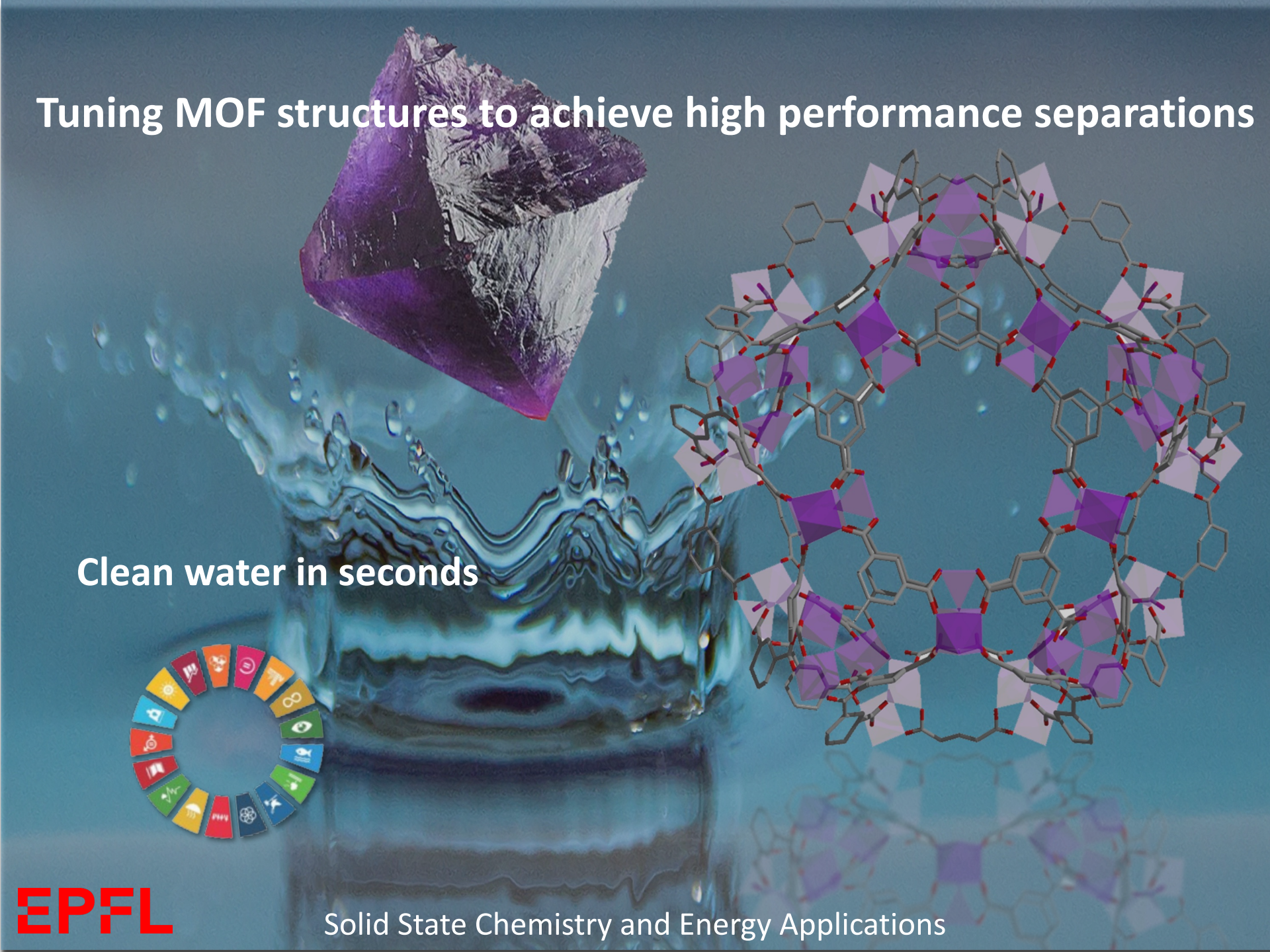
Tuning MOF structures to achieve high performance separations



Clean water in seconds

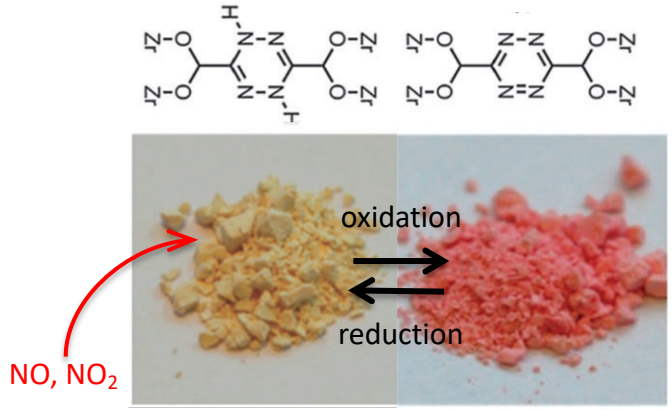
EPFL

Solid State Chemistry and Energy Applications

Four primary applications

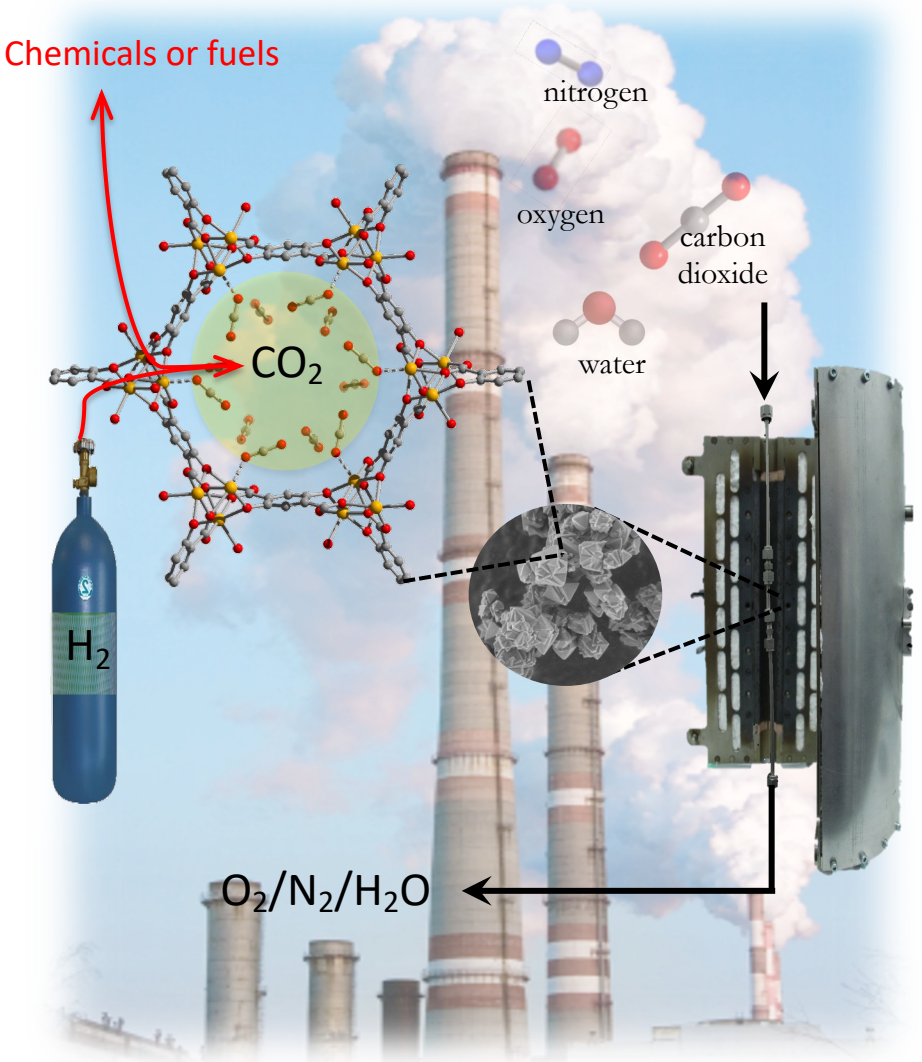
Storage/Delivery

Sensing



Nickerl, Senkovska, Kaskel *Chem. Commun.*,**2015**, 51, 2280.

Separation and conversion



EPFL

How much of the world's energy is spent on separations?

Seven separations that can change the world

1. Greenhouse gases from dilute emissions
2. Trace contaminates from water
3. Rare-metals from ore
4. Uranium from sea water

5. Alkenes from alkanes
6. Benzene derivatives
7. Hydrocarbon separation from crude oil

EPFL

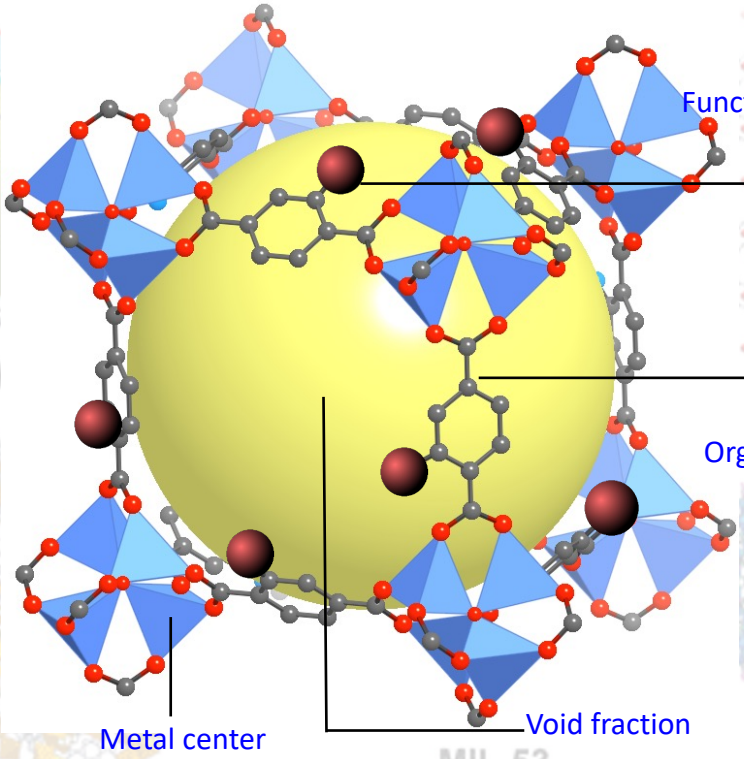
Nature, 2016, 532, 435.

Seven separations that can change the world

-reduce energy input into separations
-make impossible separations possible

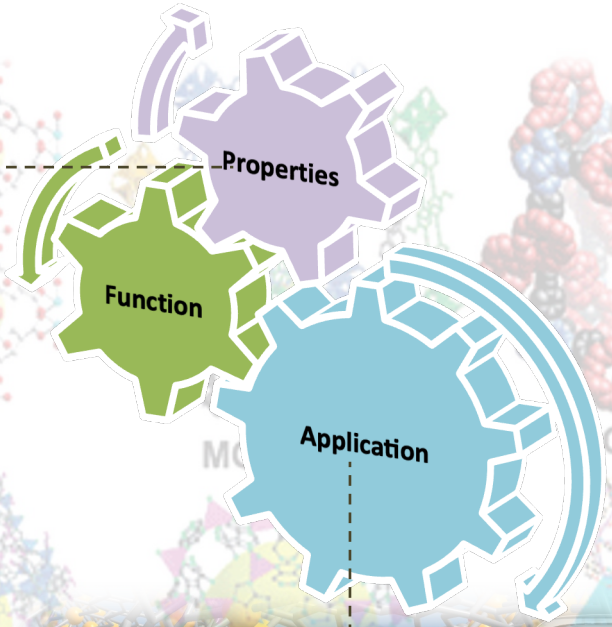
Nature, 2016, 532, 435.

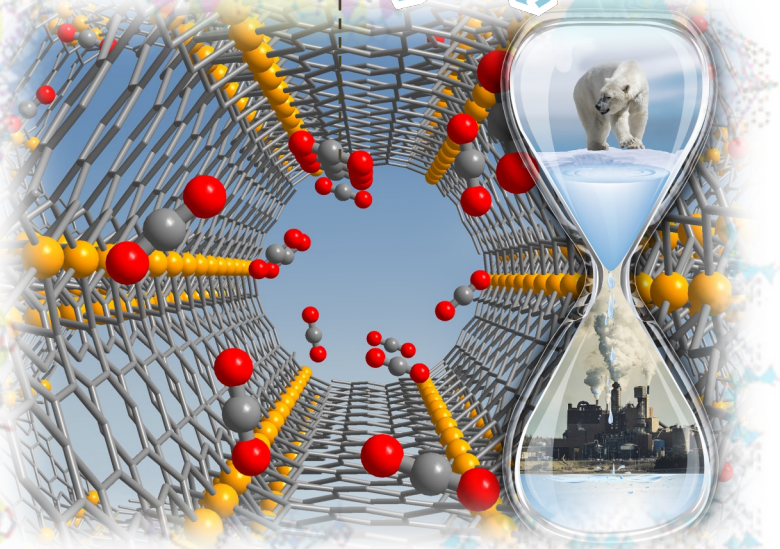
Understanding structure-derived function



Li, Eddaoudi, O'Keeffe, Yaghi, *Nature*, 1999, 402, 276.

In order to understand fully how structure dictates function we couple standard adsorption measurements with in-situ structural characterization





Chem. Sci. **2014**, 5, 4569. Featured cover article

Climate Action: Elimination of carbon dioxide

SDG 13

Global CO_2 Emissions - 30.3 Gtons/year

Automobiles

22%

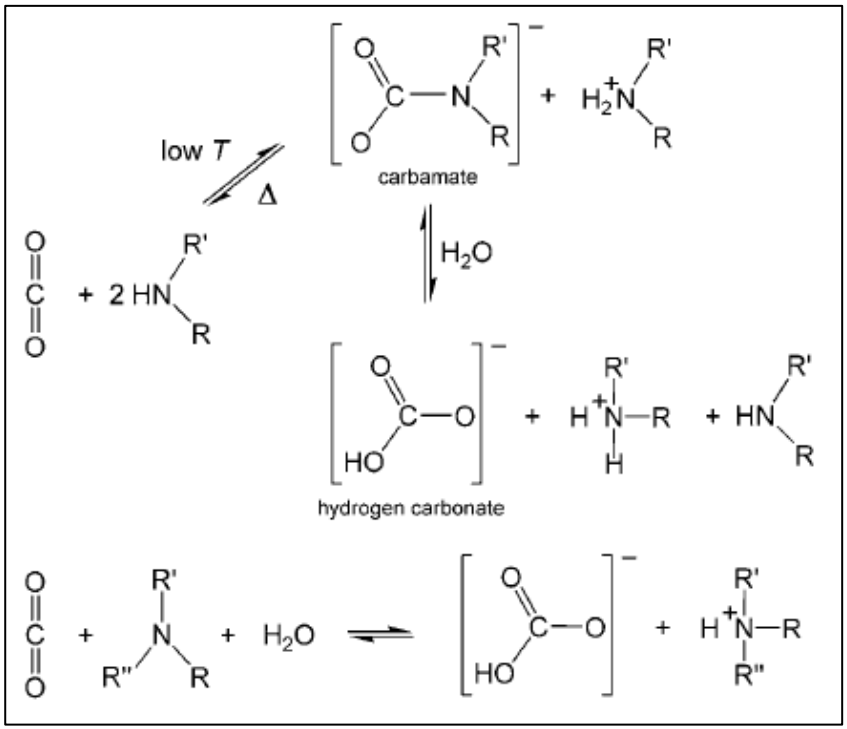
6.4 Gtons/year

electricity and heat

41%

12.4 Gtons/year

Most mature CO_2 capture technology



30% Parasitic Energy Cost

McKinsey & Co Reducing US GHG Emissions 2007; Sumida, Rogow, Mason, McDonald, Bloch, Herm, Bae, Long , *Chem. Rev*. **2012**, *112*, 724.; D'Alessandro, Smit, Long, *Angew. Chem. Int. Ed*., **2010**, *49*, 6058; IEA Statistics CO2 Emissions From Fuel Combustion, 2012.

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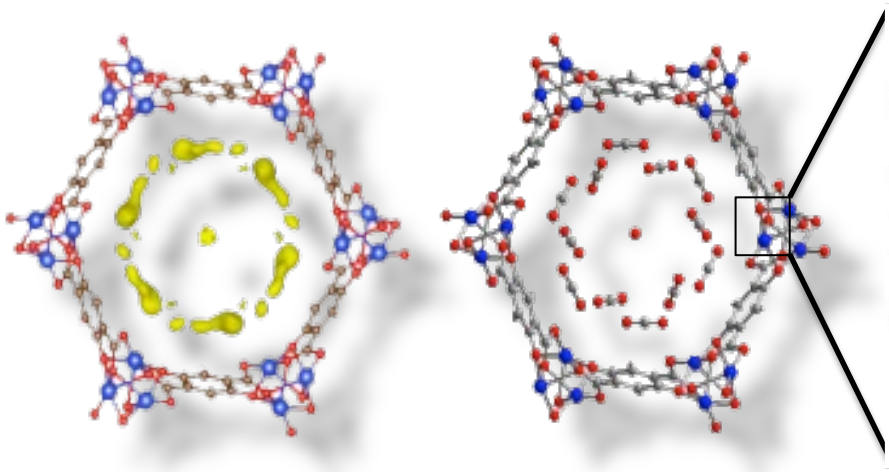
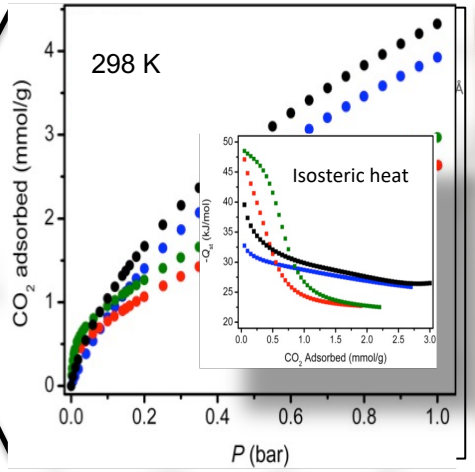
Climate Action: Capture carbon dioxide in MOFs

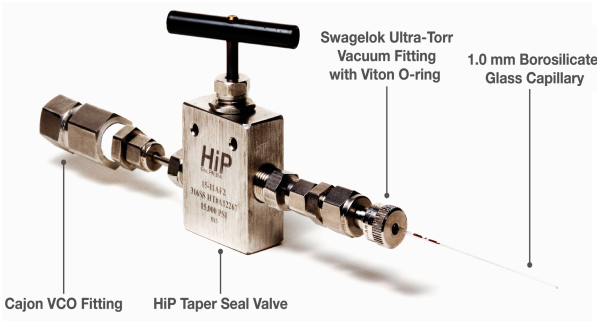
Mehrdad Asgari

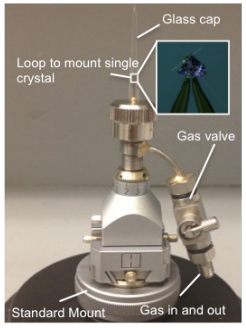


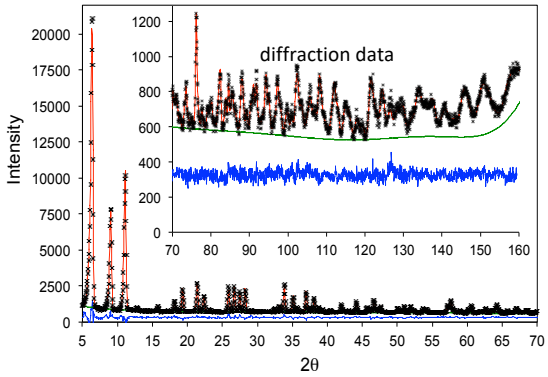


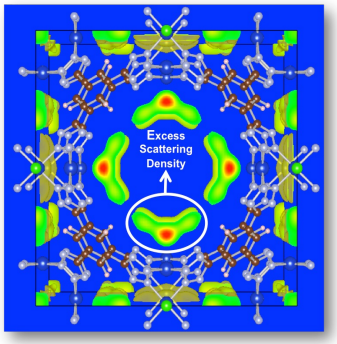
In-situ characterization

Breakthrough apparatus









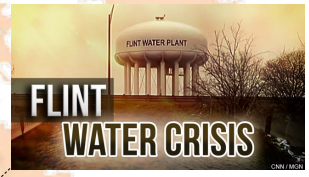
EPFL

Chem. Sci., **2017**, 8, 43
Chem. Sci. **2014**, 5, 4569. Featured cover article.
Chem.Sci., **2018**, 9, 4579. Featured cover article.

