Research activities and interests

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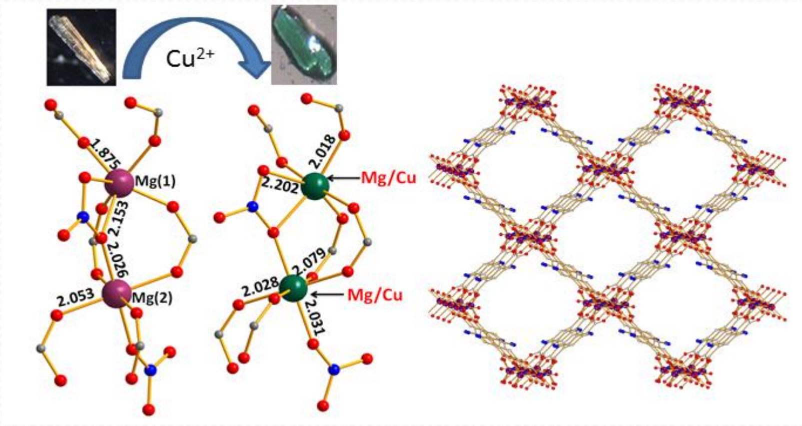
40 ΧΡΟΝΙΑ ΤΜΗΜΑ ΧΗΜΕΙΑΣ
ΠΑΝΕΠΙΣΤΗΜΙΟ ΙΩΑΝΝΙΝΩΝ

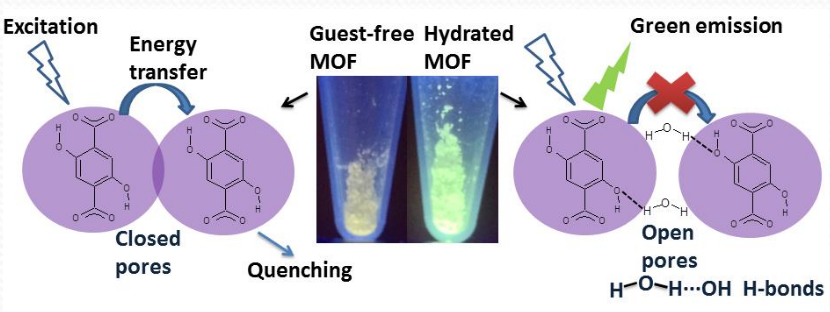
ΙΝΣΤΙΤΟΥΤΟ
ΕΠΙΣΤΗΜΗΣ ΥΛΙΚΩΝ
ΚΑΙ ΥΠΟΛΟΓΙΣΜΩΝ

Research in our group



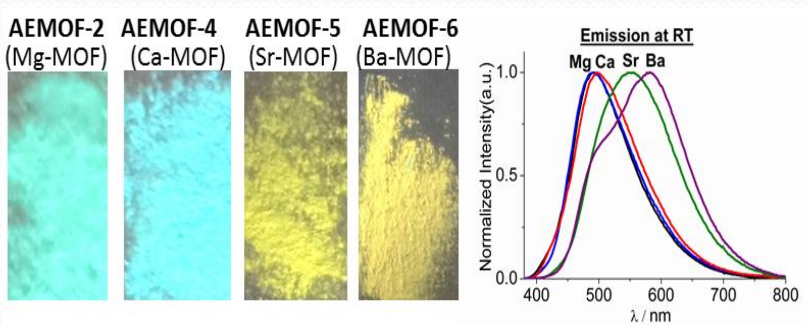
New porous MOFs (exploratory synthesis)

***CrystEngComm* 2014,** *16*, 3483
***Inorg. Chem. Front.* 2017**, *4*, 530



Luminescent MOFs-sensors

***Angew. Chem. Int. Ed.* 2015**, *54*, 1651



***Inorg. Chem.* 2015**, *54*, 5813

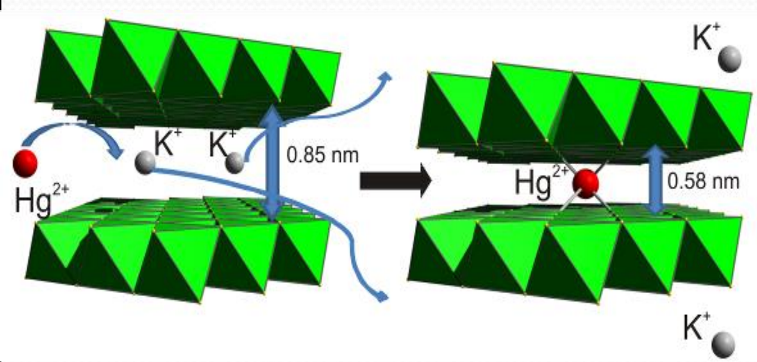
***Inorg. Chem. Front.* 2018**, *5*, 1493
***Mol. Syst. Des. Eng.* 2020**, 5, 461

Research in our group

MOF and MOF composites for water treatment applications

***Chem. Sci.*, 2016**, *7*, 2427
***Inorg. Chem. Front.* 2016**, *3*, 635
***Inorg. Chem. Front.* 2017**, *4*, 530.
***Prog. Mater. Sci.*, 2017**, *86*, 25.
***J. Mater. Chem. A*, 2017**, *5*, 14707
ChemPlusChem 2017, *82*, 1188
***J. Mater. Chem. A* 2018**, *6*, 20813
***J. Mater. Chem. A* 2019**, *7*, 15432
Sensors&Actuators B 2020, *321,128508*
Patent: **WO2017083467A1**

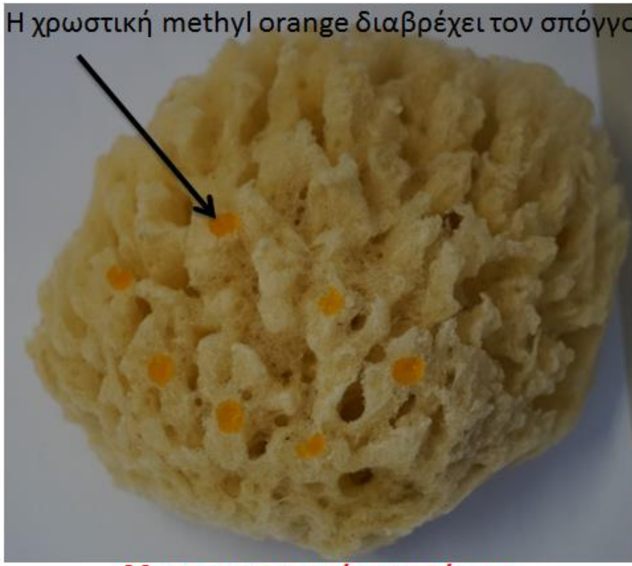
Metal sulfide ion-exchangers



***Angew. Chem. Int. Ed.* 2005**, *44*, 3552; ***J. Am. Chem. Soc.* 2006**, *128*, 8875; ***P. Natl. Acad. Sci. USA* 2008**, *105*, 3696; ***J. Am. Chem. Soc.* 2009**, *131*, 6599; ***Chem.-Eur. J*. 2009**, *15*, 4779; ***Adv. Funct. Mater*. 2009**, *19*, 1087; ***J. Am. Chem. Soc*. 2012**, *134*, 16441; ***Chem. Mater.* 2013**, *25*, 2116; ***Chem. Sci.* 2016,** 7, 4804
Patents: **US20080145305; WO2009048552-A1, US2009095684-A1, US8070959-B2; US2011290735-A1; US 20150144568 A1, WO 2015080976 A1**.

Research in our group

Hydrophobic materials



Μη τροποποιημένος σπόγγος

Τροποποιημένος σπόγγος

Ο τροποποιημένος σπόγγος απωθεί το νερό

"Sponges modified with superhydrophobic metal oxide and metal-organic nanomaterials with excellent selectivity for sorption of lipophilic pollutants from water",

GR-Patent No. 1009740.

Determination of water in organic solvents

A simple, fast and reliable chemical analysis method for the water content of organic solvents **is essential for**

A) Chemical industries producing dry solvents and moisture-sensitive chemicals
B) Industries manufacturing oils and petroleum products, in which water is a common contaminant and impurity.
C) Fuel, alcoholic beverage industries (determination of water in EtOH).

Current method used:
Karl Fisher titration
$B{\cdot}I_2 + B{\cdot}SO_2 + B + H_2O \rightarrow 2BH^+I^- + BSO_3$
(B = base, usually imidazole)

Serious disadvantages: specialized instruments, well-trained personnel, difficulty in sample manipulation, interference from other co-existing species etc

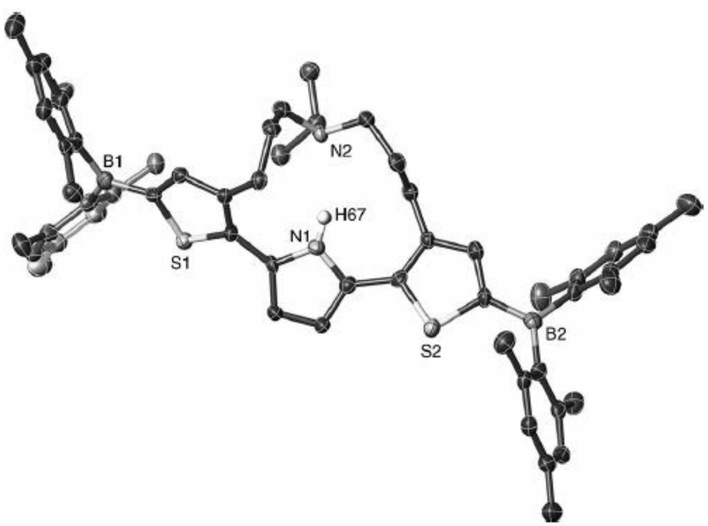
Anal. Chem. **1990**, *62*, 2504

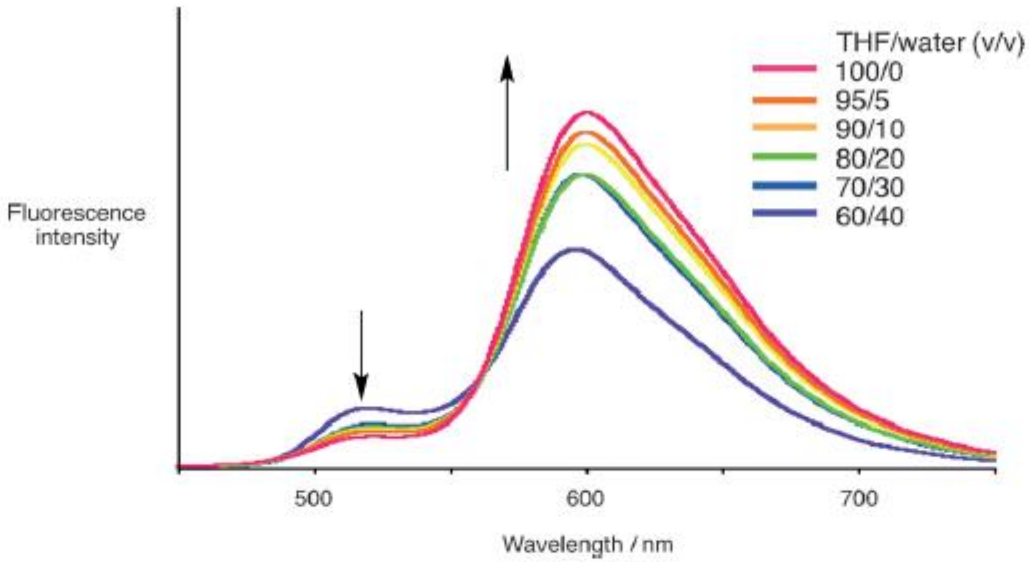
A Karl Fischer Titrator.

Luminescence water sensing

Luminescent water sensors have attracted great interest due to their significant advantages involving their capability for remote and in situ monitoring as well as the ease of their fabrication.

