SPARTE
Scintillating Porous Architectures for RadioacTivE gas detection

UNIVERSITÀ DEGLI STUDI DI MILANO BICOCCA

# Development of metal-organic frameworks (MOFs) nanocrystals with high luminescence and scintillating properties: design, preparation and characterization.

Jacopo Perego, Ph.D



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

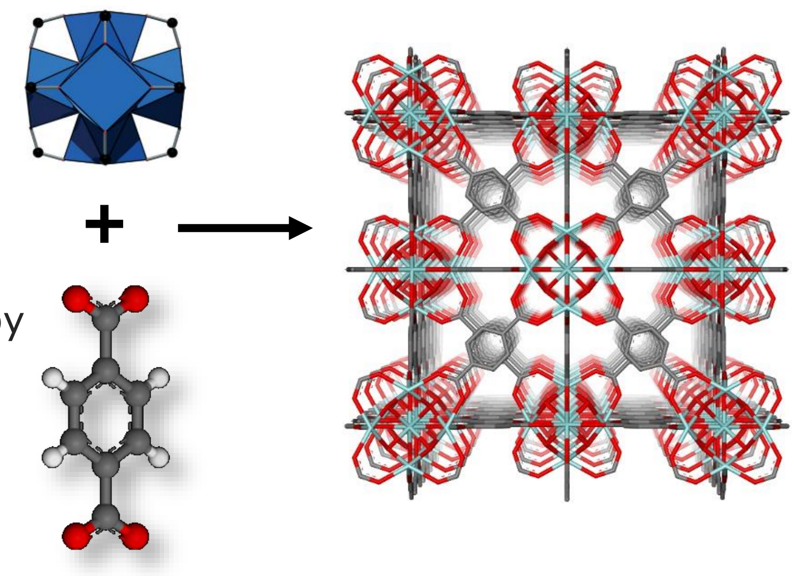
14/11/2022

# Metal-Organic Frameworks

**Metal-Organic Frameworks (MOFs) or Porous Coordination network (PCNs):**

**Crystalline hybrid materials with permanent porosity**

- **Organic-inorganic modular materials**
- **Crystalline solids** (self-assembly, reversibility)
- **High surface area,** up to 7300 $m^2\ g^{-1}$
- **Pore distribution and pore volume** defined by the crystal structure (**microporosity, IUPAC**)
- **High chemical purity**



Special issue: *Chem. Rev.*, **2012**, *112*, 2, 673–674.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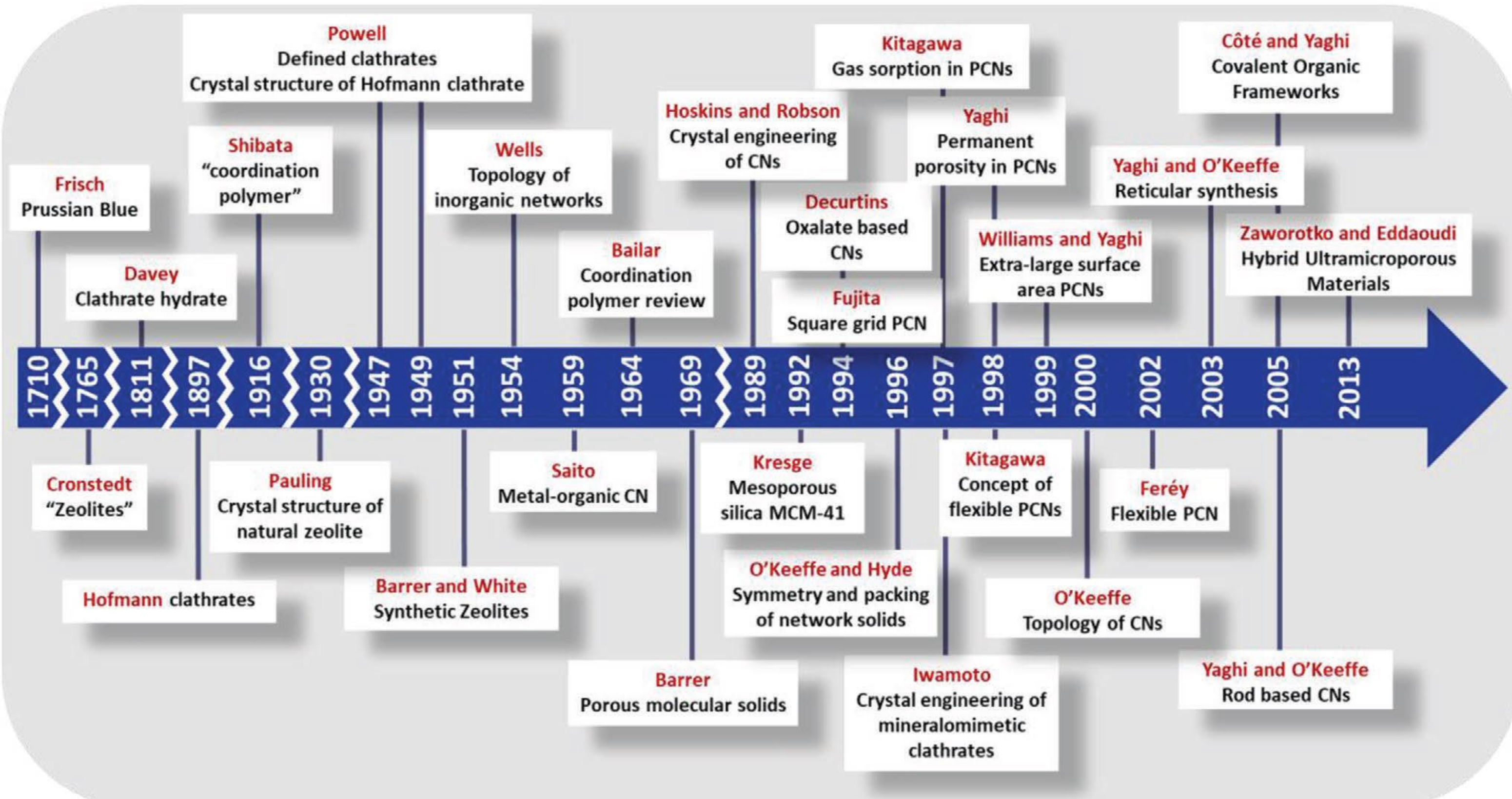
# MOFs: history

**Metal-Organic Frameworks (MOFs): standing on the shoulder of giants**




*Small*, **2021**, *17*, 2006351



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# MOFs: structure by design

**Metal-Organic Frameworks (MOFs):**

- **1700-1989**: coordination polymers (CP) and microporous/nanoporous materials are well-defined and distinct materials classes
- **1989**: **seminal work by Prof. Hoskins and Robson**: rational design of three dimensional CP using a crystal engineering approach
- **1997/1998**: Prof. Kitagawa, Prof. Yaghi described the **first examples of microporous coordination polymers**
- **2003**: **reticular synthesis** proposed as rationale approach to MOF design
- **2020: More than 100000 crystal structure** of MOF materials (CSD)

***...Find the needle in the haystack...***

*Small*, **2021**, *17*, 2006351; *Mol. Front. J.*, **2019**, *03*, 66-83.


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# Structure by design: parameters

- Primary components: inorganic cations/cluster and organic ligands
- Topology (MOF family)
- Isoreticular MOF
- Multivariate MOF
- Interpenetration
- Framework flexibility
- Morphology (powder, nanocrystalline, single crystal,…)
- Interaction with guests molecules

*Science*, **2013**, 341, 1230444; *Science*, **2010**, *327*, 846-859;


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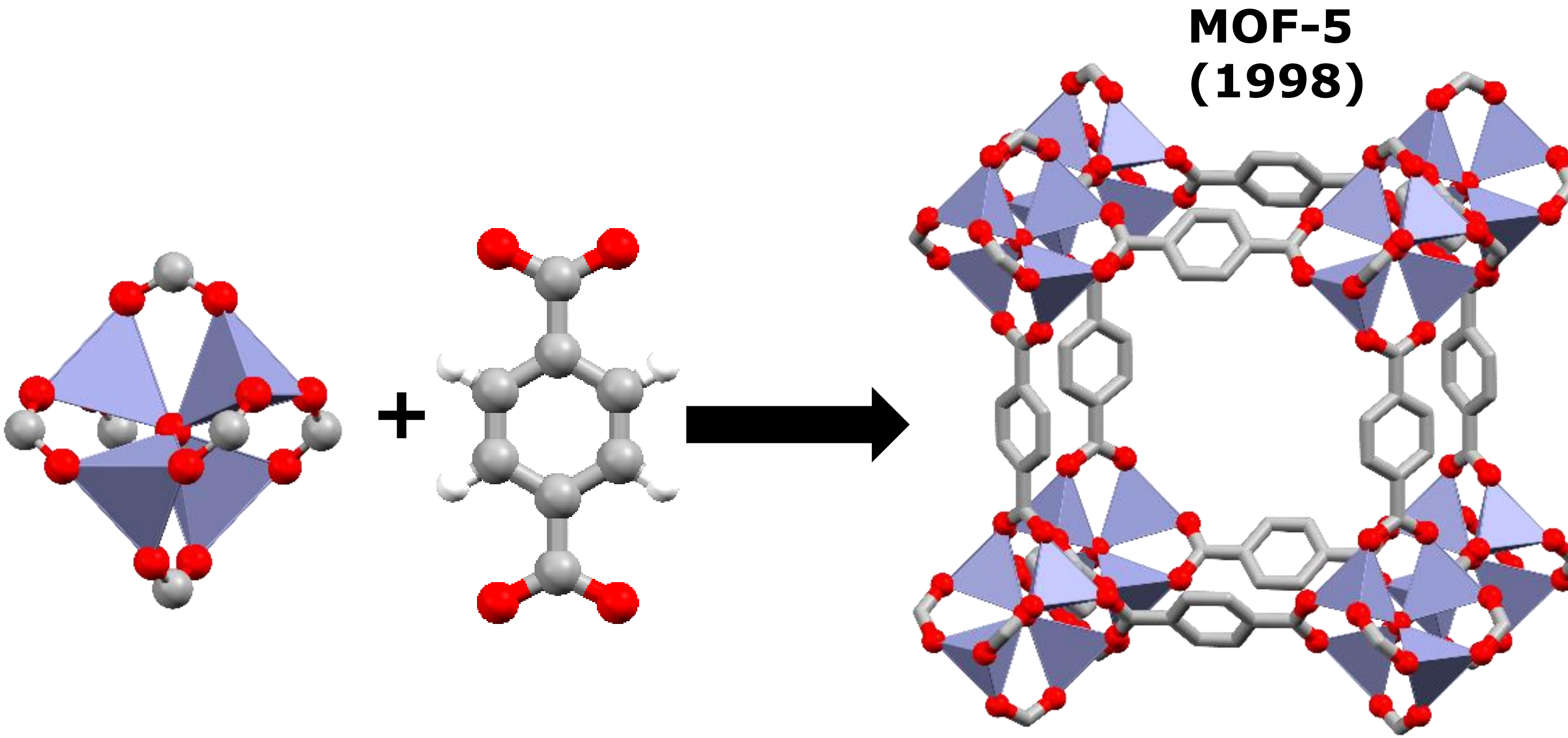
# Structure by design: example




**Basic zinc acetate cluster**

**Terephtalate ligand**

**Simple cubic structure**

<u>*Science*</u>, **2013**, 341, 1230444; <u>*Science*</u>, **2010**, *327*, 846-859;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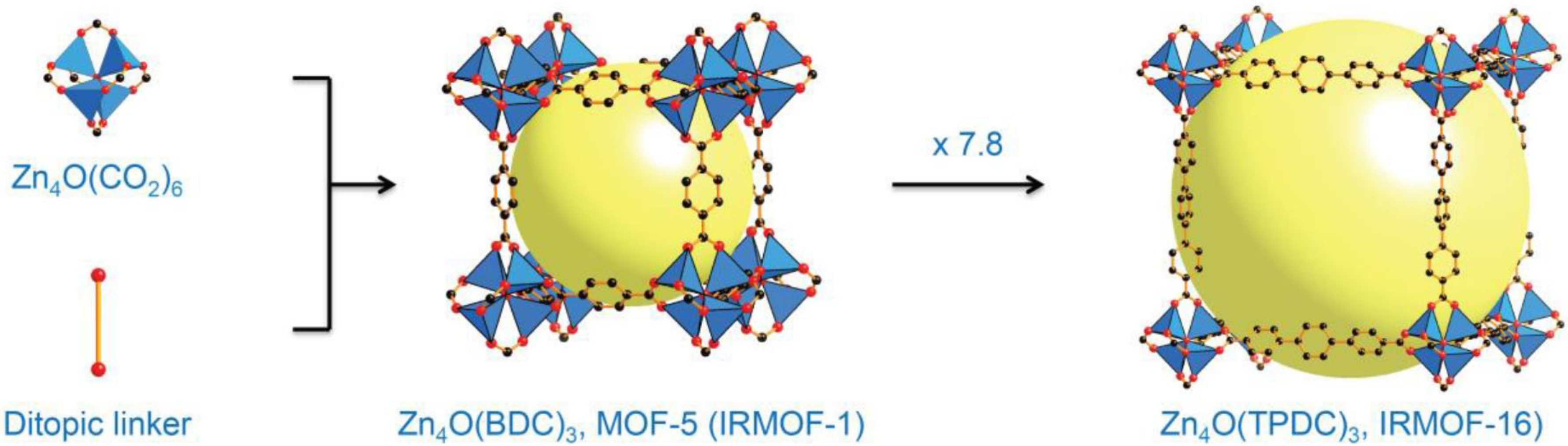
# Structure by design: isoreticular expansion