Water contamination: One of the world's leading causes of death

SDG 6

11% of the world population has no access to clean drinking water



http://www.scmp.com/news/china/article/1839337/beijing-drinking-water-reservoir-found-contain-levels-lead-20-times-who

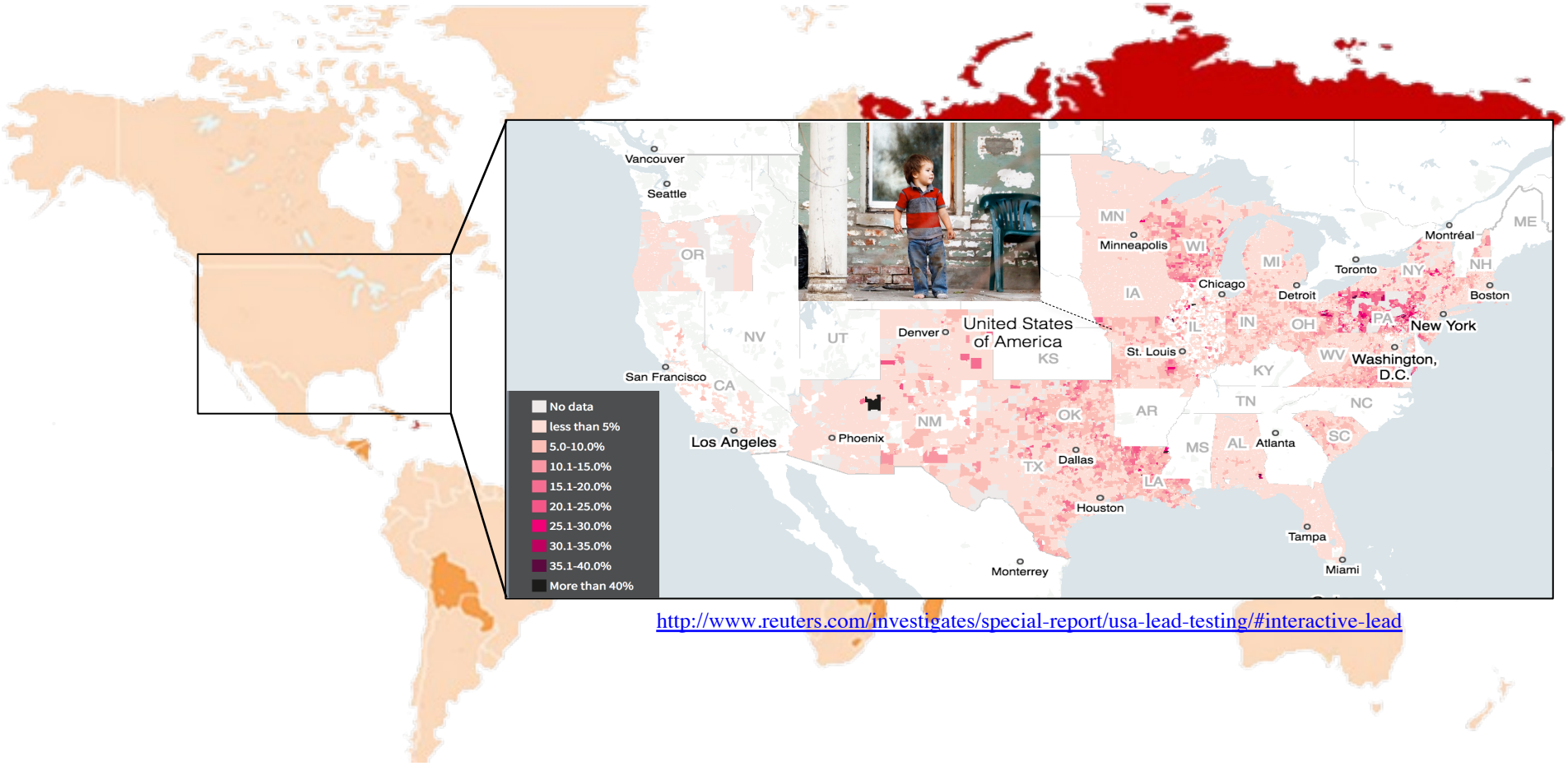
http://www.cnn.com/2016/01/11/health/toxic-tap-water-flint-michigan/index.html

EPFL

Water contamination: One of the world's leading causes of death

SDG 6

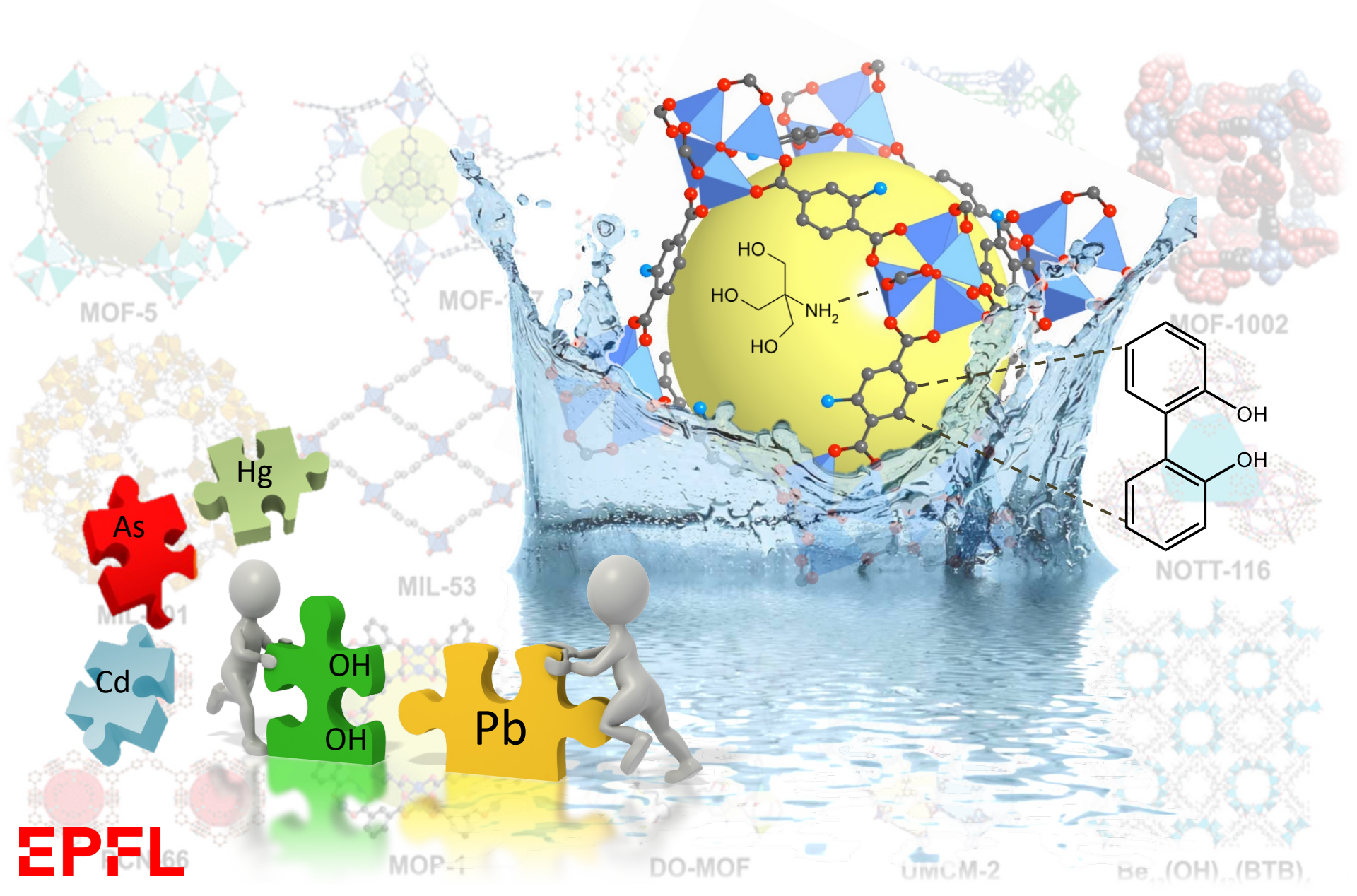
December 2016: Reuters shows 3000 areas with Pb levels twice that of Flint.



http://www.reuters.com/investigates/special-report/usa-lead-testing/#interactive-lead

EPFL

Tuning MOFs for water purifcation



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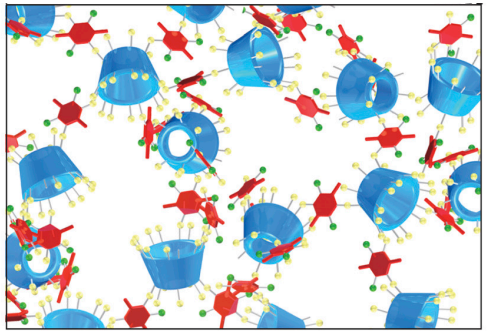
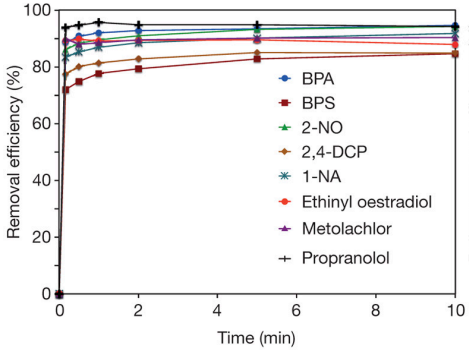
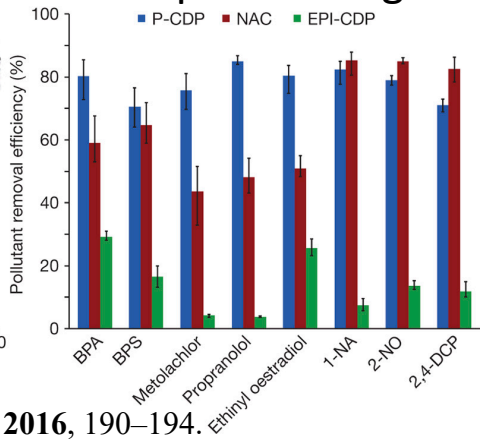
Functionalizing MOFs for enhanced performance

Porous polymers compete with commercial adsorbents for adsorption of organics



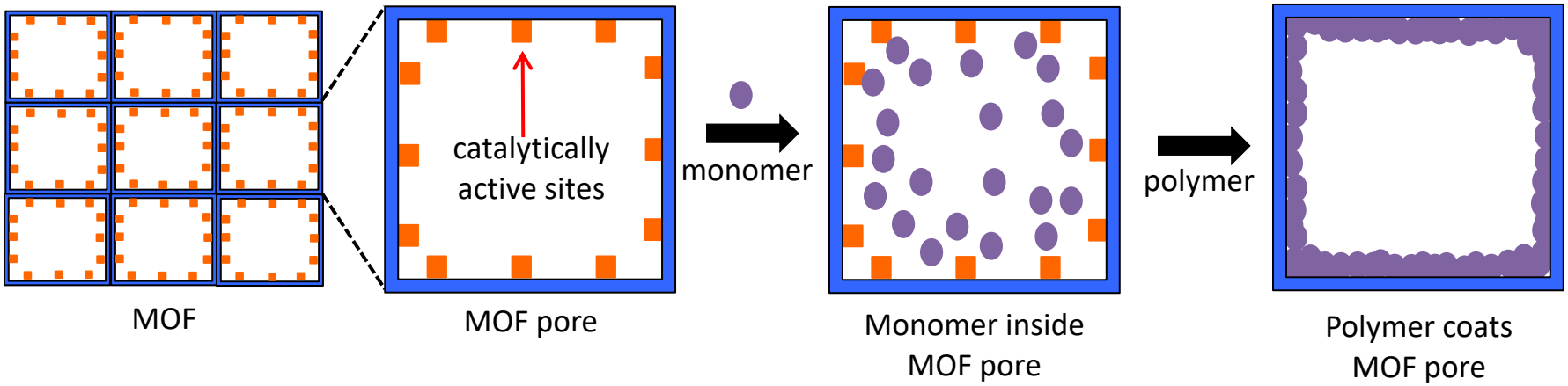
260 m^2/g





Alsbaiee, Smith, Xiao, Ling, Helbling, Dichtel, *Nature*, 529, **2016**, 190–194.

Introducing functional porosity into intrinsically nonporous materials



- Open Metal Sites that activates monomer
- Polymer Building Block

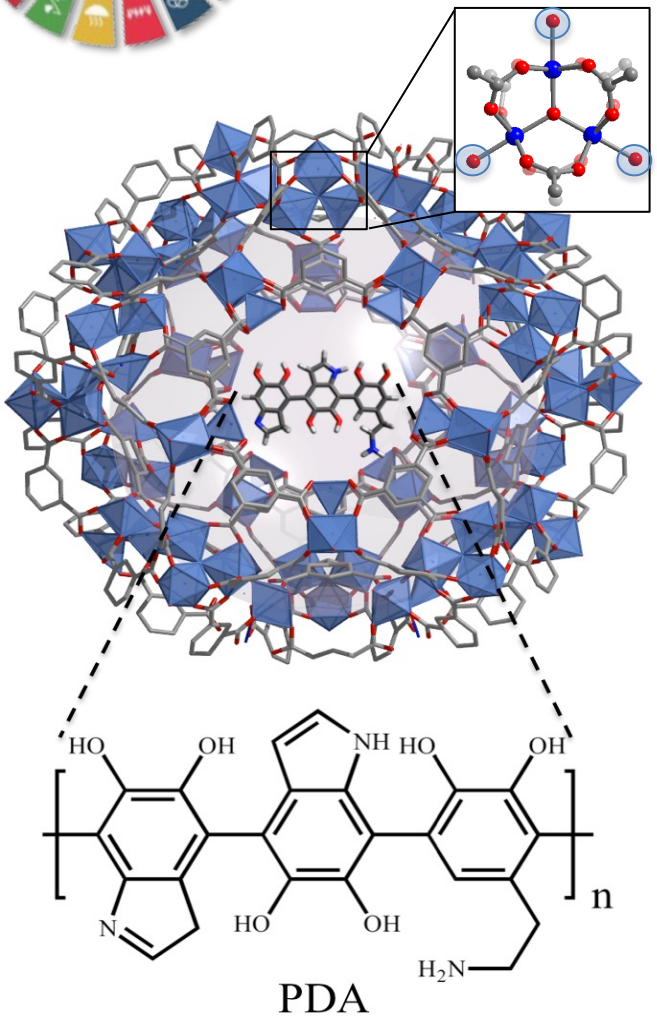
EPFL

ACS Central Science, **2018**, 4, 3, 349.
Featured cover article.

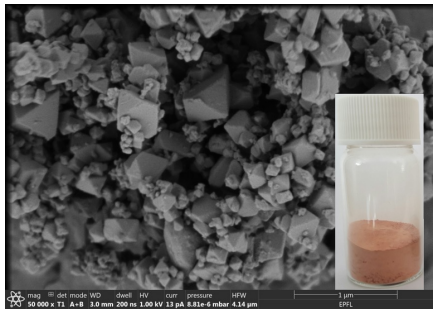
Clean water: Extracting heavy elements from water

SDG 6

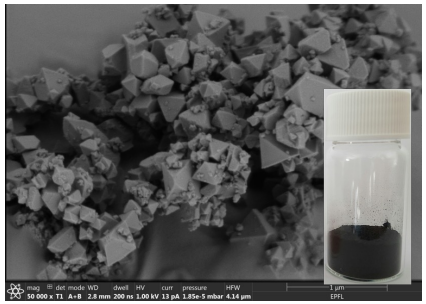
Introducing functional porosity into intrinsically nonporous materials

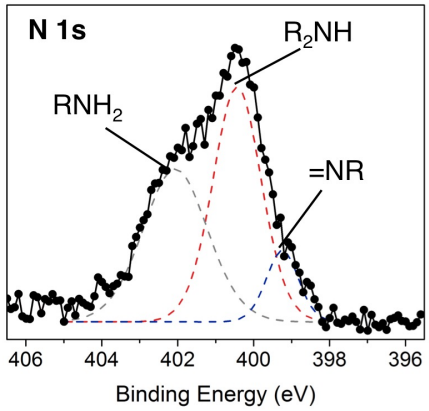


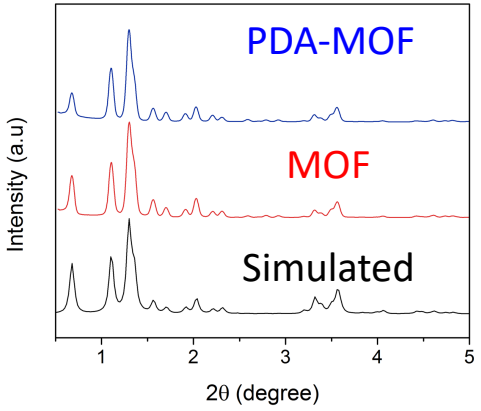
MOF

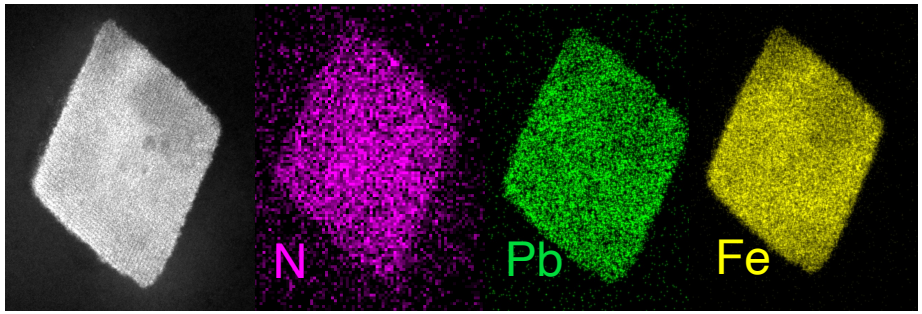


PDA-MOF









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Featured cover article.