Organic molecular sensors have been studied:





Drawbacks:

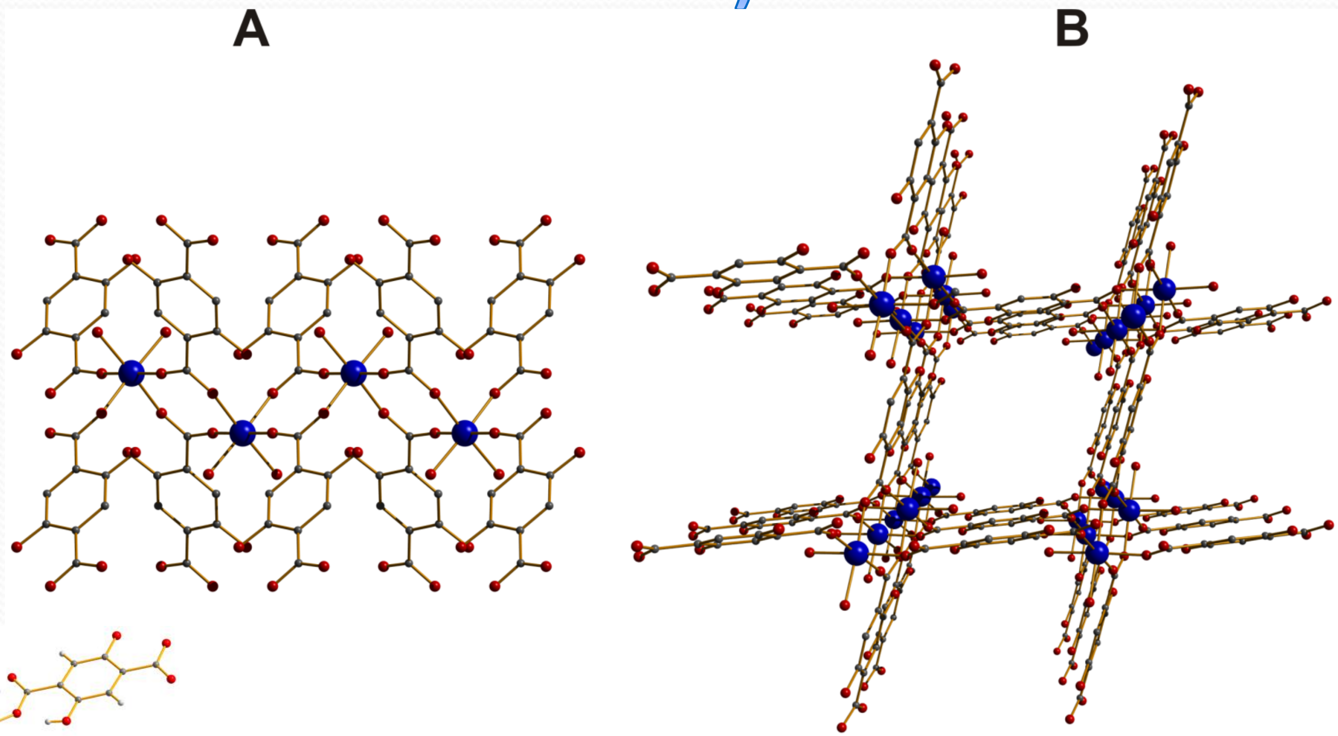
Not capable for detection of water in trace concentrations (≤1 v/v %)

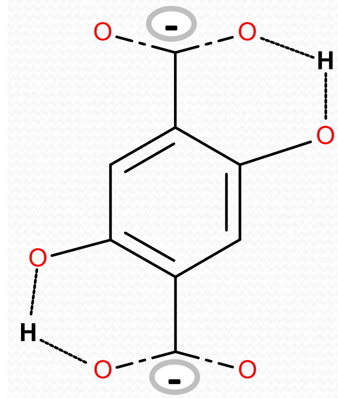
Not readily recoverable and reusable (due to the solution phase sensing)

Expensive-multistep preparation

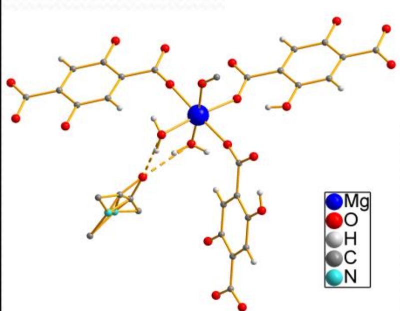
Angew. Chem. Int. Ed. **2014**,*53,* 8231

$[Mg(H_2dhtp)(H_2O)_2]\cdot DMAc$ AEMOF-1 ·DMAc (Alkaline Earth MOF-1)





H_2dhtp^{2-}

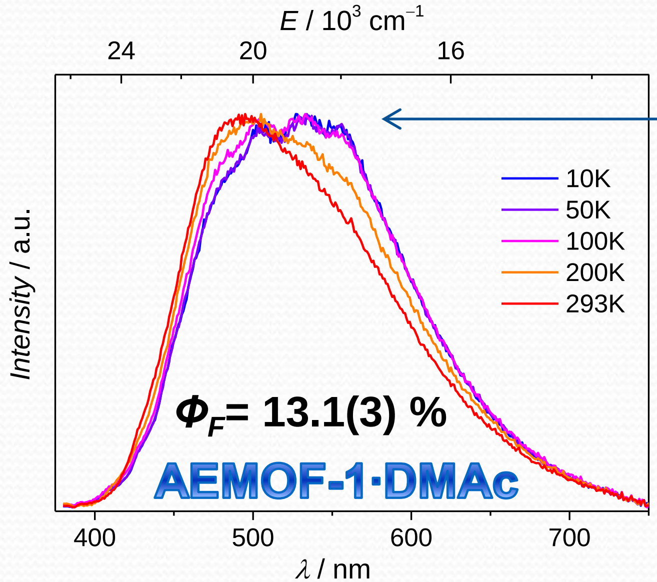


***Angew. Chem. Int. Ed.* 2015**, *54*, 1651

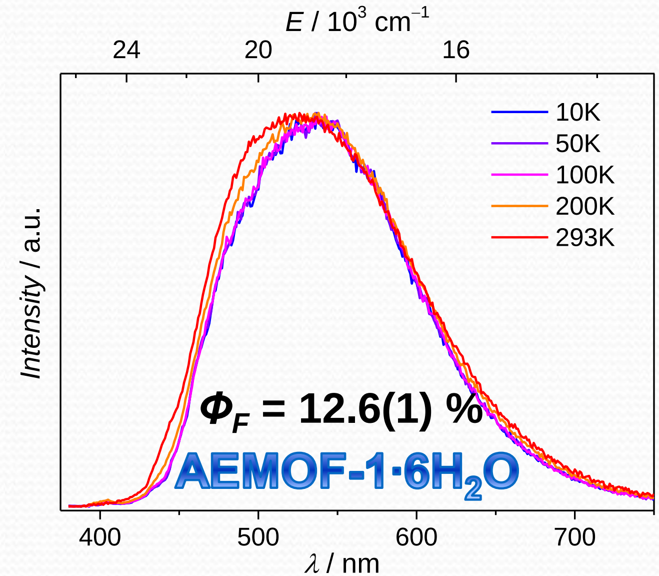
Representation of a) chain of MgO_6 octahedra and b) the 3-D structure of **AEMOF-1**. Mg, blue; O, red; C, grey. Guests DMAc and H atoms were omitted for clarity.

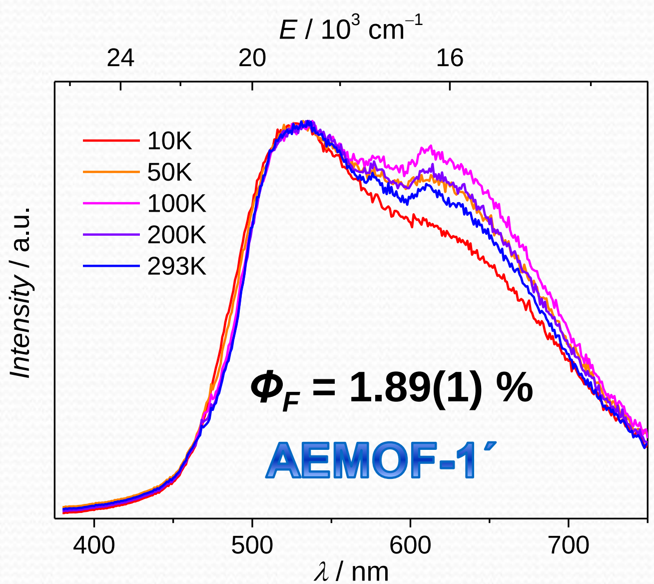
solvent-accessible volume of ~ 45 % and size of pores ~ 6 Å, calculated by PLATON

Luminescence properties

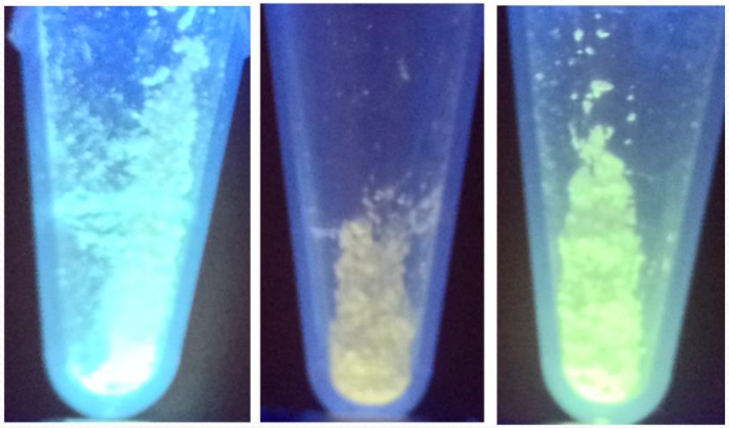


Red shift upon lowering the temperature



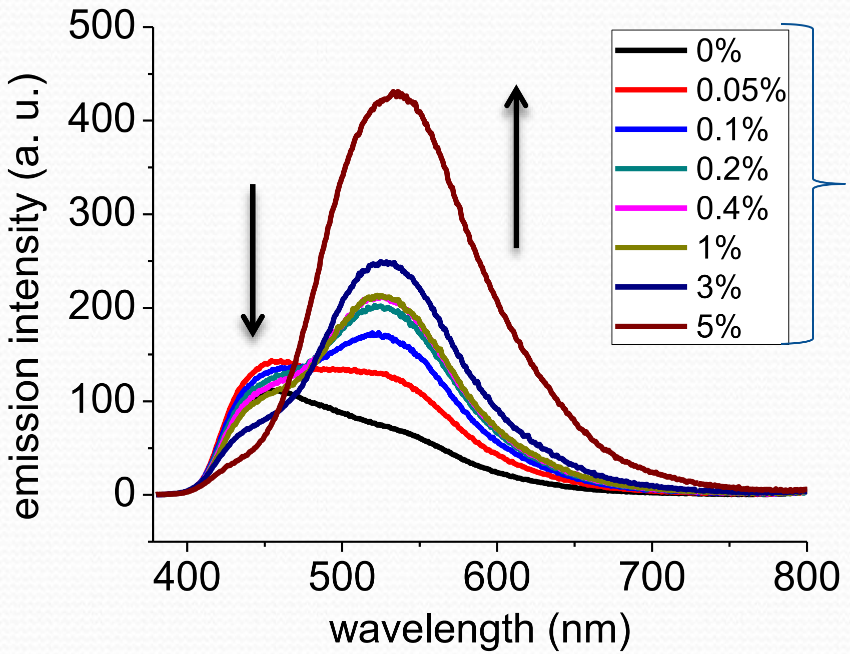


AEMOF-1·DMAc **AEMOF-1´** **AEMOF-1·6H_2O**



Real time detection of water in THF by AEMOF-1´

Measurements on continuously stirred suspension of the MOF



%H_2O (*v/v*) in THF

All measurements were performed 1-2 min after adding the water aliquots in THF

Capability for real time detection of water

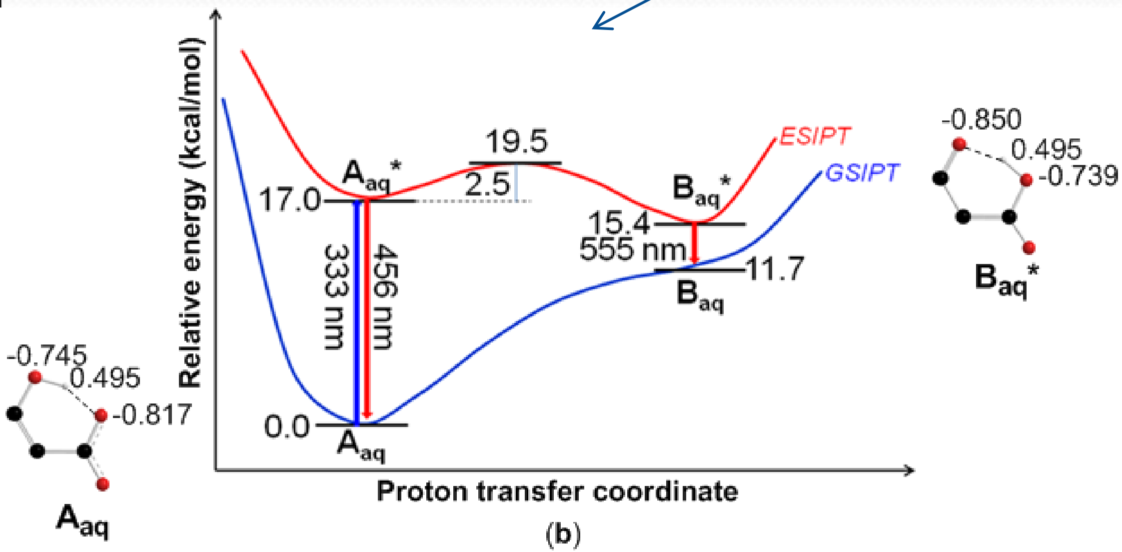
- ✓ Overall enhancement of fluorescence intensity **(turn-on)** with a concomitant red shift of the fluorescence maximum from ca. 455 to 530 nm
- ✓ **Remarkably, a considerable change in the emission profile of AEMOF-1´ is seen at a water concentration as low as 0.05% v/v!**

