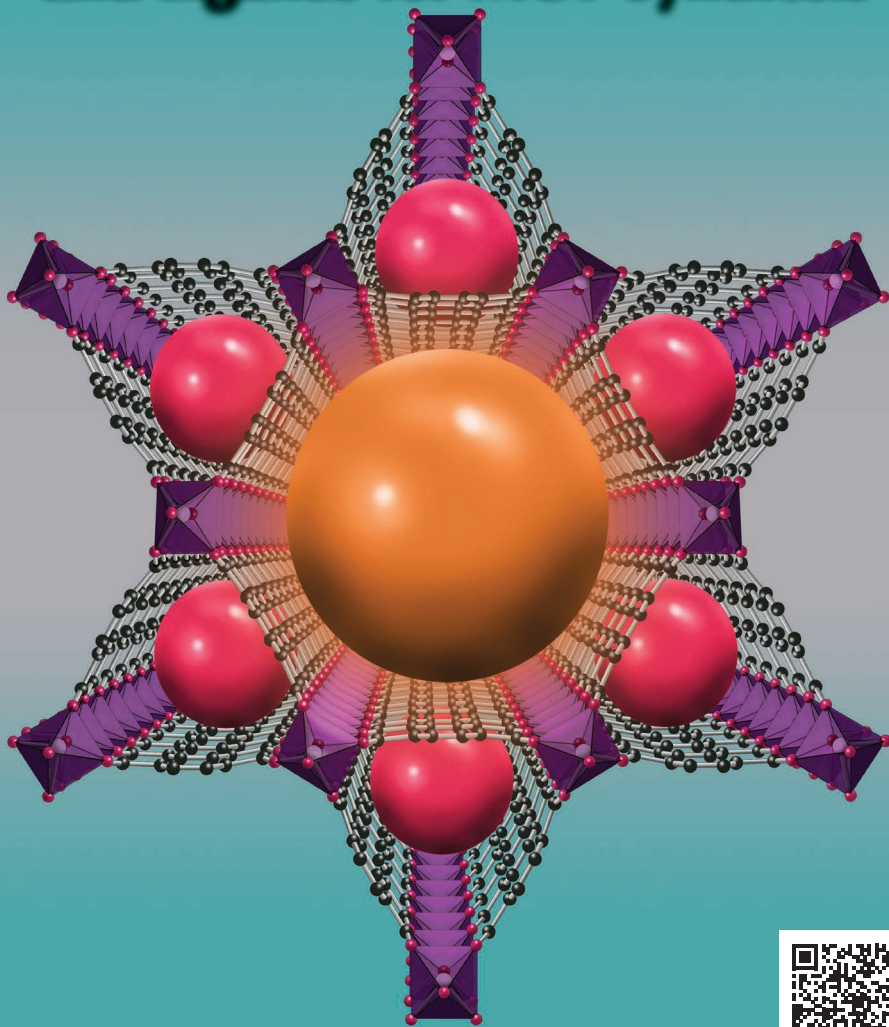


Metal Organic Frameworks and Ligands for MOF Synthesis



ETREM

MOFs and Ligands for MOF Synthesis



Strem Chemicals has been providing fine chemicals for research and commercial production for over fifty years. In this booklet you will find our selection of Metal Organic Frameworks (MOFs) and Ligands for MOF Synthesis. MOF technology is a new and exciting field that possesses great possibilities within the gas and fuel storage industries. It also has been found to have promising potential as a catalyst. We look forward to the expansion of this product line as the applications within this field continue to grow.

At Strem, we also offer a wide variety of ligands, nanomaterials and CVD/ALD precursors. Most of our products are of high purity, typically at 99%, while some are as high as 99.9999% metals purity. We continually seek to provide new technologies from around the globe and add to our product line. We have licensing agreements with industry and academia, which allow easier access to these patent-protected products for our customers. We look forward to continued growth in order to best serve our customers' needs with the quality and service they can trust from Strem.

As part of our ongoing commitment to quality, we have achieved ISO 9001 certification for the Quality Management System (QMS) at our corporate headquarters in Newburyport, Massachusetts.

In addition, custom synthesis services are provided on a contract basis. For pharmaceutical applications, manufacturing is conducted under current Good Manufacturing Practices (cGMP) in FDA inspected kilo-lab suites. Complete documentation is available, including validation and stability studies. Active Drug Master Files (DMF's) are maintained in North America and Europe.

Our other booklets, which focus on applications and product classes, are available in print per request and also on our website. Below is a list of current booklet titles that are available. Please also check our Product Resources section online to find additional literature offerings, such as the Strem Chemiker, our technical publication, and product literature sheets.

- Biocatalysts
- Buchwald Ligands and Precatalysts
- Carbon-Base Nanomaterials & Elemental Forms
- Catalysts & Ligands
Sold in Collaboration with Takasago
- Chiral Phosphoric Acids
- Gold Elements & Compounds
- Heterogeneous Catalysts
- High Purity Chiral Reagents
- Kits
- Materials for Energy Applications
- Metal Catalysts for Organic Synthesis
- Metathesis Catalysts
- MOCVD, CVD & ALD Precursors
- MOFs and Ligands for MOF Synthesis
- Nanomaterials
- New Products
- Other Ligands
- Phosphorous Ligands and Compounds
- Photocatalysts
- PURATREM: High Purity Inorganics

Ephraim S. Honig, Ph.D., M.B.A.
Chief Executive Officer



MOF 10/18
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Glossary of Terms

[α]_D	Specific rotation
AAS	Atomic Absorption Standard
ACS	Conforms to American Chemical Society specifications
air sensitive	Product may chemically react with atmospheric oxygen or carbon dioxide at ambient conditions. Handle and store under an inert atmosphere of nitrogen or argon.
amp	Ampouled
b.p.	Boiling point in °C at 760mm, unless otherwise noted
d.	Density
dec.	Decomposes
elec. gr.	Electronic Grade, suitable for electronic applications
f.p.	Flash point in °F
gran.	Granular
heat sensitive	Product may chemically degrade if stored for prolonged periods of time at ambient temperatures or higher. Store at 5°C or lower.
hydrate	Unspecified water content which may vary slightly from lot to lot
hygroscopic	Product may absorb water if exposed to the atmosphere for prolonged periods of time (dependent on humidity and temperature). Handle and store under an inert atmosphere of nitrogen or argon.
light sensitive	Product may chemically degrade if exposed to light
liq.	Liquid
m.p.	Melting point in °C
moisture sensitive	Product may chemically react with water. Handle and store under an inert atmosphere of nitrogen or argon.
NMR grade	Suitable as a Nuclear Magnetic Resonance reference standard
optical grade	For optical applications
pwdr.	Powder
primary standard	Used to prepare reference standards and standardize volumetric solutions
PURATREM	Product has a minimum purity of 99.99% (metals basis)
purified	A grade higher than technical, often used where there are no official standards
P. Vol.	Pore volume
pyrophoric	Product may spontaneously ignite if exposed to air at ambient conditions
reagent	High purity material, generally used in the laboratory for detecting, measuring, examining or analyzing other substances
REO	Rare Earth Oxides. Purity of a specific rare-earth metal expressed as a percentage of total rare-earths oxides.
SA	Surface area
store cold	Product should be stored at -18°C or 4°C, unless otherwise noted (see product details)
subl.	Sublimes
superconductor grade	A high purity, analyzed grade, suitable for preparing superconductors
tech. gr.	Technical grade for general industrial use
TLC	Suitable for Thin Layer Chromatography
v.p.	Vapor pressure mm of Hg
xtl.	Crystalline

About Purity

Chemical purity	is reported after the chemical name, e.g. Ruthenium carbonyl, 99%
Metals purity	is reported in parentheses with the respective element, e.g. Gallium (III) bromide, anhydrous, granular (99.999%-Ga) PURATREM where 100% minus the metal purity is equal to the maximum allowable percentage of trace metal impurity

PCN-250: Highly Stable Framework with Extremely High Gas Uptake

Dawei Feng, Kecheng Wang, Zhangwen Wei, Ying-Pin Chen, Cory M. Simon, Ravi K. Arvapally, Richard L. Martin, Mathieu Bosch, Tian-Fu Liu, Stephen Fordham, Daqiang Yuan, Mohammad A. Omary, Maciej Haranczyk, Berend Smit, & Hong-Cai Zhou

Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255, USA.