Clean water: Extracting heavy elements from water

SDG 6

Introducing functional porosity into intrinsically nonporous materials

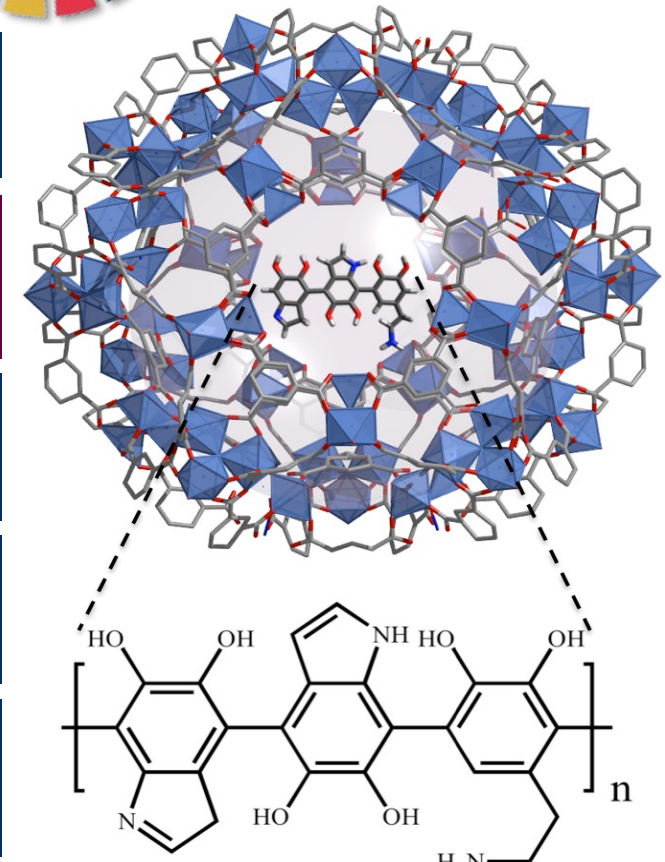
82	207.2		
1750		1.6	
327.6			
Pb			
$[Xe]4f^{14}5d^{10}6s^26p^2$			
11.4		2,4	

80	200.59		
357		1.5	
-38.72			
Hg			
$[Xe]4f^{14}5d^{10}6s^2$			
13.5		1,2	

24	51.996		
2672		1.6	
1857			
Cr			
$[Ar]3d^54s$			
7.19		2,3,6	

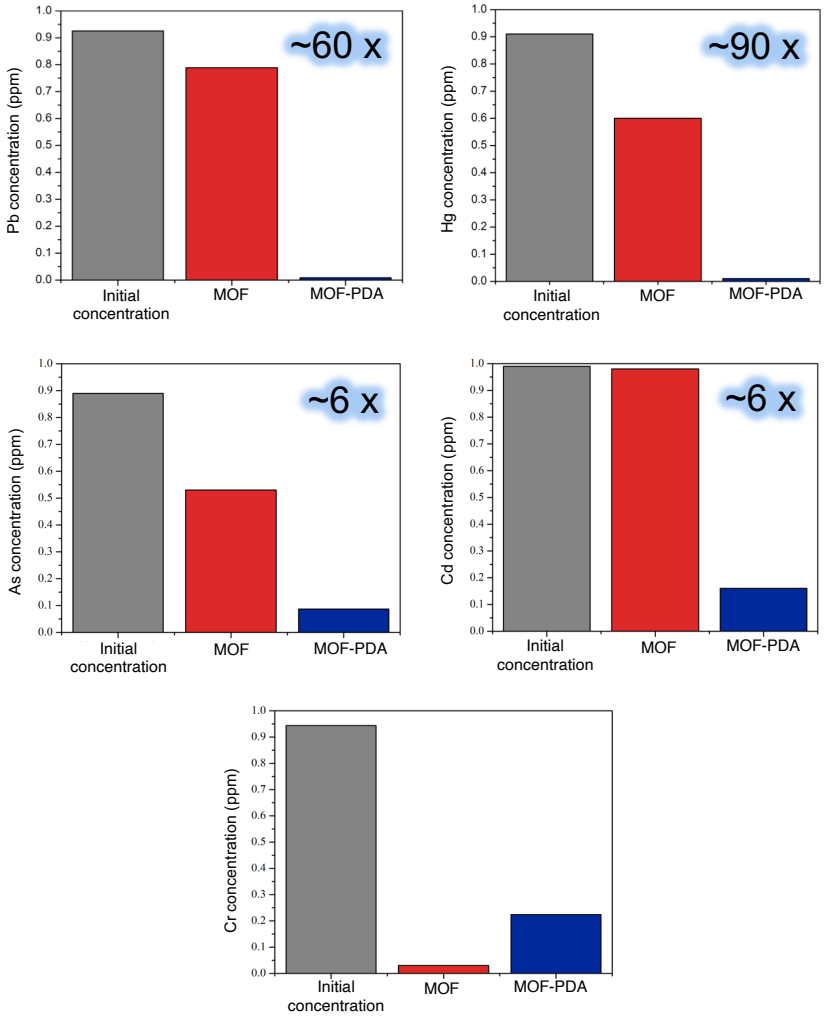
48	112.41		
767		1.5	
321.18			
Cd			
$[Kr]4d^{10}5s^2$			
8.65		2	

33	74.922		
603 (subl.)		2.2	
808 (28 atm)			
As			
$[Ar]3d^{10}4s^24p^3$			
5.73		±3,5	



PDA

Removal efficiency is improved by PDA



ACS Central Science, **2018**, 4, 3, 349.
Featured cover article.

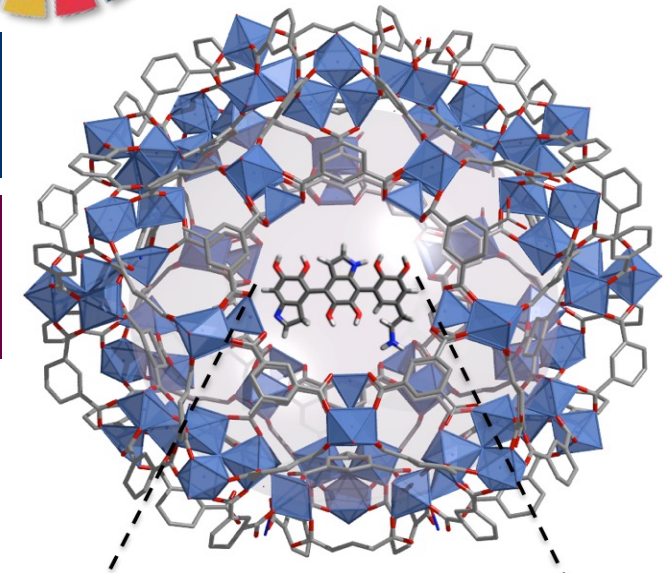
Clean water: Extracting mercury and lead from water

SDG 6

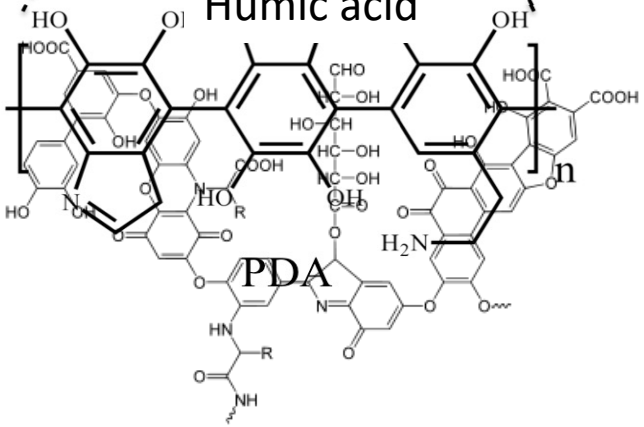
Introducing functional porosity into intrinsically nonporous materials

82 207.2
1750 1.6
327.6
Pb
[Xe]4f¹⁴5d¹⁰6s²6p²
11.4 2.4

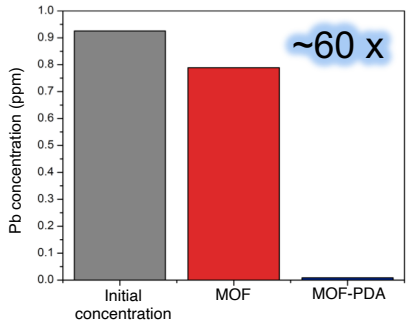
80 200.59
357 1.5
-38.72
Hg
[Xe]4f¹⁴5d¹⁰6s²
13.5 1.2

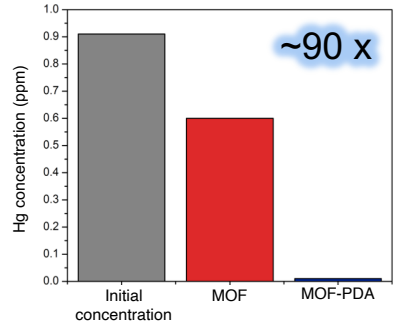


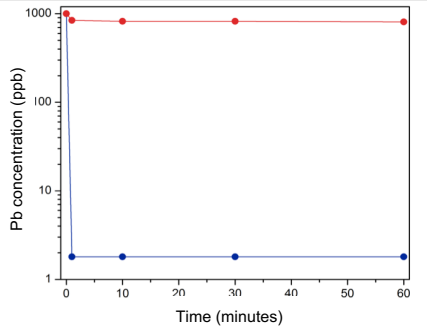
Humic acid

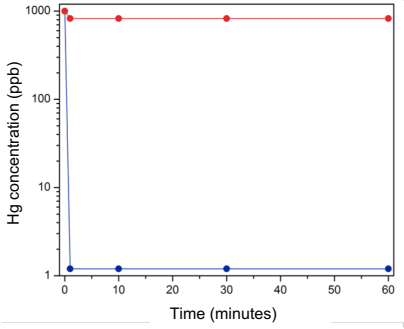


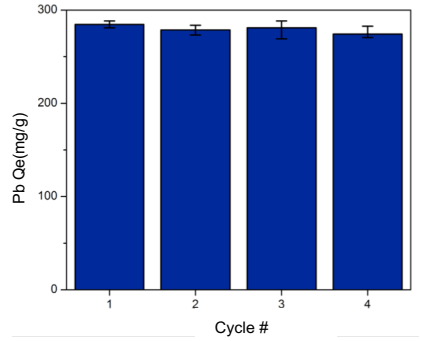
Removal capacity is improved by PDA

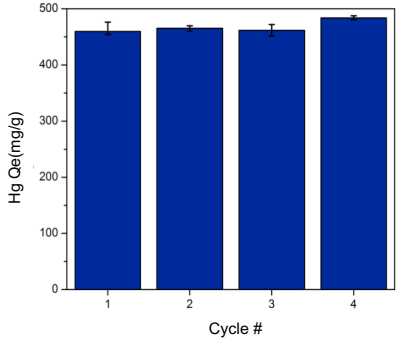












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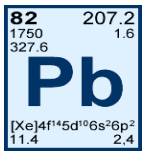
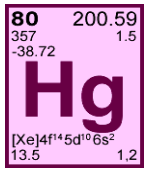
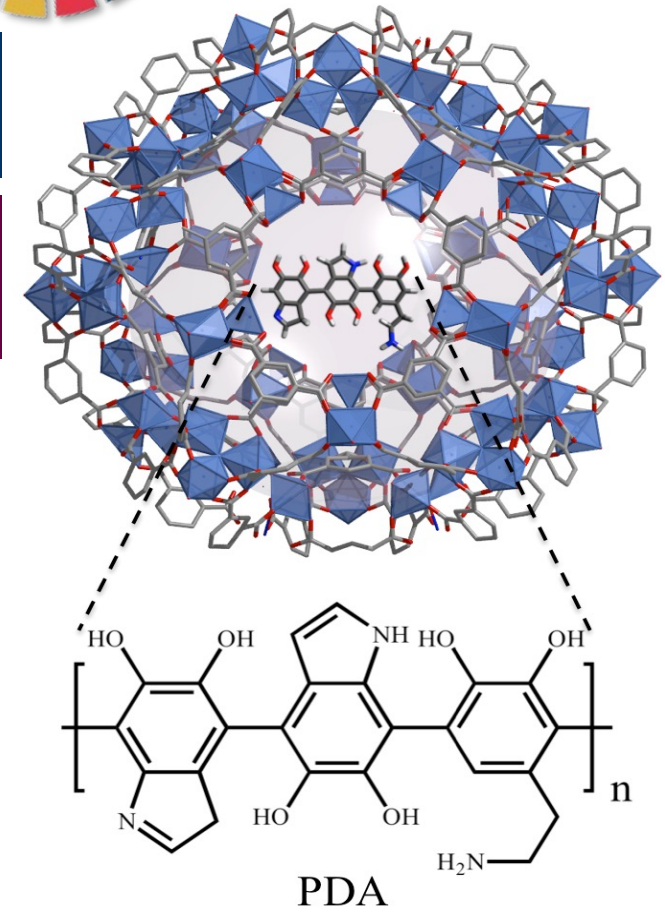
Clean water: Tuning dopamine leading

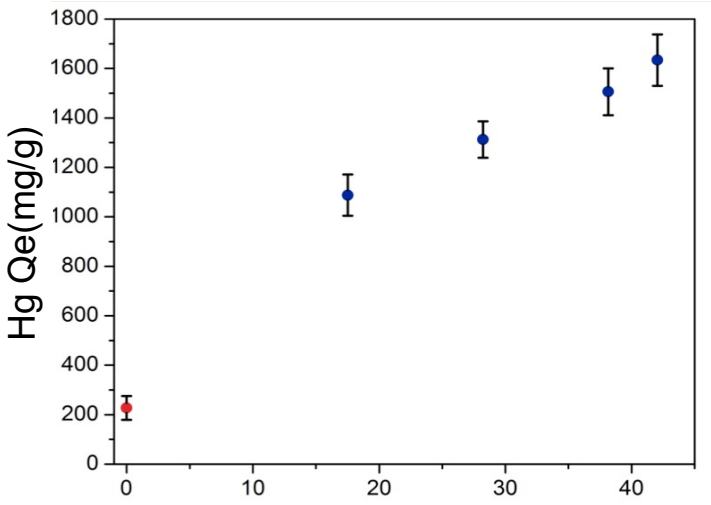
SDG 6

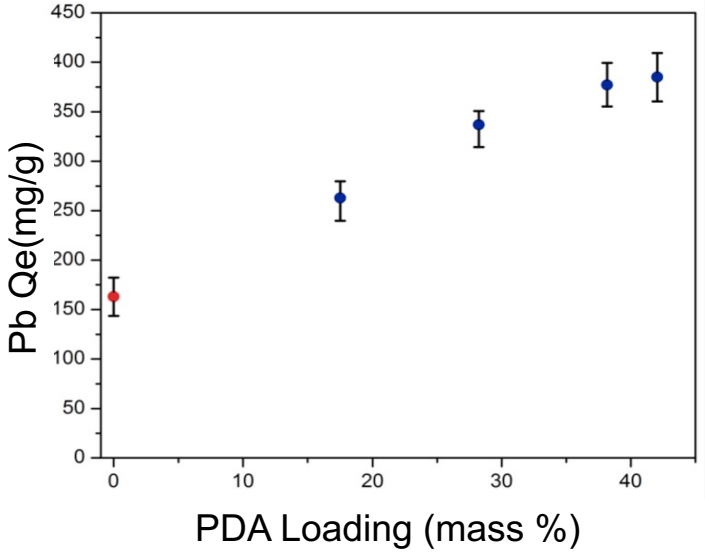
Introducing functional porosity into intrinsically nonporous materials











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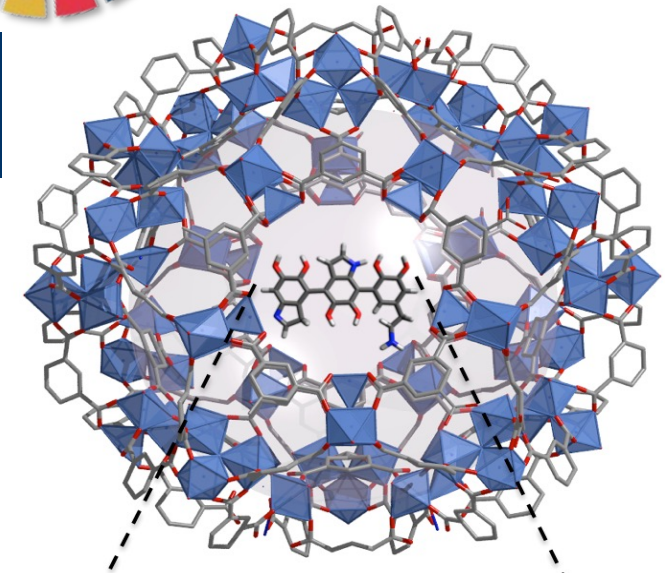
ACS Central Science, **2018**, 4, 3, 349.
Featured cover article.