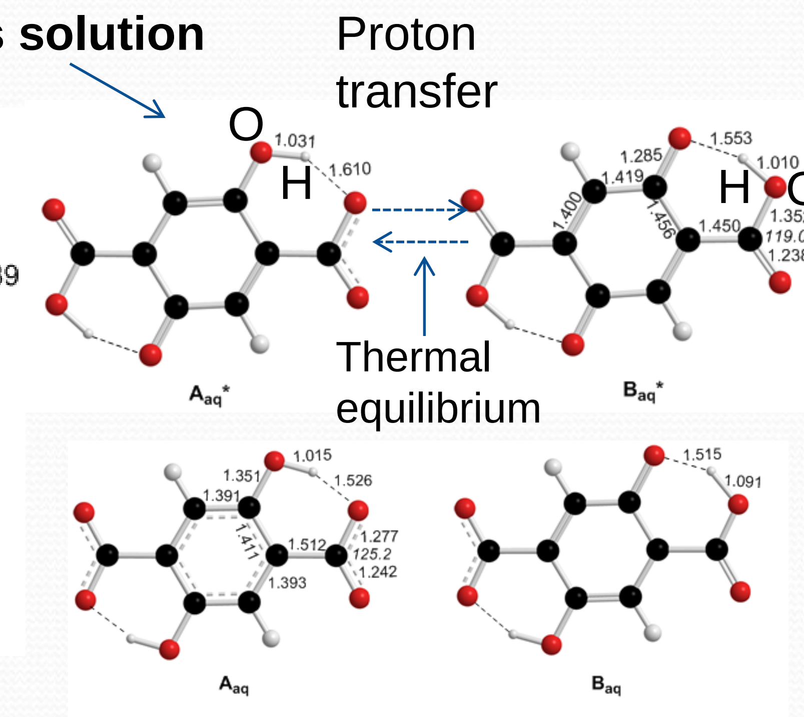
Two types of signal transduction

Increased specificity-Elimination of errors

Luminescence properties and Excited State Proton Intramolecular Transfer (ESIPT)

Calculations in aqueous solution

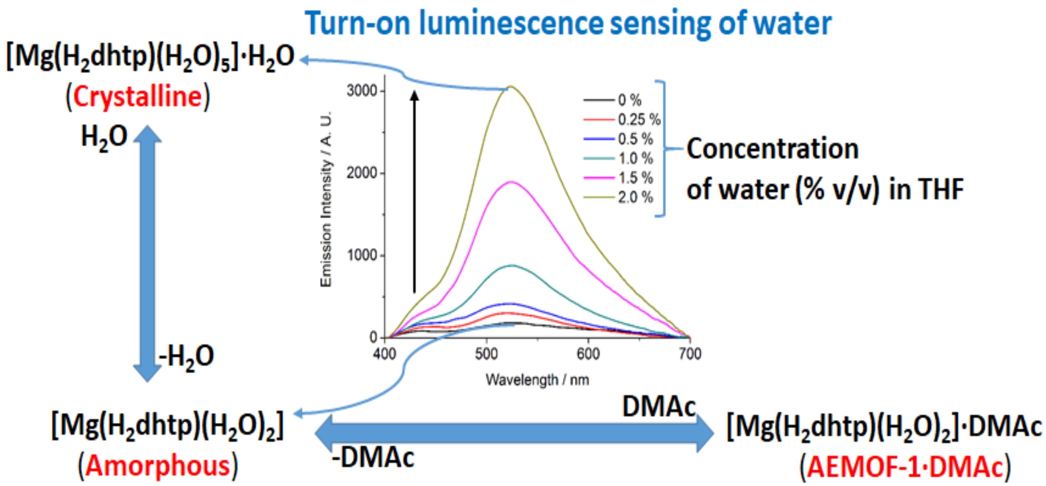




Theoretical calculations for H_2dhtp^{2-} ligand in gas phase and aqueous solution:

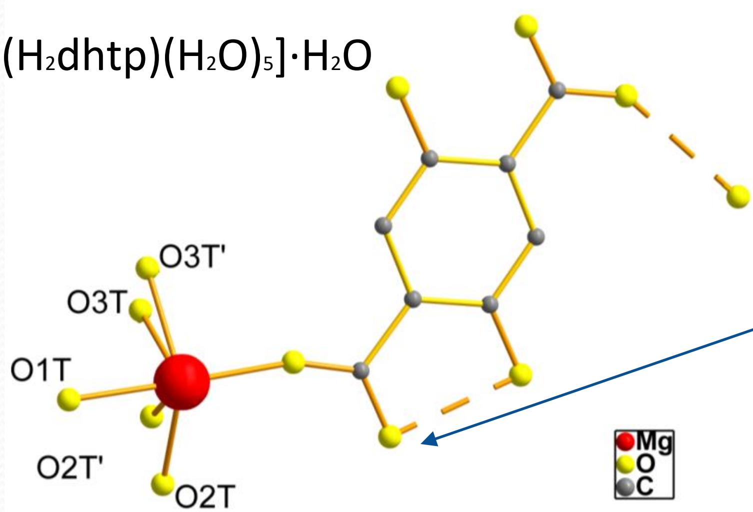
- **dual emission from two closely spaced excited states in thermal equilibrium**
- **The lowest energy excited state is more stabilized in aqueous solution (energy= 15.4 kcal/mol, stabilization vs. the high energy state=1.6 kcal/mol) than in gas phase (energy= 15.9 kcal/mol, stabilization vs. the high energy state= 0.7 kcal/mol)**
- **AEMOF-1·DMAc: RED-SHIFTED EMISSION AT LOW TEMP DUE TO THE EQULIBRIUM SHIFT TOWARDS THE LOWEST ENERGY EXCITED STATE**
- **AEMOF-1·6H_2O: RED-SHIFTED EMISSION EVEN AT RT (WHY?)**

Unravelling the mechanism of water sensing by the Mg^{2+} dihydroxy-terephthalate MOF (AEMOF-1′)



The observed changes in the fluorescence properties of AEMOF-1′ upon hydration **arise from a structural transformation to the mononuclear complex** $[Mg(H_2dhtp)(H_2O)_5]\cdot H_2O$ (H_4dhtp = 2,5-dihydroxyterepthalic acid) (1). In the latter complex, **excited state intramolecular proton transfer (ESIPT) is strongly favoured** thereby leading to enhanced and red shifted emission in comparison to AEMOF-1·DMAc.

$[Mg(H_2dhtp)(H_2O)_5]\cdot H_2O$

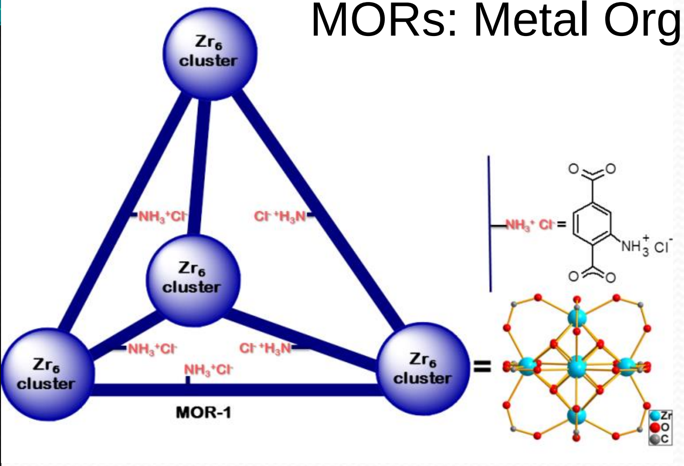


ESIPT process is not electrostatically inhibited and is thereby favoured to such an extent that practically only ESIPT emission is observed even at room temperature.

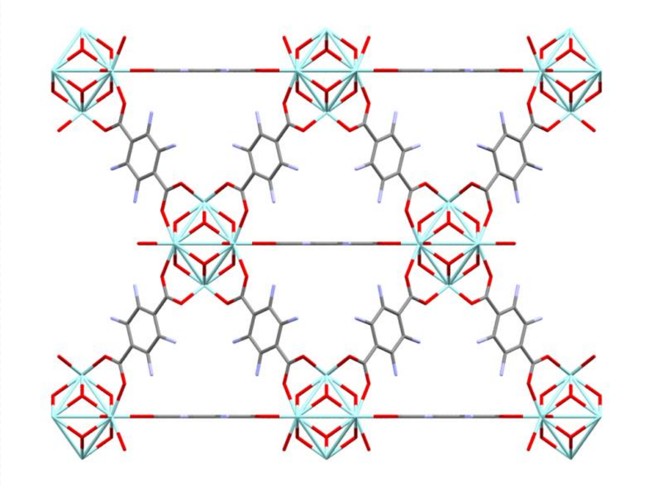
***Mol. Syst. Des. Eng.* 2020**, 5, 461

MOR-1: A Cr(VI) sorbent

MORs: Metal Organic Resins (Next Generation Ion Exchange Resins)



Weak base MOR..



MOR-1(UiO-66-NH_3^+):$[Zr_6O_4(OH)_4(NH_3^+\text{-BDC})_6]Cl_6$

Protonation of NH_2-functionalized MOF affords a highly efficient anion exchanger

However….

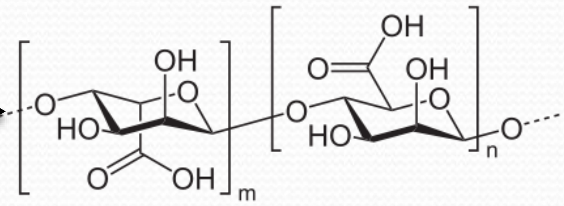
MOR-1 forms fine suspension in water, cannot be easily separated and cannot be used in ion exchange columns (required for applications).