Department of Materials Science and Engineering, Texas A&M University, College Station, Texas 77842, USA

Department of Chemical and Biomolecular Engineering,

University of California at Berkeley, Berkeley, California 94720, USA

Department of Chemistry, University of North Texas, Denton, Texas 76203, USA

Computational Research Division, Lawrence Berkeley National Laboratory, One Cyclotron Road,

MS 50F-1650, Berkeley, California 94720-8139, USA

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fujian, Fuzhou 350002, P. R. China

Institut des Sciences et Ingenierie Chimiques,

Ecole Polytechnique Fe'derale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

zhou@chem.tamu.edu

Introduction

Metal–organic frameworks (MOFs), as inorganic-organic hybrid materials based on coordination bonds, are usually less stable than covalent bond based materials. Thus, the stability of MOFs plays a vital role in real world applications.¹⁻⁴ The chemical stability of MOFs, which is defined as the resistance to reactive chemicals, is essential to a number of applications including separations, carbon capture, gas storage and catalysis⁵⁻¹⁵. MOFs that are robust, can be easily scaled up, are moisture resistant and possess high gas storage capacity are needed for the commercialization of MOFs. Nevertheless, synthesizing stable MOFs with appropriate porosity and internal surface properties has always been challenging. Moisture resistant MOFs, consisting of high-valence metals, have been made by ‘one-pot’ synthesis. That makes it hard to control the metal nodes and therefore the topology and structure of the MOFs¹⁶.

Preparing robust MOFs via a conventional one-pot synthesis method may be problematic due to the fact that an unpredictable geometry of metal clusters could be generated and even amorphous products could be seen. That makes the rational design of MOFs difficult¹⁷. To solve these problems, we use a universal approach, which is based on the kinetic and thermodynamic control of MOF crystallization, of synthesizing Fe-MOF single crystals with pre-synthesized metal building blocks $[\text{Fe}_2\text{M}(\mu_3\text{-O})(\text{CH}_3\text{COO})_6]$ ($\text{M}=\text{Fe}^{2+},^{3+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+}, \text{Zn}^{2+}$). In summary, 34 different Fe-MOF large single crystals were synthesized. Among these MOFs, PCN-250(Fe_2Co) (PCN stands for porous coordination network), shows very high total H_2 volumetric uptakes of 60 g L^{-1} at 40 bar and 77 K. It also exhibits high total CH_4 uptakes of 200V STP/V at 35 bar and 298 K^{18, 19}.

Simplification of MOFs growth using preformed $[\text{Fe}_2\text{M}(\mu_3\text{-O})(\text{CH}_3\text{COO})_6]$

$\text{M}_3(\mu_3\text{-O})(\text{COO})_6$ ($\text{M}=\text{Cr}, \text{Al}, \text{Sc}, \text{V}, \text{In}$ etc.) is one of the most common secondary building units (SBUs) that is a trivalent metal cluster in MOFs²⁰. We used $[\text{Fe}_2\text{M}(\mu_3\text{-O})(\text{CH}_3\text{COO})_6]$ as the reactant and acetic acid as the competing reagent to synthesize Fe-MOFs. These metal clusters have great solubility in common solvents, which increases their feasibility as a reactant. In terms of stability, the strong electrostatic interaction between Fe^{3+} and $\mu_3\text{-O}^{2-}$, the $[\text{Fe}_2\text{M}(\mu_3\text{-O})(\text{CH}_3\text{COO})_6]$ cluster is inherently stable to preserve the integrity of the core during carboxylate substitution process on the periphery under solvothermal conditions. Moreover, the D_{3h} cluster has six carboxylate arms in a trigonal prismatic geometry, which enables formation of 3D frameworks through simple bridging.

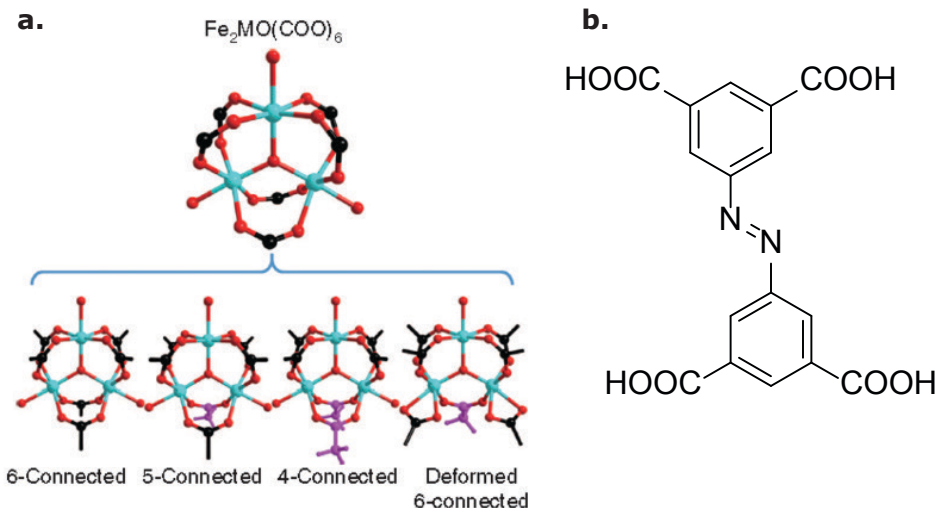


Figure 1: Different connecting modes and organic linkers used. (a) Four different connecting modes of the $[\text{Fe}_2\text{M}(\mu_3\text{-O})]$ cluster. Carboxylates on ligands and terminal acetates are represented by black and purple, respectively. (b) Ligand used in constructing PCN-250.

The amount of acetic acid, as the competing reagent, can easily adjust both the ligand substitution and dissociation processes. As a result, we successfully synthesized large single crystals of many Fe-MOFs, including PCN-250, with the $[\text{Fe}_2\text{M}(\mu_3\text{-O})]$ cluster.

Discussion on synthetic conditions of PCN-250

This novel synthetic approach could be regarded as a “dimensional augmentation” process. This means that pre-formed isolated clusters, or zero-dimensional nodes of $[\text{Fe}_2\text{M}(\mu_3\text{-O})]$, have been connected together to form three-dimensional nets of the MOF. Partial substitution on the $[\text{Fe}_2\text{M}(\mu_3\text{-O})]$ clusters has also happened when symmetry requirements or steric hindrance prohibits complete substitution.

Based on our hypothesis, the substitution rate of the MOF formation process would be lower with extra acetic acid, which indicates the kinetic control. Gels or amorphous products were obtained when the amount of acetic acid was much less than the optimal value. If the concentration of acetic acid is much higher than the optimal value, no crystal or even solid would be generated after a long time. If MOF crystallization is considered to be an equilibrium and the formation of clear solution is regarded as the point of transition to a positive Gibbs free energy, then the concentration of acetic acid is actually an indicator of the MOF's ΔG of crystallization.

High volumetric gas uptake of PCN-250

High methane uptake of PCN-250 is a key feature of this material. It is highly related to the structure of the MOF used¹⁹. Computational studies give a good prediction of its methane uptake. Figure 2a shows the simulated deliverable capacities of PCN-250(Fe_3), PCN-250(Fe_2Co) and other predicted structures. Our computational simulations indicate that PCN-250 is potentially an outstanding absorbent for methane storage using a pressure range between 1 and 35 bar. Our simulations also prove that PCN-250 has the highest methane loading of all structures considered in this analysis at 35 bar.

PCN-250 is made of 6-connected $[\text{Fe}_2\text{M}(\mu_3\text{-O})]$ SBUs and a rectangular tetratopic ligand (Fig. 2b–d), which is isostructural to a reported indium MOF²¹. It is interesting that PCN-250', a MOF isomer of PCN-250, is formed in different solvothermal conditions. In PCN-250', the ligand has

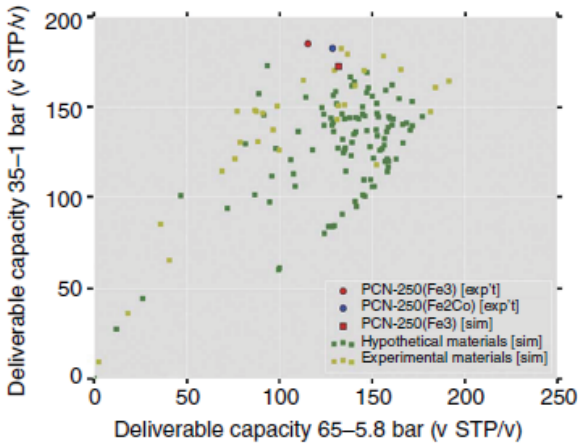
the same configuration in the one cube and mirror configuration in the adjacent cubes along any axis. The isothermal data shows that PCN-250(Fe₂Co) has total methane uptake of 200 v/v at 35 bar and 298 K (Fig. 2e), which is one of the highest methane uptake among all the reported MOFs. PCN-250(Fe₂Co) also possesses a record high H₂ uptake of 3.07 wt% and 28 g L⁻¹ at 1.2 bar and 77 K. In terms of hydrogen uptake, it also has one of the highest total volumetric H₂ uptakes, 60 g L⁻¹, at high pressure because of its high crystal density.