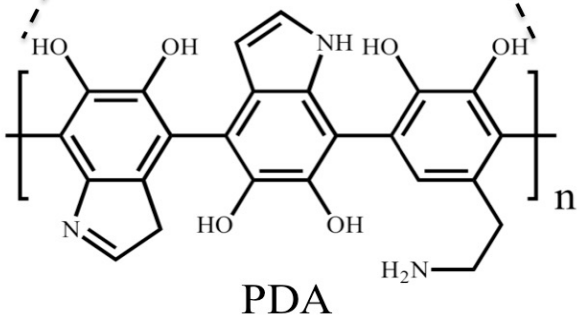
Clean water: Highly selective heavy metal extraction

SDG 6

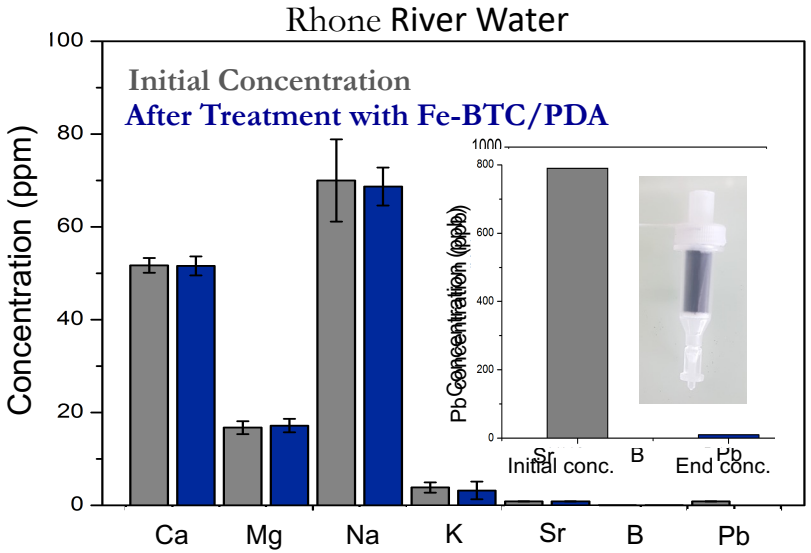
Introducing functional porosity into intrinsically nonporous materials

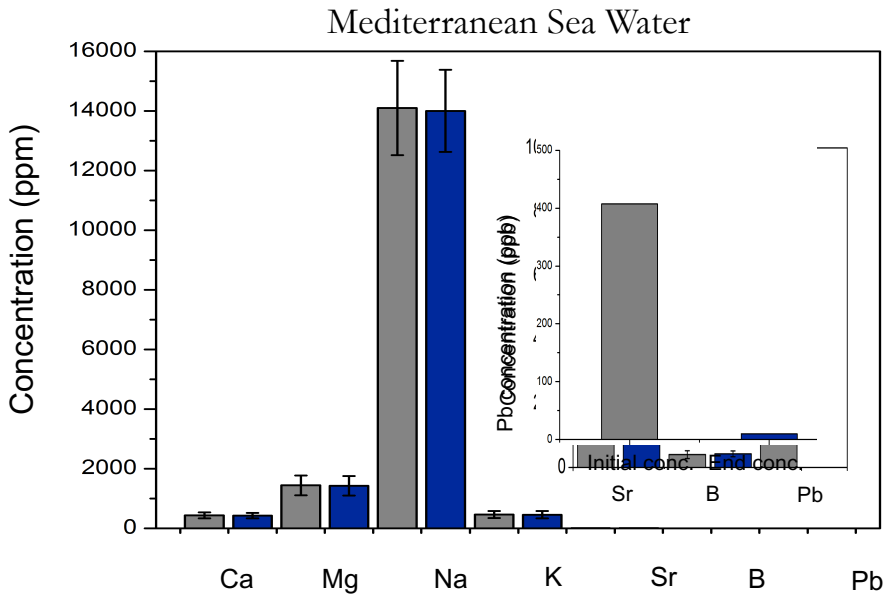
82 207.2
1750 1.6
327.6
Pb
[Xe]4f¹⁴5d¹⁰6s²6p²
11.4 2.4





PDA





EPFL

ACS Central Science, **2018**, 4, 3, 349.
Featured cover article.

Clean water: How do we compare?

- ✓ High capacities: 1690 and 400 mg/g for Hg^{2+} and Pb^{2+}, respectively.
- ✓ High k_ds: $5.5*10^6$ for Hg^{2+} and $1.7*10^6$ for Pb^{2+}

$$k_d = \frac{C_o - C_e}{C_e}\left(\frac{V}{m}\right)$$

C_o = initial concentration, C_e = end concentration, V = volume (mL), m = mass (g)

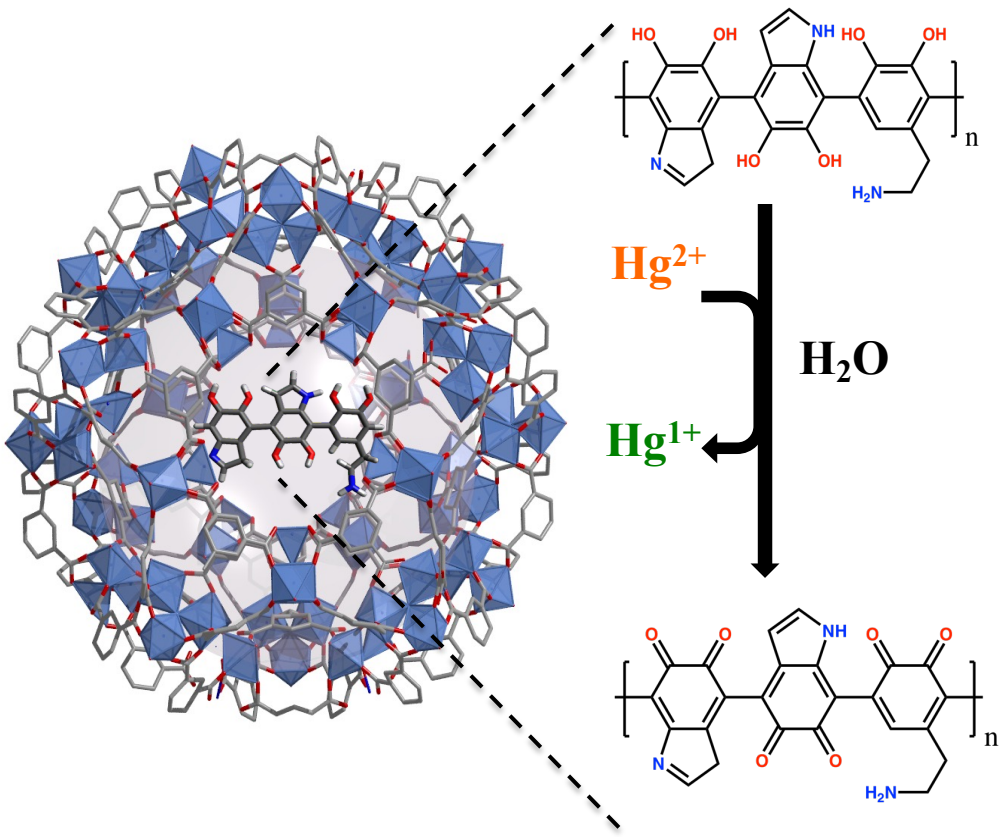
- ✓ Cost: 2.50 USD per kg composite for starting materials
- ✓ Rates: a few seconds
- ✓ Reversibility: 5 cycles
- ✓ Stablility: In water for several months
- ✓ Selectivity: resists clogging of common organic interferents and inorganics

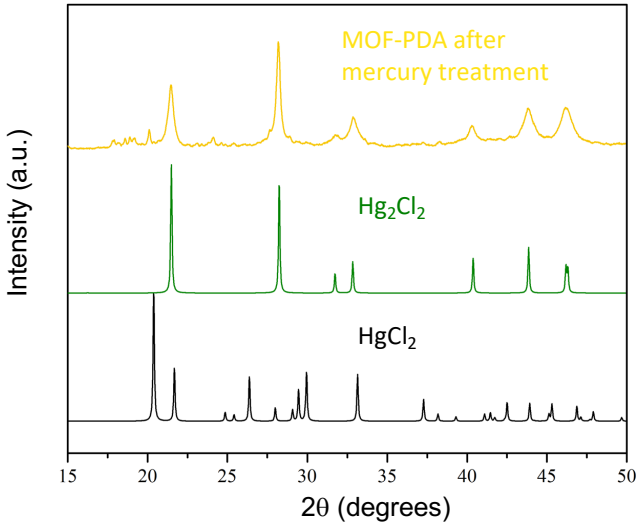
ACS Central Science, **2018**, 4, 3, 349.
Featured cover article.

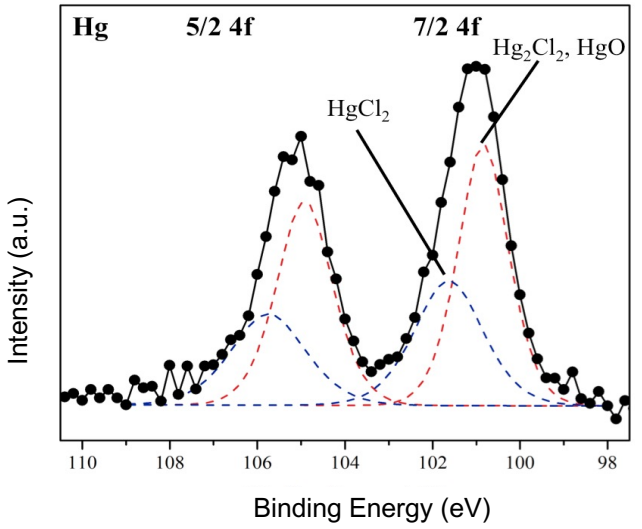
Clean water: Reduction of Hg^{2+}

SDG 6

$2Hg^{2+} \rightarrow Hg_2^{2+}$ ~ 0.92 V







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Clean water: Reduction of Cr^{6+}

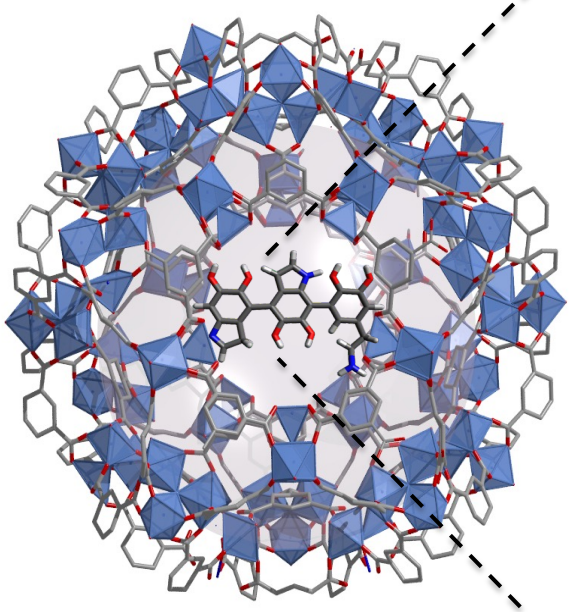
SDG 6

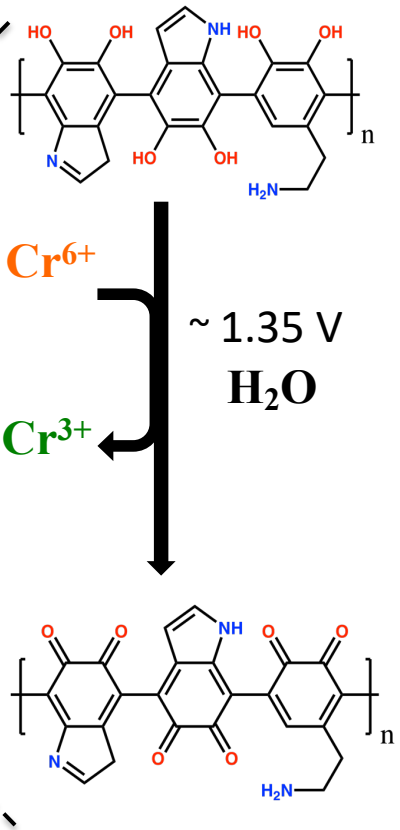
$Au^{3+} \rightarrow Au(s)$ ~ 1.50 V

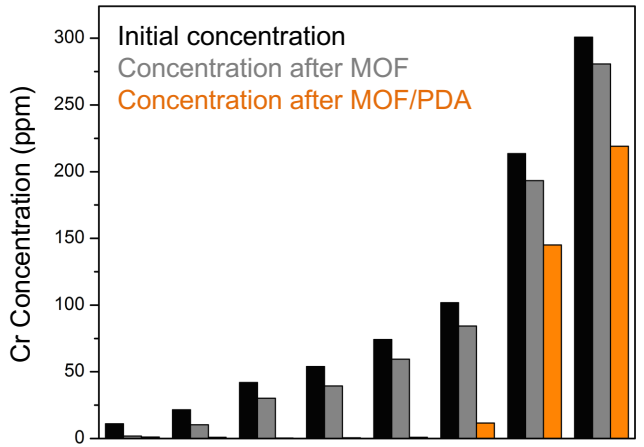
$Pt^{2+} \rightarrow Pt(s)$ ~ 1.18 V

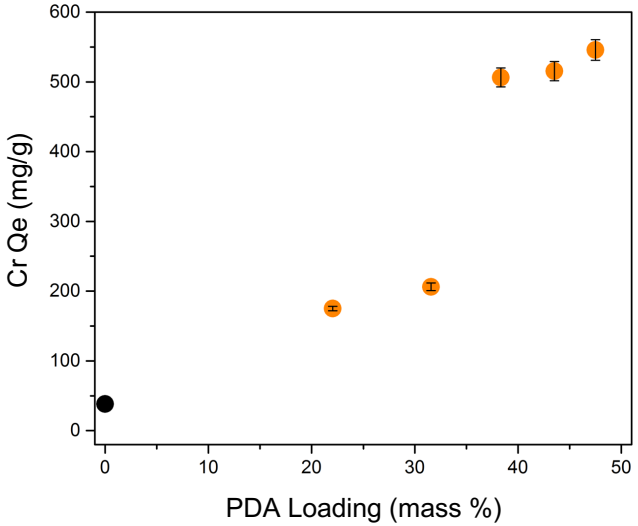
$Pd^{2+} \rightarrow Pd(s)$ ~ 0.95 V

$Ag^{+} \rightarrow Ag(s)$ ~ 0.80 V







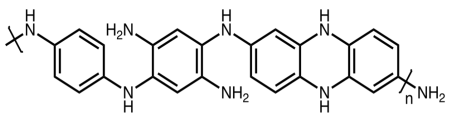


EPFL unpublished, **2019**

Other MOF/polymer composites

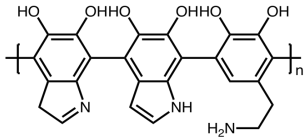
PpPDA

1800 m^2 / g



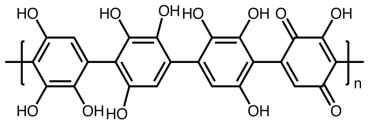
PDA

1100 m^2 / g



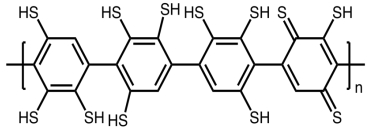
PHQ

900 m^2 / g



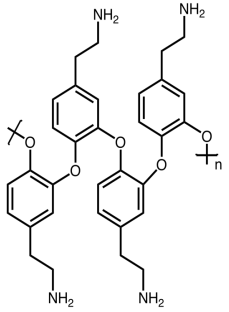
PBDT

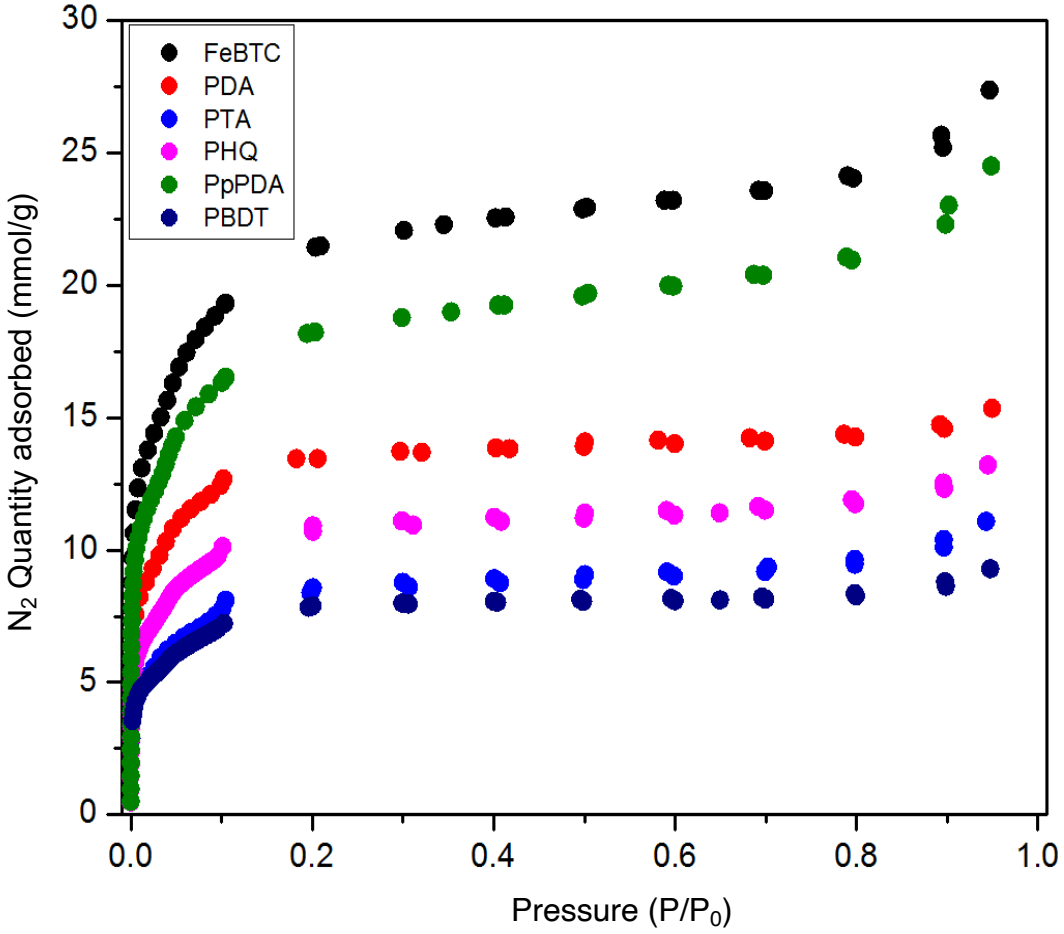
650 m^2 / g



PTA

700 m^2 / g





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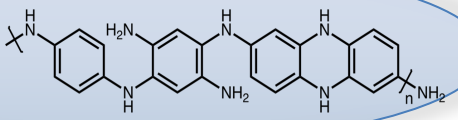
ACS Central Science, **2018**, 4, 3, 349.
Featured cover article.