“Composite materials containing organic polymer encapsulated metal organic frameworks”,
Patent Number: **WO2017083467A1**

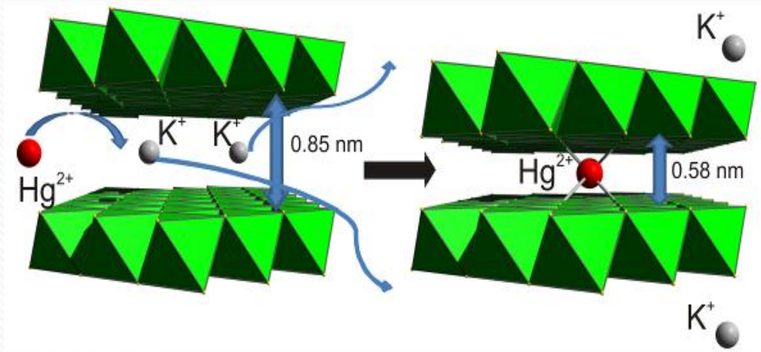
Chem. Sci. **2016**, *7*, 2427

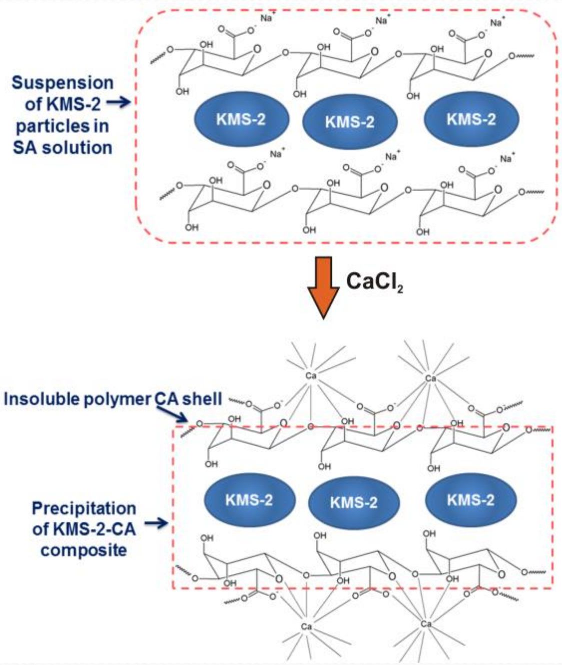
ALGINIC ACID (HA) AND CALCIUM ALGINATE (CA) composites

Brown algae

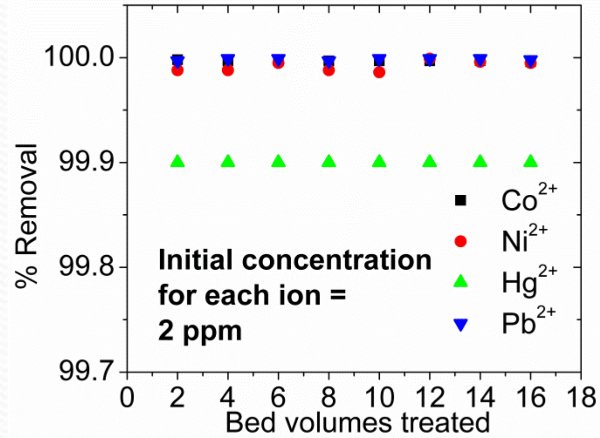


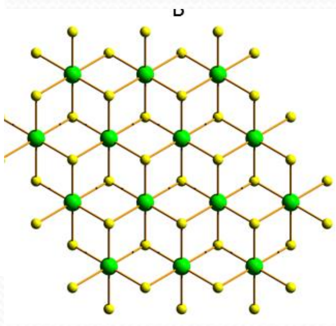
ALGINIC ACID





KMS-2 KMS-2-CA

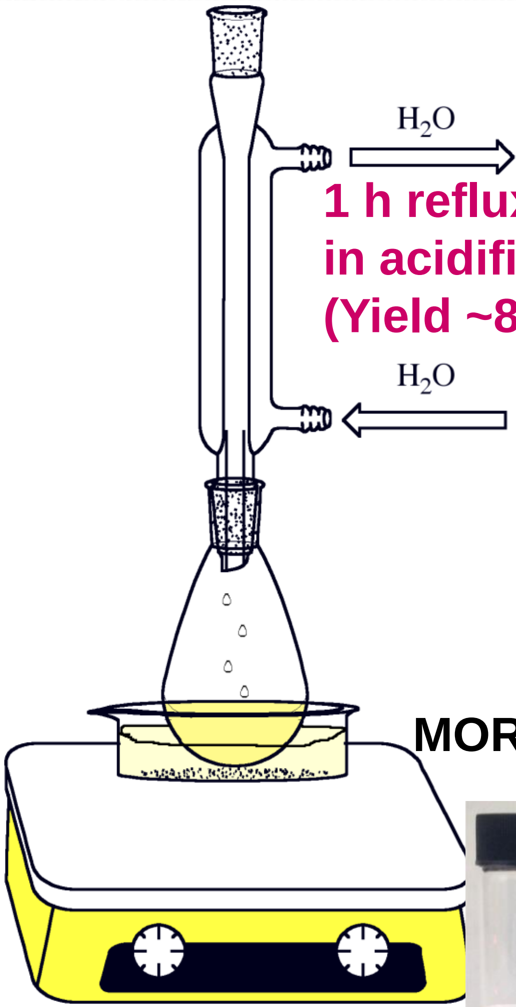




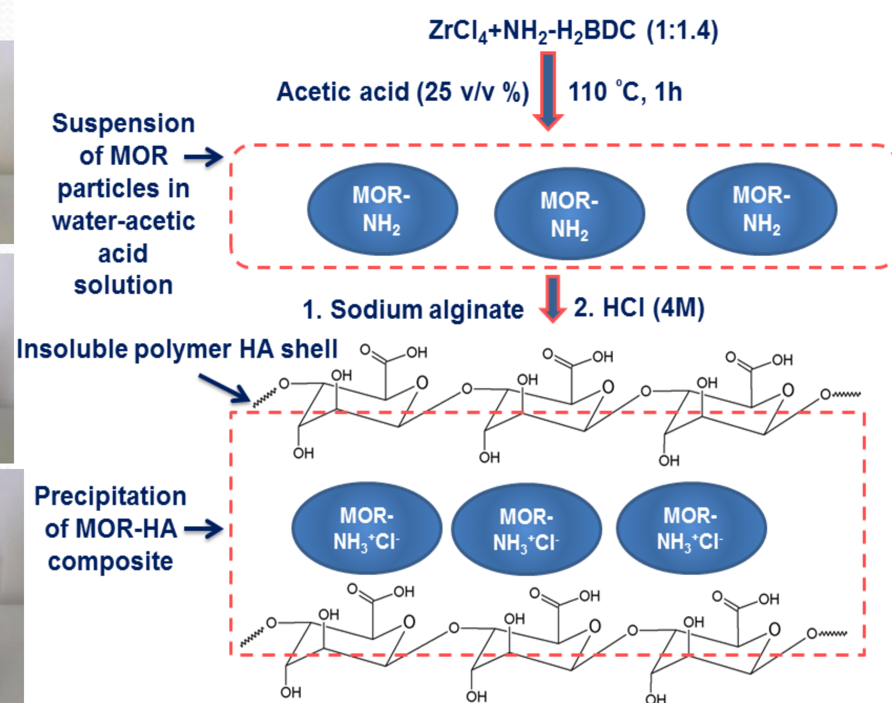
KMS-2: $K_2MgSn_2S_6$

"Column Material for the Capture of Heavy Metal and Precious Metal Ions", Patent Number: **US 20150144568 A1; WO 2015080976 A1.**

Green, rapid synthesis of MOR-1-HA



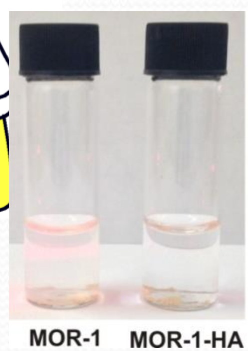
1 h reflux synthesis in acidified water (Yield ~80%)

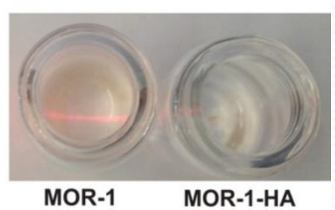


MOR-1-HA is less H_2O-dispersed

alginic acid ~ 2.1% wt

MOR-1-HA: BET surface area 1182 m²/g

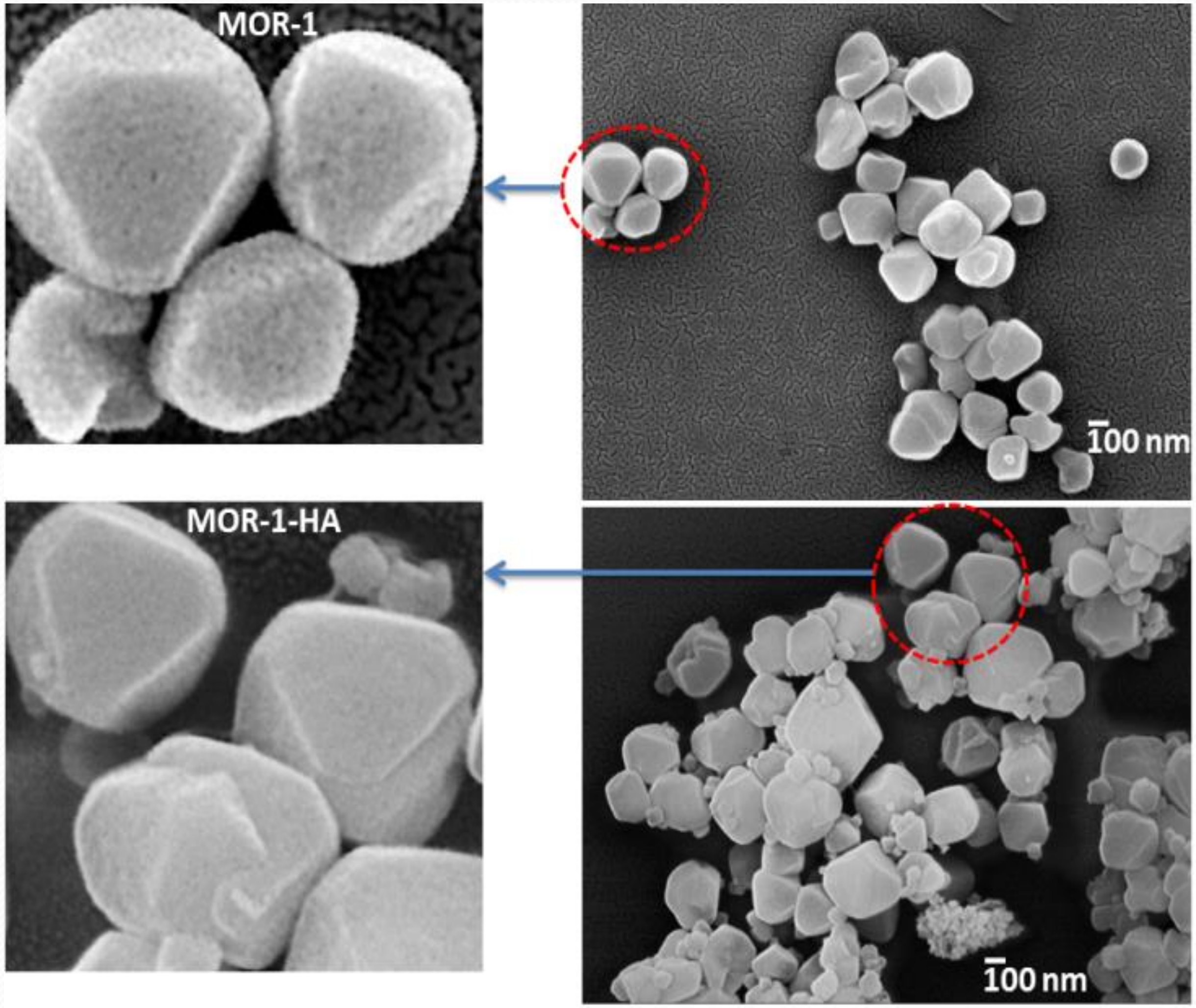




Inorg. Chem. Front. **2016**, *3*, 635

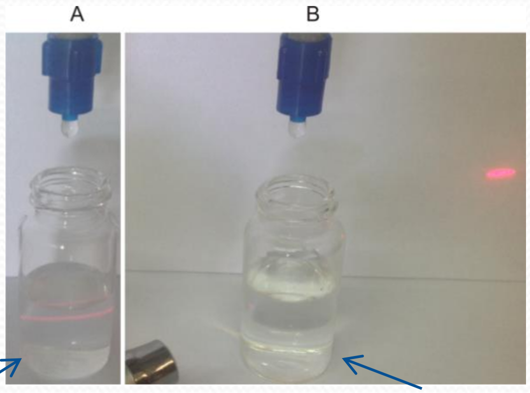
Patent number: ***WO2017083467A1***

FE-SEM studies



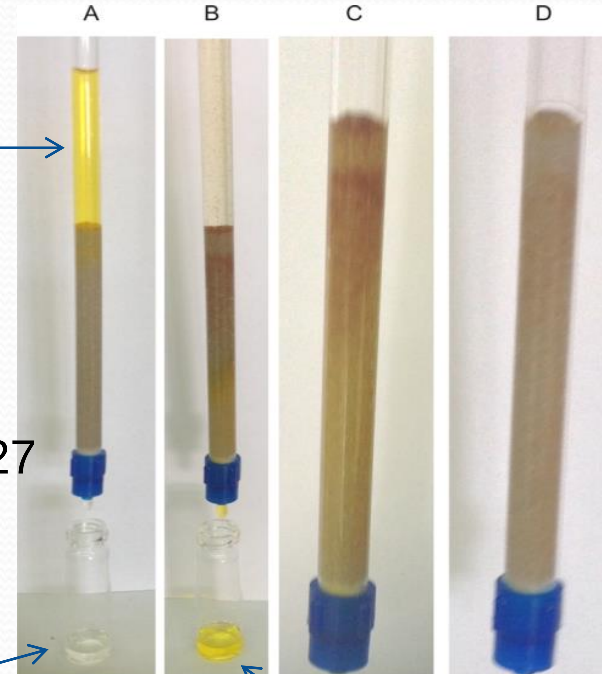
- The nanoparticles of **MOR-1** are spongy with relatively large voids
- Those of **MOR-1-HA** contain significantly smaller pores in their surface
- a thin layer of alginic acid covers the large pores in the surface of **MOR-1** nanoparticles