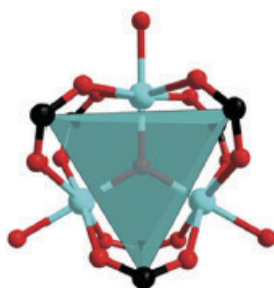
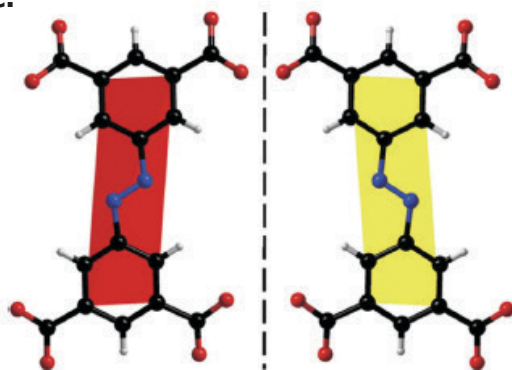
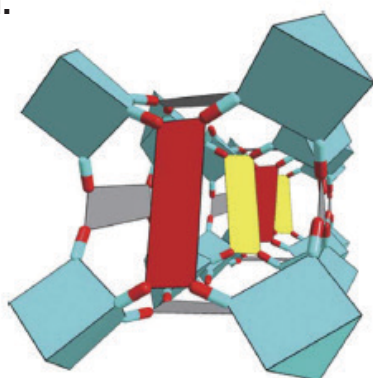
Both high uptake of methane and hydrogen results from the high valent open metal sites and suitable size of the pores in PCN-250 (Fig. 2f). As shown in Fig. 2b, the ligand covers the faces of every other cube in PCN-250 and highly charged open metal sites are around the channels between each cube. Thus, all of the inter space is available for gas adsorption. The interspace of PCN-250 has strong interaction with both H₂ and CH₄ molecules. Therefore, highly efficient space utilization for high volumetric gas uptake is achieved by inducing polarization of gas molecules via charge-induced dipole interaction. This high valence metal ion and induced dipole interaction is not limited within the first layer of gas molecules. Additional layers of gas molecules could be polarized, which would result in relatively insignificant adsorption enthalpy drop for multi-layer gas adsorption.

Extraordinary chemical stability of PCN-250

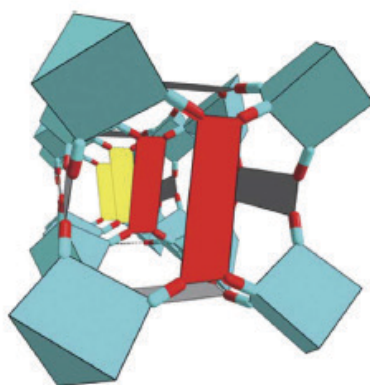
The PCN-250 series exhibits excellent chemical stability even after the replacement of the one iron atom to softer Lewis acid metal, M(II), in the μ₃-oxo cluster. PCN-250(Fe₂Co) is intact in a range of pH values from 1 to 11 for 24 h. This is shown in the PXRD results that the peaks remained sharp with the treatment of glacial acetic acid and pH=1 to pH=11 aqueous solutions for 24 h (Fig. 2g, h). Under neutral condition, PCN-250(Fe₂Co) remained robust in H₂O after 6 months (Fig. 2g, h). Additionally, with almost no change in N₂ adsorption isotherms of PCN-250(Fe₂Co) after all these pH treatments, we can conclude that no MOF decomposition or phase transition happened. The rare combination of high gas uptake and chemical robustness gives PCN-250 a reusability of the sorbent for real world applications. With its extraordinary stability, high gas uptake, and excellent scalability, PCN-250 is a promising material for natural gas storage for a variety of applications.

a.

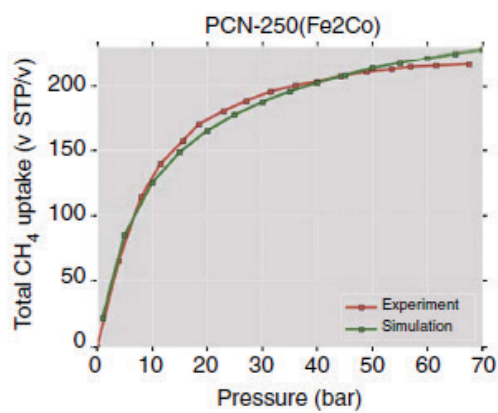
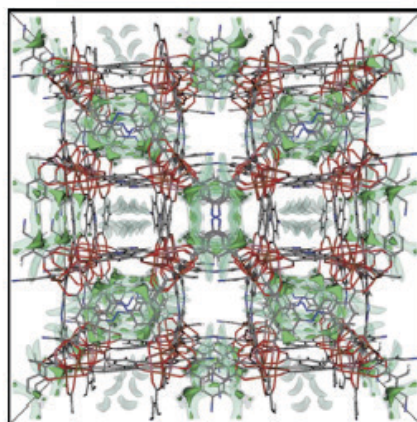


b.**c.****d.**

PCN-250



PCN-250'

e.**f.**

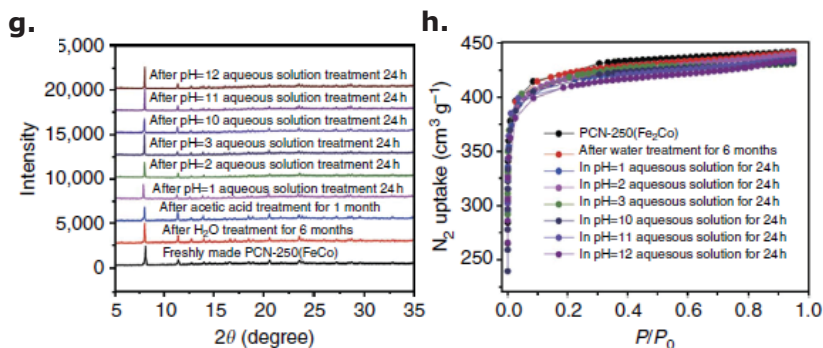


Figure 2: Simulated and experimental CH₄ adsorption of Fe-MOFs. (a) Performance plot of deliverable capacities using two different pressure swings. Shown are the predictions for the Fe-MOFs synthesized here (yellow) and in silico predicted structures (green). Red and blue points show PCN-250. (b–d) Structures of PCN-250 and PCN-250'. (e) Total CH₄ adsorption uptake of PCN-250 at 298 K and (f) contours of the computed potential energy surface of adsorbed CH₄ in PCN-250. (g) Powder X-ray patterns and (h) N₂ adsorption isotherms of PCN-250(Fe₂Co) after stability tests.

Conclusion

Highly stable metal–organic frameworks (MOFs) have been under investigation for a long period of time because of the interest in the material sustainability for real world applications. Nevertheless, synthesizing highly porous, chemically robust, and single crystalline MOFs has been extremely challenging. In this article, we report a novel robust porous Fe-MOF, PCN-250, prepared by kinetically tuned dimensional augmentation (KTDA) synthetic approach for the preparation of PCN-250. PCN-250(Fe₂Co) shows high volumetric uptake of H₂ and CH₄, and remains intact in water and aqueous solutions with a wide range of pH, which provides potential applications in gas storage for a variety of power systems and gas purification.

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ALUMINUM (Compounds)

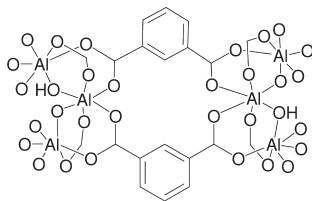
13-0300

NEW

Aluminum hydroxide isophthalate MOF (CAU-10, Isophthalate:Al=0.9-1.0)

(1416330-84-1)

Al(OH)(C₈H₄O₄)_x, X = 0.9-1.0; white solid;
SA: 620-640 m²/g; P.Vol. 0.23-0.27 cm³/g
Note: Particle size: 0.4-0.7 micron, Thermal
stability: 400°C, Activation temperature: 150°C
Sold under license from Inven2 AS for
research purposes only.
PCT/GB2009/001087.