Responsible consumption: Gold extraction from river water

SDG 7

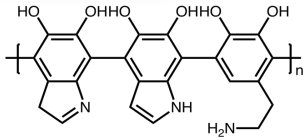
PpPDA

1800 m² / g



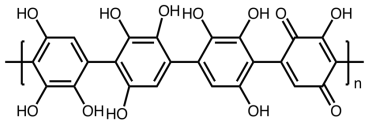
PDA

1100 m² / g



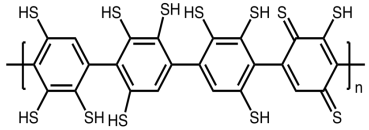
PHQ

900 m² / g



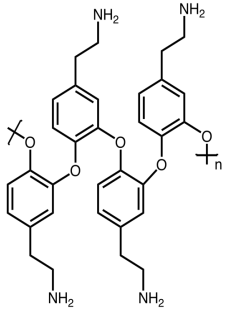
PBDT

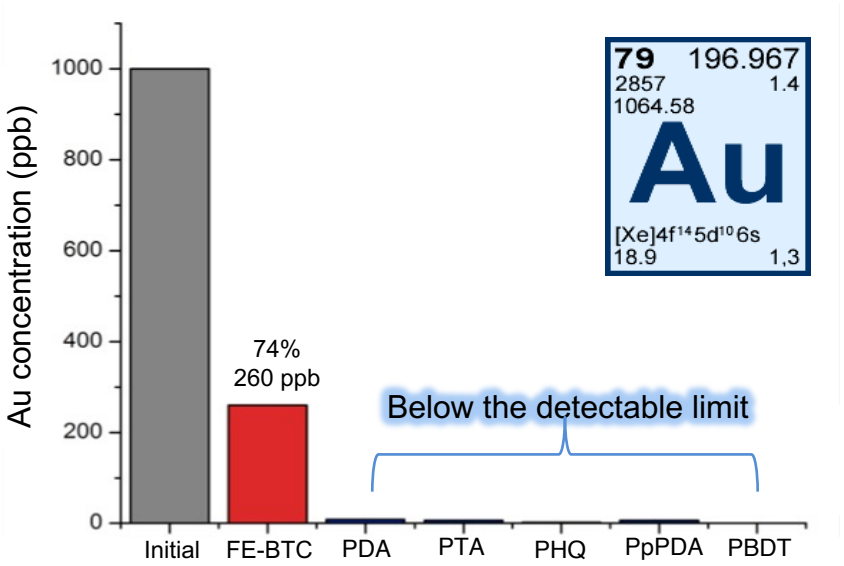
650 m² / g

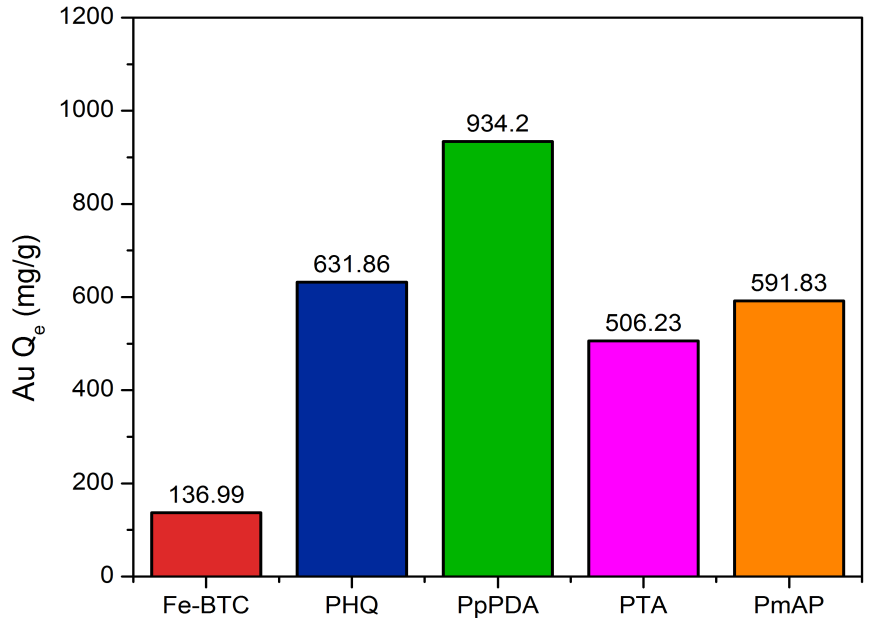


PTA

700 m² / g







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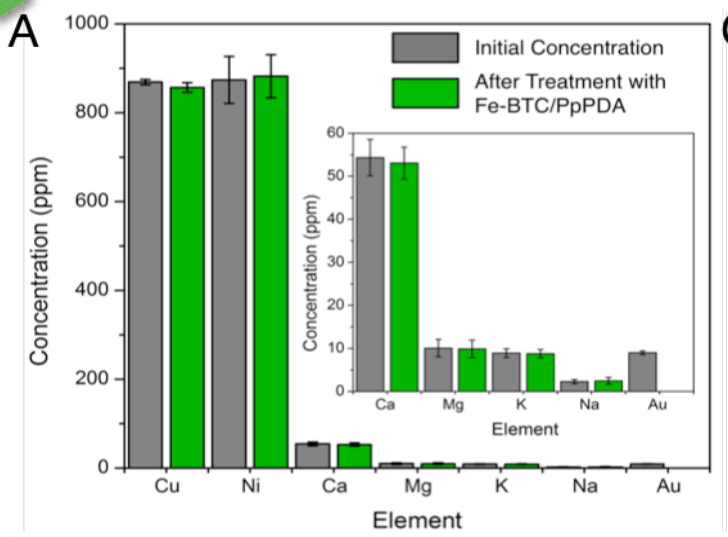
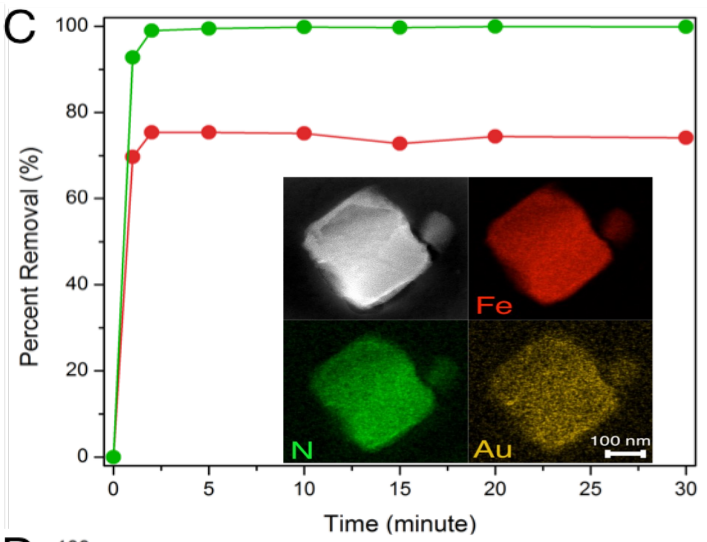
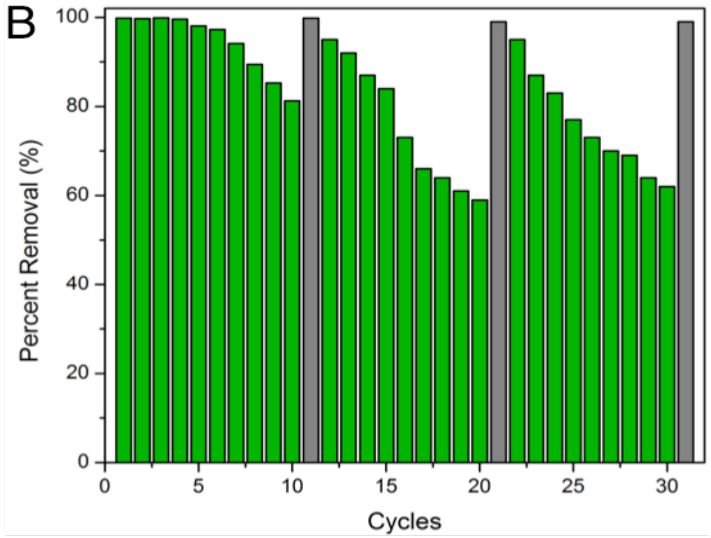
J. Am. Chem. Soc, **2018**, 140, 16697.
C&E News, 2018, 96, 47. *ACS Editors Choice*

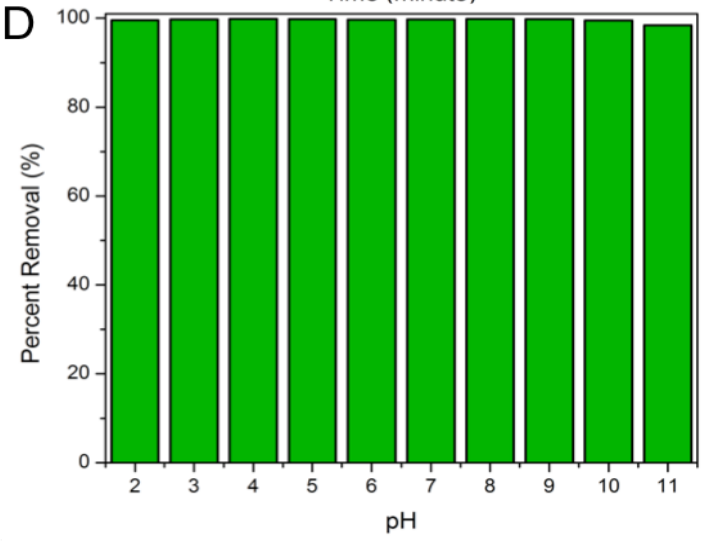
Responsible consumption: Gold extraction from river water

SDG 7









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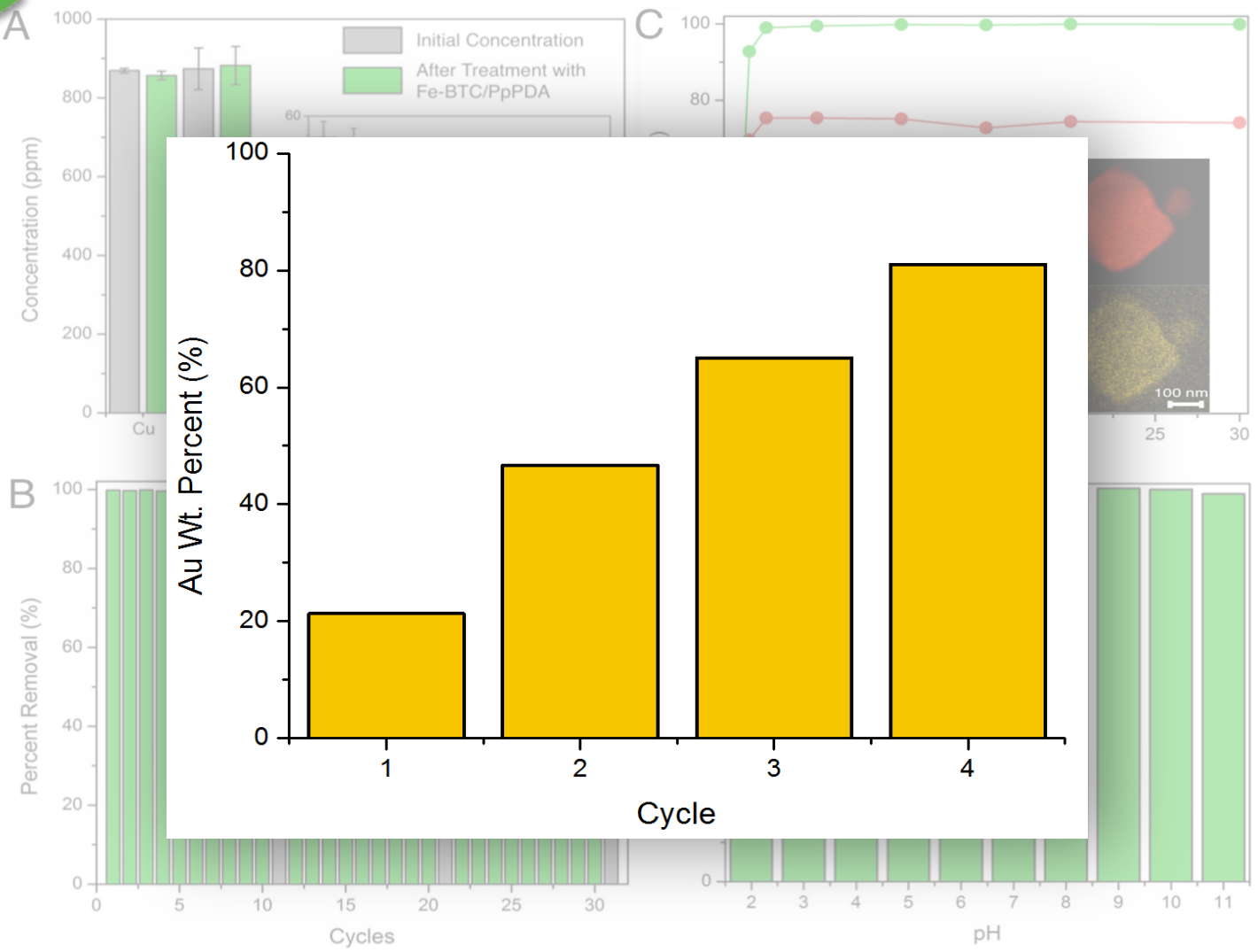

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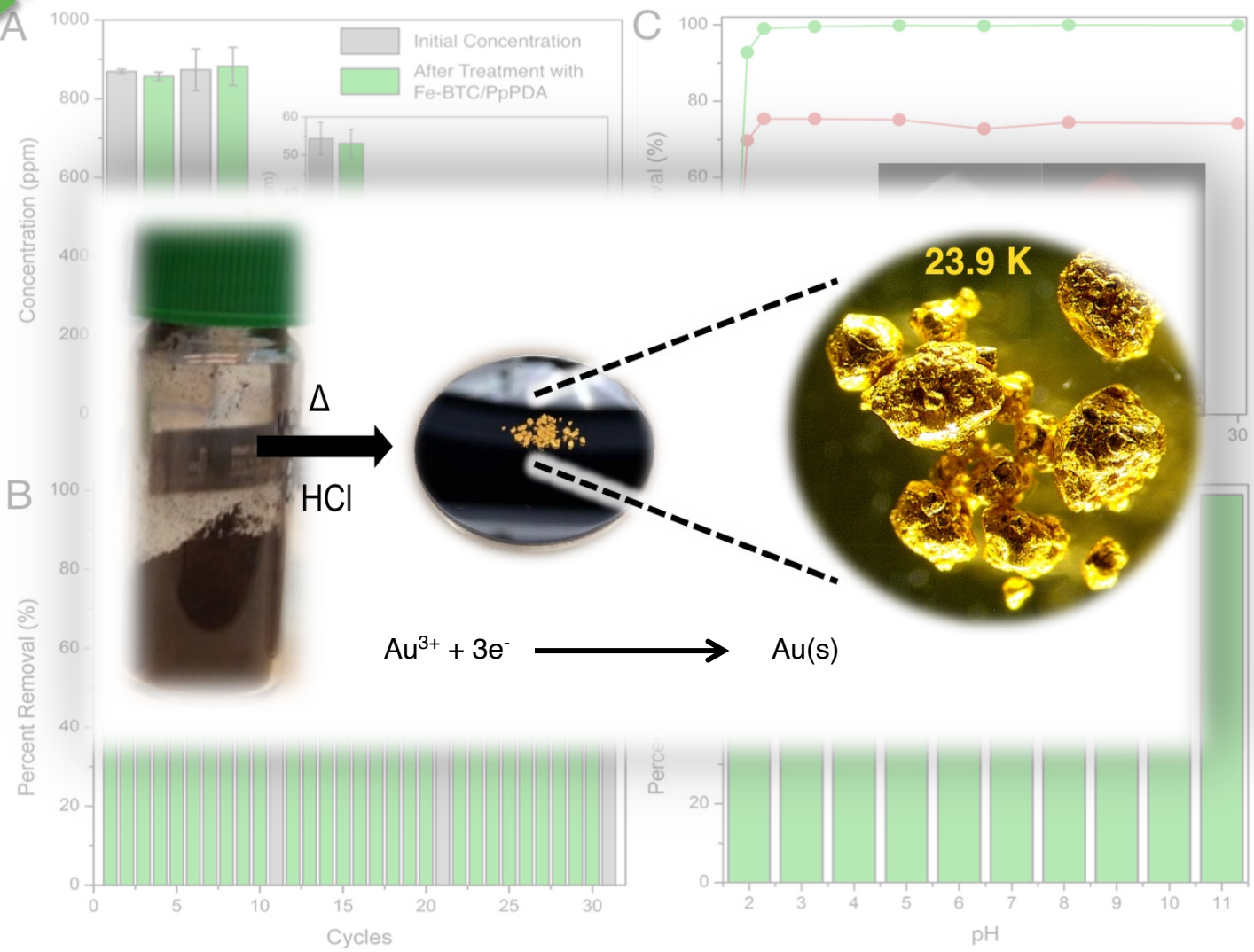
C&E News, 2018, 96, 47. *ACS Editors Choice*

Responsible consumption: Gold extraction from river water

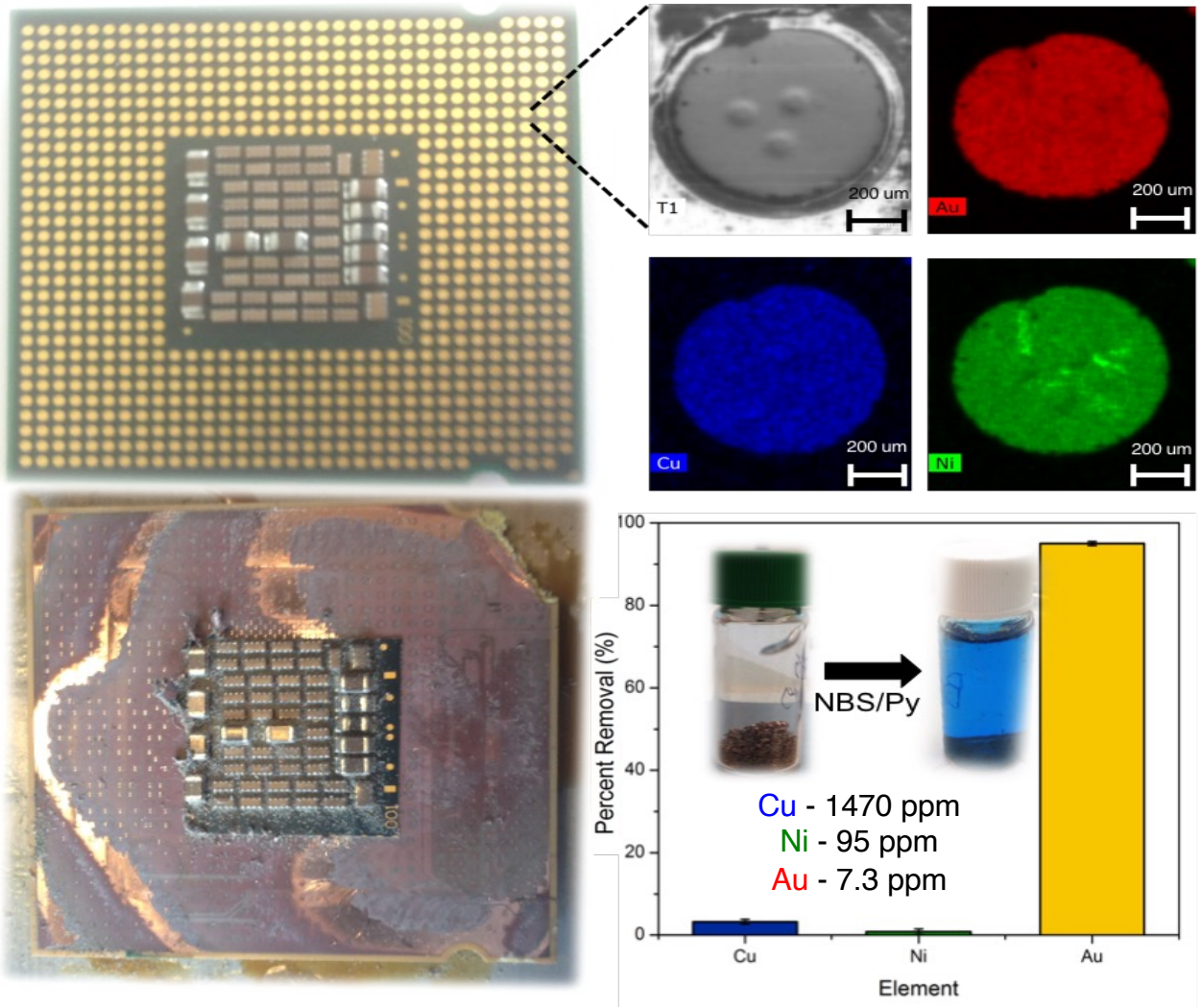
SDG 7



J. Am. Chem. Soc, **2018**, 140, 16697.
C&E News, 2018, 96, 47. *ACS Editors Choice*

Responsible consumption: Gold recovery from electronic waste

SDG 7



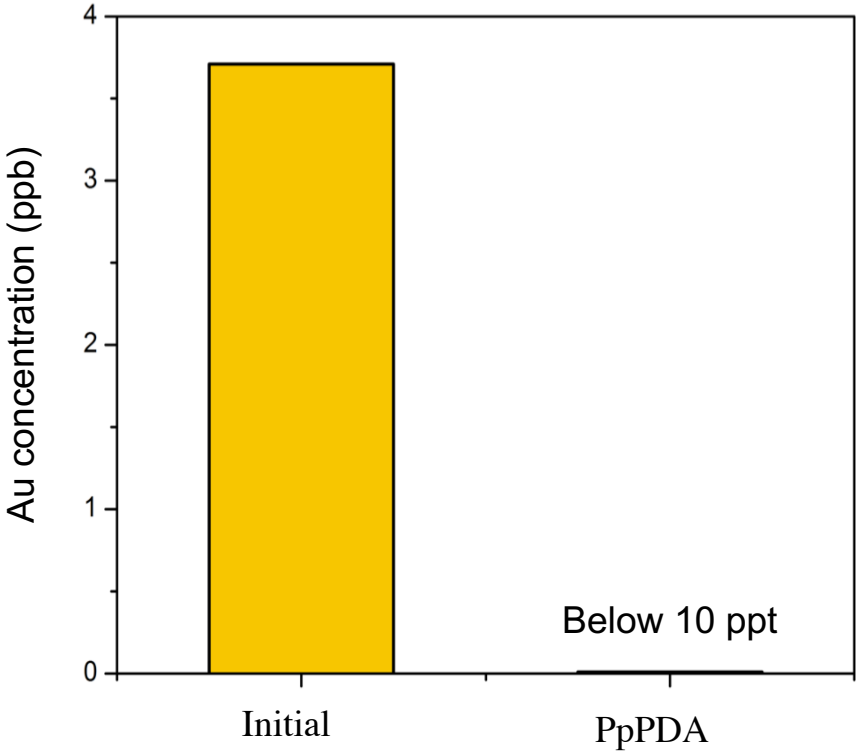
J. Am. Chem. Soc, **2018**, 140, 16697.
C&E News, 2018, 96, 47. *ACS Editors Choice*