Column ion exchange with MORs



MOR MOR-HA

Chem. Sci., **2016**, *7*, 2427



Cr(VI)

Cr-free effluent

Regeneration with acid

The columns prepared contain only 1-2 wt.% of MOR-HA, so the main component of the stationary phase was sand.

The stationary phase in the columns is a mixture of MOR-HA and sand. The use of such mixtures instead of the pure composite has several advantages (stable flow, distribution of active material in longer column length, low cost)

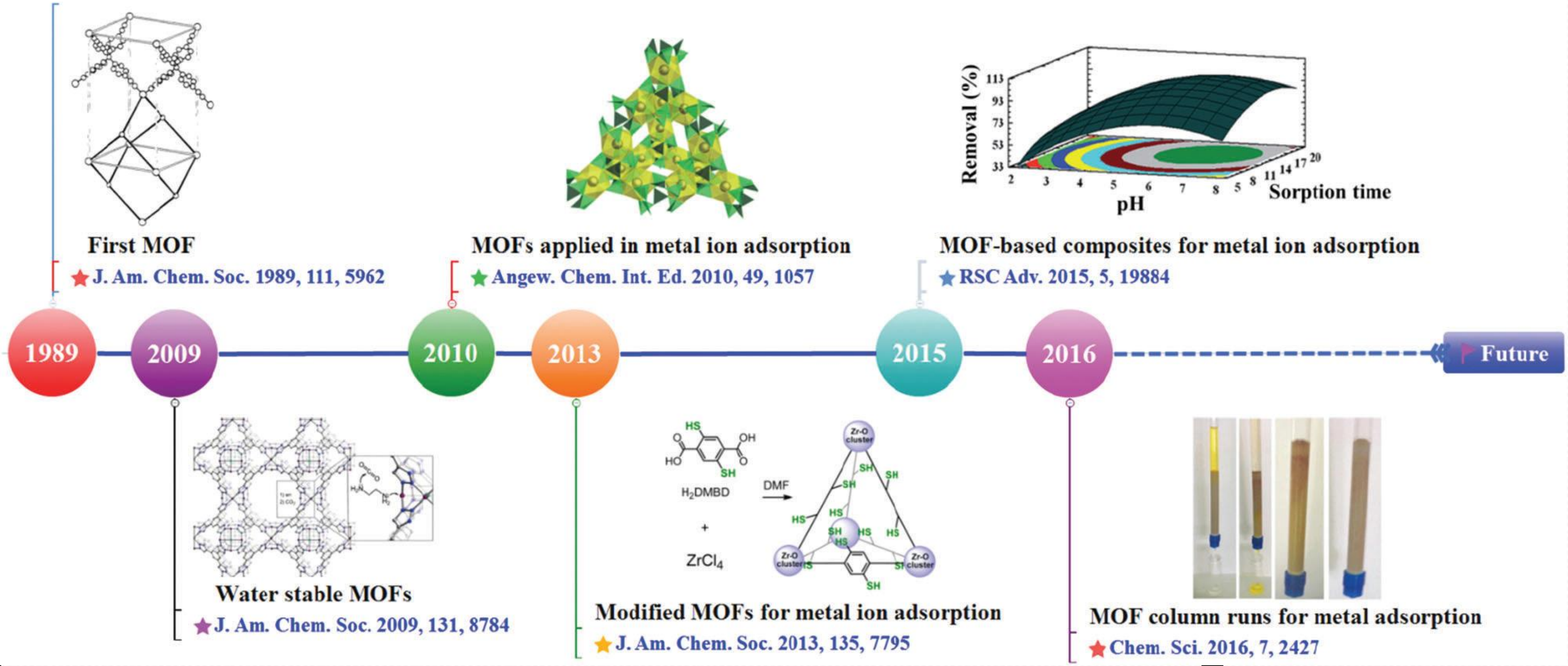


Fig. 1 Developmental milestones of MOF-based materials for the adsorption of toxic and nuclear waste-related metal ions….

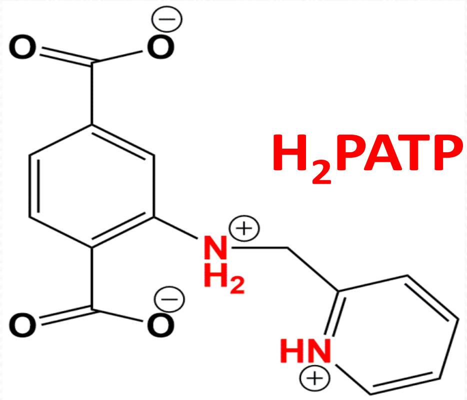
Chem. Soc. Rev. **2018**,*47*, 2322

Looking for even better sorbents…

Use of pre-functionalized ligand to incorporate maximum number of functional groups

Aiming to…..

$[Zr_6O_4(OH)_4(H_2PATP)_6]Cl_{12}$

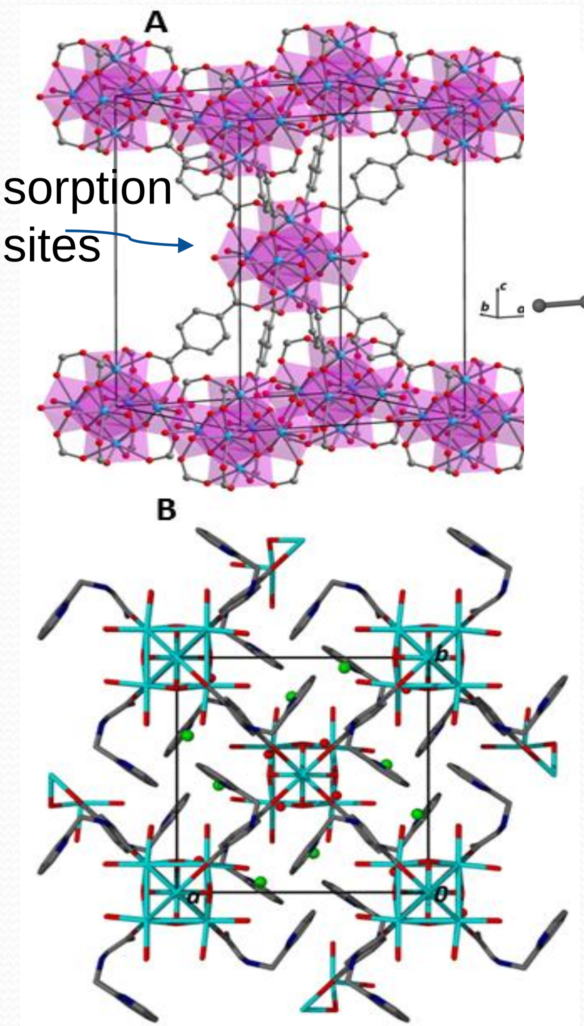


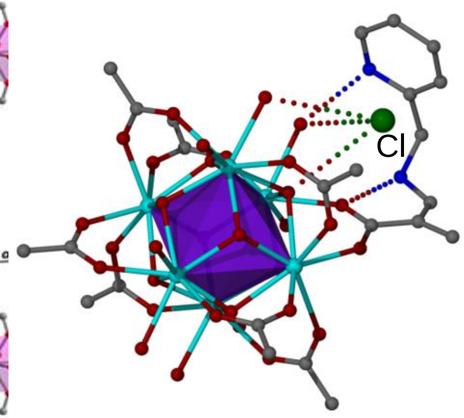
However…..

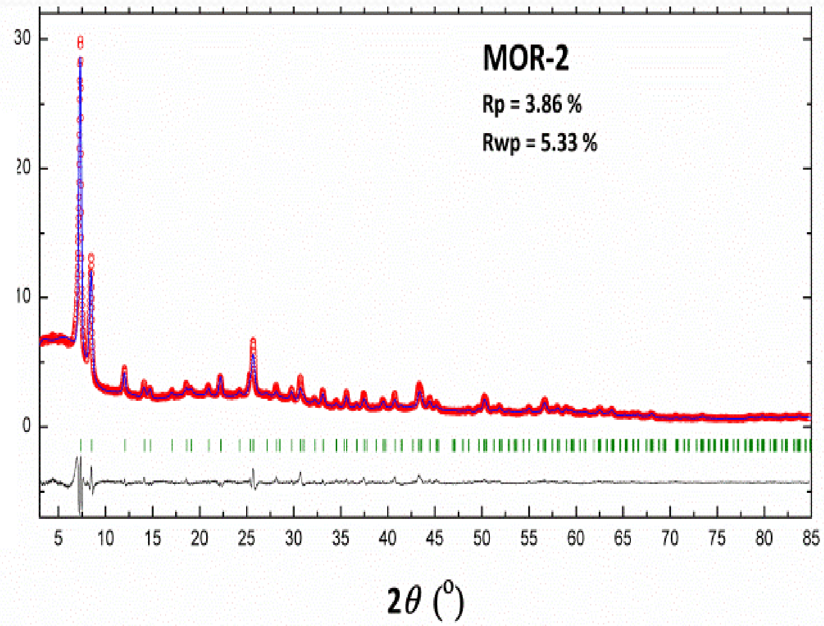
A series of analytical data (C,H,N, EDS, Zr analyses and TGA) were consistent with the formula $H_{16}[Zr_6O_{16}(H_2PATP)_4]Cl_8 \cdot xH_2O$ (x =8-12) for the **MOR-2** material.

