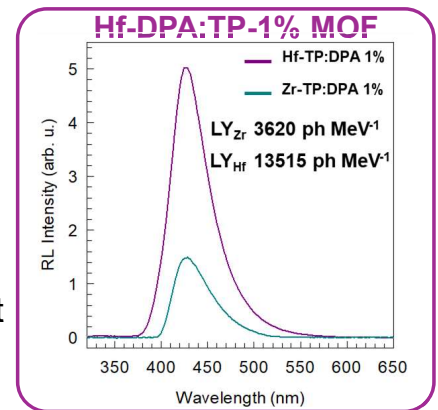
Heteroligand MOFs for improved radioactive gas detection



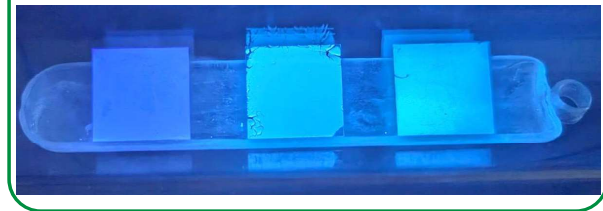
Conclusions

- **MOFs are versatile emitters.** Energy transport and energy transfer processes can be fine-tuned exploiting ligand and structural properties. **Massive Stokes shift** has been obtained while keeping **fast emission properties** → *use in TOF- PET, HEP experiments, metrology...*
- **MOFs can be grown on substrates,** opening the development of real devices with potentially also electric interfaces and useful for charge transport. → *TOF- PET detectors where ultrafast time resolution is required are being fabricated*
- **Nanoporosity allows the development of innovative solid-state nanoporous scintillators** for effective radioactive gas detection at ultra-low concentrations.

What is next?



MOF films



Acknowledgements and funding



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

Prof. P. Sozzani
Prof. A. Comotti
Prof. S. Bracco
Dr. C. X. Bezuidenhout
Dr. L. Dharmo
S. Piva
A. Rigamonti
Master and Undergraduated students

Thank you!

Prof. A. Monguzzi	Prof. C. Dujardin	Dr. E. Auffray
Prof. A. Vedda	Dr. P. Mai	Dr. M. Salomoni
Dr. M. Orfano	Dr. B. Sabot	Dr. F. Pagano
Dr. F. Cova	Dr. S. Pierre	Dr. I. Franck
Dr. I. Villa	Prof. C. Daniel	Dr. N. Kratochwil
Prof. F. Meinardi	Dr. M. Antico	Dr. S. Gundacker
Prof. L. Gironi		

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



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 and **PRIN-2022 – HYSTAR** no. H53D23004720006 and **grant MINERVA** no. H25E22000490006. The Lombardy Region for “**Enhancing Photosynthesis**” grant (2021-2023) was acknowledged for the financial support. We thank the **ESRF synchrotron facility** in Grenoble (France) for access to the ID22 beamline (Project: HC-5193).