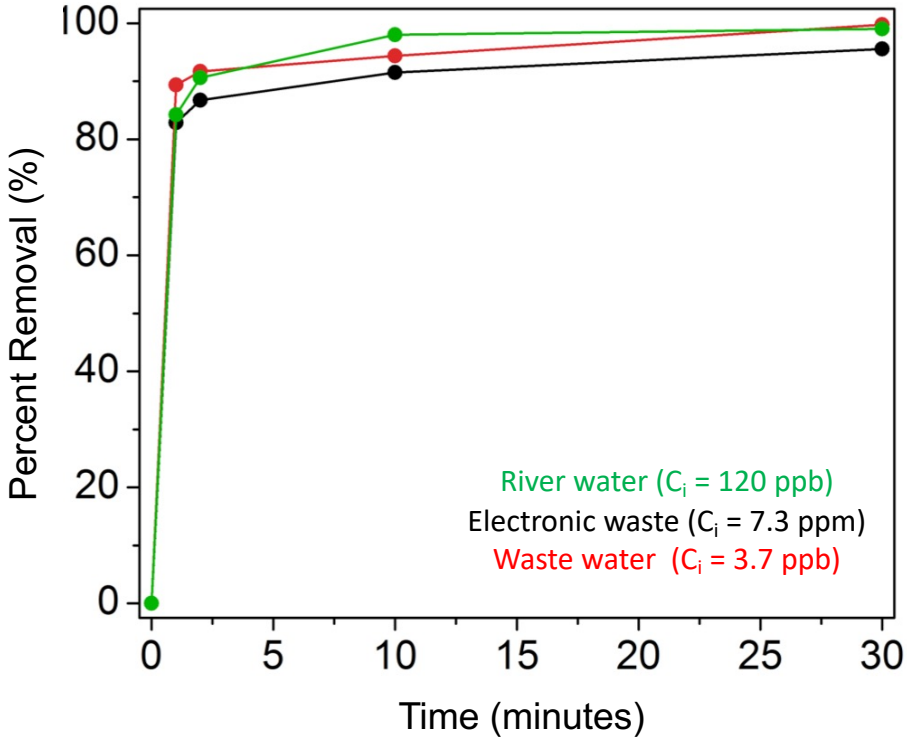
Responsible consumption: Gold recovery from wastewater

SDG 7

Scientists find gold worth $2 million in Swiss sewage

by Alanna Petroff @AlannaPetroff





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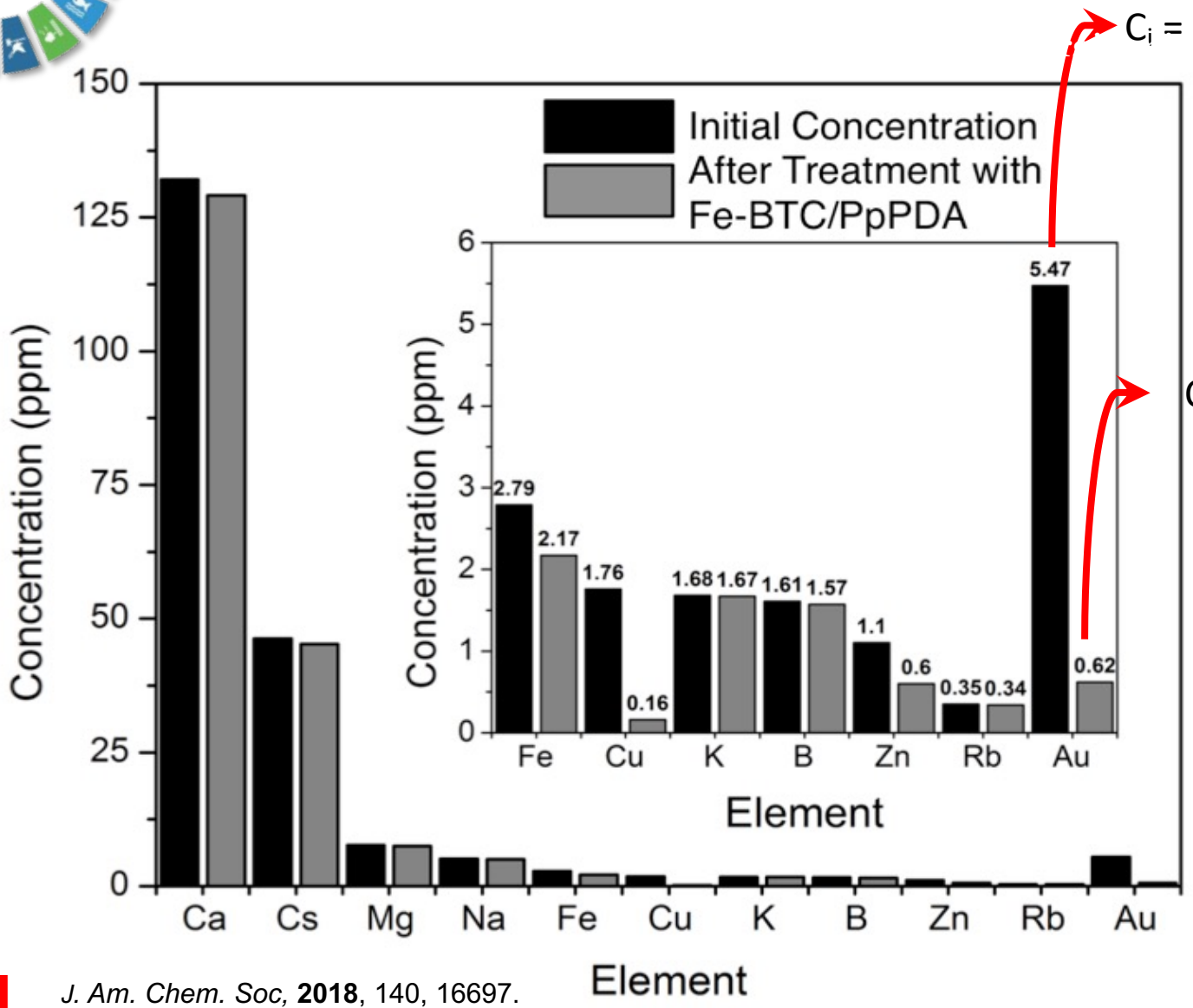
J. Am. Chem. Soc, **2018**, 140, 16697.
C&E News, 2018, 96, 47. *ACS Editors Choice*

Responsible consumption: Gold recovery from sewage sludge ash

SDG 7



C_i = 5.47 ppm

C_f = 0.62 ppm

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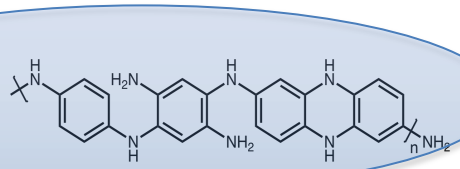
J. Am. Chem. Soc, **2018**, 140, 16697.
C&E News, 2018, 96, 47. *ACS Editors Choice*

Varying Polymer building blocks

SDG 7

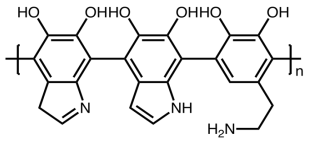
PpPDA

1800 m^2 / g



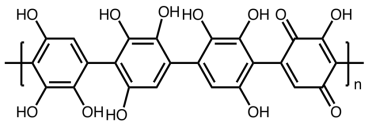
PDA

1100 m^2 / g



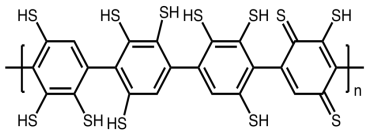
PHQ

900 m^2 / g



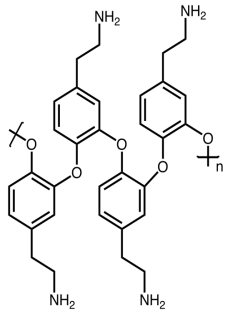
PBDT

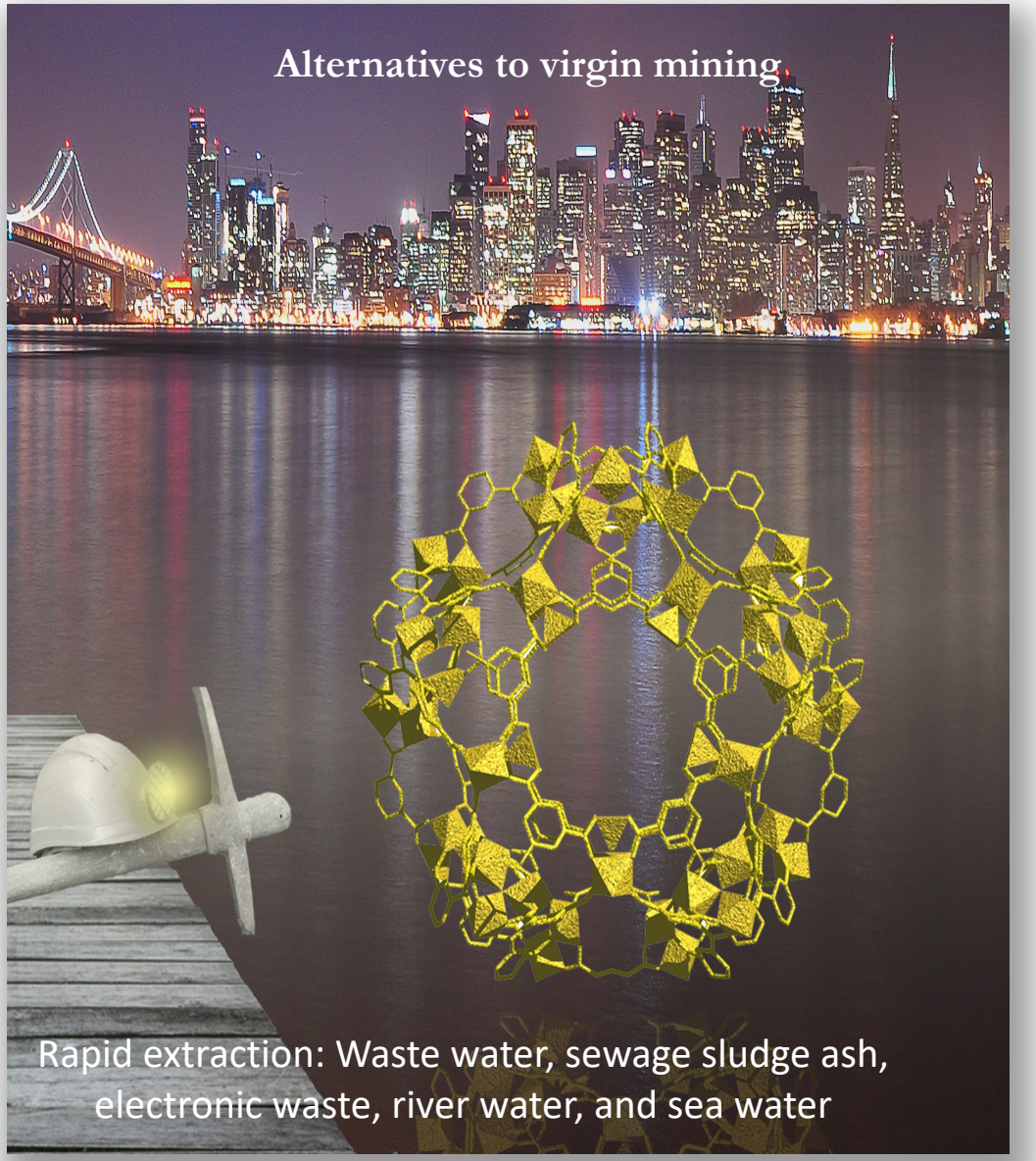
650 m^2 / g



PTA

700 m^2 / g





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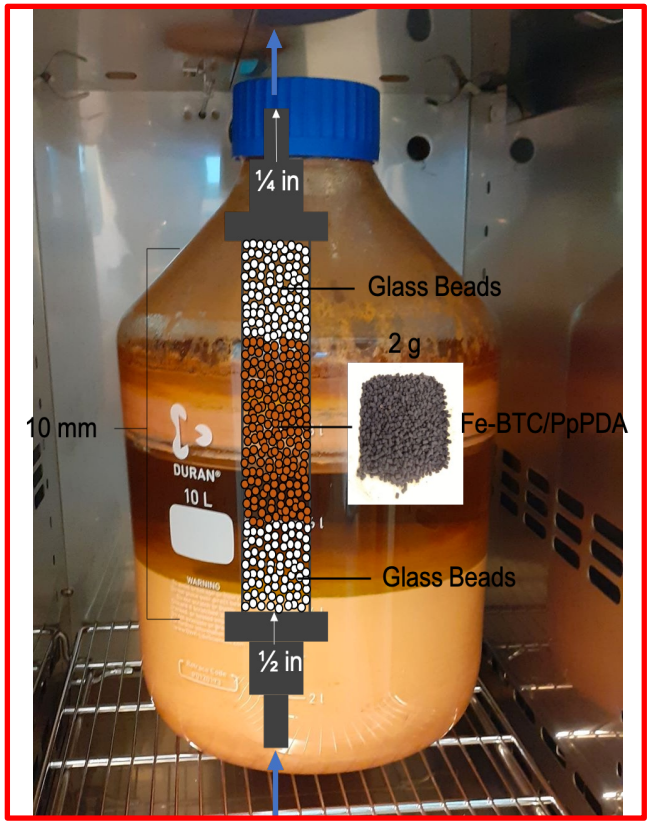
J. Am. Chem. Soc, **2018**, 140, 16697.
C&E News, 2018, 96, 47. *ACS Editors Choice*

Where shall we go from here…

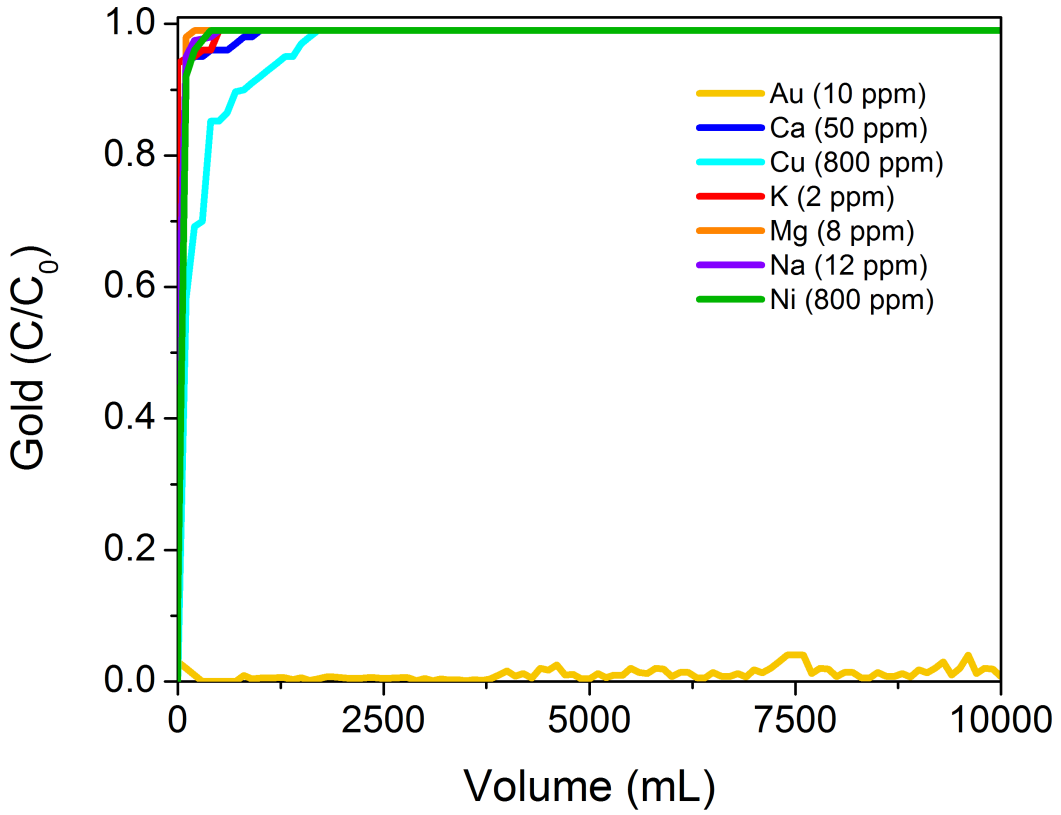
SDG 7

enable

600 gram synthesis in water, reuse solvent



Installation of a flow through apparatus



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Where shall we go from here…