Lenghtening or functionalization of the organic ligand produces MOF with expanded frameworks without affecting the framework topology




<u>*Science*</u>, **2013**, 341, 1230444; <u>*Science*</u>, **2010**, *327*, 846-859;



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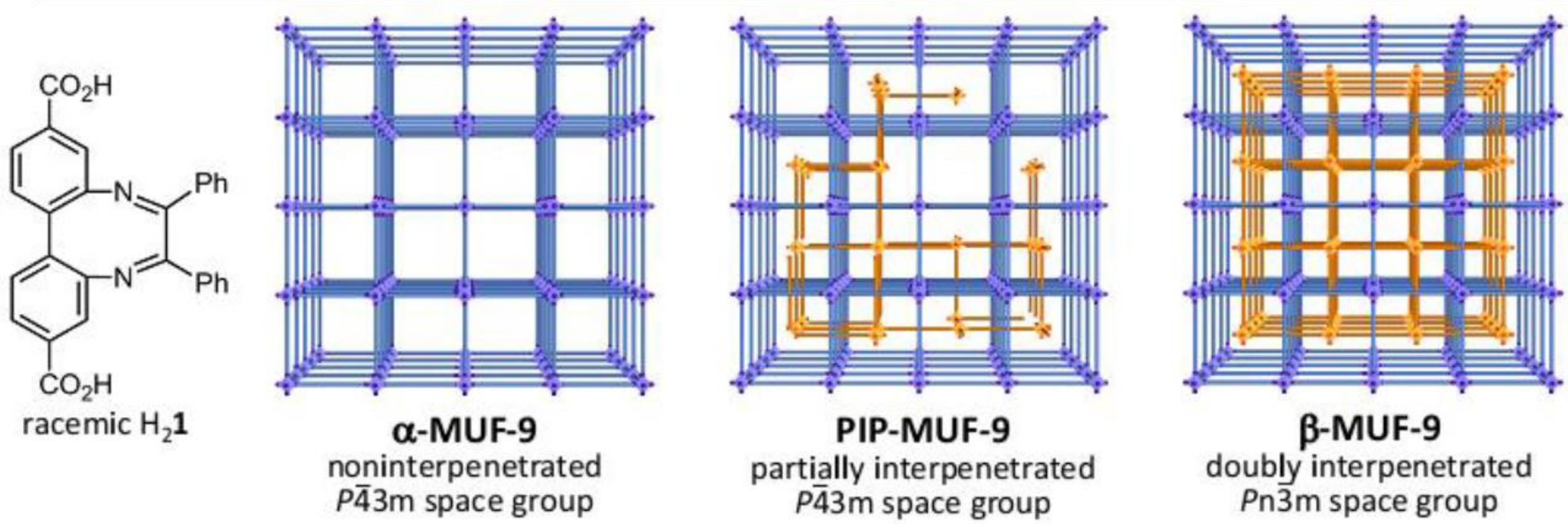
# Structure by design: interpenetration

Different frameworks can be entangled one another generating a mechanical linkage.




*Nature Chemistry*, **2016**, *8*, 250-257.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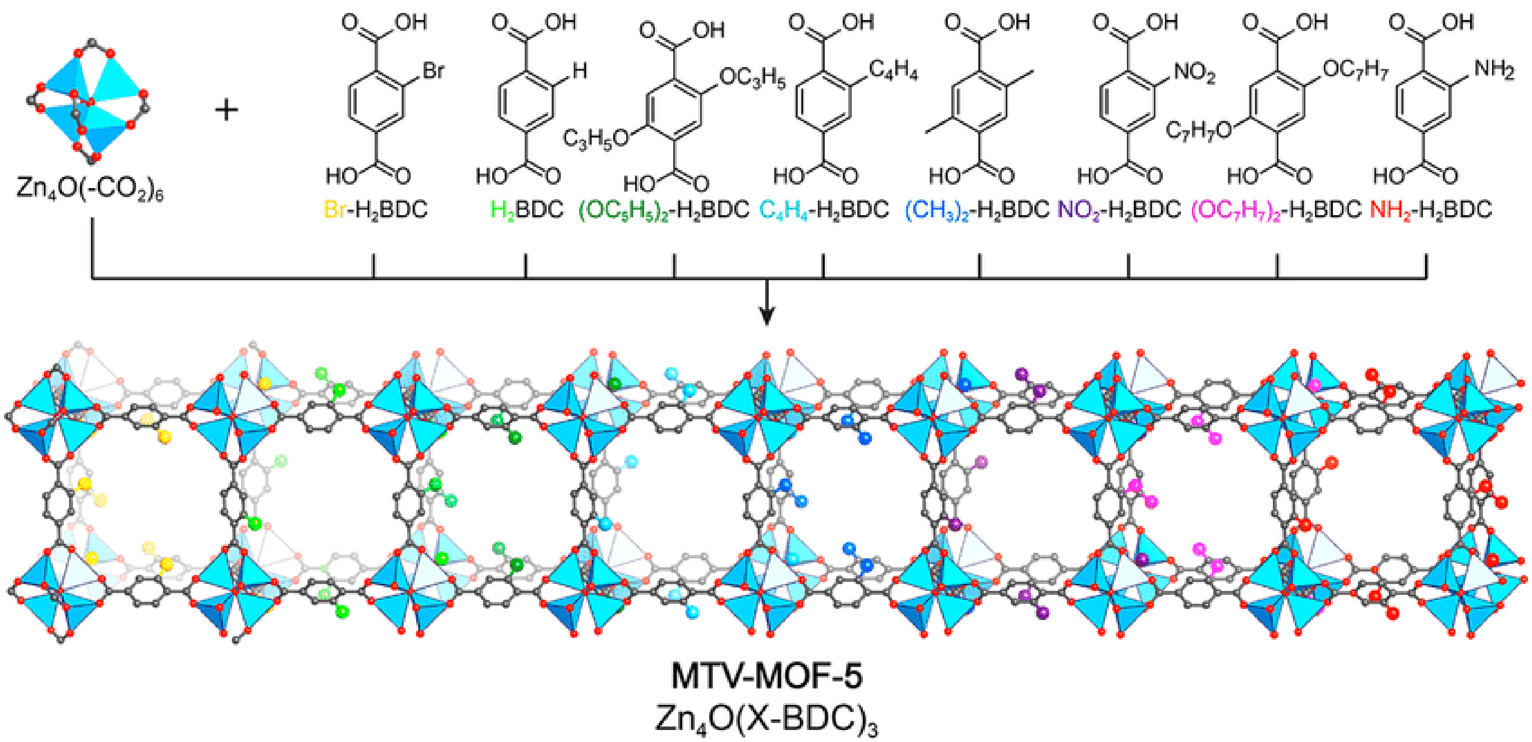
# Structure by design: multivariate MOF

Functionalized ligands installed at random or in precise sequence to tune MOF properties and pore surface properties.




<u>*ACS Cent. Sci.*</u>, **2018**, *4*, 11, 1457–1464.



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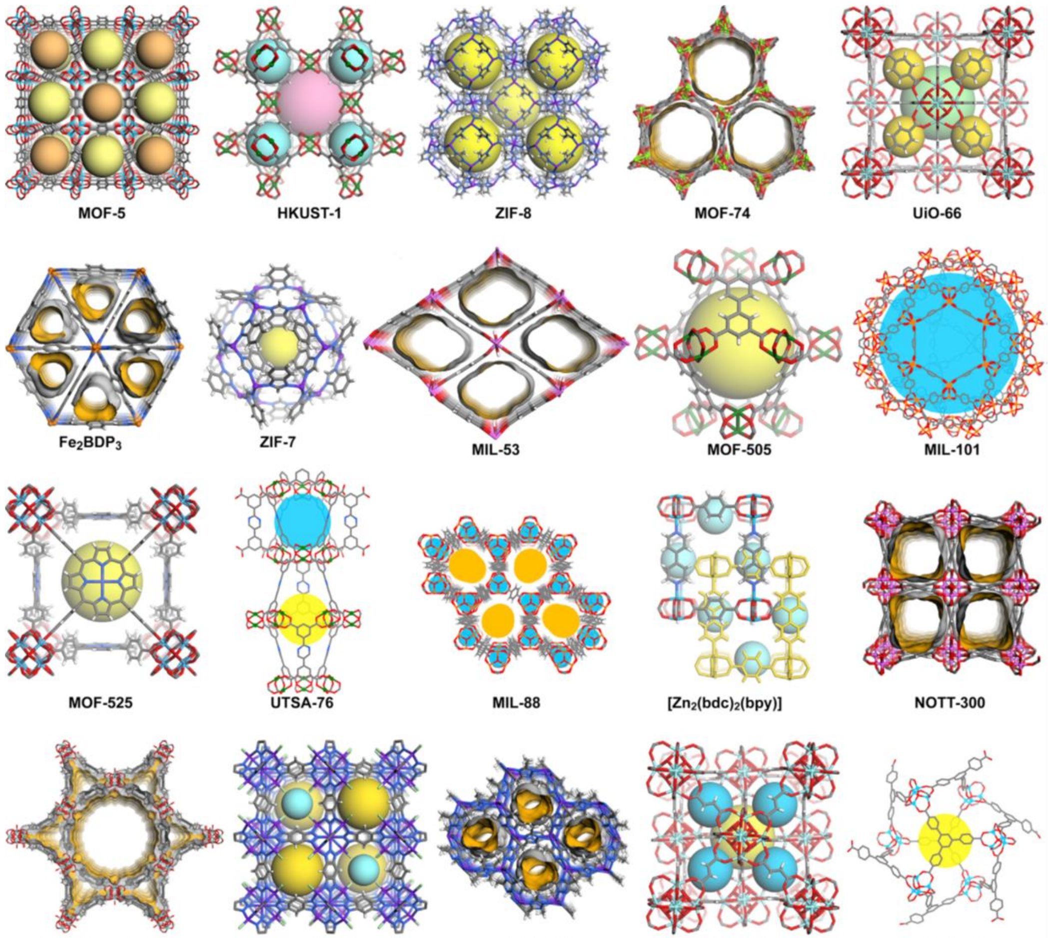
# Structure by design: towards complexity




<u>*Chem*</u>, **2020**, *6*, 337-363.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# Synthetic strategies

The **synthetic method strongly affects the characteristics and properties of the material.**

- New polymorphs, different crystal structures
- Particle size, size distribution, morphology
- Defectivity and purity

The size, shape, morphology and surface properties of crystals modify the physico-chemical properties of MOFs: dispersibility, PL quantum yield, gas diffusivity, ...

*Chem. Rev.*, **2012**, *112*, 933–969; *Adv. Funct. Mater.*, **2020**, 30, 1909062


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# Synthetic strategies

**Targeting Nanocrystalline Metal-Organic Frameworks:**

***Solvothermal synthesis***

***Microwave assisted synthesis***

***Modulated solvothermal synthesis***

***Mechanochemistry***

***Emulsion or confined synthesis***

***Flow chemistry***

*Chem. Rev.*, **2012**, *112*, 933–969; *Adv. Funct. Mater.*, **2020**, 30, 1909062


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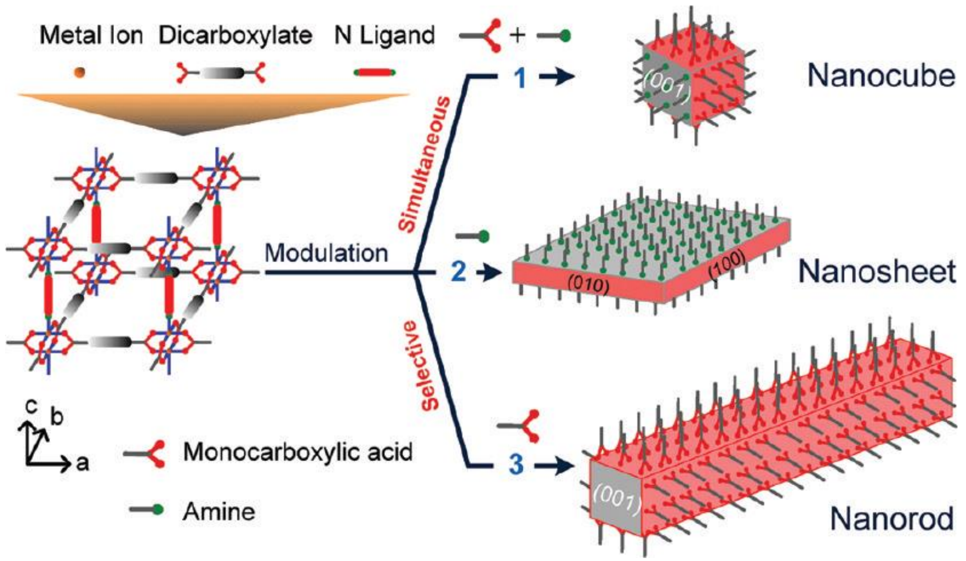
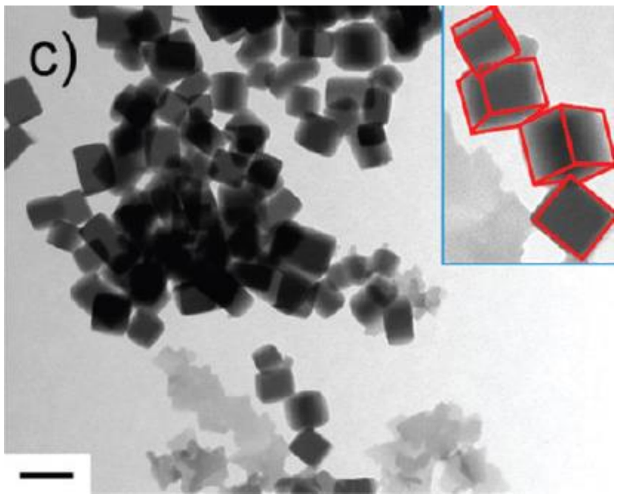
# Solvothermal synthesis

