Research activities and interests

M. J. Manos

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Research in our group

**New porous MOFs (exploratory synthesis)**

CrystEngComm 2014, 16, 3483  

**Luminescent MOFs-sensors**

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

**Emission at RT**

Inorg. Chem. 2015, 54, 5813  
Research in our group

**MOF and MOF composites for water treatment applications**

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


Research in our group

Hydrophobic materials

“Sponges modified with superhydrophobic metal oxide and metal-organic nanomaterials with excellent selectivity for sorption of lipophilic pollutants from water”,
GR-Patent No. 1009740.
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

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
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 \(\sim 6\, \text{Å}\), calculated by PLATON

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

Red shift upon lowering the temperature

$\Phi_F = 13.1(3) \%$

AEMOF-1·DMAc

$\Phi_F = 12.6(1) \%$

AEMOF-1·6H$_2$O

$\Phi_F = 1.89(1) \%$

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

Measurements on continuously stirred suspension of the MOF

- **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!

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

  *Capability for real time detection of water*

Two types of signal transduction

- Increased specificity
- Elimination of errors
Theoretical calculations for $\text{H}_2\text{dhtp}^2-$ 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 EQUILIBRIUM SHIFT TOWARDS THE LOWEST ENERGY EXCITED STATE
- AEMOF-1·6$\text{H}_2\text{O}$: 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

$$[\text{Mg(H}_2\text{dhtp)(H}_2\text{O)}_5\] \cdot \text{H}_2\text{O} \ (\text{H}_4\text{dhtp} = \text{2,5-dihydroxyterephthalic 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.

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.

MOR-1: A Cr(VI) sorbent

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


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).**


*Chem. Sci.* 2016, 7, 2427
ALGINIC ACID (HA) AND CALCIUM ALGINATE (CA) composites

Brown algae

ALGINIC ACID

KMS-2

KMS-2-CA

KMS-2: $\text{K}_2\text{MgSn}_2\text{S}_6$

Green, rapid synthesis of MOR-1-HA

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

MOR-1-HA is less H$_2$O-dispersed

alginic acid ~ 2.1% wt

MOR-1-HA: BET surface area 1182 m$^2$/g

ZrCl$_4$+NH$_2$H$_2$BDC (1:1.4)

Acetic acid (25 v/v %)  110 °C, 1h

1. Sodium alginate  2. HCl (4M)

Suspension of MOR particles in water-acetic acid solution

Precipitation of MOR-HA composite

Insoluble polymer HA shell


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

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…..

\[ \text{[Zr}_6\text{O}_4\text{(OH)}_4\text{H}_2\text{PATP)}_6\text{]}\text{Cl} \]

However…..

A series of analytical data (C,H,N, EDS, Zr analyses and TGA) were consistent with the formula \( \text{H}_{16}\text{[Zr}_6\text{O}_{16}\text{(H}_2\text{PATP)}_4\text{]}\text{Cl}_8\cdot\text{xH}_2\text{O (x =8-12)} \) for the MOR-2 material.

\[ J. \text{Mater. Chem. A 2017, 5, 14707} \]
Solution and Rietveld refinement

- \( l4/m \)
- \( a = 14.677(3) \, \text{Å} \)
- \( b = 20.794(6) \, \text{Å} \)

- \( \text{Zr}_6\text{O}_8 \) 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

Collaboration with Prof. J. Plakatouras
Comparison with other sorbents

Selected Cr(VI) sorption characteristics of reported MOFs.

<table>
<thead>
<tr>
<th>MOF</th>
<th>Sorption capacity (mg Cr(VI)/g)</th>
<th>Kinetic studies-Equilibrium time at RT</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-CIO₄</td>
<td>28.2</td>
<td>CrO₄²⁻</td>
</tr>
<tr>
<td>SLUG-21</td>
<td>26.9</td>
<td>6 h</td>
</tr>
<tr>
<td>Zn-Co-SLUG-35</td>
<td>30.7</td>
<td>48 h</td>
</tr>
<tr>
<td>MOR-2</td>
<td>118.3</td>
<td>2 h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 min</td>
</tr>
<tr>
<td>ABT·2ClO₄</td>
<td>102.6-130.5</td>
<td>Cr₂O₇²⁻</td>
</tr>
<tr>
<td>FIR-53</td>
<td>35.6</td>
<td>48 h</td>
</tr>
<tr>
<td>FIR-54</td>
<td>49.6</td>
<td>10 min</td>
</tr>
<tr>
<td>ZJU-101</td>
<td>118</td>
<td>30 min</td>
</tr>
<tr>
<td>MOF-867</td>
<td>25.5</td>
<td>10 min</td>
</tr>
<tr>
<td>MOR-1-HA</td>
<td>116.5-134.8</td>
<td>&gt;12 h</td>
</tr>
<tr>
<td>1-SO₄</td>
<td>79.9</td>
<td>3-9 min</td>
</tr>
<tr>
<td>MOR-2</td>
<td>193.7</td>
<td>72 h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 min</td>
</tr>
</tbody>
</table>

MOR-2 shows particularly high Cr(VI) sorption capacity and extremely fast Cr(VI) sorption.
A. Decontamination of the chrome plating solution B, after passing it through the MOR-2-HA/sand column.

B. CrO₄²⁻-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

MOR-2@Cr₂O₇²⁻

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 Zr₆ clusters constitute the sorption sites in which the Cr(VI) anions are finally grafted.

Novel type of ion sorption process involving both ion exchange and chemisorption.
Sorption of radioactive TcO$_4^-$ anions

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$_4^-$. The Re species were found above a triangular face of the Zr$_6$O$_8$ octahedron at close proximity to the $\mu_3$-O atom.

J. Mater. Chem. A 2018, 6, 20813
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$_3$!**

\[
q_m = 3.21 \pm 0.18 \text{ mmol/g}
\]

\[
q_m = 3.58 \pm 0.27 \text{ mmol/g}
\]
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).

*J. Mater. Chem. A, 2018 (DOI:10.1039/C8TA07901C)*
Comparison with other MOFs

MOR-2 most efficient ReO$_4^-$ sorbent reported

*J. Mater. Chem. A* 2018, 6, 20813
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*
“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)
Group members

PhD
Mrs. Sofia Rapti (MSc)

MSc
Mr. Petros Georgianos

Mrs. Christina Bika.

Mrs. Sofia Rizogianni

Mr. Dimitris Evangelou

Post doc
Dr. Anastasia Pournara

Funding:

[Logos and text indicating funding sources]