500mg
2g

Technical Note:

1. MOF exhibits water adsorption characteristics which make it a promising adsorbent for application in heat-exchange processes ¹

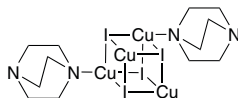
References:

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COPPER (Compounds)

29-3015

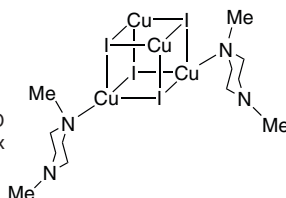
**Bis(1,4-diazabicyclo [2.2.2]octane)tetra
(copper(I) iodide) (CuI)₄(DABCO)₂** (928170-42-7)
C₁₂H₂₄Cu₄I₄N₄; FW: 986.15; yellow powdr.; SA: >514;
P.Vol. 0.25
air sensitive



500mg
2g

29-0550

**Bis(N,N'-dimethylpiperazine)tetra[copper(I)
iodide], 98% MOF** (1401708-91-5)
(CuI)₄(C₆H₁₄N₂)₂; FW: 990.18; white powdr.
moisture sensitive, (store cold)



500mg
2g

Technical Note:

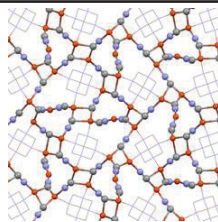
1. The copper iodide, N,N'-dimethylpiperazine complex is a 3D photoluminescent, fairly open network, with a lambda max excitation of 321 nm and a lambda max emission of 525nm.

References:

1. *Dalton Trans.*, **2012**, 41, 11663

29-0565

**(Hexamethylenetetramine)penta[copper(I) cyanide],
98% MOF** (1042093-98-0)
C₆H₁₂N₄(CuCN)₅; FW: 588.00; white powdr.
hygroscopic, (store cold)



500mg
2g

Technical Note:

1. The copper cyanide hexamethylenetetramine complex is a 3D photoluminescent, very densely-packed, network of tetradentate ligands with a lambda max excitation of 282 and 304nm, and a lambda max emission of 417 and 522nm.

References:

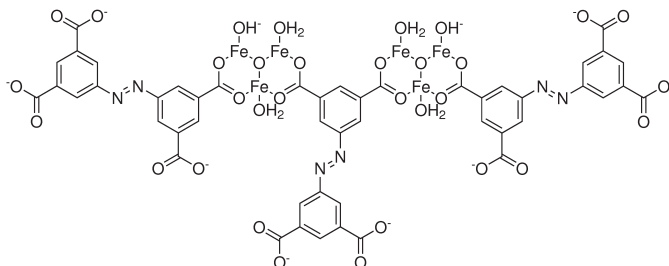
1. *Inorg. Chem.*, **2007**, 46, 8897
2. *Inorg. Chem.*, **2008**, 47, 6947
3. *Inorg. Chem. Acta.*, **2010**, 364, 102
4. *Dalton Trans.*, **2012**, 41, 11663

IRON (Compounds)

26-3725	Iron azobenzene tetracarboxylic, Porous [PCN-250(Fe)], AYRSORB™ F250 (1771755-22-6) Dark red-brown powd. Note: Sold in collaboration with framergy for research purposes only. Patent: US 9,724,668 B2.	500mg 2g 10g
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Technical Note:

- Please refer to the article on page 1 for a detailed look at this product. A full technical note is also available at www.strem.com



26-2340	Iron(III) 1,3,5-benzenetricarboxylate hydrate, porous (F-free MIL-100(Fe), KRICT F100) [Iron trimesate] (1257379-83-1) [Fe ₃ O(H ₂ O) ₂ (OH){C ₆ H ₃ (COO) ₃ }] ₂ ·xH ₂ O; red solid; SA: 2120 (Langmuir); 1950 (BET); P.Vol. 1.075 Note: Sold under agreement with KRICT for research and development purposes only. Patents US 8507399 B2, US 8252950 B2.	500mg 2g
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Technical Note:

Large-pore Iron(III) carboxylate

As hybrid organic-inorganic structures, porous metal-organic frameworks (MOFs) have interesting coordination structures and topologies, with notable features including well-defined crystalline structures, regular pore structures, and very high porosities and surface areas. Consequently, these advanced functional materials have potential use in gas/liquid storage, gas separation, adsorption chiller, dehumidification, catalysis, drug delivery, magnetic and optical devices, and many other applications.

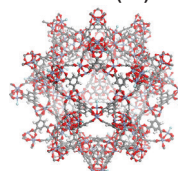
MIL-100(Fe) is a new iron(III) carboxylate that has initially been developed by the collaboration between the CNRS-Institute for Lavoisier (ILV; Prof. G. Férey and Dr. C. Serre) and the Korea Research Institute of Chemical Technology (KRICT; Dr. J.-S. Chang and Dr. Y.K. Hwang). KRICT F100 is a fluorine-free version of MIL-100(Fe) prepared by KRICT with similar physicochemical properties. It would be actually one of the highest porous MOFs that can be produced by the large-scale hydrothermal synthesis. The hierarchically mesoporous crystalline three-dimensional iron(III) trimesate has two sets of mesoporous cages (24 Å and 29 Å) that are accessible through microporous windows (ca. 8.6 Å and ca. 4.7-5.5 Å).

The incorporation of transition metals into the skeleton of MOFs imparts new sorption and catalytic properties to these functional materials. Iron is attractive because it is readily available, inexpensive, environmentally benign, nontoxic, and exhibits interesting redox behavior.

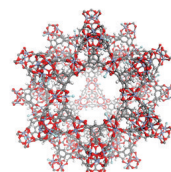
In fact, KRICT F100 has been shown to be biocompatible and hydrothermally stable in boiling water at 100°C. It has also been found to catalyze several types of Lewis acid catalysis such as Friedel–Crafts acylation, Prins reaction, etc. In addition, this large-pore iron trimesate can be reduced under controlled conditions to generate sites that strongly interact with unsaturated gas molecules and enable selective gas sorption and separation.

Finally, the rapid preparation of KRICT F100 on a 15 Kg-scale has been demonstrated using fluorine-free hydrothermal conditions.

Mesoporous Cages in MIL-100(Fe)



Medium cage (24 Å)

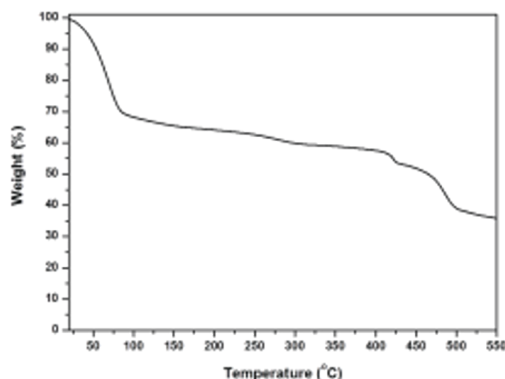


Large cage (29 Å)

IRON (Compounds)

26-2340 Iron(III) 1,3,5-benzenetricarboxylate hydrate, porous (F-free MIL-100(Fe), (continued) KRICT F100) [Iron trimesate] (1257379-83-1)

TGA Profile of KRICT F100



Characterization of KRICT F100

KRICT F100 has been characterized using powder X-ray diffraction (XRD) analysis, Fourier transform infrared (FTIR) spectroscopy, and thermogravimetric analysis (TGA). It has also been shown to have high hydrothermal and chemical stability.

The terminal water molecules in the assynthesized MOF are removable upon heating above 100 °C under vacuum or a gas stream. The removal of the water molecules from fully saturated KRICT F100 can be seen in the TGA profile.

Reactivity of KRICT F100

The effectiveness of MIL-100(Fe) or KRICT F100 as a heterogeneous catalyst was demonstrated for the Friedel-Crafts benzylation of benzene by benzyl chloride (BZC) to yield diphenylmethane (DPM). At 70 °C, 100% BZC

conversion with nearly 100% DPM selectivity was achieved within 5 min over MIL-100(Fe). Solid acid zeolite catalysts were significantly less reactive and slightly less selective for DPM. These results suggest that the unsaturated iron(III) metal sites have potential activity for new catalytic applications.

Removal of the terminal water molecules from KRICT F100 leads initially to the generation of a large number of coordinatively unsaturated Fe(III) sites that act as Lewis acid sites in the pores. After activation, the reduced framework iron sites in octahedral iron trimers strongly interact with unsaturated gas molecules, such as CO and propylene, and also exhibit improved preferential sorption properties for unsaturated gases, such as propylene over propane. Thus, KRICT F100 and its derivatives have the potential to serve as environmentally friendly gas adsorbents with preferential gas sorption properties.

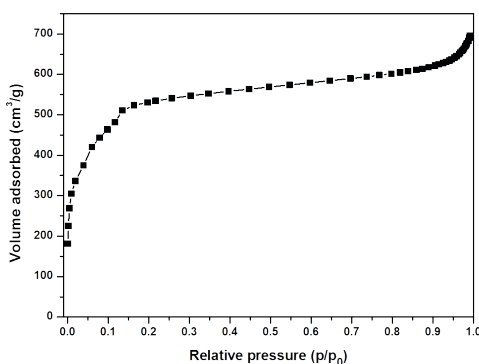
Activation: KRICT F100 is generally activated by heating at 150°C for 6 h under a vacuum or nitrogen flow.