Solvothermal synthesis can produce nanocrystalline MOF

- **High reagent concentration, high temperature, fast nucleation and precipitation** (anti-solvents,…)

**External agents: capping agents**




200 nm

*Cryst. Growth Des.*, **2012**, *12*, 3091-3095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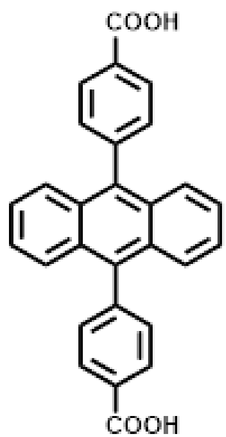
# Modulated synthesis: Zr and Hf-based MOFs

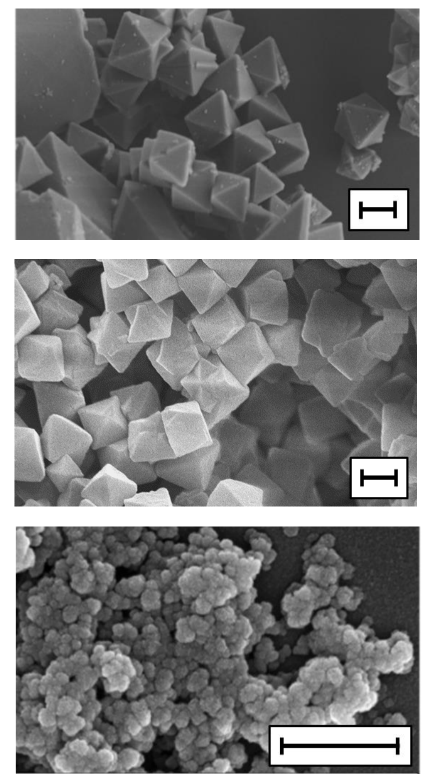
**Modulator**: mono-functionalized molecules with the same or similar functional groups of the ligands compete during the generation of the metal-based cluster or during MOF growth, controlling the size and shape of MOF nanocrystals.

$HfCl_4$ +




\+ **Formic acid**

**$CH_3COOH$** →



2 μm

400 nm

400 nm



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# Microwave-assisted reaction

The direct interaction of the microwave radiation with the molecular dipoles/ions in solution generates a very energy efficient method of heating.


- **Fast and homogeneous (local) heating**
- **Higher nucleation rate** and fast growth rate

Small and monodispersed (nano)crystals (< 5 μm), fast reaction time

*J. Mater. Chem. A*, **2017**, *5*, 7333-7338


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# Mechanochemistry and liquid-assisted grinding

Mechanochemistry is a well-developed discipline, especially in the pharmaceutical industry.

Metal-Organic Frameworks can be synthesized under mechanochemical conditions producing mostly nanoparticles.

- Fast, cheap and scalable approach
- Dry conditions or minimal solvent required
- Use of a wide range of chemical reagents
- New phases, post-modification

*CrystEngComm*, **2020**, *22*, 4511–4525; *J. Am. Chem. Soc.*, **2016**, 138, 2929−2932


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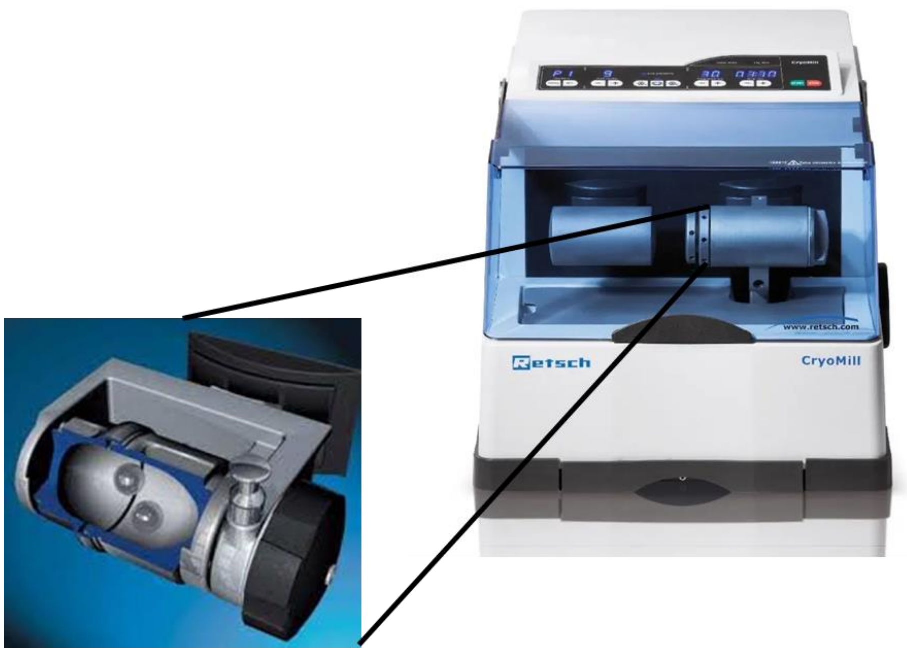
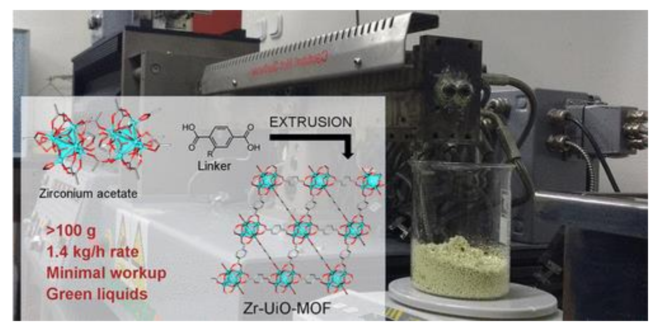
# Mechanochemistry and liquid-assisted grinding

Technology: ball millers and twin-screw extruder

Batch process




Continous process




<u>*ACS Sustainable Chem. Eng.*</u>, **2018**, *6*, 11, 15841–15849.



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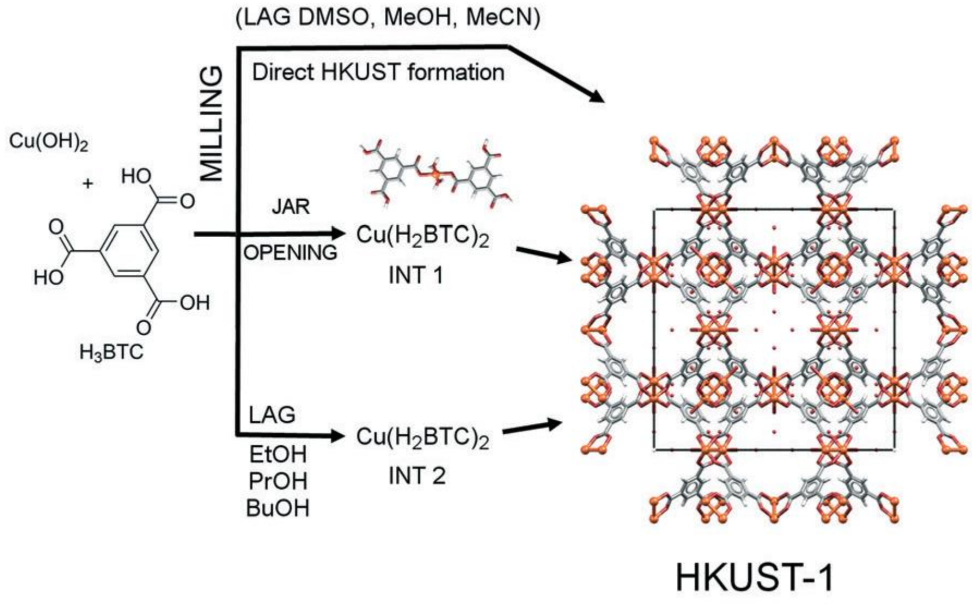
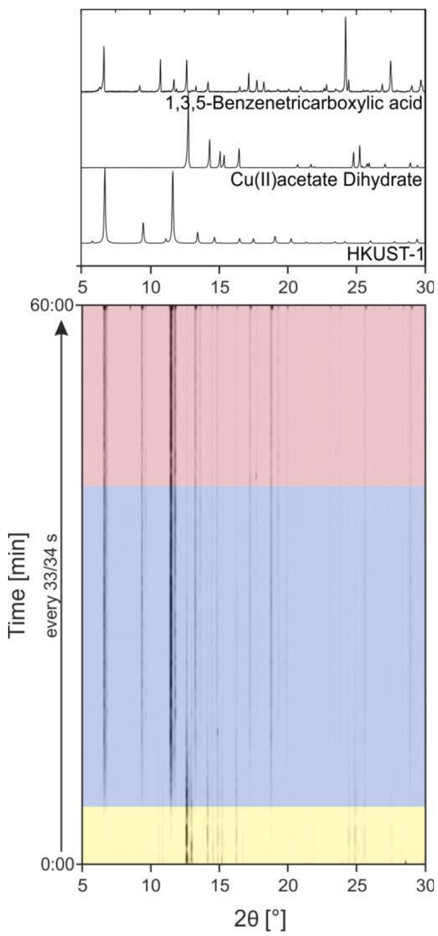
# Mechanochemistry and liquid-assisted grinding

MOF preparation by mechanical milling: HKUST-1




HKUST-1

Cu(II) acetate
HKUST-1

REAGENTS

*Inorg. Chem.*, **2017**, *56*, 11, 6599–6608.



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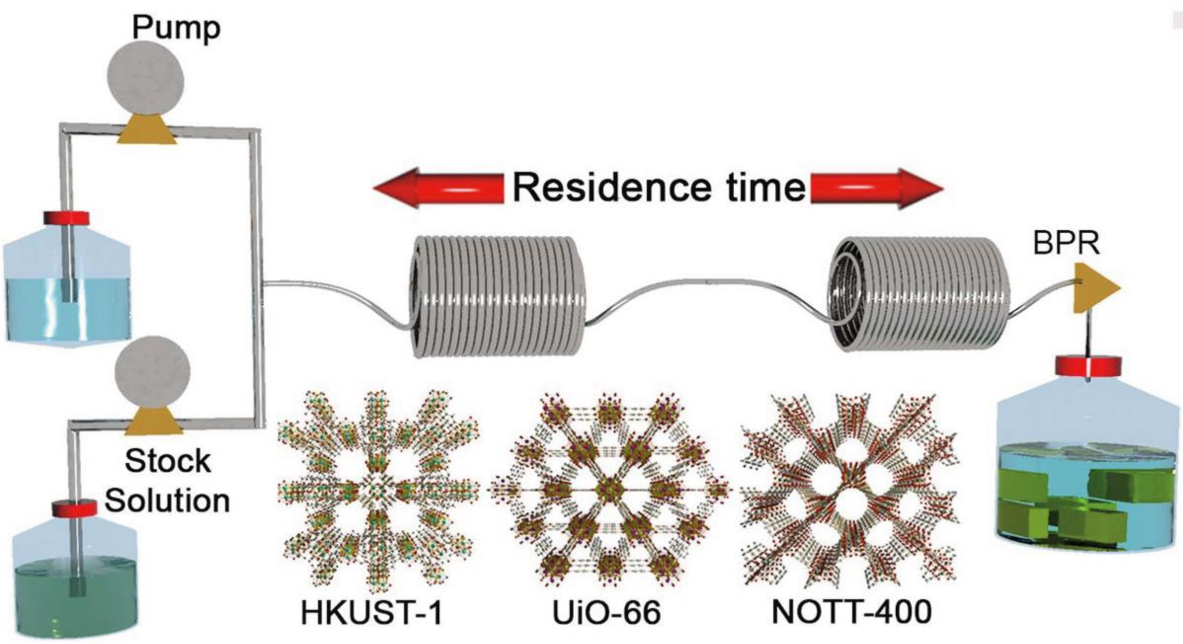
# Flow chemistry

Continuous process promise easy scalability on the industrial scale.

Flow chemistry achieves high production rates with minimum energy requirements




*Scientific Reports*, **2014**, *4*, 5443.



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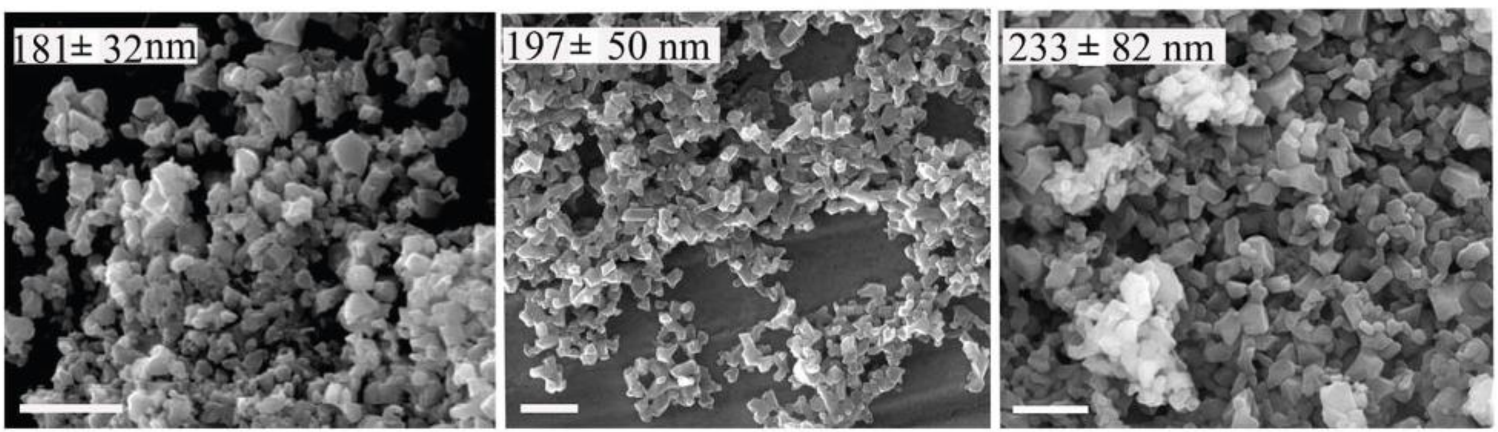
# Flow chemistry

Flow chemistry is particularly suited for the production of MOF nanoparticles.