J. Mater. Chem. A **2017**, *5*, 14707

Solution and Rietveld refinement







I4/m
a =14.677(3) Å
b = 20.794(6) Å

Collaboration with Prof. J. Plakatouras

- Zr_6O_8 core was found using direct methods
- 8-connected model of the structure of **MOR-2** was built with Materials Studio and then it was optimized
- The best solution was used as the starting point for the Rietveld refinement

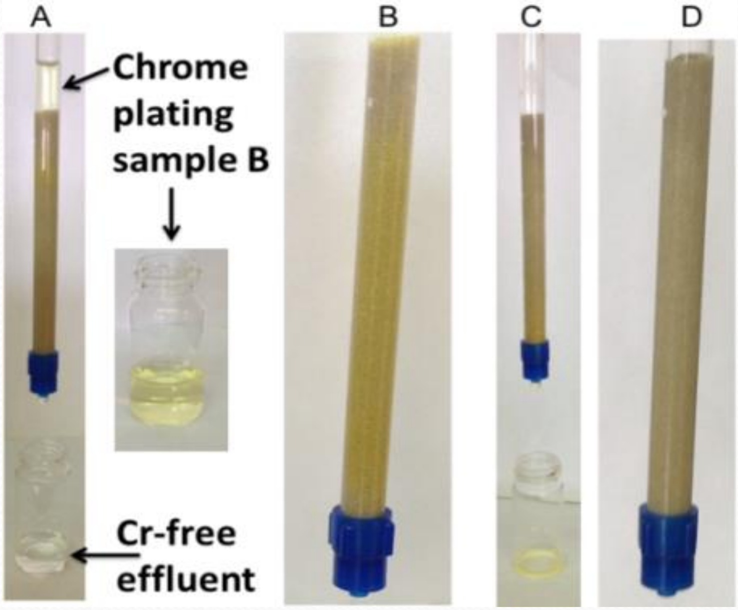
Comparison with other sorbents

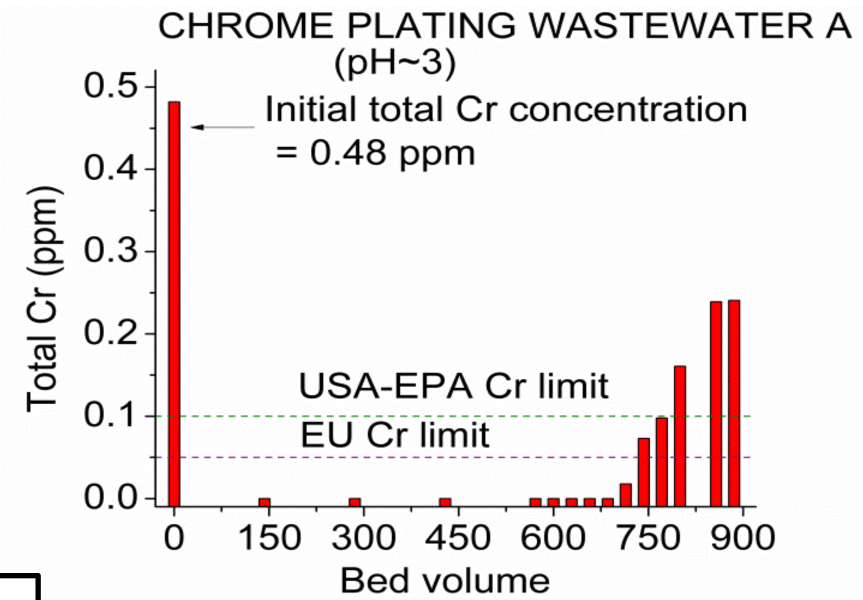
Selected Cr(VI) sorption characteristics of reported MOFs.

MOF	Sorption capacity (mg Cr(VI)/g)	Kinetic studies-Equilibrium time at RT
		CrO_4^{2-}
1-ClO_4	28.2	6 h
SLUG-21	26.9	48 h
Zn-Co-SLUG-35	30.7	2 h
MOR-2	**118.3**	**1 min**
		$Cr_2O_7^{2-}$
ABT·2ClO_4	102.6-130.5	48 h
FIR-53	35.6	10 min
FIR-54	49.6	30 min
ZJU-101	118	10 min
MOF-867	25.5	>12 h
MOR-1-HA	116.5-134.8	3-9 min
1-SO_4	79.9	72 h
MOR-2	**193.7**	**1 min**

MOR-2 shows particularly high Cr(VI) sorption capacity and extremely fast Cr(VI) sorption

Column ion exchange studies-industrial waste





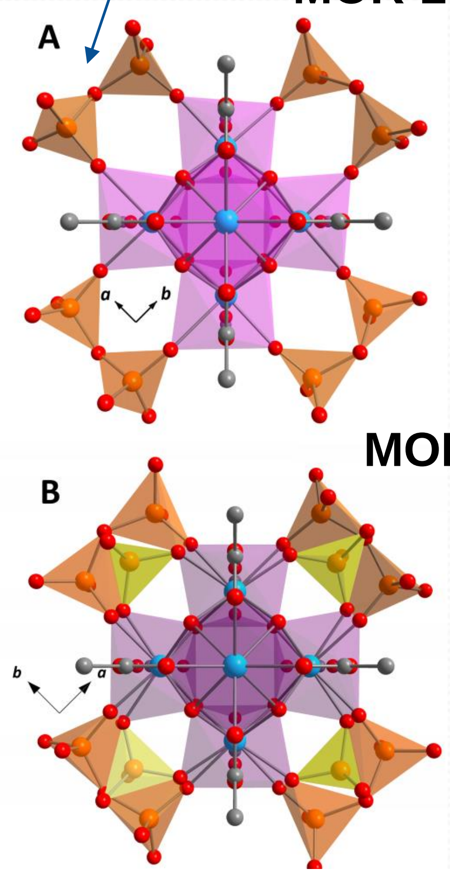
A. Decontamination of the chrome plating solution B, after passing it through the **MOR-2-HA**/sand column.
B. CrO_4^{2-}saturated column.
C. Regeneration of the column by washing it with 4 M HCl solution.
D. Column after the regeneration process (it looks identical with the pristine one).

2.5 L (~714 bed volumes) of the diluted chrome plating solution had a total Cr content <18 ppb, after passing it through the **MOR-2-HA**/sand column.

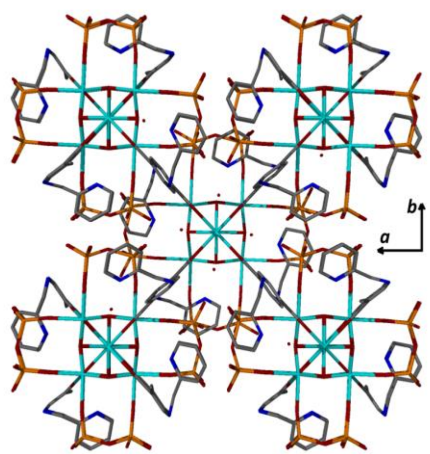
Mechanism of the ion exchange process

Determination of the structures of Cr(VI)-loaded materials

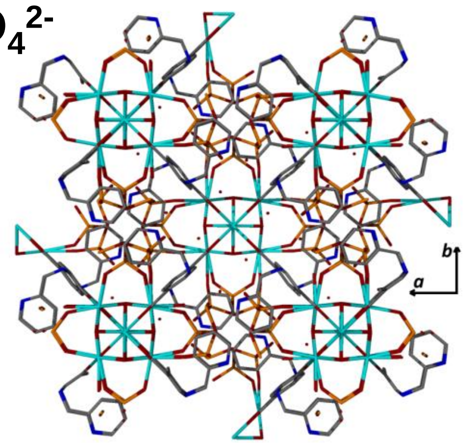
$Cr_2O_7^{2-}$



MOR-2@$Cr_2O_7^{2-}$



MOR-2@CrO_4^{2-}



Mechanism of ion exchange process

- The pyridyl-methyl-ammonium functional groups may strongly interact with either chromate or dichromate anions, thus providing a driving force for the Cr(VI) exchange process

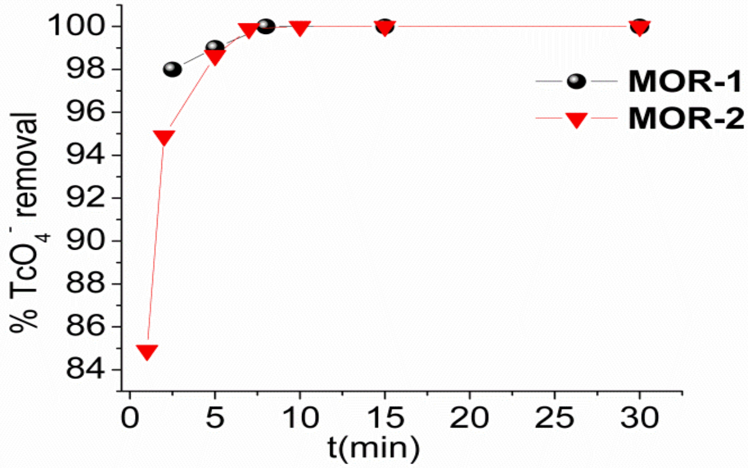
- The labile terminal ligands of the Zr_6 clusters constitute the sorption sites in which the Cr(VI) anions are finally grafted.

$$H_{16}[Zr_6O_{16}(H_2PATP)_4]Cl_8 + 4Cr_2O_7^{2-} \rightarrow [Zr_6O_8(Cr_2O_7)_4(H_2PATP)_4] + 8Cl^- + 8H_2O$$

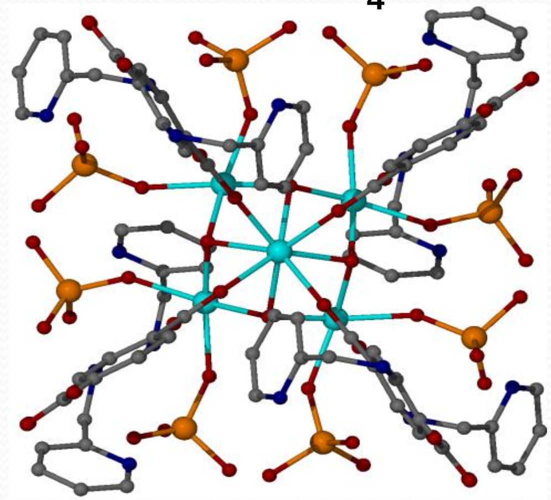
$$H_{16}[Zr_6O_{16}(H_2PATP)_4]Cl_8 + 2CrO_4^{2-} + 2Cr_2O_7^{2-} \rightarrow [Zr_6O_8(Cr_2O_7)_2(CrO_4)_2(H_2PATP)_4] + 8Cl^- + 8H_2O$$

Novel type of ion sorption process involving both ion exchange and chemisorption

Sorption of radioactive TcO_4^- anions

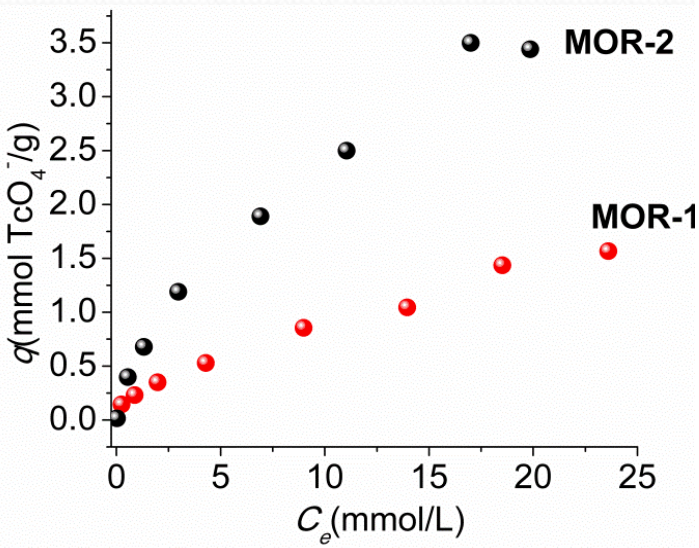


MOR-2/ReO_4^-

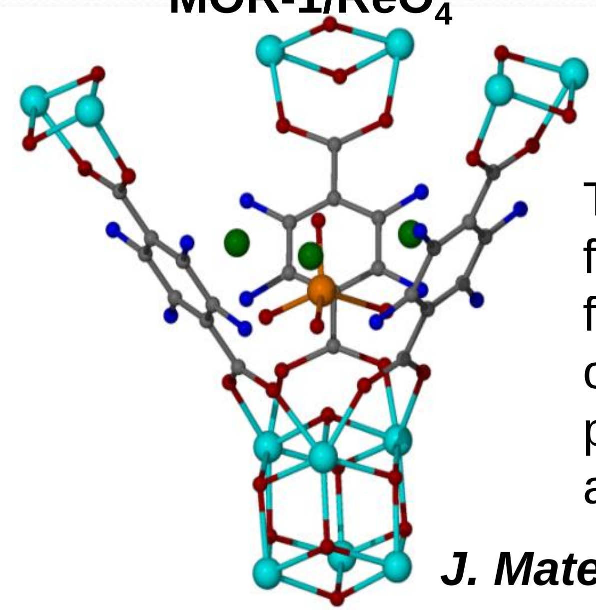


A representation of the refined structure of **MOR-2/ReO_4^-** showing the coordination of 8 ReO_4^- anions to the Zr_6 unit