Large-scale Preparation of KRICT F100

The highly productive rapid (>1700 Kg/m³-day), large-scale (15 Kg) synthesis of KRICT F100 via hydrothermal reactions in the absence of HF has been achieved using a highly concentrated reactant mixture. The HF-free route is both less time-consuming and less expensive, and the KRICT F100 obtained using this method has similar physicochemical properties as MIL-100(Fe) and is the highest surface area MOF produced at this scale with such a high space-time yield. KRICT F100 can also be formed into spheres, pellets, monoliths or washcoated honeycombs for ease of handling on a large scale.

Storage conditions: No special storage conditions are required. It is recommended, however, that KRICT F100 be placed in a desiccator prior to use.

NH₂ Physisorption Isotherm for KRICT F100 at 77 K



IRON (Compounds)

26-2340 Iron(III) 1,3,5-benzenetricarboxylate hydrate, porous (F-free MIL-100(Fe), (continued) KRICT F100) [Iron trimesate] (1257379-83-1)

Key Properties of KRICT F100

Purity: > 99%

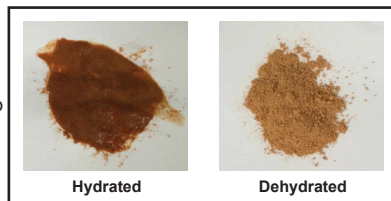
Color: Dark brown (hydrated), Pale brown (dehydrated)

Sensitivity (air, heat, light, water): KRICT F100 is insensitive to air, light, and water, but it is sensitive to heat above 150°C in air

Specific surface area (after dehydration at 150°C): 2120 m²/g (Langmuir); 1950 m²/g (BET)

Pore volume: 1.075 cm³/g

Gas/liquid uptake: much higher than conventional zeolite beta and commercial iron trimesate; both nonpolar and polar molecules due to the presence of both hydrophilic and hydrophobic sites in the framework.



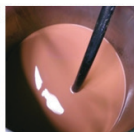
KRICT F100



Spheres



Washcoated
Honeycomb



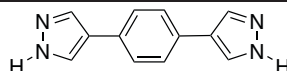
Slurry Solution

References:

1. P. Horcajada, et al., "Synthesis and Catalytic properties of MIL-100(Fe), an iron(III) carboxylate with Large Pores," Chem. Commun., 2820-2822 (2007).
2. J.W. Yoon, et al., "Controlled Reducibility of a Metal-Organic Framework with Coordinatively Unsaturated Sites for Preferential Gas Sorption," Angew. Chem. Int. Ed., 49, 5949-5952 (2010).
3. Y.-K. Seo, et al., "Large Scale Fluorine-Free Synthesis of Hierarchically Porous Iron(III) Trimesate MIL-100(Fe) with a Zeolite MTN Topology," Micropor. Mesopor. Mater., 157, 137-145 (2012).
4. Y.-K. Seo, et al., "Energy-Efficient Dehumidification over Hierarchically Porous Metal-Organic Frameworks as Advanced Water Adsorbents," Adv. Mater., 24, 806-810 (2012).
5. P. Horcajada, et al., "Porous Metal-organic-framework nanoscale carriers as a potential platform for drug delivery and imaging," Nature Mater., 9, 172-178 (2010).

NITROGEN (Compounds)

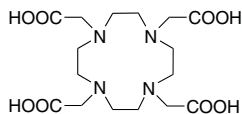
07-0435 1,4-Di(4'-pyrazolyl)benzene, min. 97% H₂BDP (1036248-62-0)
C₁₂H₁₀N₄; FW: 210.24; pale yellow solid
Note: Ligand for MOF synthesis.



500mg

2g

07-1942 1,4,7,10-Tetraazacyclododecane-N,N',N'',N'''-tetraacetic acid, min. 98% DOTA (60239-18-1)
C₁₆H₂₈N₄O₈; FW: 404.42; white powdr.
Note: Ligand for MOF synthesis.

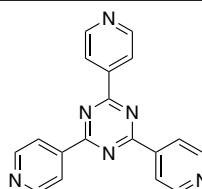


250mg

1g

5g

07-3235 2,4,6-(Tri-4-pyridinyl)-1,3,5-triazine, min. 97% TPT (42333-78-8)
C₁₈H₁₂N₆; FW: 312.33; off-white powdr.
Note: Ligand for MOF synthesis



250mg

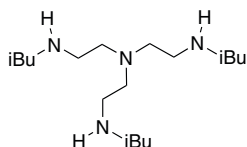
1g

5g

MOFs and Ligands for MOF Synthesis

NITROGEN (Compounds)

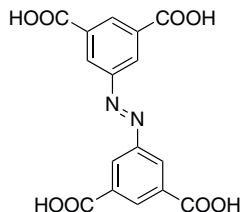
07-3110 **Tris(isobutylaminoethyl)amine, min 97%**
 (331465-73-7)
 $C_{18}H_{42}N_4$; FW: 314.55;
 colorless to pale yellow, viscous liq.
hygroscopic
 Note: Ligand for MOF synthesis.



500mg
2g

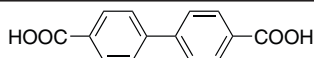
OXYGEN (Compounds)

08-0125 **3,3',5,5'-Azobenzene tetracarboxylic acid, TazbH₄, 97% (365549-33-3)**
 $C_{16}H_{10}N_2O_8$; FW: 358.26; yellow-orange powdr.
 Note: Ligand for MOF Synthesis



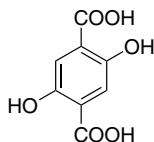
1g
5g

08-0175 **[1,1'-Biphenyl]-4,4'-dicarboxylic acid, min. 98% (787-70-2)**
 $C_{14}H_{10}O_4$; FW: 242.23; white to pale-yellow solid
 Note: Ligand for MOF synthesis.



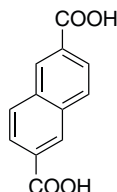
5g
25g

08-1220 **2,5-Dihydroxyterephthalic acid, 98% H₄DOBDC (610-92-4)**
 $C_6H_2(OH)_2(COOH)_2$; FW: 198.13; yellow powdr.
 Note: Ligand for MOF Synthesis



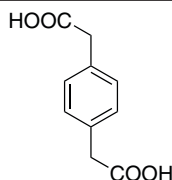
1g
5g
25g

08-1235 **2,6-Naphthalenedicarboxylic acid, min. 98% (1141-38-4)**
 $C_{10}H_6(COOH)_2$; FW: 216.19; white powdr.; m.p. >300°
 Note: Ligand for MOF synthesis.



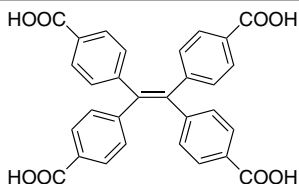
5g
25g

08-1165 **1,4-Phenylenediacetic acid, 97% (7325-46-4)**
 $C_8H_8(CH_2COOH)_2$; FW: 194.18; white to off-white solid
 Note: Ligand for MOF synthesis.



1g
5g

08-3060 **1,1,2,2-Tetra(4-carboxyphenyl)ethylene, 99% H₄TCPE (1351279-73-6)**
 $C_{30}H_{20}O_8$; FW: 508.48; pale yellow powdr.
 Note: Ligand for MOF synthesis.

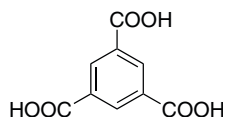


25mg
100mg

MOFs and Ligands for MOF Synthesis

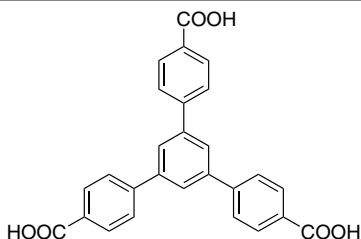
OXYGEN (Compounds)

08-0195 **1,3,5-Tricarboxybenzene, min. 95% (Trimesic acid)**
BTC (554-95-0)
 $C_6H_3(COOH)_3$; FW: 210.14; white powdr.
 Note: Ligand for MOF synthesis.



50g
250g

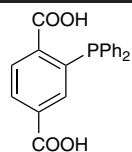
08-0635 **1,3,5-Tris(4-carboxyphenyl)benzene, min. 98%**
BTB (50446-44-1)
 $C_{27}H_{18}O_6$; FW: 438.43; white to yellow solid;
 m.p. 322-327°
 Note: Ligand for MOF synthesis.