- **Fast heating and heat transfer**
- Use of **activated reagents**

| **Sample** | **Surface area ($m^2/g$)** | **Time (min)** |
|---|---|---|
| Flow chemistry | 1852 | 10 |
| Basolite C300 | 1820 | 150 |




*Scientific Reports*, **2014**, *4*, 5443.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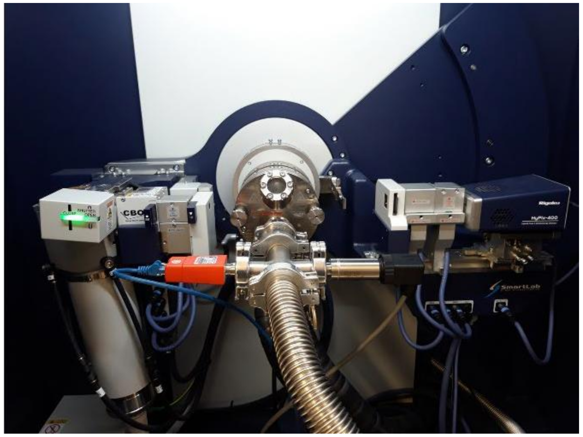
# Structure determination

Structure refinement from powder x-ray diffraction and modelling

- *In-situ* techniques (controlled atmosphere/pressure and controlled temperature) allowed precise structural characterizations under controlled conditions. Flexibility with guests can play a great role in the photophysical response of MOFs.



- Structure solution and refinement are based on Rietveld refinement combined with molecular modeling (e.g. DFT methods,…).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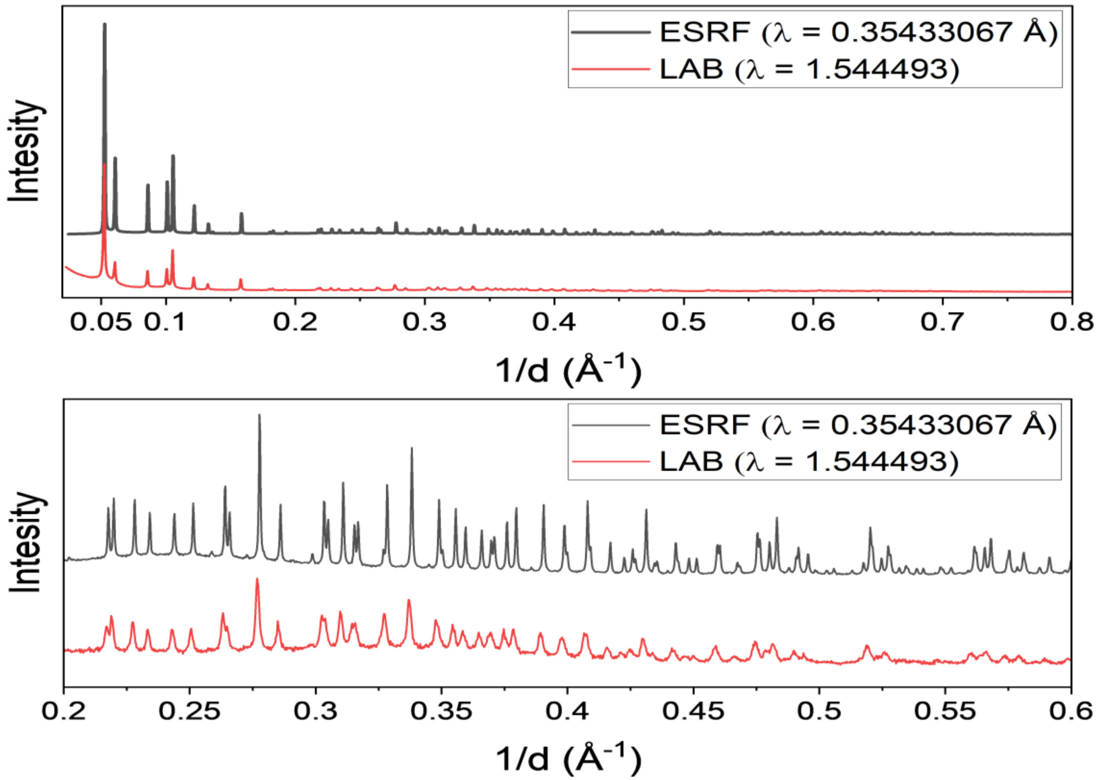
# Structure determination

Structure refinement from powder x-ray diffraction and modelling

- Synchrotron radiation offers high resolution data suitable for structure refinement and validation



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# Particle size and shape

**SEM and TEM microscopy**

Particle size and shape are fundamental for nanomaterials characterization and affect strongly the physical properties. For example, anysotropic properties of crystals, high surface to volume ratio,… led to different properties.


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# Porosity

**Special techniques:**

- **Interaction between gases and framework.** Measurement of guest-host interaction *via* direct calorimetry

- **Molecular sieving effects and selective gas adsorption from gas mixtures** can be evaluated using continous flow separation measurements (Gas breakthrough experiment)

- **Pore accessibility and pore size/shape analysis by hyperpolarized $^{129}$Xe NMR**


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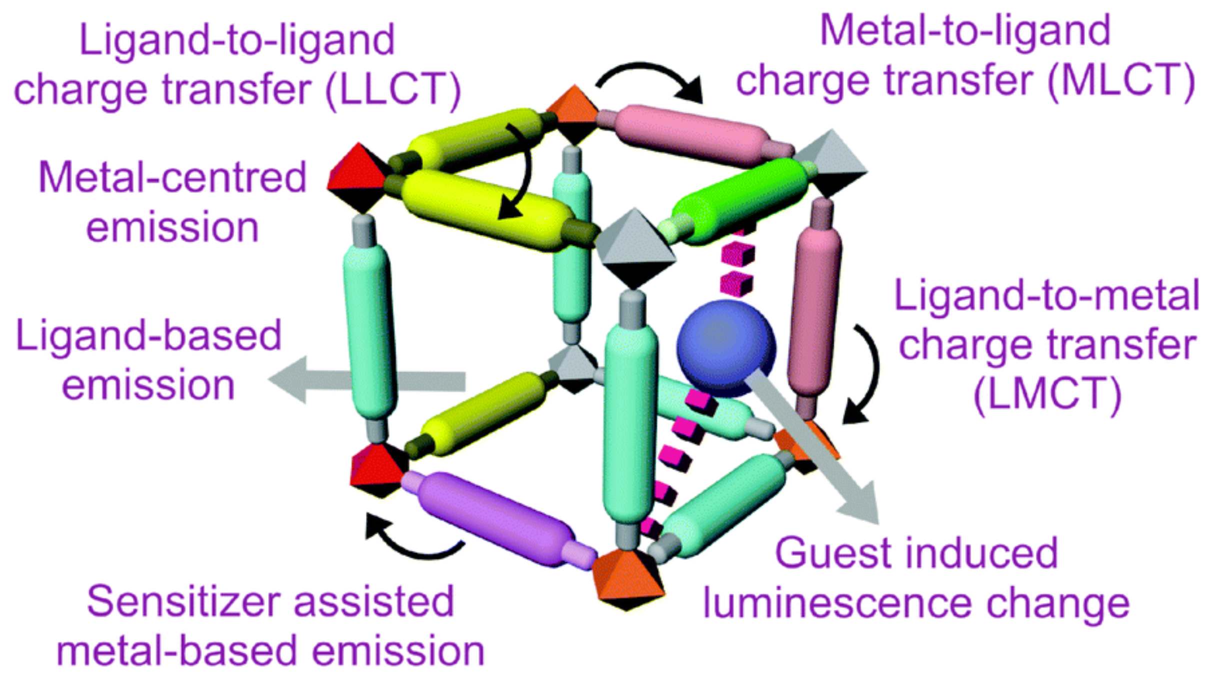
# Photophysical properties of MOFs

Photophysical processes in MOFs can involve inorganic clusters, ligands or guest molecules, with cross-talking between all these units.



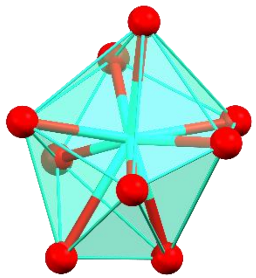

<u>*Chem. Soc. Rev.*</u>, **2017**, 46, 3242-3285; <u>*Coord. Chem. Rev.*</u>, **2018**, *377*, 259-306.



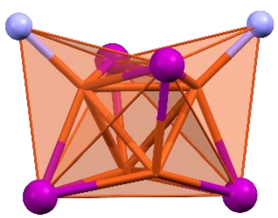
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 899293

# Photophysical properties of MOFs

## Luminescent building blocks

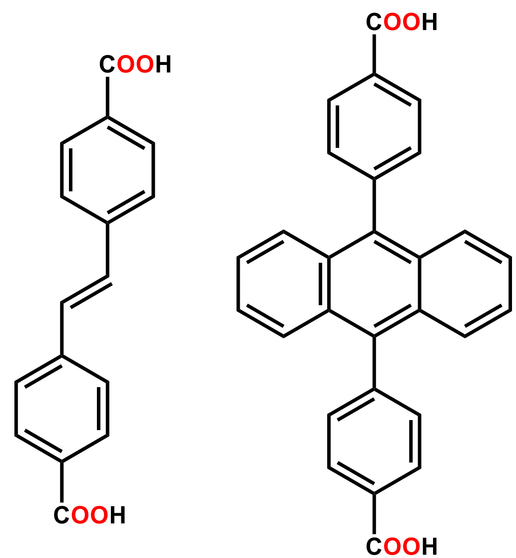


9-coordinated lanthanide clusters

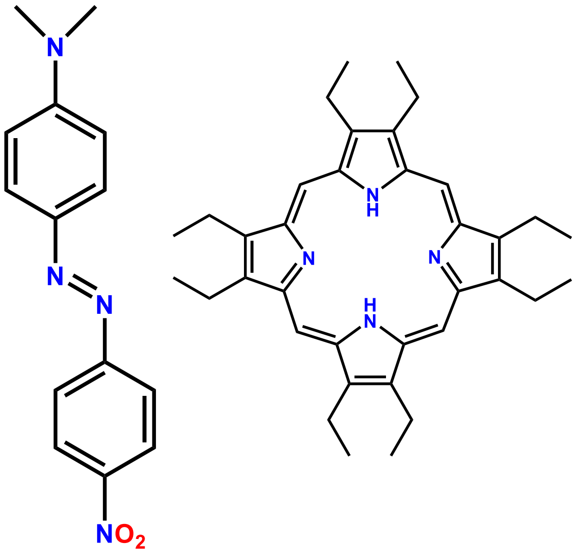


$Cu_4I_4$ cluster

**Inorganic nodes or clusters**




**Organic ligands**




**Guest species**

<u>*Chem. Soc. Rev.*</u>, **2017**, 46, 3242-3285; <u>*Coord. Chem. Rev.*</u>, **2018**, *377*, 259-306.



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# Photophysical properties of MOFs

Properties and applications:

- High luminescence QY.
- Highly tunable emission.
- Upconversion.

- White-light phosphors.
- Fluorescence imaging (bioimaging).
- Luminescent sensing (optical thermometers, pH sensors, sensing of liquids, gases,…).
- Photosensitizers.