SDG 7

1). Material design

Electronic Waste

Waste Water

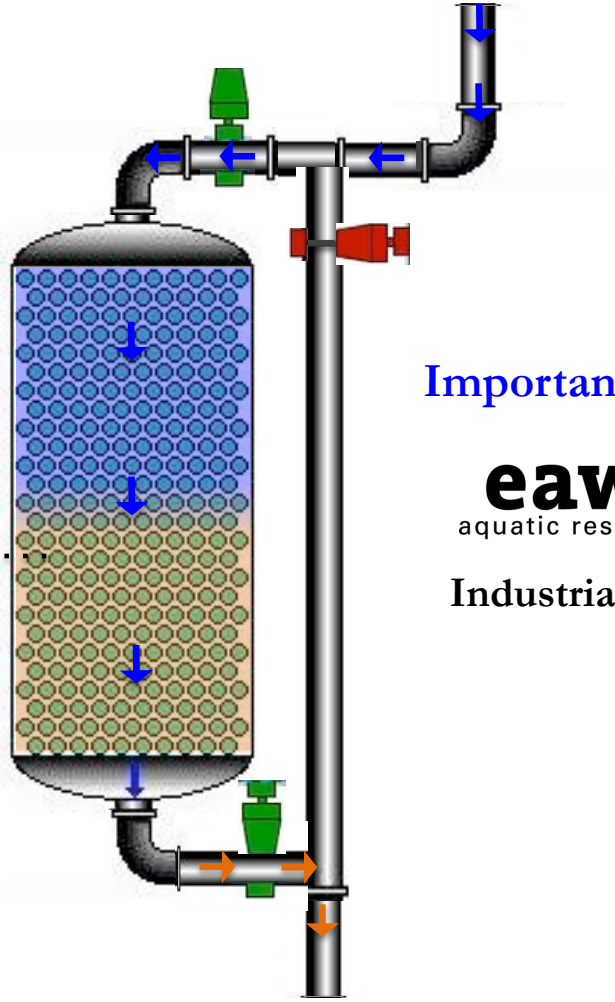
Fresh Surface Water

Sea Water

Sponge

2). Structuring

3). Scaled -up demonstration (kg)
Flow contaminated mixture in



Important Partners

eawag aquatic research

Industrial partners…

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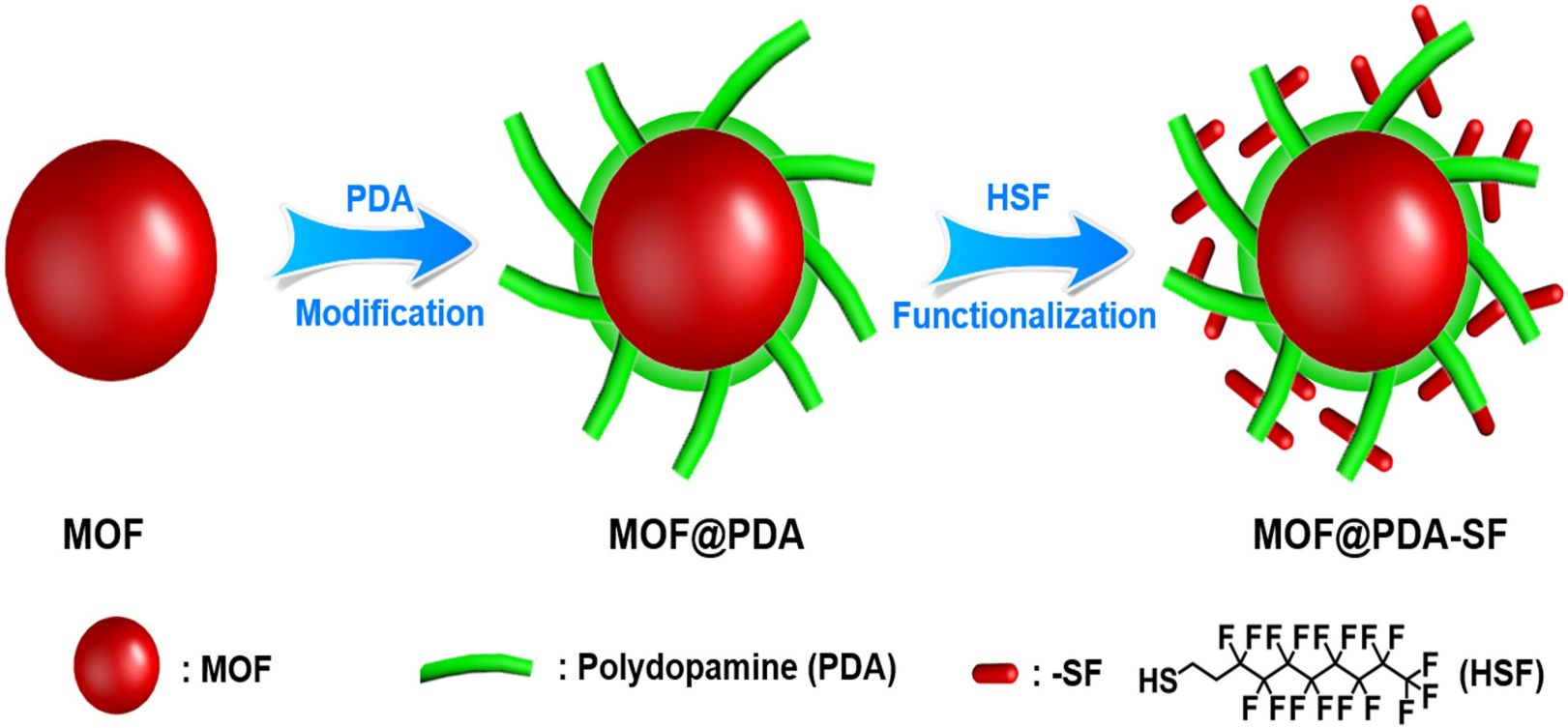
Overcoming limitations at extreme pH

"A new post-synthetic polymerization strategy makes MOFs more stable"



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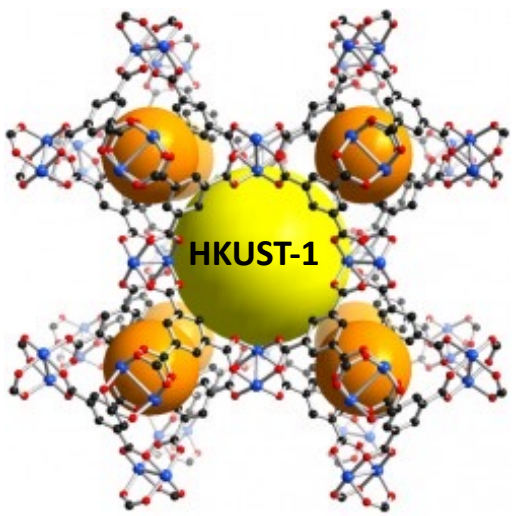
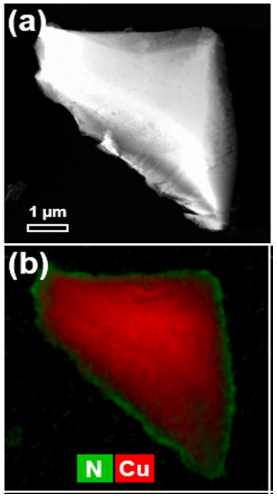
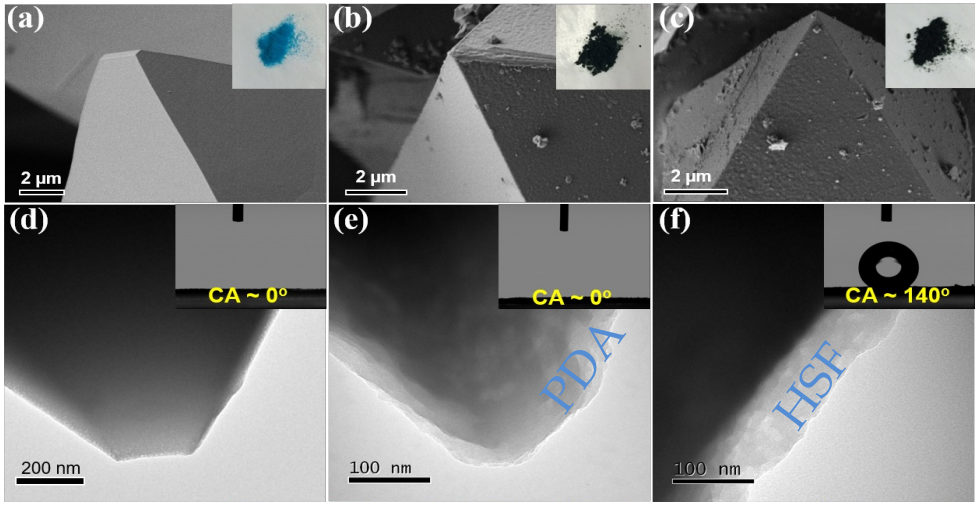
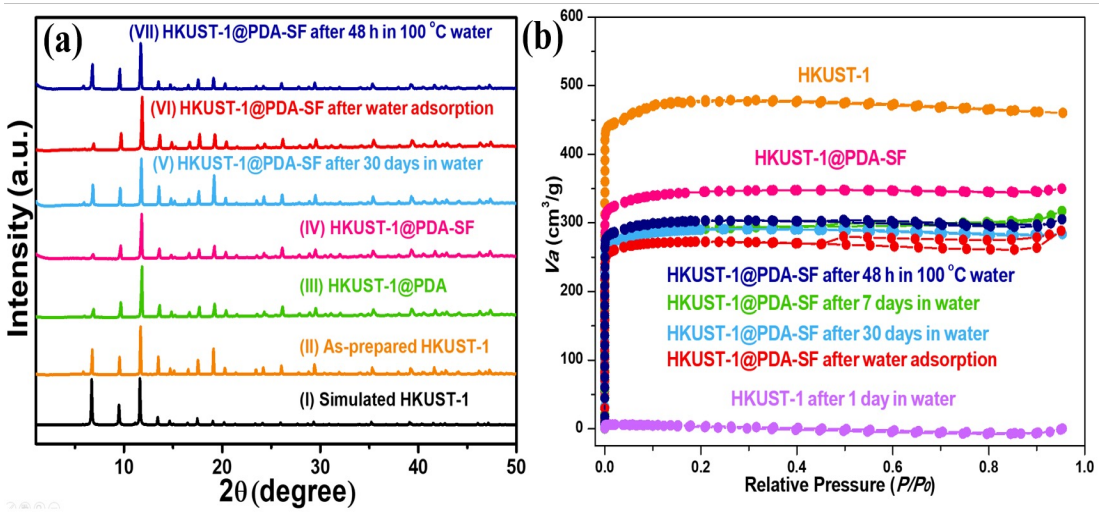
Chem Sci. **2019**, 10, 4542. Featured cover article.

Hydrophobic coatings on HKUST-1









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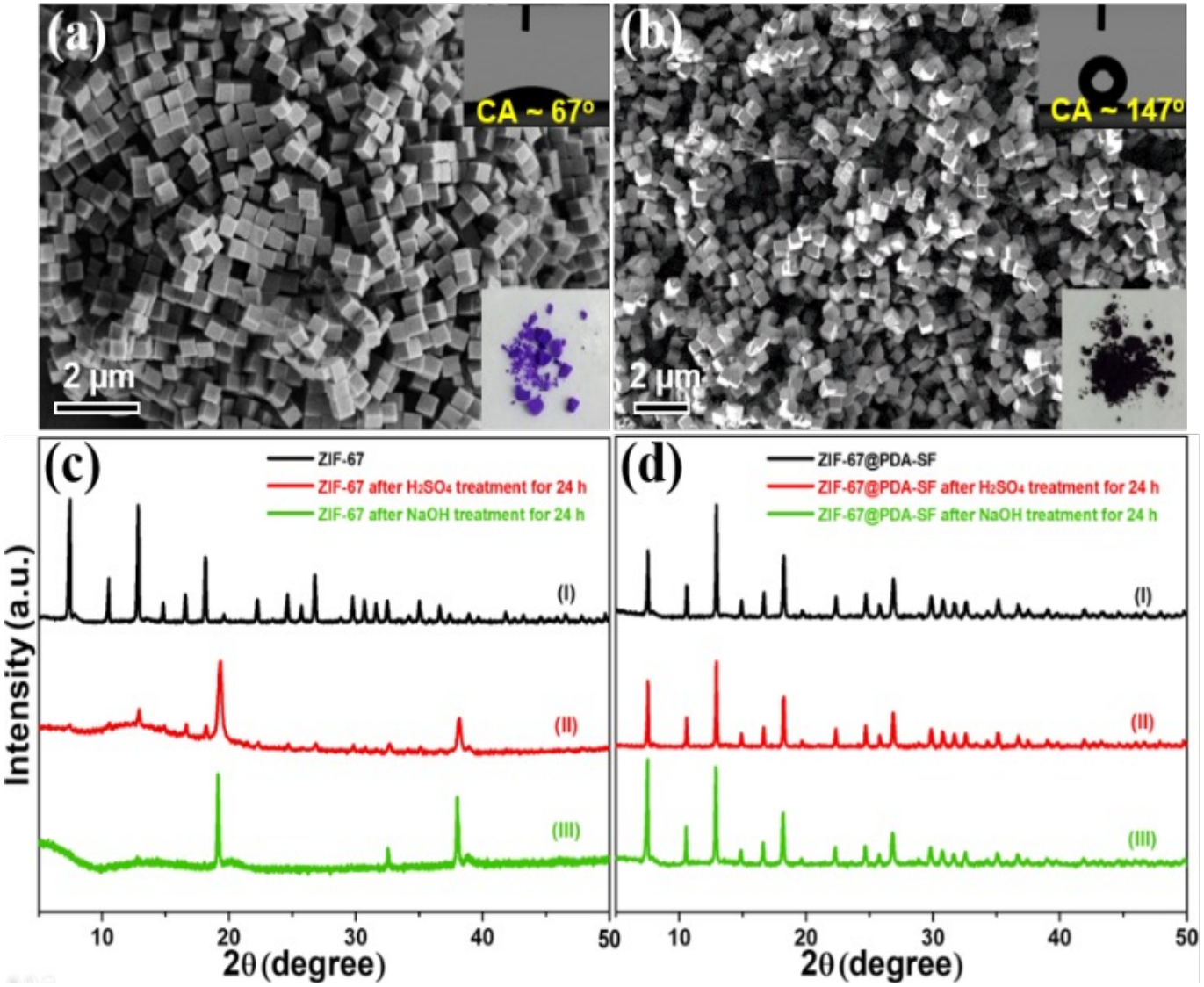
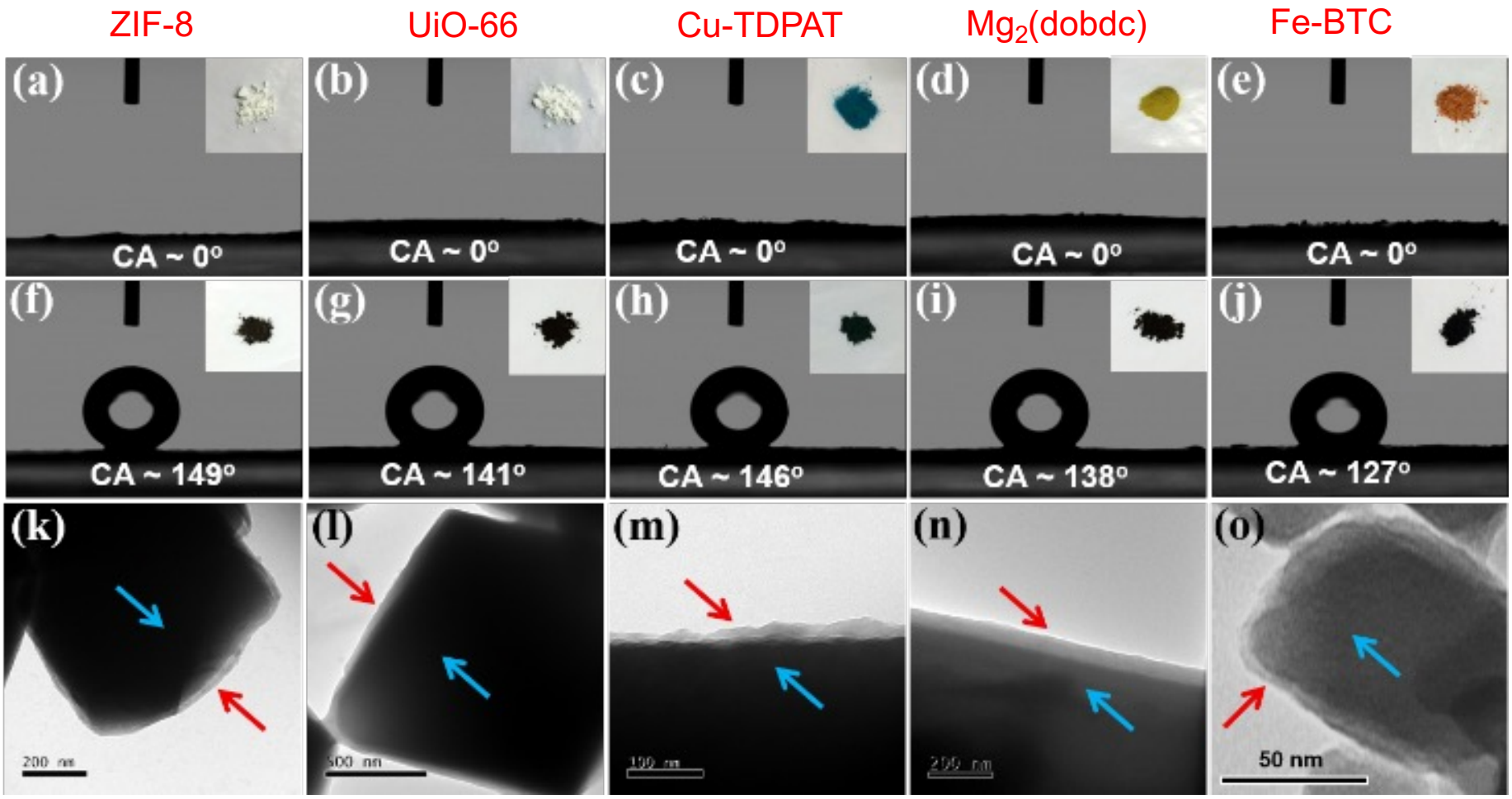
Hydrophobic coating on ZIF-67



Chem Sci. **2019**, 10, 4542. Featured cover article.