ReO_4^- non-radioactive analogue of TcO_4^-



MOR-1/ReO_4^-



The Re species were found above a triangular face of the Zr_6O_8 octahedron at close proximity to the μ_3-O atom

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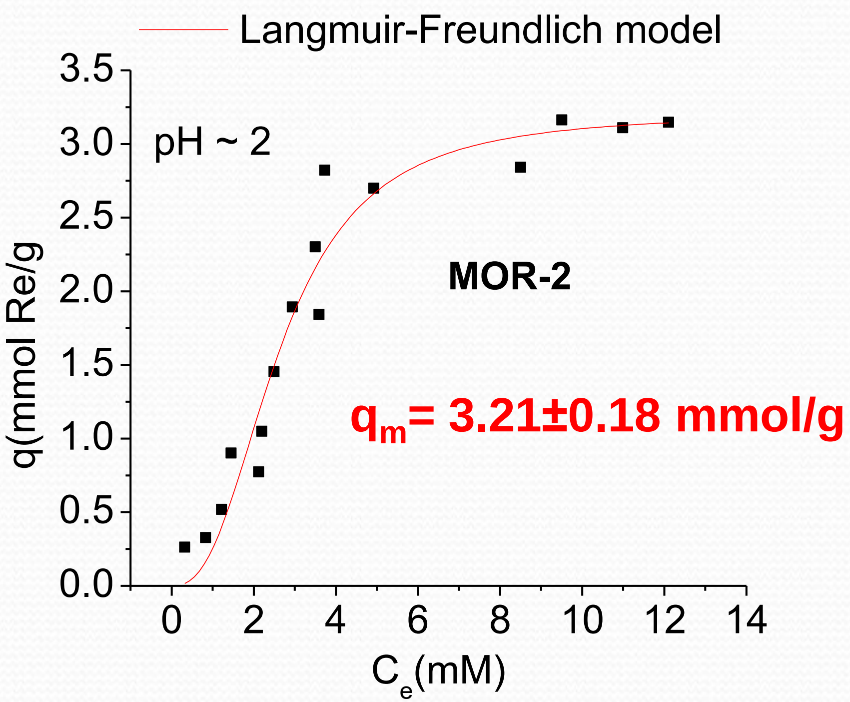
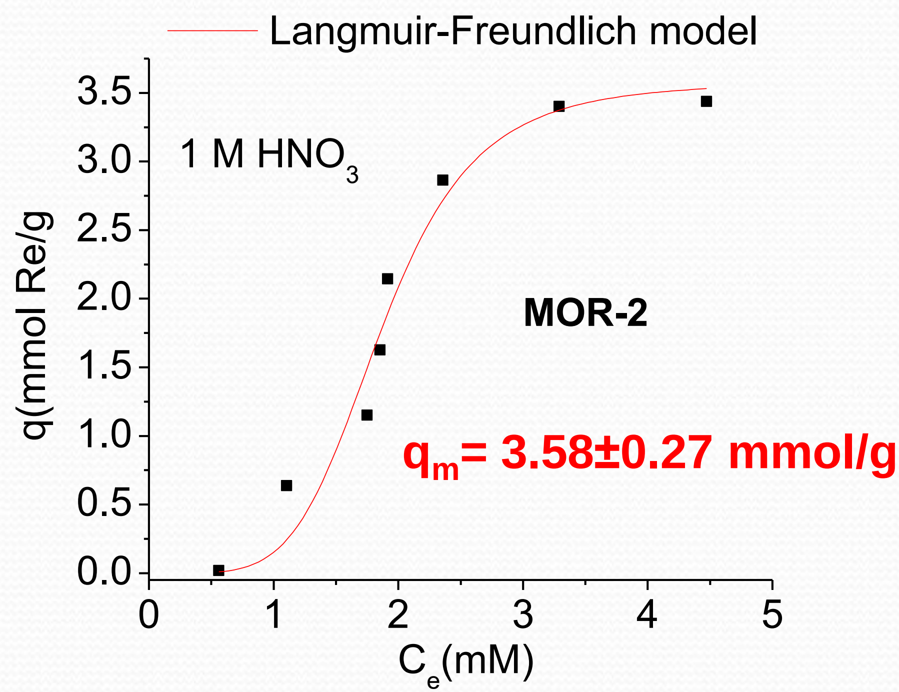
MOR-2 for capture of ReO_4^- under acidic conditions

- Nuclear waste is usually either highly acidic (1-2 M HNO_3 acid) or highly basic (5 M NaOH)

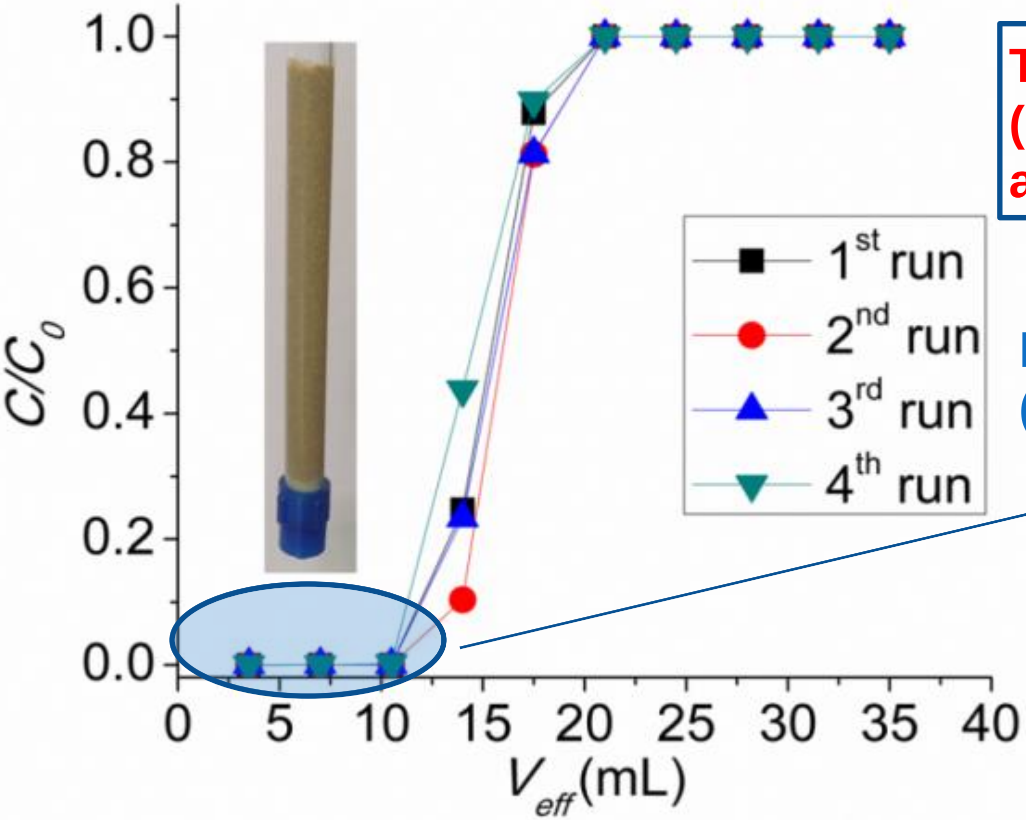
- Zr^{4+} MOFs are stable under extreme acidic conditions (e.g. MOR-2 stable in 4 M HCl)

MOR-2 exceptional ReO_4^- sorption capacity even in the presence of 1 M HNO_3!





Column ReO_4^- sorption data for MOR-2-HA



The column is regenerated (by washing with acid) and reused with no loss of capacity

Re concentrations ≤25 ppb (ICP-MS) (almost 100 % removal)

C= ReO_4^- concentration of the effluent, C_0 = initial ReO_4^- concentration = 1.14 mM, pH~ 7, flow rate ~ 1.75 mL/min, one bed volume =3.5 mL, stationary phase **MOR-2-HA**/sand =0.05 g:5 g).

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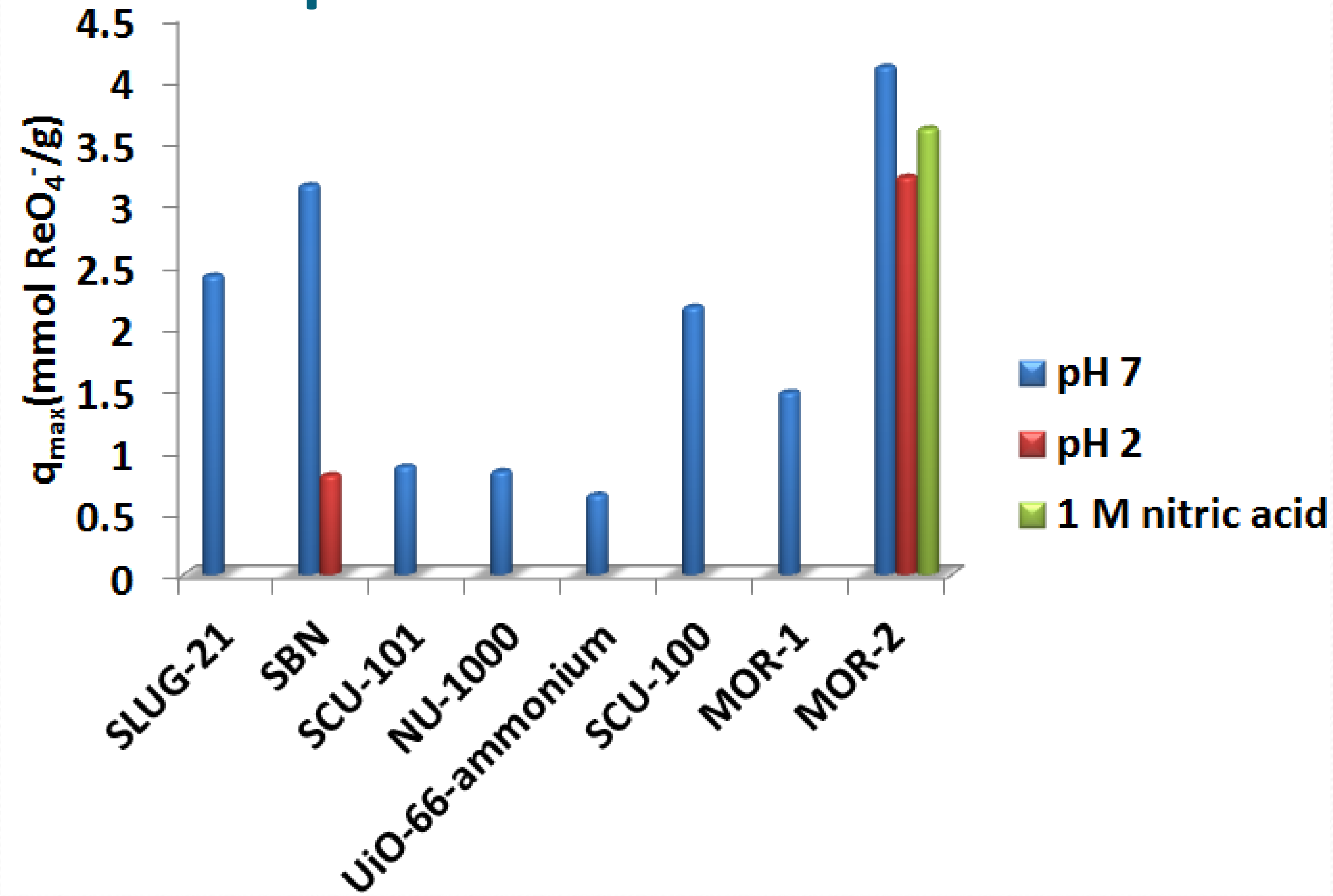
Comparison with other MOFs