1g
5g

PHOSPHORUS (Compounds)

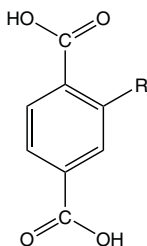
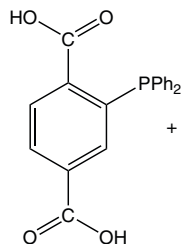
15-7170 **2-(Diphenylphosphino)terephthalic acid, 98%**
 (1537175-69-1)
 $C_{20}H_{18}O_4P$; FW: 350.30; white powdr.
 Note: Ligand for MOF synthesis. Developed at the Paul
 Scherrer Institute, Switzerland PCT/EP2013/051405.



50mg
250mg

Technical Note:

- Starting material for the construction of diphenylphosphino-substituted MOFs.



R = H, NH₂

MOF-5 PPh₂ sub.
MIL-101 PPh₂ sub.

Tech. Note (1)
Ref. (1)

References:

- Ind. Eng. Chem. Res.*, **2014**, 53, 9120.

TITANIUM (Compounds)

22-1070

NEW

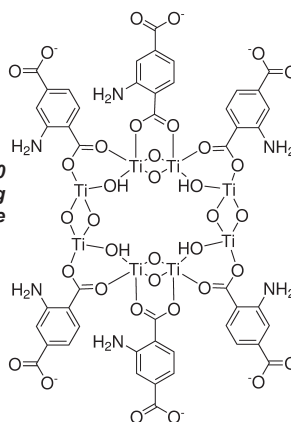
**Hexakis[μ-(2-amino-1,4-benzenedicarboxylato)]
[tetra-μ-hydroxyocta-μ-oxooctatitanium], NH₂-
MIL-125(Ti), AYRSORB™ T125 (1309760-94-8)**

C₄₈H₃₄N₆O₃₆Ti₈; FW: 1653.74; yellow powder;
SA: ~1530; P.Vol. ~0.74

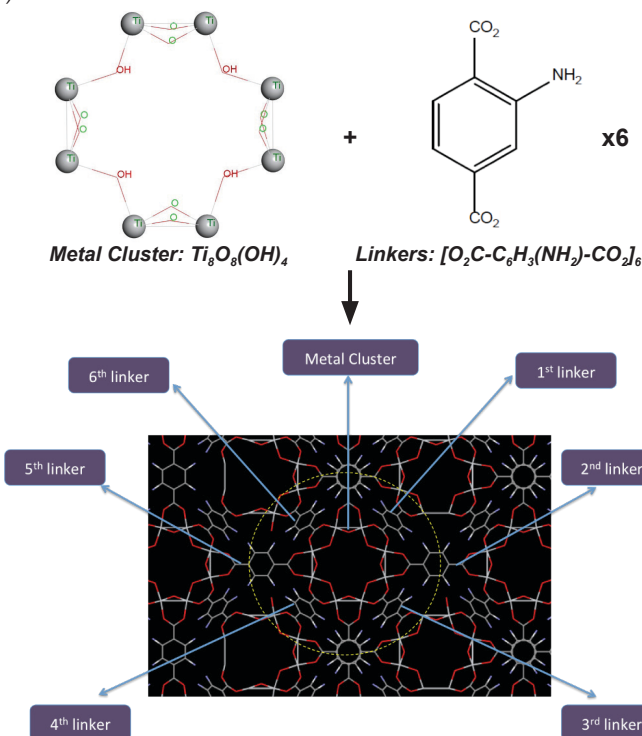
Note: Sold in collaboration with framergy for research purposes only. Patent: US 8,940,392 B2.

Activation of this material requires heating at 200 °C for 6 hours under vacuum. Upon cooling under vacuum, the activated product should be stored and handled under an inert atmosphere.

250mg
1g



This metal-organic framework (MOF) material is composed of a repeating unit cell. The unit cell is composed of a metal cluster and six linkers (ligands). The linkers connect the metal clusters together and they form a porous network, which is called a MOF. To clarify the structure in the above figure, the cluster is depicted with its elemental components to help the reviewer match the structure to its formula. (please see below)



Using an appropriate choice of solvent mixtures (dimethylformamide (DMF) and methanol, solid denoted MIL-125(Ti)-NH₂ or $Ti_8O_8(OH)_4(2OC-NH_2-C_6H_3-CO_2)_6 \cdot 18(CH_3OH) \cdot 3((CH_3)_2NCHO)$ has been isolated (MIL stands for Material from Institute Lavoisier). The synthesized solid was heated to 200 °C for 6 hours under vacuum to remove the molecules of solvent (see Thermogravimetric analysis in Figure 2).

MIL-125-NH₂ is thermally robust. After the departure of the guest molecules below 200 °C, X-ray diffractometry does not indicate any change in crystallinity.

Nitrogen sorption experiments reveal that MIL-125-NH₂ is highly porous characteristic of microporous solids, a BET surface area of 1530 m²·g⁻¹, and a micropore volume (V_p) of 0.74(2) cm³·g⁻¹ (Figure 3)

TITANIUM (Compounds)

22-1070
(continued)

Hexakis[μ -(2-amino-1,4-benzenedicarboxylato)] [tetra- μ -hydroxyocta- μ -oxooctatitanium], NH2-MIL-125(Ti), AYRSORB™ T125 (1309760-94-8)

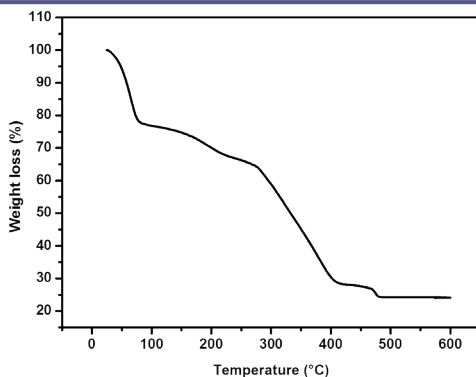


Figure 2: Thermogravimetric analysis

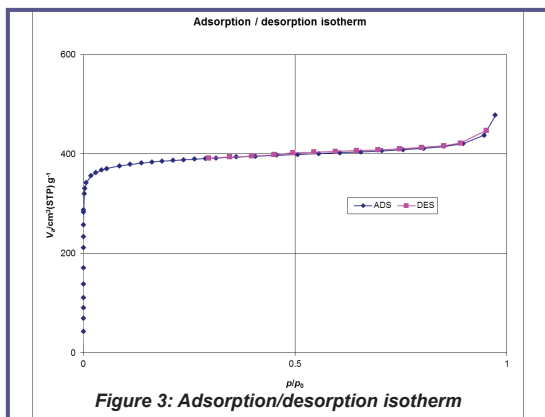


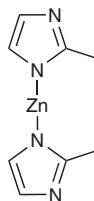
Figure 3: Adsorption/desorption isotherm

References:

1. A New Photoactive Crystalline Highly Porous Titanium(IV) Dicarboxylate, Meenakshi Dan-Hardi, Christian Serre, Theo Frot, Laurence Rozes, Guillaume Maurin, Clement Sanchez, and Gerard Ferey, *J. Am. Chem. Soc.*, **2009**, 131, 10857–10859.
2. A robust amino-functionalized Titanium (IV) based MOF for an improved separation of acid gases, Sébastien Vaesen, Vincent Guillermin, Qingyuan Yang, Andrew Wiersum, Bartosz Marszalek, Barbara Gil, Alexandre Vimont, Marco Daturi, Thomas Devic, Philip L. Llewellyn, Christian Serre, Guillaume Maurin and Guy De Weireld, *Chem. Commun.*, **2013**, 49, 10082-10084.
3. Adsorption/catalytic properties of MIL-125 and NH2-MIL-125, Se-Na Kim, Jun Kim, Hee-Young Kim, Hye-Young Cho, Wha-Seung Ahn, *Catalysis Today* **2013**, 204, 85–93.