Tests on many structurally diverse MOFs

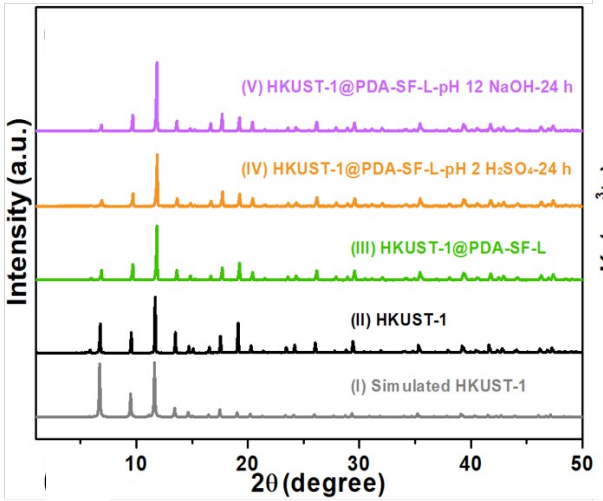


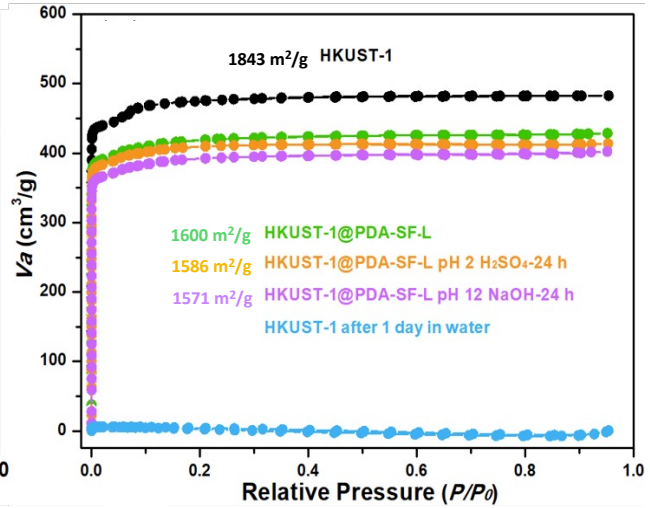
Chem Sci. **2019**, 10, 4542. Featured cover article.

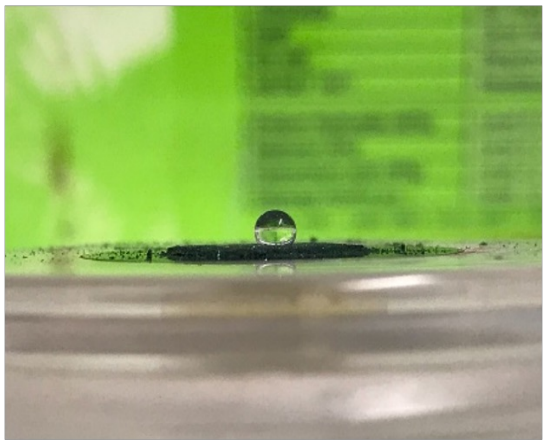
Optimizing surface coatings

Sample Name / Formula	BET Surface Area (m^2/g)	Contact Angle (°)	Polymer Loading (wt%)	H_2SO_4 Treatment, pH = 0, 1, 2 or 3 for 24 h	BET Surface Area after H_2SO_4 Treatment (m^2/g)	NaOH Treatment, pH = 11, 12 or 13 for 24 h	BET Surface Area after NaOH Treatment (m^2/g)
UiO-66 $Zr_6O_4(OH)_4(BDC)_6$, BDC^{2-}= 1,4-dicarboxybenzene	1430	~0	---	X	---	X	---
UiO-66@PDA-SF	638	141	10.3	✓	626	✓	581
Cu-TDPAT Cu_3(TDPAT), TDPAT=2,4,6-tris(3,5 dicarboxylphenylamino)-1,3,5-triazine	2254	~0	---	X	---	X	---
Cu-TDPAT@PDA-SF	1835	146	12.5	✓	1784	✓	1778

6.8 wt % PDA







Chem Sci. **2019**, 10, 4542. Featured cover article.

Tests on many structurally diverse MOFs

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HKUST-1 $Cu_3(BTC)_2$, BTC^{3-}= benzene-1,3,5-tricarboxylate	1854	~0	---	X	---	X	---
HKUST-1@PDA-SF	1286	140	16.8	✓	1247	✓	1242
ZIF-67 $Co(MIm)_2$, MIm=2-methylimidazolate	1466	67	---	X	---	X	---
ZIF-67@PDA-SF	683	147	16.8	✓	729	✓	738
ZIF-8 $Zn(MIm)_2$, MIm=2-methylimidazolate	1788	~0	---	X	---	✓	1710
ZIF-8@PDA-SF	1389	149	7.6	✓	1387	✓	1411
Mg-MOF-74 $Mg_2(dobdc)$, $dobdc^{4-}$ = 2,5-dioxido-1,4-benzenedicarboxylate	1182	~0	---	X	---	✓	1138
Mg-MOF-74@PDA-SF	918	138	12.8	✓	867	✓	952
MIL-100-Fe $Fe_3(BTC)_2$, BTC^{3-}= benzene-1,3,5-tricarboxylate	1587	~0	---	X	---	✓	1579
MIL-100-Fe@PDA-SF	1266	127	14.7	✓	1369	✓	1262
UiO-66 $Zr_6O_4(OH)_4(BDC)_6$, BDC^{2-}= 1,4-dicarboxybenzene	1430	~0	---	X	---	X	---
UiO-66@PDA-SF	638	141	10.3	✓	626	✓	581
Cu-TDPAT $Cu_3(TDPAT)$, TDPAT=2,4,6-tris(3,5 dicarboxylphenylamino)-1,3,5-triazine	2254	~0	---	X	---	X	---
Cu-TDPAT@PDA-SF	1835	146	12.5	✓	1784	✓	1778

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Chem Sci. **2019**, 10, 4542. Featured cover article.

Optimizing surface coatings

Sample Name / Formula	BET Surface Area (m^2/g)	Contact Angle (°)	Polymer Loading (wt%)	H_2SO_4 Treatment, pH = 0, 1, 2 or 3 for 24 h	BET Surface Area after H_2SO_4 Treatment (m^2/g)	NaOH Treatment, pH = 11, 12 or 13 for 24 h	BET Surface Area after NaOH Treatment (m^2/g)
HKUST-1 $Cu_3(BTC)_2$, BTC^{3-}= benzene-1,3,5-tricarboxylate	1843	~0	---	✗	---	✗	---
HKUST-1@PDA-SF	1286	140	16.2	✓	1247	✓	1242
HKUST-1@PDA-SF-2	1600	135	6.8	✓	1586	✓	1571
ZIF-67 $Co(MIm)_2$, MIm=2-methylimidazolate	1466	67	---	✗	---	✗	---
ZIF-67@PDA-SF	683	147	16.8	✓	729	✓	738
ZIF-67@PDA-SF-2	1312	139	11.5	✓	1303	✓	1293
ZIF-8 $Zn(MIm)_2$, MIm=2-methylimidazolate	1788	~0	---	✗	---	✓	1710
ZIF-8@PDA-SF	1389	149	7.6	✓	1387	✓	1411
Mg-MOF-74 $Mg_2(dobdc)$, $dobdc^{4-}$ = 2,5-dioxido-1,4-benzenedicarboxylate	1182	~0	---	✗	---	✓	1138
Mg-MOF-74@PDA-SF	918	138	12.8	✓	867	✓	952
MIL-100-Fe $Fe_3(BTC)_2$, BTC^{3-}= benzene-1,3,5-tricarboxylate	1587	~0	---	✗	---	✓	1579
MIL-100-Fe@PDA-SF	1266	127	14.7	✓	1369	✓	1262
UiO-66 $Zr_6O_4(OH)_4(BDC)_6$, BDC^{2-}= 1,4-dicarboxybenzene	1430	~0	---	✗	---	✗	---
UiO-66@PDA-SF	638	141	12.3	✓	630	✓	724

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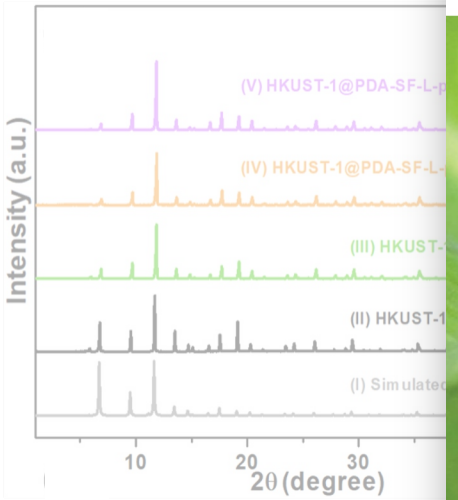
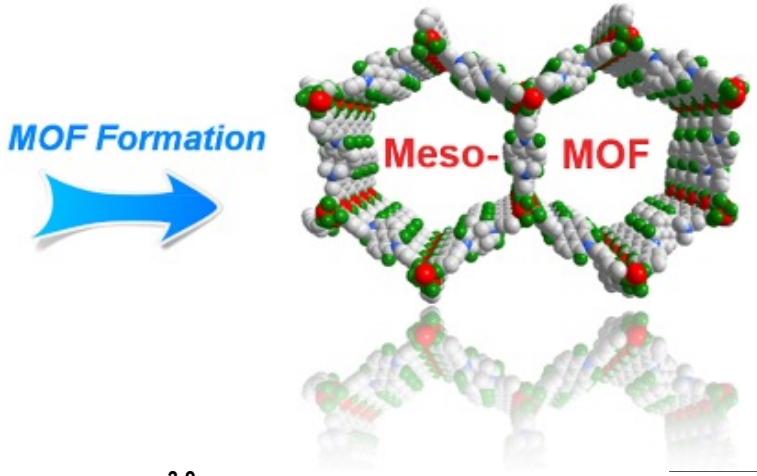
Optimizing surface coatings

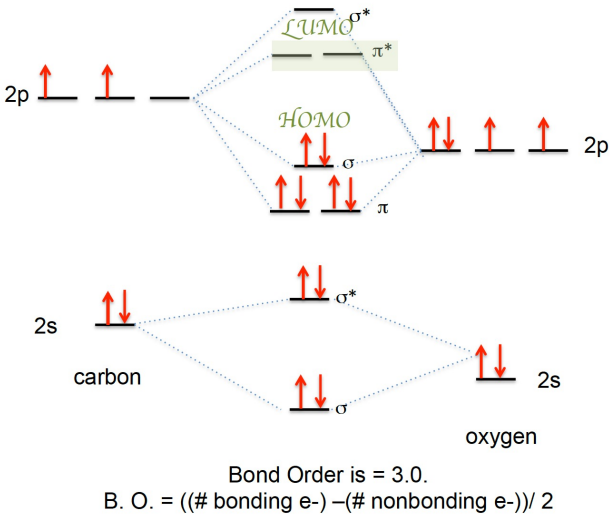


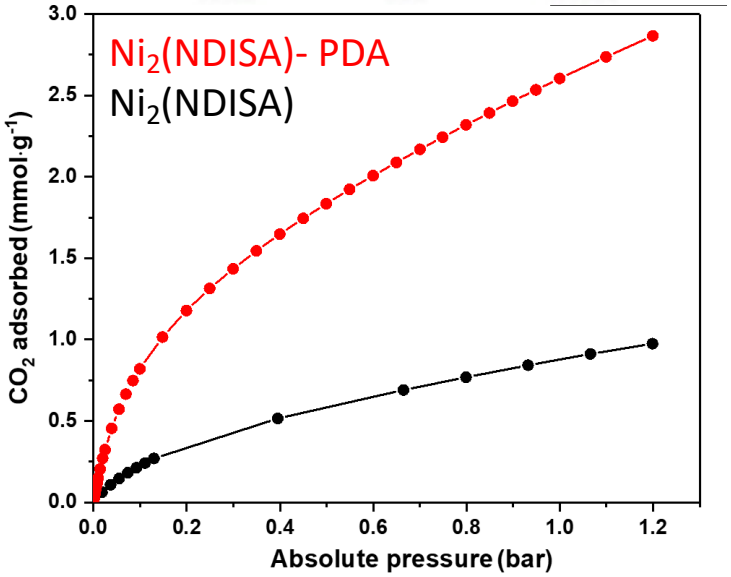
Chem Sci. **2019**, 10, 4542. Featured cover article.

Achieving larger pore volumes and higher capacities

"Preserving Porosity of Mesoporous Metal-Organic Frameworks through the Introduction of Polymer Guests"







J. Am. Chem. Soc, **2019**, 141, 12397.
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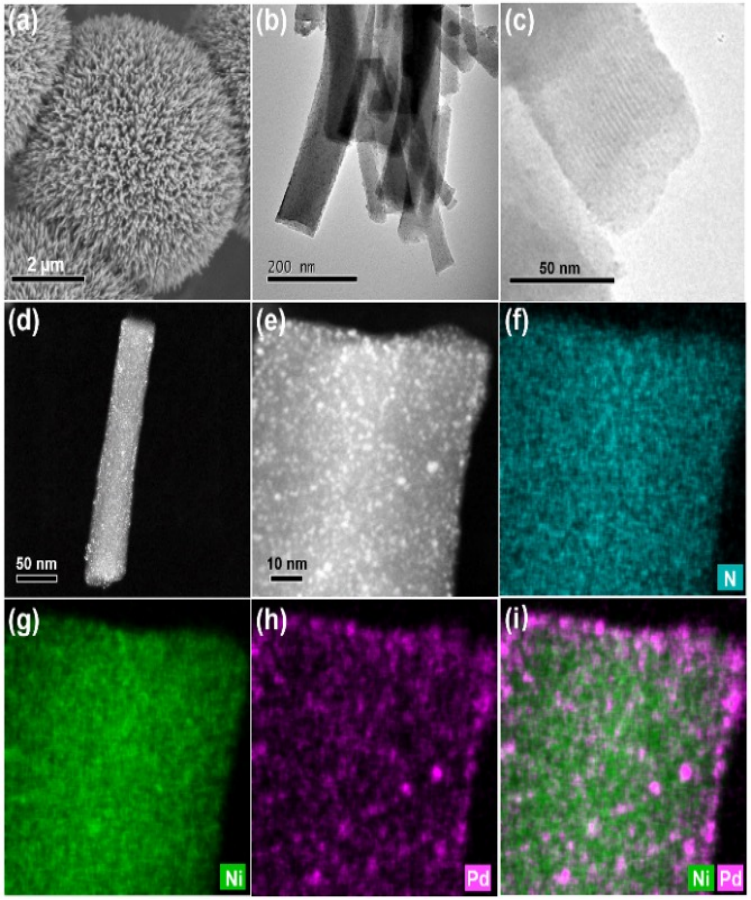

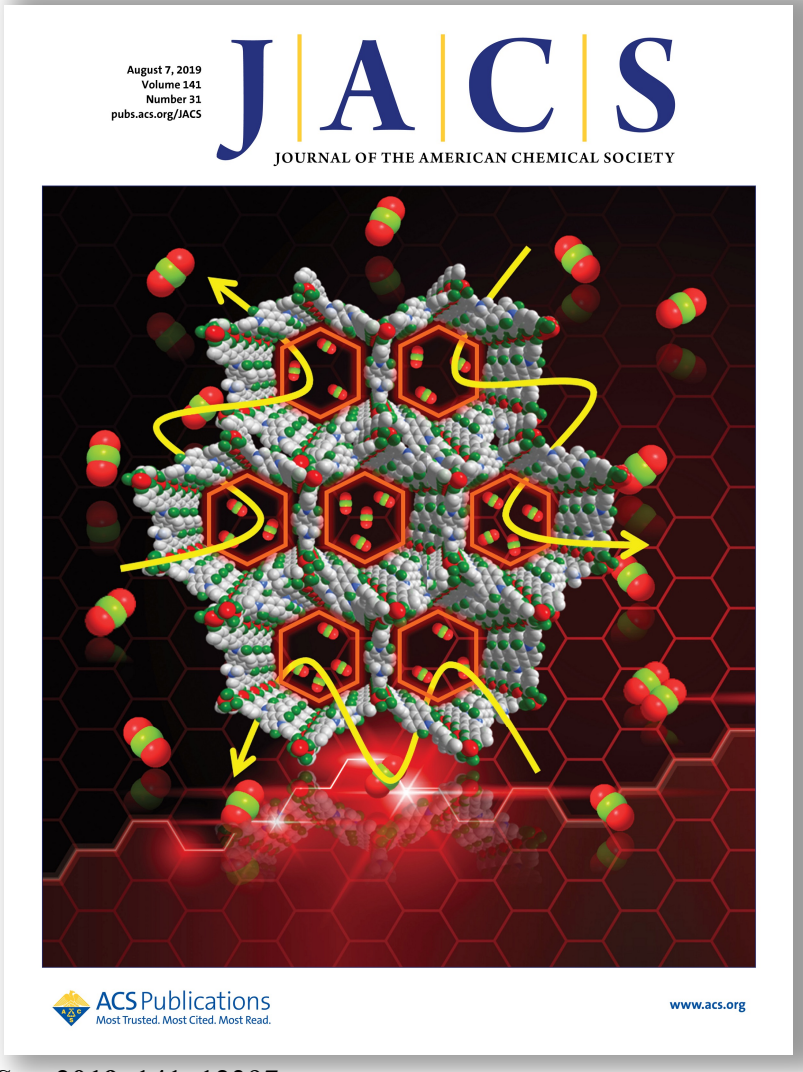

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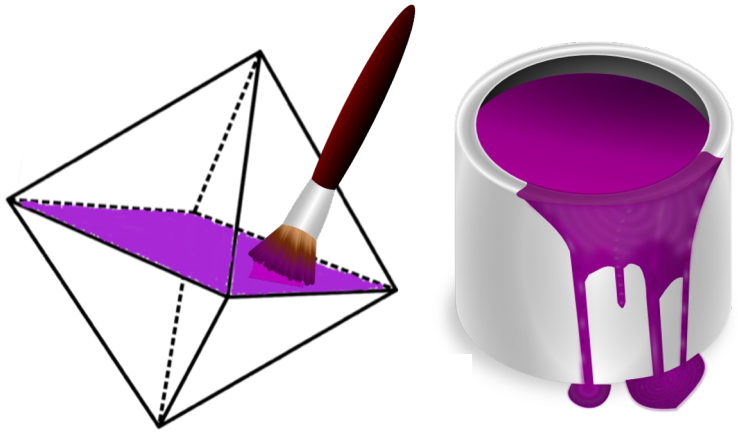
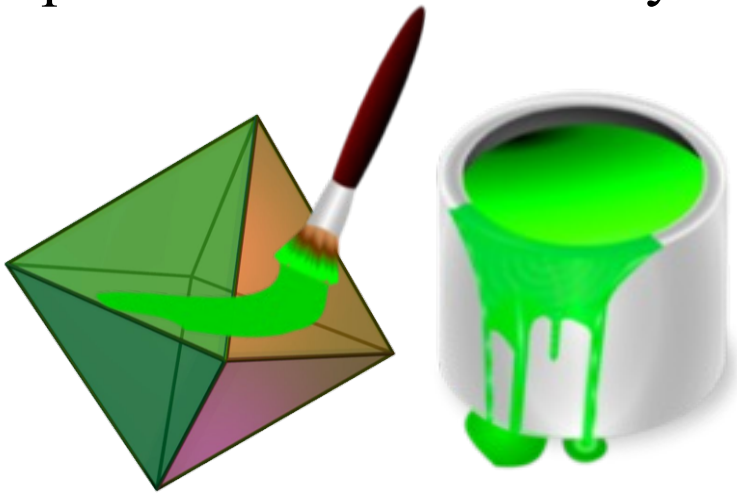
End goals

Objective 1: enhance adsorption/separation

Applications:
1. Heavy metal extraction
2. High value commodities
3. Harmful organics
4. Gas separations



Objective 2: enhance performance in humidity and acidic/basic media



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