MOR-2 most efficient ReO_4^- sorbent reported

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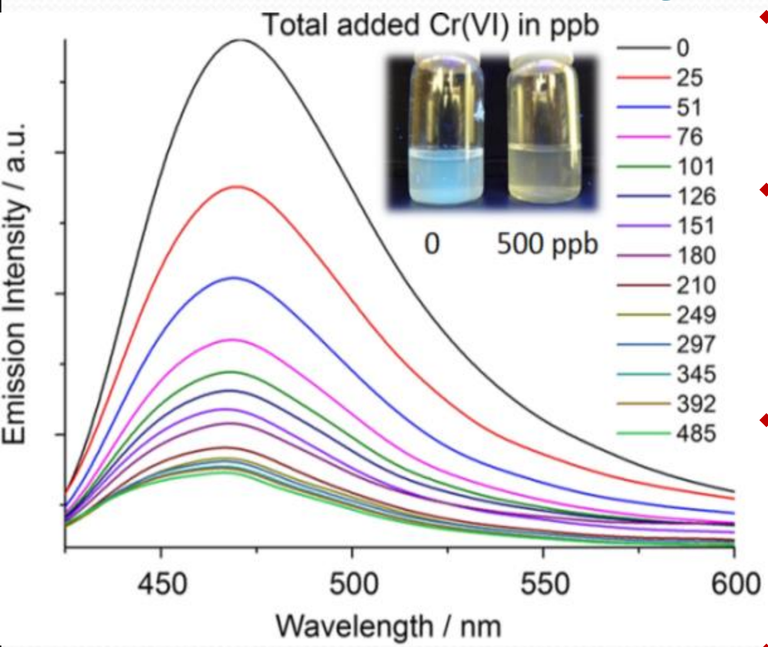
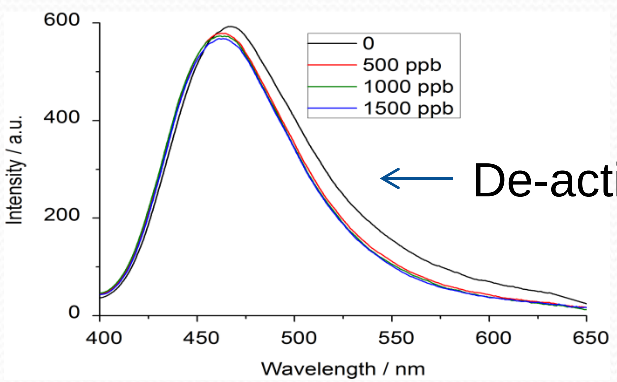
Not only a sorbent…



- **MOR-2** readily forms stable suspensions in aqueous media (ideal for sensing applications)
- Strong fluorescence quenching (loss of more than 80% of the initial emission signal) upon Cr(VI) addition
- Limits of detection (LOD) and quantification (LOQ) were found at 4 and 13 ppb respectively(well below acceptable Cr(VI) levels)
- Energy/electron transfer phenomena (enhanced by the coordination of Cr(VI) in the Zr_6 cluster) explain the strong fluorescence quenching



← De-activated (deprotonated sample) shows no sensing capability

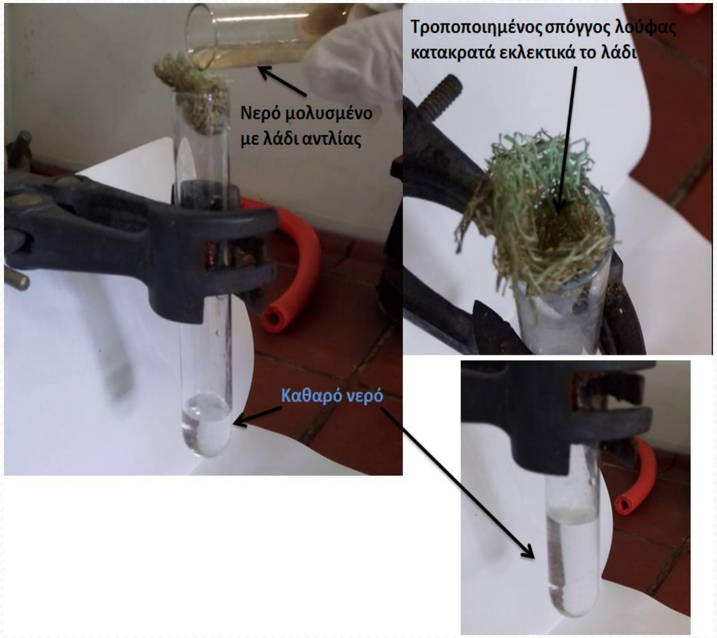
↓

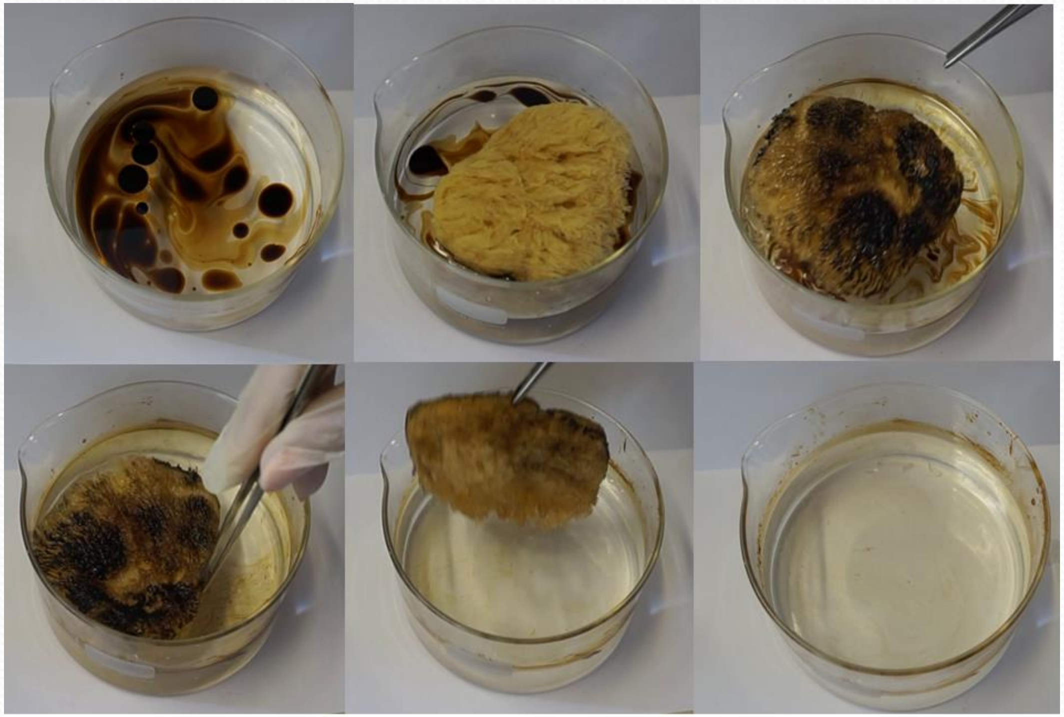
Sensing is facilitated by the rapid insertion of Cr(VI) in the pores of MOR-2 material

Collaboration with Mr S. Diamantis, Dr. T. Lazarides

SUPERHYDROPHOBIC MATERIALS

Ο τροποποιημένος σπόγγος απωθεί το νερό





Ο τροποποιημένος σπόγγος απομακρύνει ταχύτατα ακάρθατο πετρέλαιο απο το νερό

"Sponges modified with superhydrophobic metal oxide and metal-organic nanomaterials with excellent selectivity for sorption of lipophilic pollutants from water",

GR-Patent No. 1009740.

COLLABORATIONS WITH MEMBERS OF INSTITUTE
CONTRIBUTION FROM MY GROUP

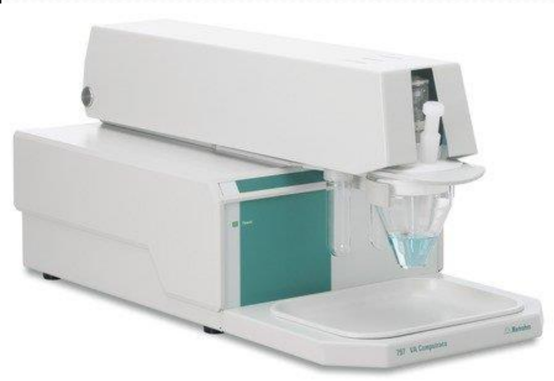
- ✓ Prof. S. Hadjikakou, Prof. A. Garoufis (single crystal X-ray crystallography)
- ✓Prof. J. Plakatouras (powder X-ray structural determination and refinement)
- ✓Prof. I. Deligiannakis, Prof. M. Louloudi (Arsenic(III) sorption studies)
- ✓Assoc. Prof. D. Giokas (oil sorption, environmental remediation studies)
- ✓ Assistant Prof. P. Papadopoulos(water contact angle measurements)
- ✓ Assoc. Prof. A. Douvalis (Mössbauer spectroscopy studies)

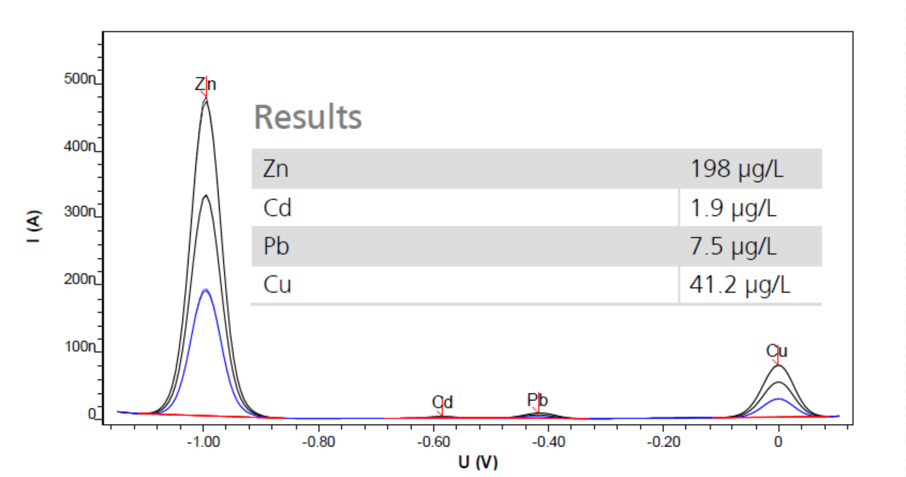
Our expertise (fields we can contribute)

1. **Synthesis of MOFs and composites for various applications**
2. **Synthesis of purely inorganic materials (e.g. metal chalcogenides) and composites for various applications**
3. **Investigation of sorption properties of materials in liquid phase**
4. **Single crystal and powder X-ray determination of crystal structures**

Instrumentation

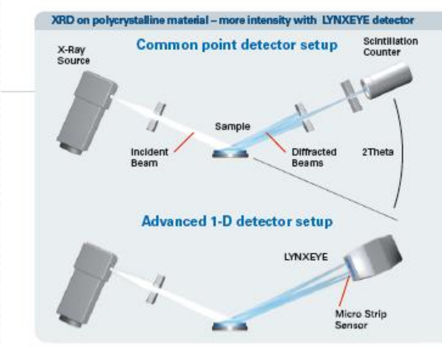
- ✓ Instruments of Chemistry Department and University of Ioannina
- ✓ Voltammetry

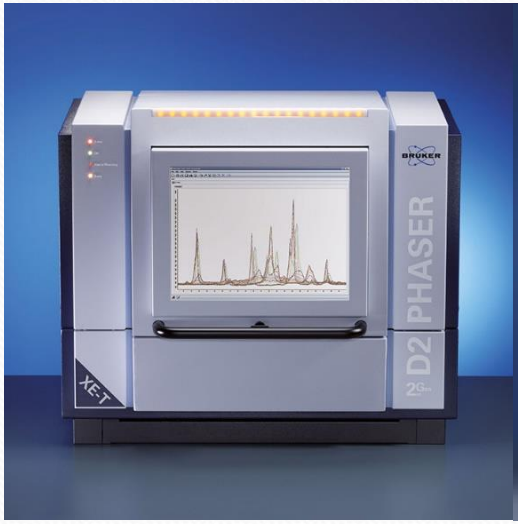




- ✓ Benchtop PXRD

(coming soon)





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Funding:

Περιφέρεια Ηπείρου
Region of Epirus

Patras Science Park
Επιστημονικό Πάρκο Πατρών

H.F.R.I.
Hellenic Foundation for Research & Innovation

European Union
European Social Fund

Operational Programme
Human Resources Development, Education and Lifelong Learning
Co-financed by Greece and the European Union

ΕΣΠΑ 2014-2020