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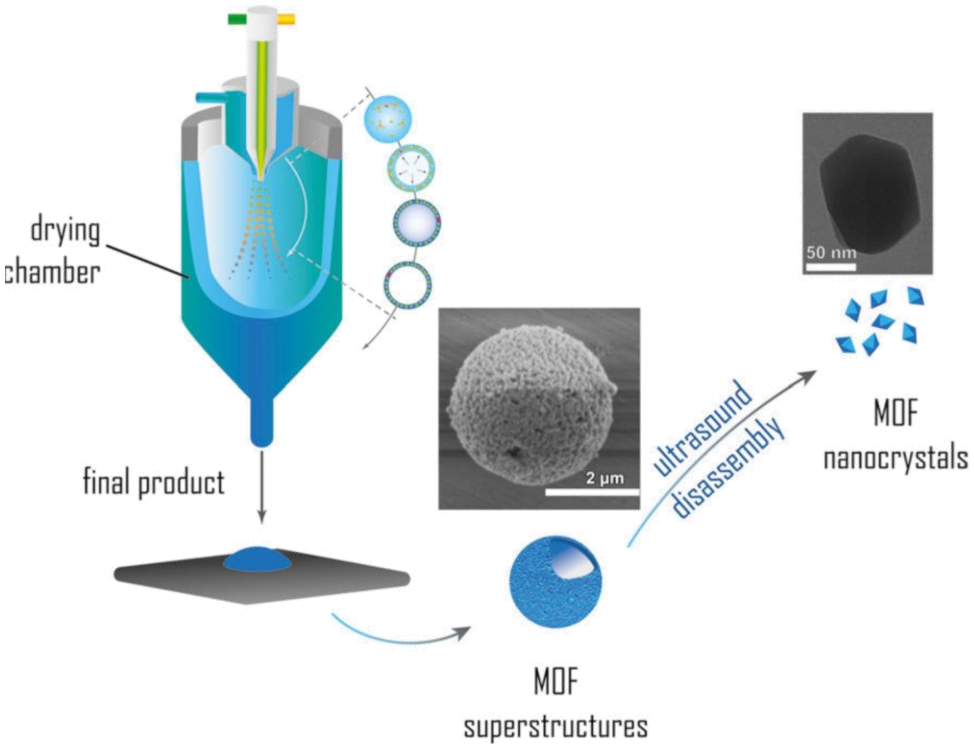
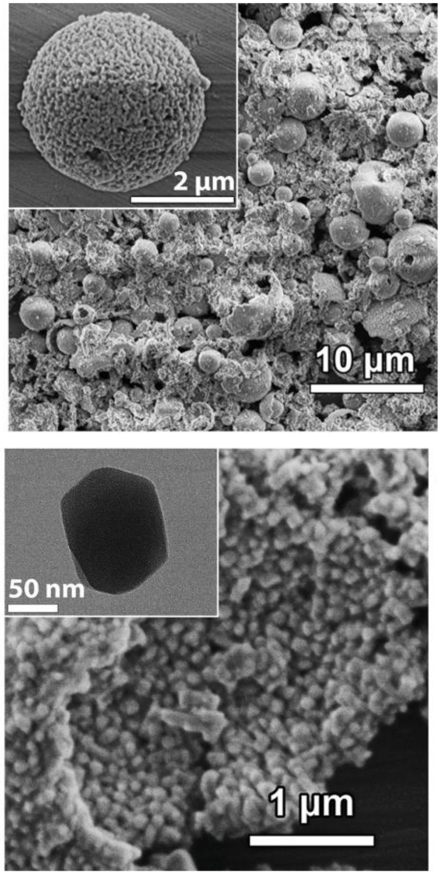
# Luminescent MOFs: Lanthanide nanothermometers

Lanthanide-based MOF are exploited as optical thermometer for applications in microelectronics, biomedicine.




*Chem. Eur. J.*, **2016**, *22*, 14782-14795.



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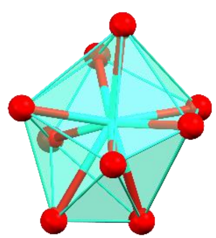
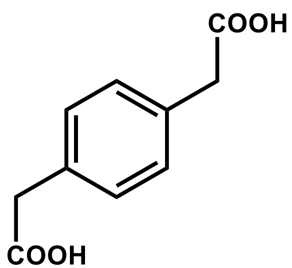
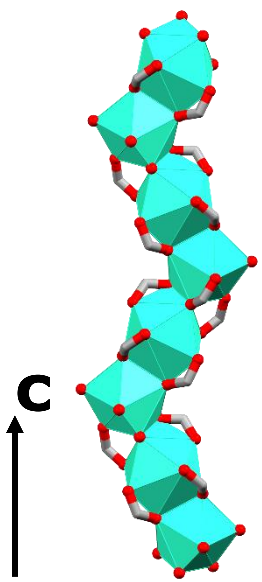
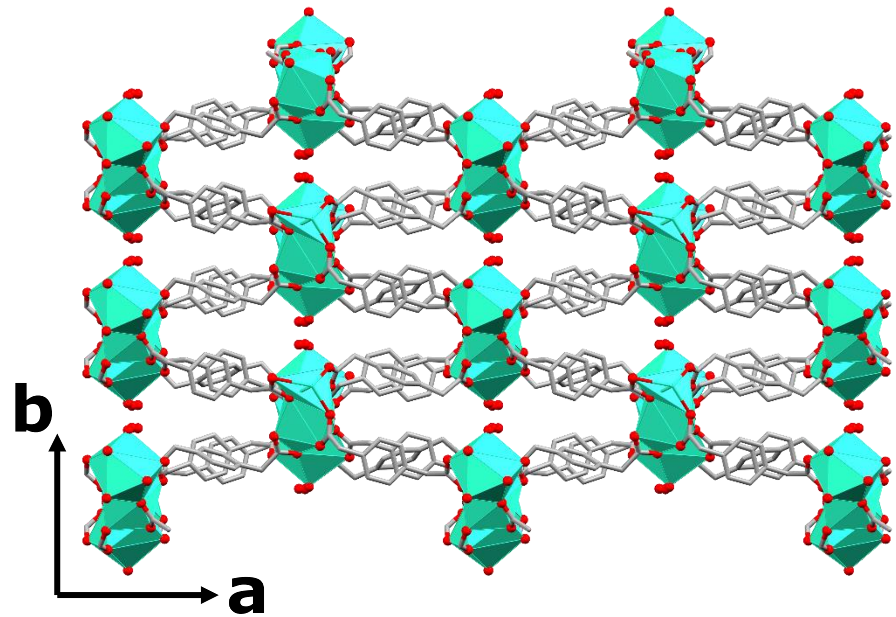


$Eu^{3+}$ and $Tb^{3+}$ cations




1,4 phenylenediacetic acid




*Adv. Funct. Mater.*, **2015**, *25*, 2824-2830.



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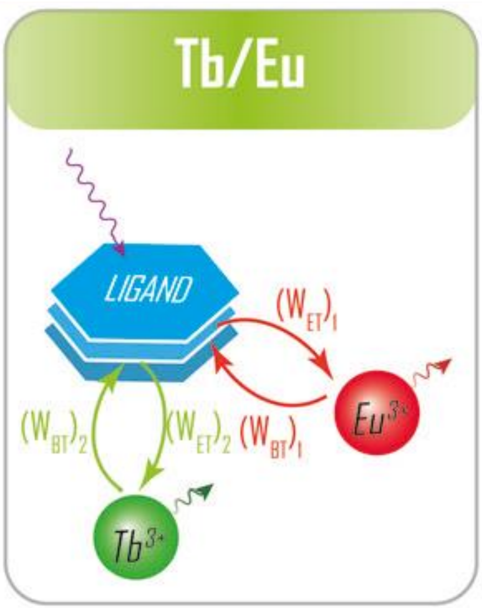
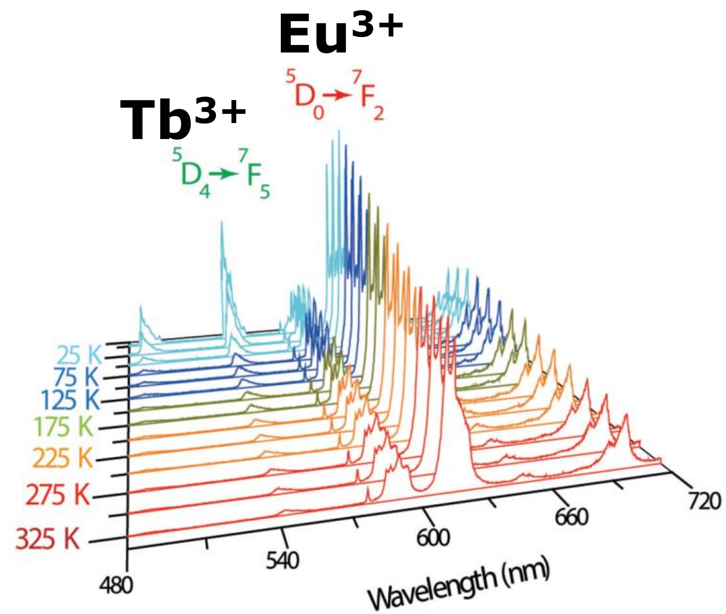
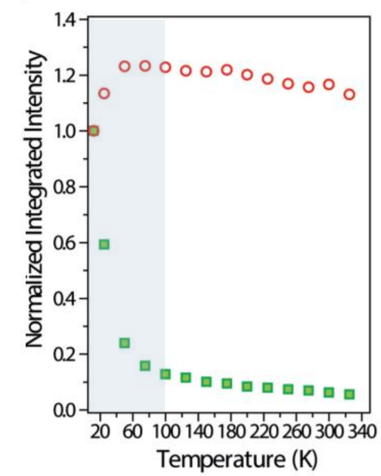
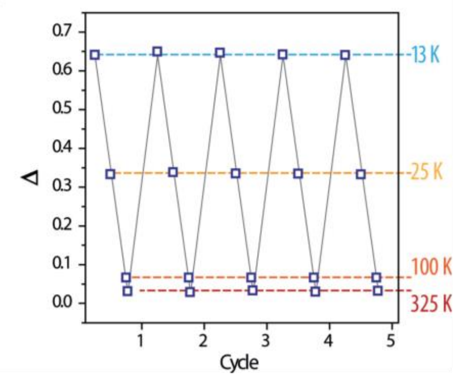
Lanthanide-based MOF are exploited as optical thermometer for applications in microelectronics, biomedicine.




$Tb_xEu_{y...}$

*Adv. Funct. Mater.*, **2015**, *25*, 2824-2830.



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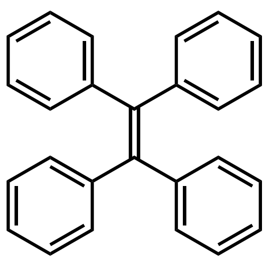
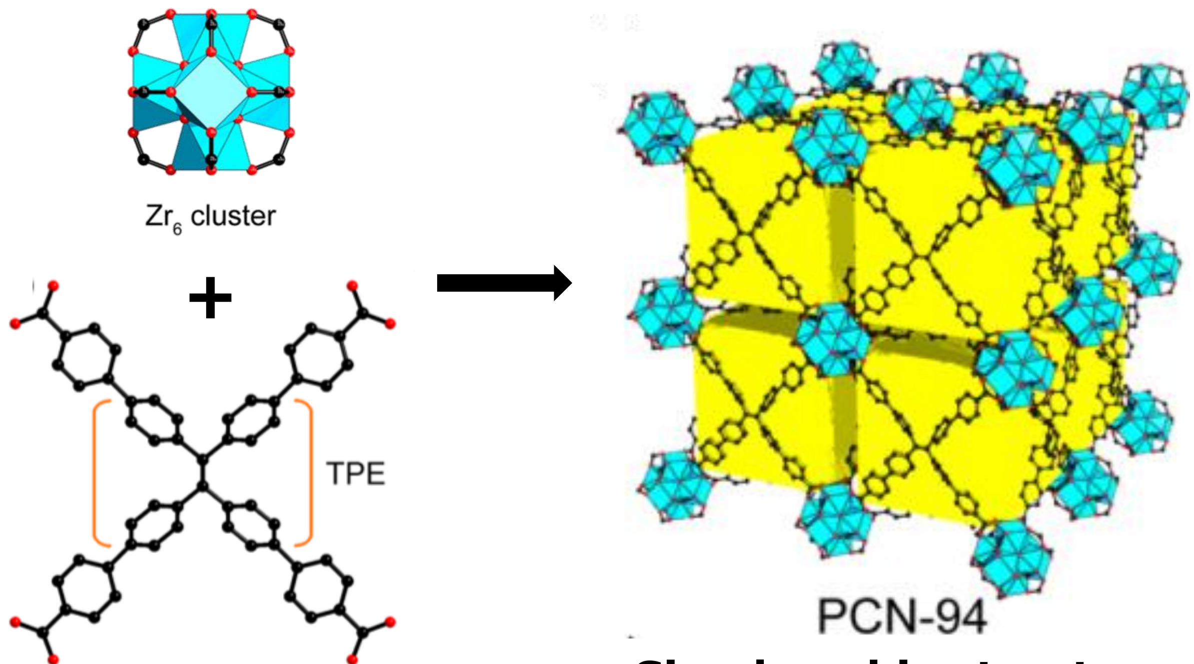
# Luminescent MOFs: light-emitting ligands

Immobilization of ligands in rigid MOF structures: PL enhancement due to suppression of luminescence quenching and conformational control.

Aggregation induced emitting (AIE) chromophore



Tetraphenylethylene (TPE)




**Simple cubic structure**

*J. Am. Chem. Soc.*, **2014**, *136*, 8269-8276.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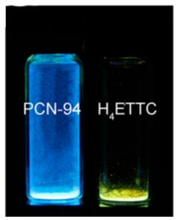
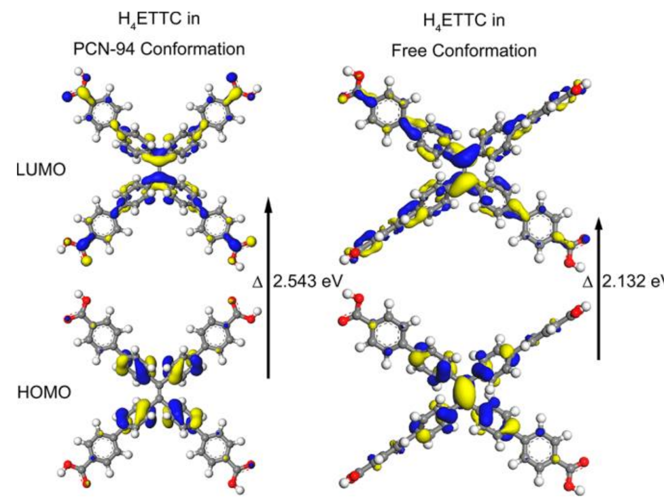
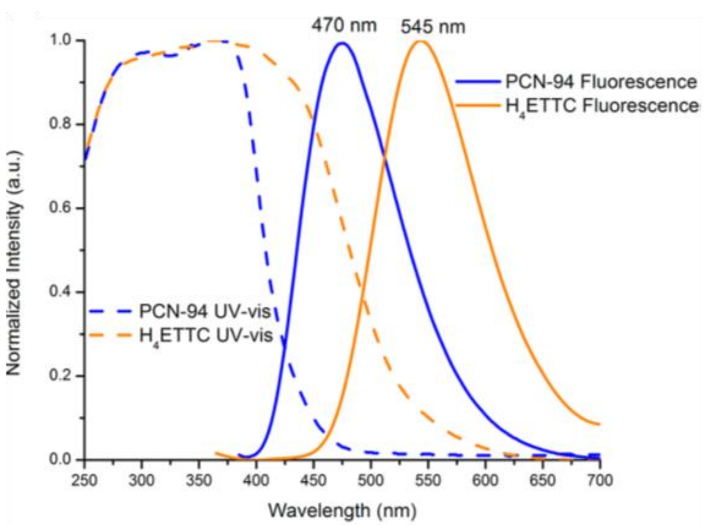
# Luminescent MOFs: light-emitting ligands

PCN-94 dispays a bathochromic shift of the PL emission (470 nm) and an improved QY ~ 0.99. The results were rationalized using TD-DFT calculations.


| Sample | PL QY (%) | Lifetime (s) |
|---|---|---|
| $H_4ETTC$ | 30 | $\tau_1$ = 24.74<br>$\tau_2$ = 4.15 |
| PCN-94 (air) | 76 | $\tau$ = 2.06 |
| PCN-94 (Ar) | 99 | $\tau$ = 1.87 in $N_2$ |

<u>*J. Am. Chem. Soc.*</u>, **2014**, *136*, 8269-8276.