ZINC (Compounds)

30-4015 **Zinc 2-methylimidazole MOF (ZIF-8) (59061-53-9)**
 HAZ $C_8H_{10}N_4Zn$; FW: 227.58; white solid; SA: 1813; P.Vol. 0.65



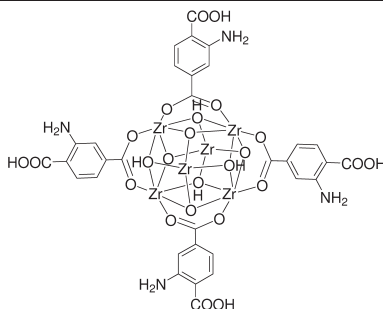
1g
5g

Technical Notes:

1. Use of ZIF-8 in the separation of alkanes, alkenes and aromatics
 - a. Separation of xylene isomers
Micropor. Mesopor. Mat., **2013**, 173, 1.
 - b. Separation of C6 Paraffins
Ind. Eng. Chem. Res., **2012**, 51, 4692.
 - c. Effective separation of propylene/propane binary mixtures
J. Membrane Sci., **2012**, 390-391, 93.
2. Use of ZIF-8 as a catalyst and catalyst-support
 - a. Catalytic activity of ZIF-8 in the synthesis of styrene carbonate
Chem. Commun., **2013**, 32, 36.
 - b. Iridium nanoparticles stabilized by metal organic frameworks: synthesis, structural properties and catalytic performance
Dalton Trans., **2012**, 41, 12690.
 - c. Zeolitic imidazole frameworks: Catalysts in the conversion of carbon dioxide to chloropropene carbonate
ACS Catalysis, **2012**, 2, 180.
 - d. Expanding applications of metal-organic frameworks: zeolite imidazolate framework ZIF-8 as an efficient heterogeneous catalyst for the Knoevenagel reaction
ACS Catalysis, **2011**, 1, 120.
3. Use of ZIF-8 in gas purification
 - a. MOF-containing mixed-matrix membranes for CO₂/CH₄ and CO₂/N₂ binary gas mixture separations
Sep. Purif. Technol., **2011**, 81, 31.
 - b. Porous polyethersulfone-supported Zeolitic Imidazolate Framework Membranes for hydrogen separation
J. Phys. Chem. C., **2012**, 116, 13264.

ZIRCONIUM (Compounds)

40-1109 **Zirconium aminobenzenedicarboxylate**
MOF (UiO-66-BDC-NH₂, BDC-NH₂:
Zr=0.9-1.0) (1260119-00-3)
 $Zr_6O_4(OH)_4(C_8H_5NO_4)_x$, X = 5.4-6.0;
 yellow solid; SA: 800-1075 m²/g;
 P.Vol. 0.31-0.41 cm³/g
 Note: Particle size: 0.1-0.5 micron,
 Thermal stability: 300°C, Activation
 temperature: 150°C
 Sold under license from Inven2 AS for
 research purposes only.
 PCT/GB2009/001087.



500mg
2g

Technical Notes:

1. Useful MOF for adsorption of CO₂ applications¹
2. Catalyst MOF used in the conversion of toxic agents to non-toxic products²

References:

1. *Carbon Dioxide Adsorption in Amine-Functionalized Mixed-Ligand Metal-Organic Frameworks of UiO-66 Topology.*, Chem.Sus.Chem. **2014**, 7, 3382-3388.
2. *Tailoring the Pore Size and Functionality of UiO-Type Metal-Organic Frameworks for Optimal Nerve Agent Destruction*, Inorg. Chem. **2015**, 54, 9684-9686.
3. *Towards Metal-Organic Framework based Field Effect Chemical Sensors: UiO-66-NH₂ for Nerve Agent Detection*, Chem. Sci., **2016**, 7, 5827.

ZIRCONIUM (Compounds)

40-1108

NEW

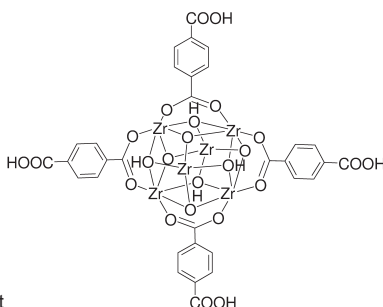
Zirconium benzenedicarboxylate MOF (UiO-66-BDC, BDC:Zr=0.66-0.98)

$Zr_6O_4(OH)_4(C_6H_4O_2)_x$, $X = 3.96-5.88$;
white solid; SA: 1050-1400 m²/g;
P.Vol. 0.42-0.58 cm³/g

Note: Particle size: 0.2-0.5 micron,
Thermal stability: 400°C, Activation
temperature: 300°C

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research purposes only.
PCT/GB2009/001087.

500mg
2g



Technical Note:

1. New zirconium-based inorganic building brick that allows the synthesis of very high surface area MOF's with unprecedented stability³

References:

1. *Tuned to Perfection: Ironing Out the Defects in Metal-Organic Framework UiO-66* Chem. Mater. **2014**, 26, 4068-4071.
2. *H₂ storage in isostructural UiO-67 and UiO-66 MOFs* Phys. Chem. Chem. Phys., **2012**, 14, 1614-1626.
3. *A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability*. J. Am. Chem. Soc. **2008**, 130, 13850-13851.

40-1112

NEW

Zirconium biphenyldicarboxylate MOF (UiO-66-BPDC/UiO-67, BPDC:Zr=0.9-1.0)

$Zr_6O_4(OH)_4(C_{12}H_8O_4)_x$, $X = 5.4-6.0$;
white solid; SA: 2400-2500 m²/g;
P.Vol. 0.85-0.98 cm³/g

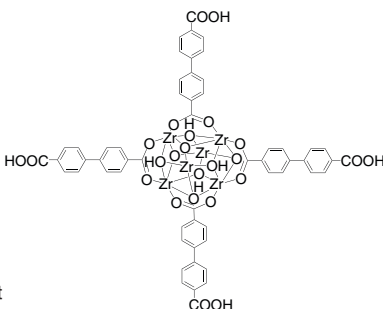
moisture sensitive

Note: Particle size: 0.4-0.7μ,

Thermal stability: 450°C

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research purposes only.
PCT/GB2009/001087.

250mg
1g



Technical Notes:

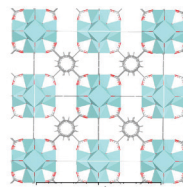
1. Metal-organic framework showing excellent stability to water, reversible water vapor adsorption, and increased volumetric capacity for methane adsorption¹
2. Remarkable stability at high temperatures, high pressures and in the presence of different solvents, acids and bases^{2,3}

References:

1. *UiO-67-type Metal-Organic Frameworks with Enhanced Water Stability and Methane Adsorption Capacity*, Inorg. Chem. **2016**, 55, 1986-1991.
2. *H₂ storage in isostructural UiO-67 and UiO-66 MOFs*, Phys. Chem. Chem. Phys., **2012**, 14, 1614-1626.
3. *A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability*. J. Am. Chem. Soc. **2008**, 130, 13850-13851.

ZIRCONIUM (Compounds)

40-1105 Zirconium 1,4-dicarboxybenzene MOF (UiO-66, BDC:Zr=1) (1072413-89-8)
 $C_{48}H_{28}O_{32}Zr_6$; FW: 1664.06; white powdr.;
 SA: 1180-1240m²/g; P.Vol. 0.45-0.48
 Note: Particle size: 0.2-0.5 micron, Thermal stability:
 400°C, Activation temperature: 300°C
 Sold under license from Inven2 AS for research
 purposes only. EP 09738396 and US 12/989,64

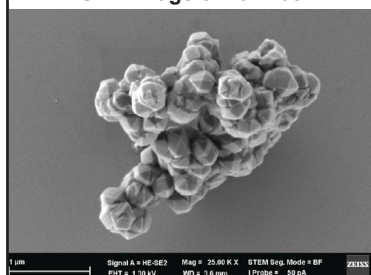


500mg
2g

The Special Nature of UiO-66

The stability of MOFs is largely determined by the structure of the inorganic brick and the nature of the chemical bonds it forms with the linker. To date, most MOFs have exhibited weak thermal, chemical, and mechanical stability, which has limited their use in large-scale industrial applications.

SEM image of 40-1105



UiO-66 (and isorecticular UiO-67 and UiO-68), however, is a zirconium-based MOF with very high surface area (1180-1240 m²/g) and unprecedented stability.

Developed by Prof. Karl Petter Lillerud of the Department of Chemistry at the University of Oslo, UiO-66 is comprised of $Zr_6O_4(OH)_4$ octahedra that are 12-fold connected to adjacent octahedra through a 1,4-benzenedicarboxylate (BDC) linker, resulting in a highly packed fcc structure.

The Zr-O bonds formed between the cluster and carboxylate ligands is believed to be the source of increased stability of Zr-based MOFs. Specifically, the combination of strong Zr-O bonds and the ability of the inner Zr_6 -cluster to rearrange reversibly upon removal or addition of μ_3 -OH groups without any changes in the connecting carboxylates are thought to contribute to the greater stability of UiO-66.