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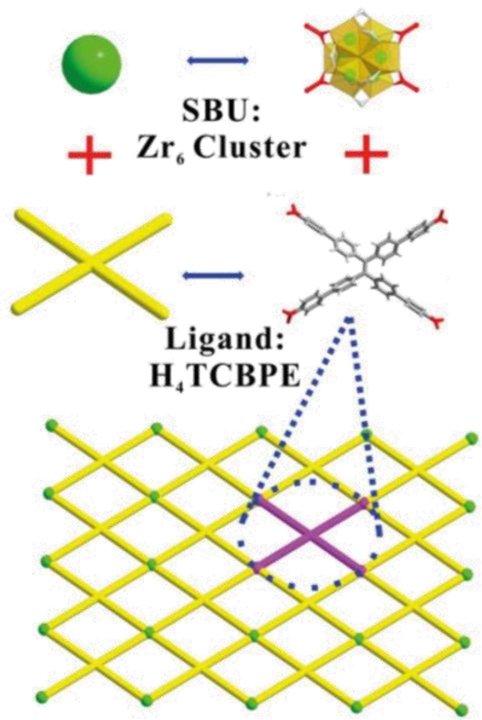
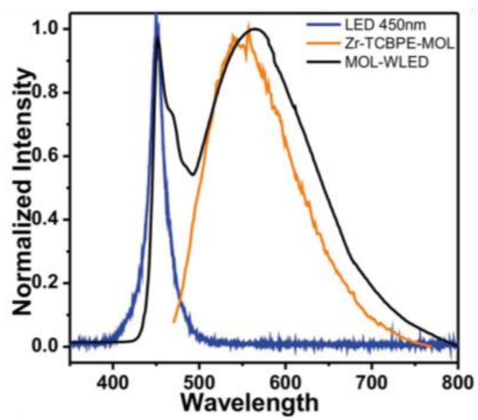
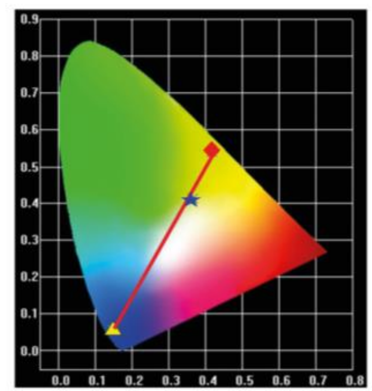
# Luminescent MOFs: phosphor for white-light emission

A similar material can be assembled as layered structure (MOL = Metal-Organic Layer) with a few layer thickness.



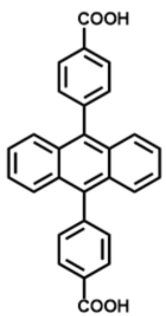



*Chem. Eur. J.*, **2017**, *23*, 8390-8394.

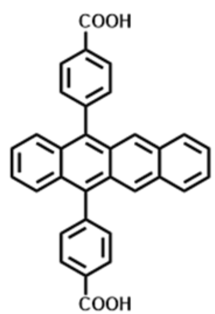

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 899293

# Large Stokes shift luminescent MOFs

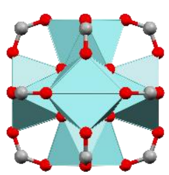
Self-assembly of complementary chromophores in fast emitting large-Stokes shift MOF nanocrystals




**DPA**

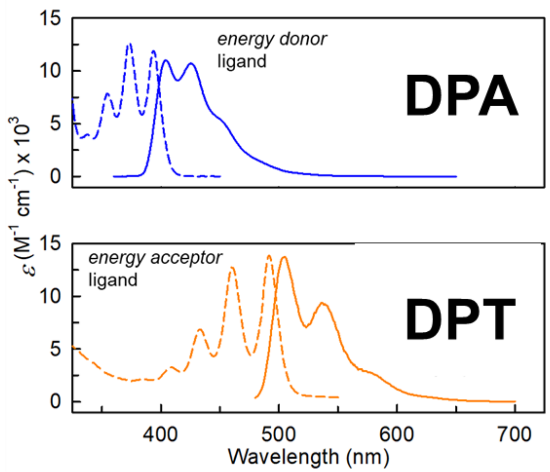



**DPT**

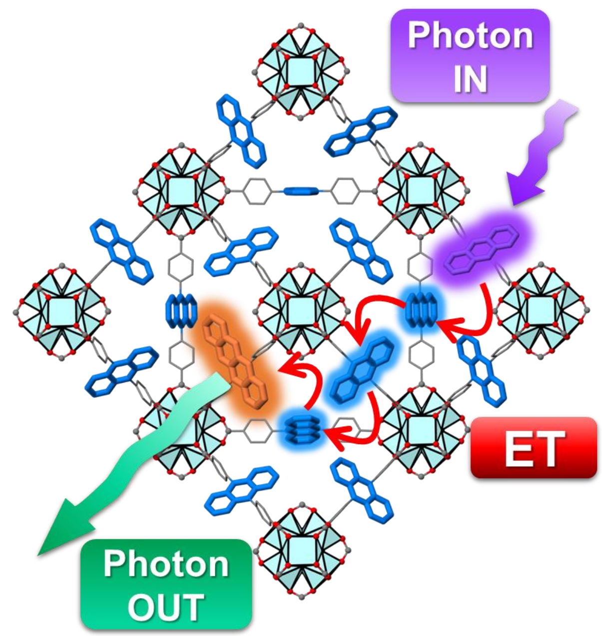


**Zirconium cluster**

**Complementary photophysical properties**




**Fast emitting reabsorption-free MOF nanocrystals**




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



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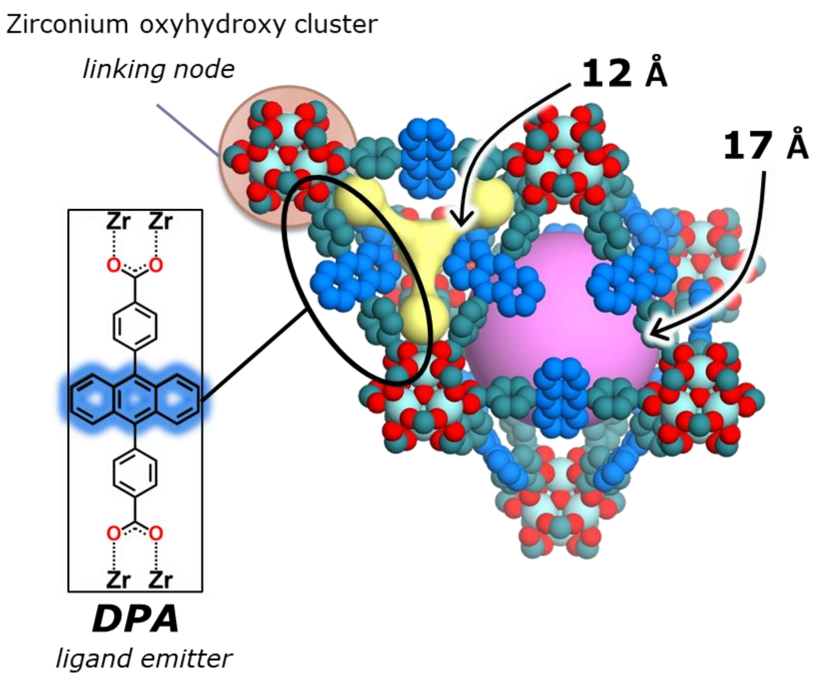
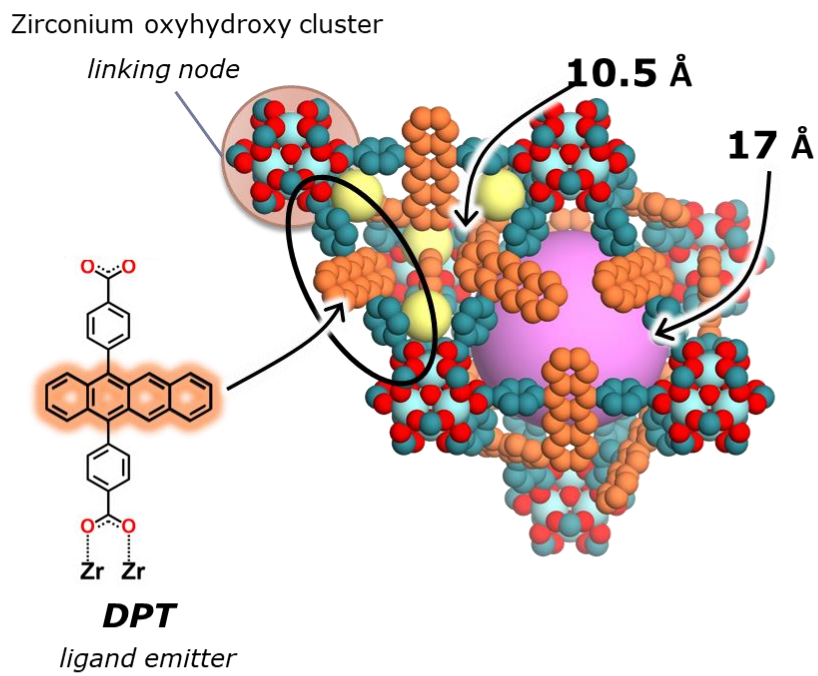
# Zr-based luminescent MOF: Zr-DPA and Zr-DPT

Zr-based MOFs with light-emitting linkers: Zr-DPA and Zr-DPT

**Zr-DPA**




**Zr-DPT**



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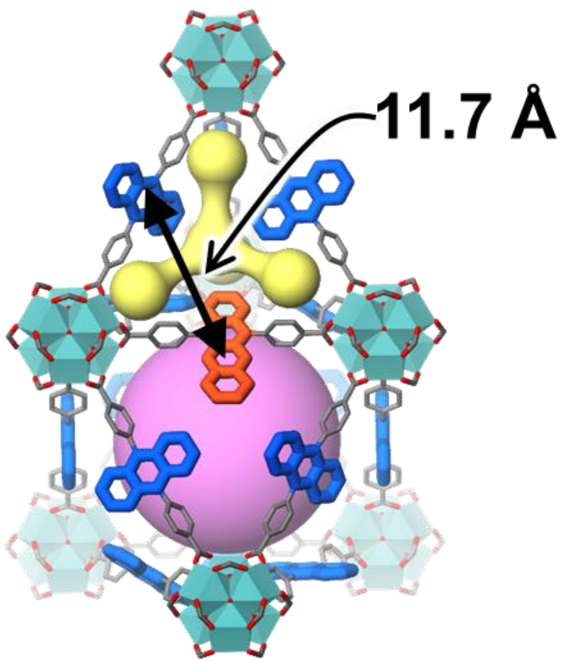
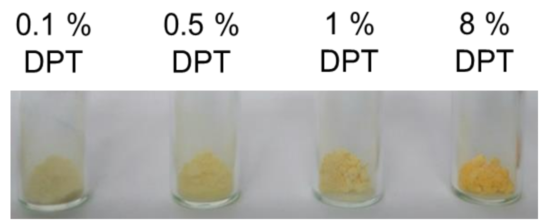
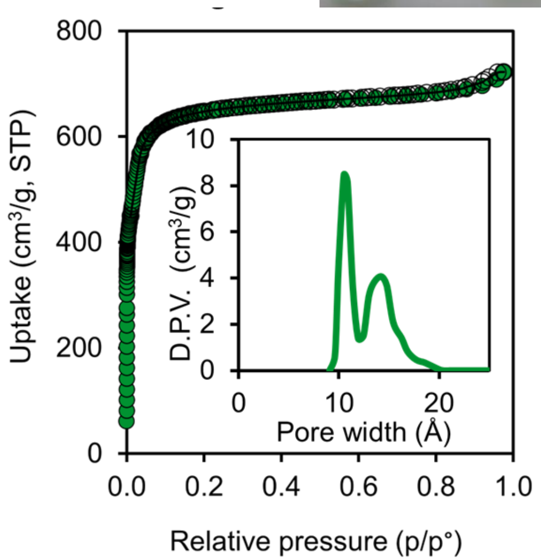
# Large Stokes shift luminescent MOFs

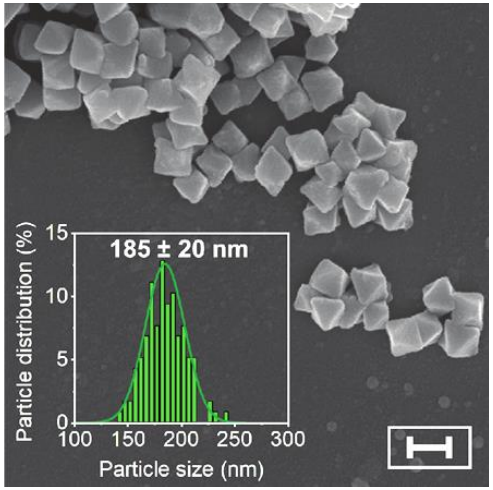
Co-assembly of the 2 different ligands in various ratio generate a family of doped MOFs with different concentration of DPT units

**Zr-DPT:DPA-X% (0.1 %< X < 8 %)**



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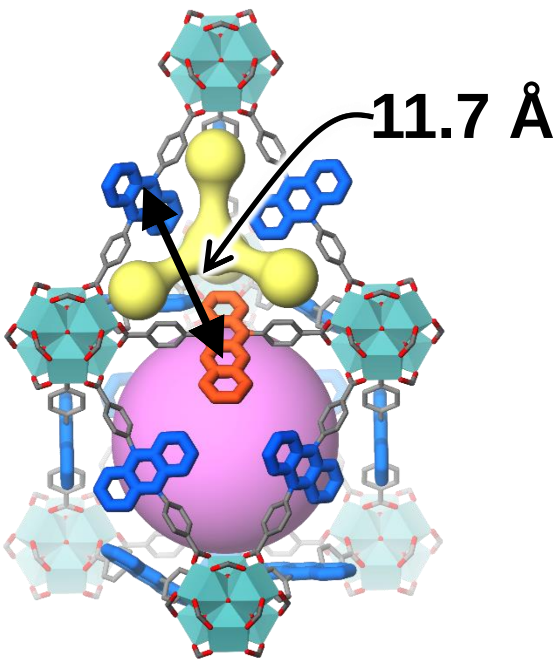
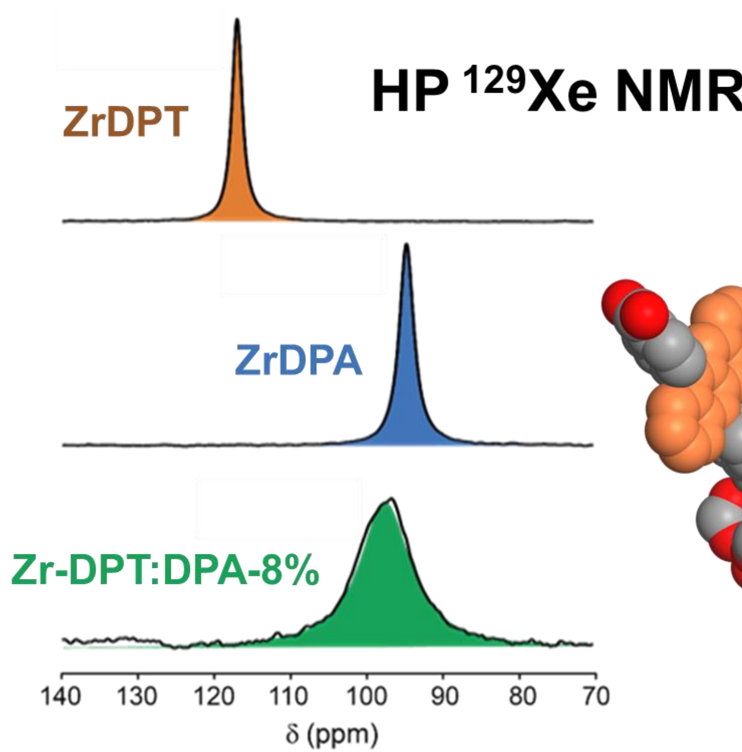
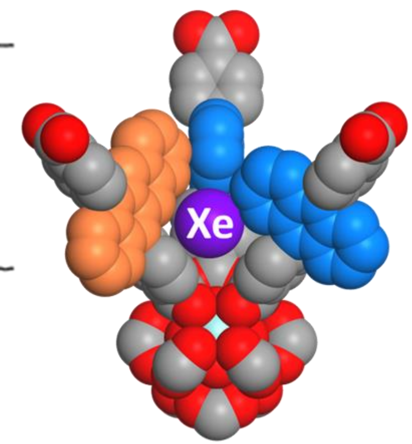
# Large Stokes shift luminescent MOFs

Mixed ligand MOFs display high surface area (up to 3040 $m^2/g$). Hyperpolarized $^{129}Xe$ NMR provide a unique method to prove the homogeneous distribution of the 2 ligands inside the structure.




**Zr-DPT:DPA-8%**



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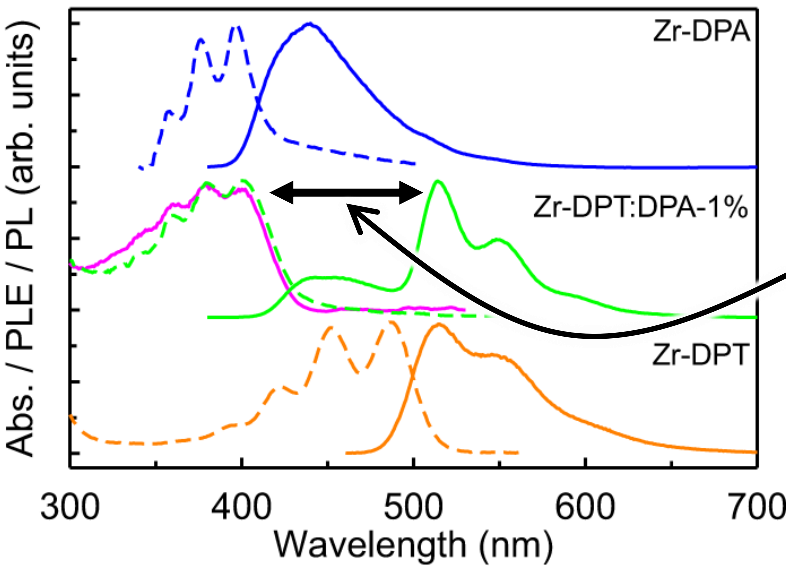
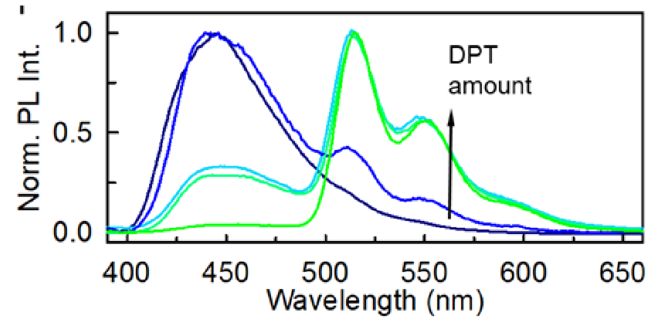
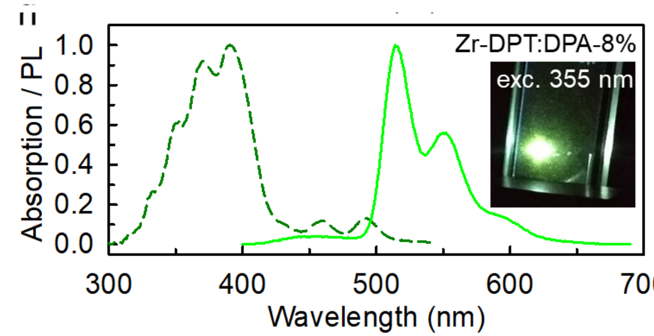
# Zero-reabsorption MOFs

## Large Stokes Shift emission




**Large Stokes shift emission**

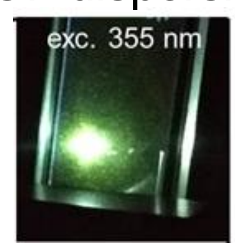



Natural light

UV light

MOF dispersion



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# Luminescent MOFs: other properties and applications

- Thin films for tunable **OLED emitters**.
- **Biological imaging**.
- **Lasing materials**.
- **Luminescent sensors**: highly accessible porosity allowed the intimate contact between guests and host, thus producing highly sensitive sensors.
- **Light-collectors and sensitizers** for heterogeneous photocatalysis and photosynthesis.
- **Upconverting materials** for imaging and photocatalysis.


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# Radioluminescent and scintillating MOFs

**MOF provide a versatile platform for the development of hybrid scintillators**

The potential application of MOFs as scintillating materials were reported by research groups of Prof. Allendorf (2009) and Prof. Lin (2014). These research led to groundbreaking studies related to the development of nanocrystalline MOF for biological applications: bioimaging and therapeutic agents excited by X-ray irradiation.

*J. Mater. Chem.*, **2012**, *22*, 10235-10248; *J. Am. Chem. Soc.*, **2014**, *136*, 6171-6174.



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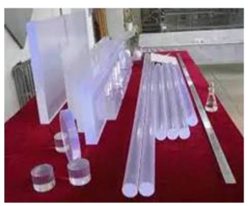
# Fast composite MOF@polymer scintillators

High-energy radiation detection with MOF-based composites

## Current technologies: advantages and drawbacks of scintillating materials

**Plastic (organic) scintillator**

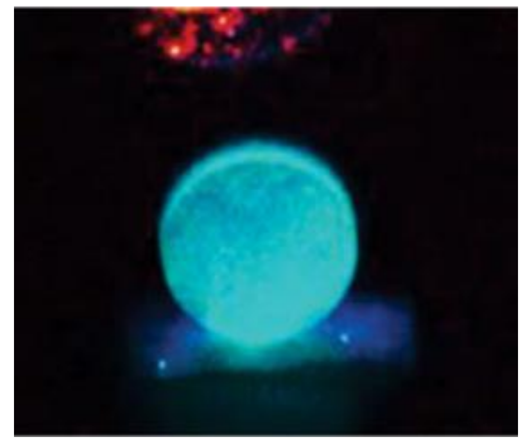


✓ Fast time response, cheap
× Low light yield

**Inorganic scintillator**


✓ High light yield
× Slow time response, expensive

## MOF@polymer based composite scintillator



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

J.Perego et al., <u>*Nature Photonics*</u>, **2021**, *15*, 393–400.



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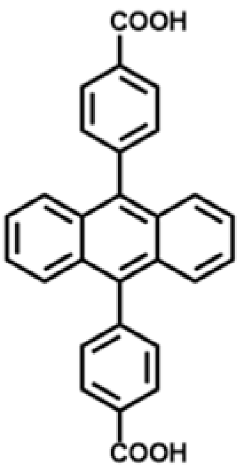
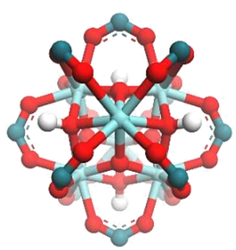
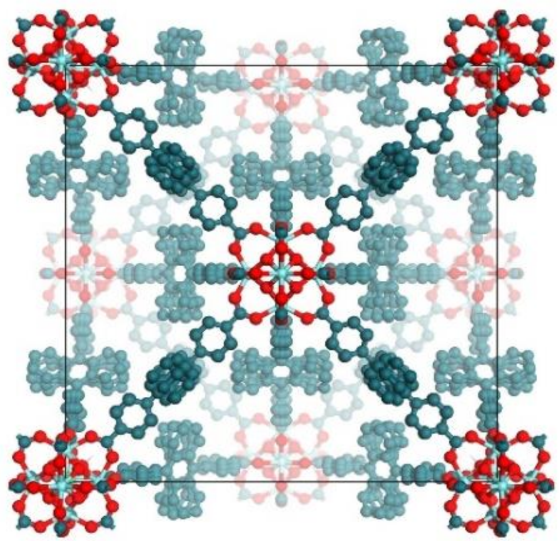
# Fast composite MOF@polymer scintillators

**Combine two components in a precise way at nanometric distances**

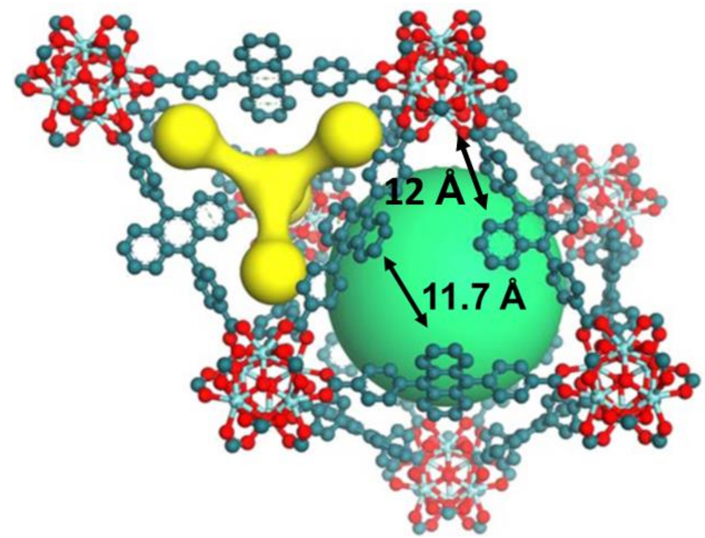


$Zr_6O_4(OH)_4(COO^-)_{12}$
cluster



**Zr-DPA**
**Fcc structure**



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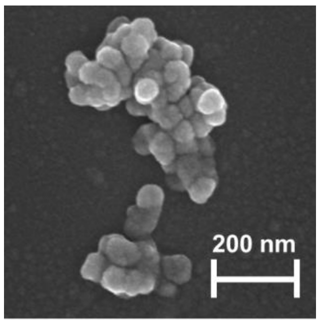
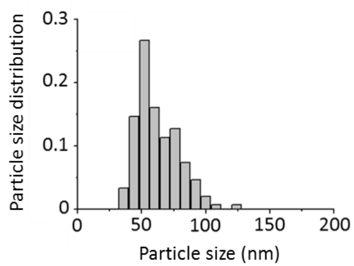
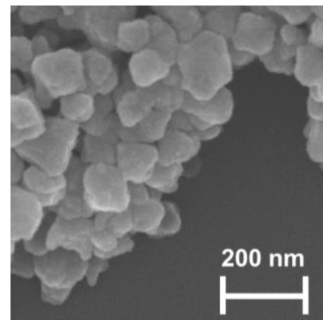
# Fast composite MOF@polymer scintillators