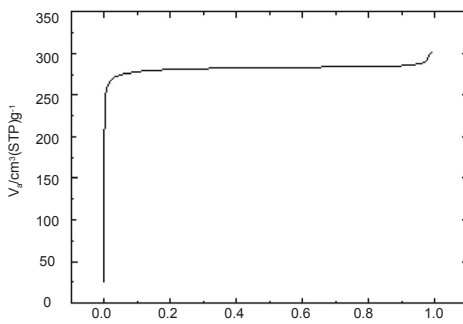
Key Properties of UiO-66

- The particle size of UiO-66 is 0.25-0.35µm, and the particles have clearly visible facets.
- The specific surface area of UiO-66 after heating to 300 °C is 1147 m²/g.
- The pore size of the UiO-66 is 6 Å. That means that a molecule the size of fully methylated benzene can enter the UiO-66 structure.
- The toughness of UiO-66 is demonstrated in its physical properties:
 - Stable upon washing in boiling water and after heating in air to 300 °C for 6h
 - Decomposition above 500 °C
 - Resistance to most chemicals
 - Retention of crystallinity even after exposure to 10 tons/cm² of external pressure.

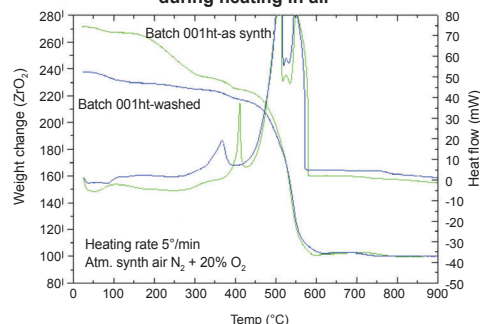
References:

1. *J. Am. Chem. Soc.*, **2008**, 130, 13850.
2. *J. Phys. Chem. Lett.*, **2013**, 4(6), 925.
3. *Chemistry – An Asian Journal* **2011**, 6(12), 3270.
4. *Chem. Mater.*, **2011**, 23 (7), 1700.

UiO-66 N₂ adsorption at 77K



Thermogravimetric response of UiO-66 during heating in air



ZIRCONIUM (Compounds)

40-1114

NEW

Zirconium Fumarate MOF

(UiO-66-FA, FA:Zr=0.66-0.98)

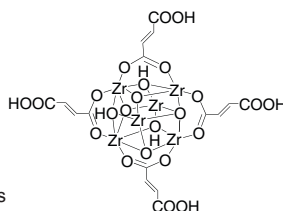
$Zr_6O_4(OH)_4(C_4H_2O_4)_x$, $X = 3.96-5.88$;

white solid; SA: 650-960 m²/g;

P.Vol. 0.26-0.4 cm³/g

Note: Particle size: 0.1-0.5 micron, Thermal stability: 200°C, Activation temperature: 130°C
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500mg
2g



Technical Notes:

1. Metalorganic framework used in a large number of studies for the storage of hydrogen or methane²
2. Water adsorption in MOF's for many applications such as dehumidification, thermal batteries, and delivery of drinking water in remote areas³

References:

1. *Water harvesting from air with metal-organic frameworks powered by natural sunlight.* Science, **2017**, 356, 430-434.
2. *A Facile "Green" Route for Scalable Batch Production and Continuous Synthesis of Zirconium MOFs.* Eur. J. Inorg. Chem. **2016**, 4490-4498.
3. *Water Adsorption in Porous Metal-Organic Frameworks and Related Materials,* J. Am. Chem. Soc., **2014**, 136, 4369-4381.
4. *A water-born Zr-based porous coordination polymer: Modulated synthesis of Zr-fumarate MOF.* Microporous and mesoporous materials , **2015**, 203,186-194.

40-1106

NEW

Zirconium trans-1, 2-ethylenedicarboxylic acid MOF (UiO-66-FA, FA:Zr=1)

$Zr_6O_4(OH)_4(C_2H_2O_4)_6$; cream solid;

SA: 720-770 m²/g; P.Vol. 0.29-0.32 cm³/g

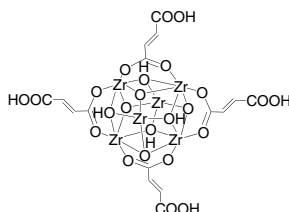
Note: Particle size: 0.1-0.5 micron,

Thermal stability: 200°C,

Activation temperature: 150°C

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500mg
2g



Technical Notes:

1. Metalorganic framework used in a large number of studies for the storage of hydrogen or methane²
2. Water adsorption in MOF's for many applications such as dehumidification, thermal batteries, and delivery of drinking water in remote areas³

References:

1. *Water harvesting from air with metal-organic frameworks powered by natural sunlight.* Science, **2017**, 356, 430-434.
2. *A Facile "Green" Route for Scalable Batch Production and Continuous Synthesis of Zirconium MOFs.* Eur. J. Inorg. Chem. **2016**, 4490-4498.
3. *Water Adsorption in Porous Metal-Organic Frameworks and Related Materials,* J. Am. Chem. Soc., **2014**, 136, 4369-4381.
4. *A water-born Zr-based porous coordination polymer: Modulated synthesis of Zr-fumarate MOF.* Microporous and mesoporous materials , **2015**, 203,186-194.

ZIRCONIUM (Compounds)

40-1111

NEW

Zirconium trimellitate MOF (UiO-66-BDC-COOH, BDC-COOH:Zr=0.9-1.0)

$Zr_6O_4(OH)_4(C_6H_4O_6)_x$, X = 5.4-6.0;

white solid; SA: 550-600 m²/g;

P.Vol. 0.25-0.27 cm³/g

Note: Particle size: 0.2-0.5 micron,

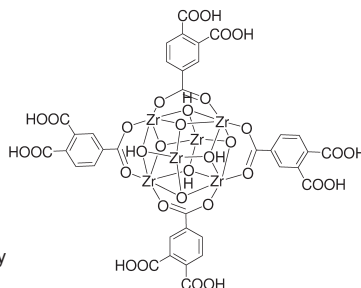
Thermal stability: 350°C,

Activation temperature: 150°C

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PCT/GB2009/001087.

500mg
2g



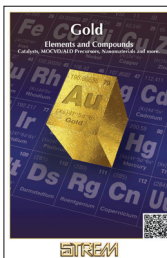
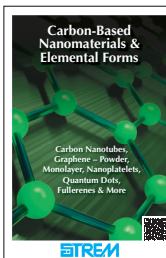
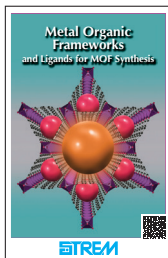
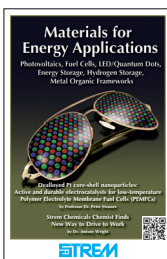
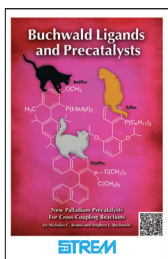
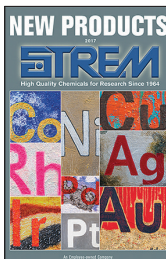
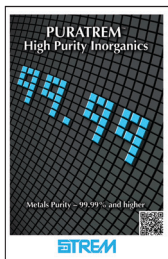
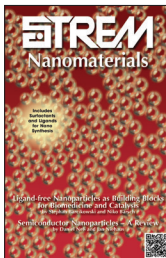
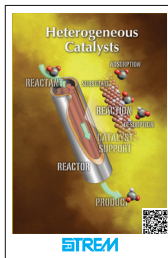
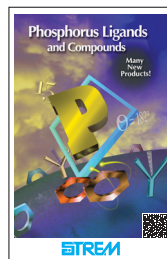
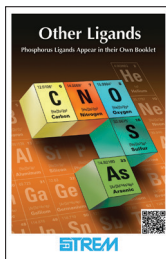
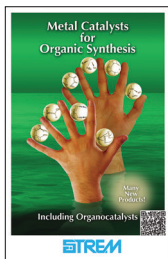
Technical Notes:

1. MOF for which the introduction of copper markedly increases ammonia adsorption capacities¹
2. Functionalized forms show the highest selectivity, good working capacity and medium ranged CO₂ adsorption enthalpy that make these materials very promising for physi-sorption-based processes²

References:

1. *Engineering Copper Carboxylate Functionalities on Water Stable Metal–Organic Frameworks for Enhancement of Ammonia Removal Capacities.* J. Phys. Chem. C, **2017**, 121, 3310–3319.
2. *Functionalizing porous zirconium terephthalate UiO-66(Zr) for natural gas upgrading: a computational exploration.*, Chem. Commun., **2011**, 47, 9603–9605.

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Strem Chemicals, Inc.

15, rue de l'Atome
Zone Industrielle
F-67800 BISCHHEIM (France)
Tel.: +33 (0) 3 88 62 52 60
Fax: +33 (0) 3 88 62 26 81
Email: info.europe@strem.com

Strem Chemicals, Inc.

Postfach 1215
D-77672 KEHL, Germany
Tel.: +49 (0) 7851 75879
Fax: +33 (0) 3 88 62 26 81
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