**Controlled growth of MOF nanocrystals through a modulated self-assembly synthesis**

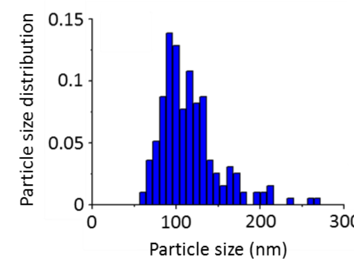



**58 ± 20 nm**

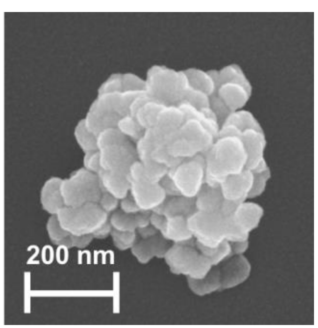


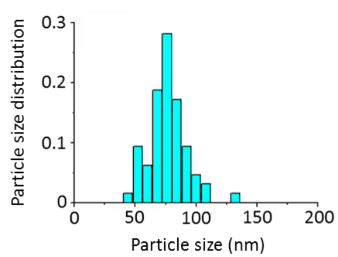

**130 ± 40 nm**

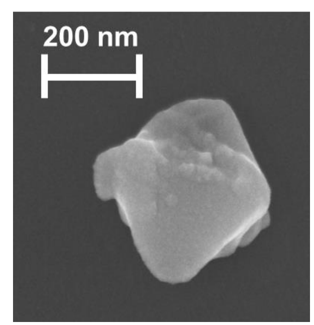



**Increasing modulator concentration**

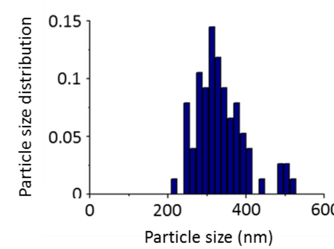



**85 ± 20 nm**




**350 ± 60 nm**



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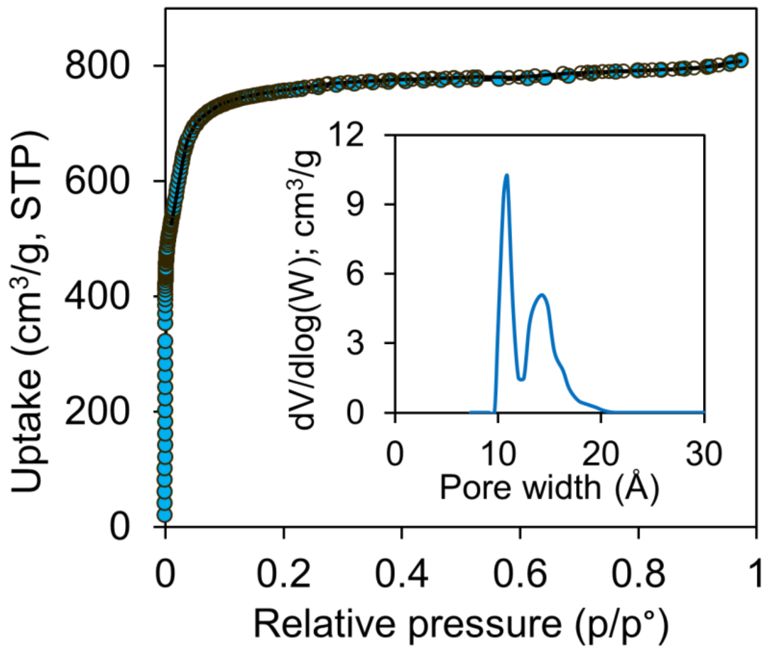
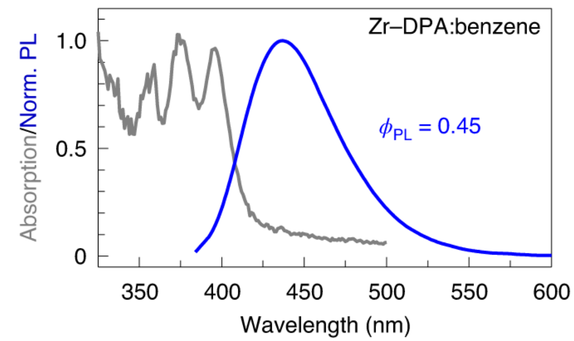
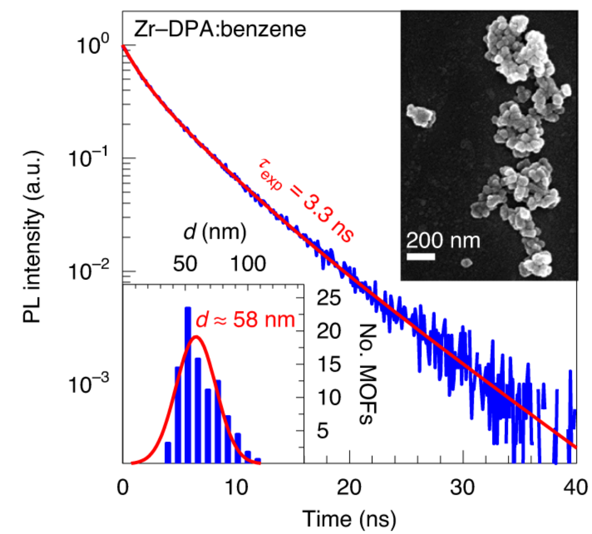
# Fast composite MOF@polymer scintillators

## MOF nanocrystals: structural and luminescent properties




| | |
|---|---|
| **Langmuir surface area (m²/g)** | **3410** |
| **BET surface area (m²/g)** | **3010** |
| **Pore volume (cm³/g)** | **1.11** |



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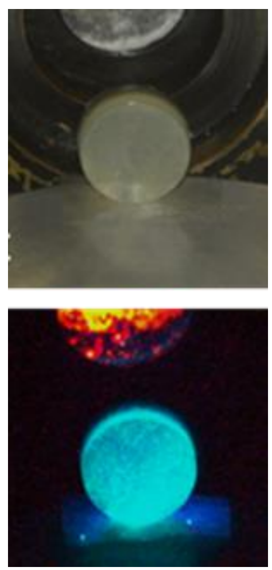
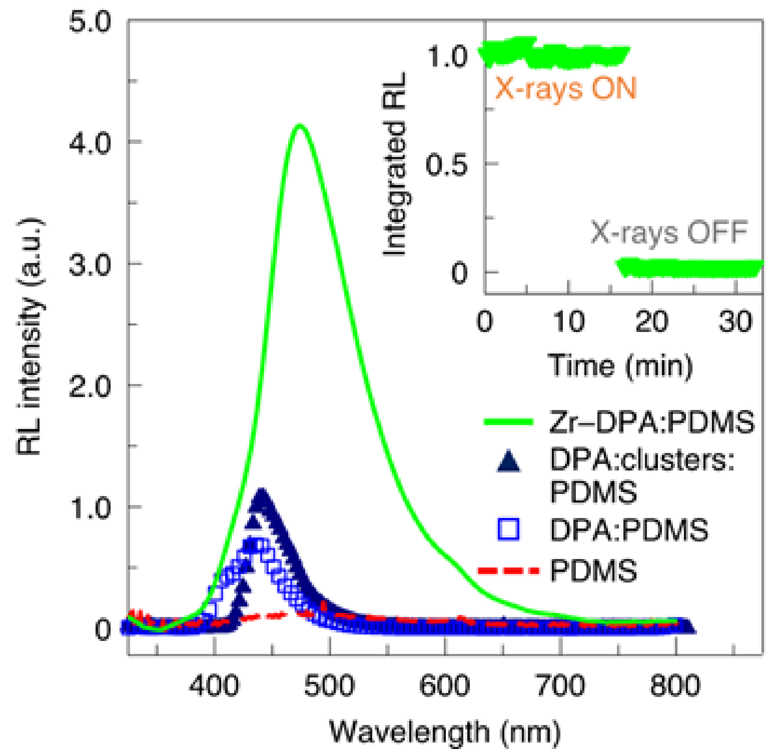
# Fast composite MOF@polymer scintillators

## MOF nanocrystals: Radioluminescence and scintillation

**MOF-based composite scintillator**


**Ionizing radiation (α, β, γ- and x-rays)**






**Fast scintillation time decay**

**$\tau_{decay}$ = 4.1 ns**



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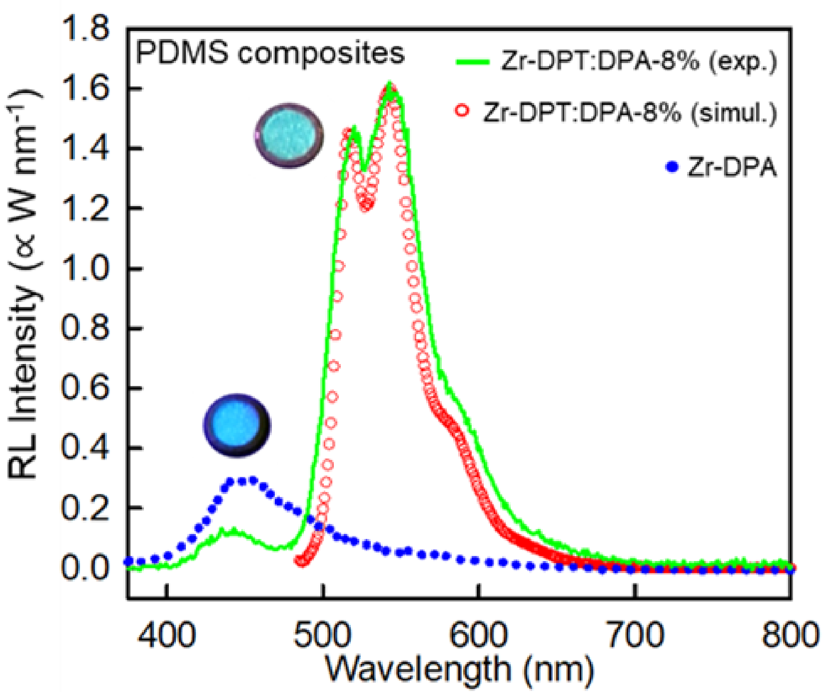
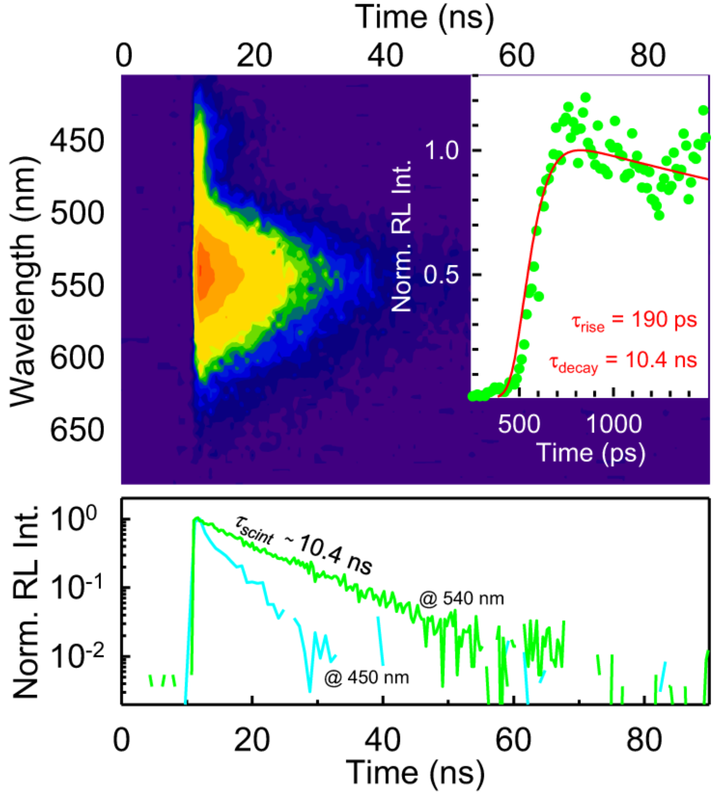
# Fast composite MOF@polymer scintillators

**Zr-DPT:DPA-8% mixed ligand MOFs: bulk scintillating materials without self-reabsorption**




Nature Communications, **2022**, *13*, 3504. Nature Photonics, **2021**, *15*, 393–400



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# MOF nanocrystals for X-ray diagnostic and therapy

- Nanocrystalline MOFs as **contrast agent in x-ray imaging** (e.g. computed tomography).
- They can also be engineered to promote therapeutic effects due to **x-ray sensitized production of ROS species** in targeted tumors.
- Moreover, they find application as **drug-delivery nanoparticles** with high cargo load.

*Chem. Eur. J.*, **2021**, *27*, 3229-3237; *Chem. Rev.*, **2015**, *115*, 19, 11079-11108.


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

# Conclusion: a "bright" future ahead

- Understanding the photophysical processes in MOF nanocrystals of increasing complexity.
- Hybridization of MOF nanocrystals with other nanomaterials for enhanced and synergistic functions and properties.
- Reliable, scalable and sustainable synthesis of MOF nanocrystals.
- Shaping of nanocrystalline MOFs in self-standing materials (films, membrane, fiber, bulk).


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