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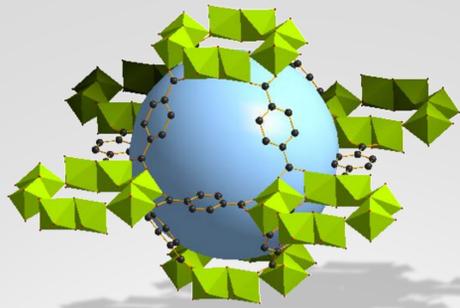
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Introduction

So far, the synthesis of porous MOFs has been focused mainly on the use of divalent or trivalent cations. Recently, the first porous zirconium^{IV} and titanium^{IV} dicarboxylates have been reported,¹ with both high thermal stabilities and large specific surface areas. Besides, the water stability of MOFs is of a crucial importance with most M(II) based carboxylates unstable under moisture while most trivalent metal-based carboxylates exhibit a significantly higher stability under similar conditions.² Therefore, this would be a of great interest to discover new porous metal^{IV} carboxylates MOFs in order to obtain porous hybrid solids with a high degree of chemical stability.

Photochromism of MIL-125(Ti)

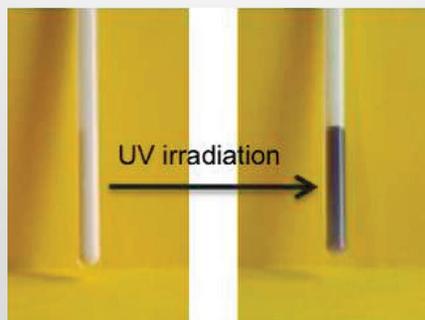


View of the octahedral cage of MIL-125

The first highly crystalline and porous titanium dicarboxylate has been recently reported, exhibiting a high specific surface area ($S_{\text{BET}}=1550(2)\text{m}^2\cdot\text{g}^{-1}$), with large octahedral and tetrahedral cages.

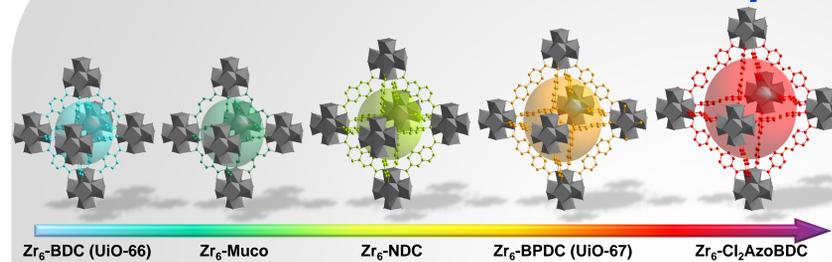
As expected, this titanium terephthalate possesses not only a high thermal stability (>300°C), but also exhibit interesting photochromism properties.

When alcohols (R-OH) such as methanol, ethanol, and benzylalcohols are adsorbed inside the MIL-125 framework in the absence of oxygen, a fast photochromic effect is observed upon UV-visible excitation. The light irradiation changes the color of the materials from white to purple-gray-blue within a few seconds. After a few minutes, an intense gray-blue color is observed.



View of MIL-125 in a capillary filled with benzyl alcohol before and after UV irradiation

Zr-MOFs with UiO-66 extended topology

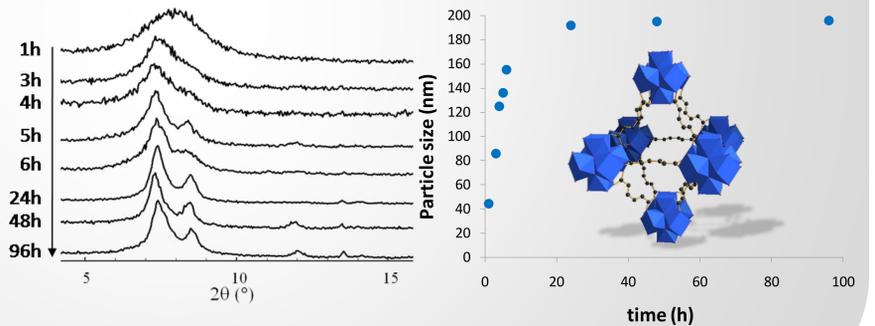


View of the octahedral cages of MOFs with the UiO-66 topology (scale chemistry)

The recently reported series of isorecticular MOFs built up from "Zr₆" zirconium oxoclusters building units and dicarboxylate moieties has been extended by the use of other linkers (muconic acid, naphthalene dicarboxylic acid, azobenzene dicarboxylic acid),³ of different lengths.

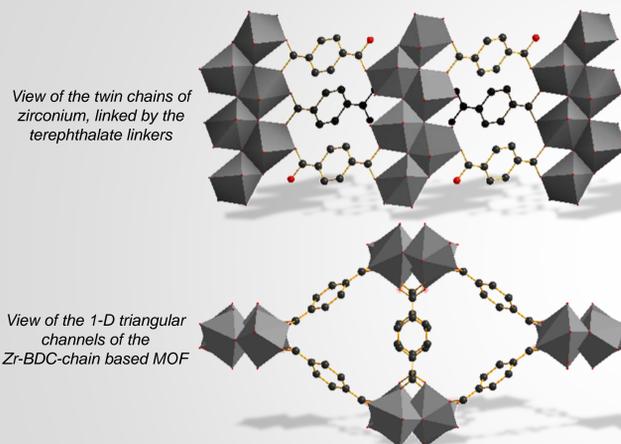
We have also shown recently that the use of a preformed Zr₆ oxocluster⁴ allows the low temperature synthesis of the Zr₆-muconate solid together with a control of the size of the nanoparticles, in agreement with the Sherrer equation, which paves the way for future thin films applications.⁵

linker	Space Group	a (Å)	V (Å ³)
BDC	Fm -3 m	20.76(10)	8946.6(8)
Muconic	Fm -3 m	20.82(10)	9022.6(8)
NDC	Pn -3 m	24.18(10)	14137.4(1)
BPDC	F 2 3	27.10(10)	19906.9(0)
Cl ₂ AzoBDC	P 2 3	29.91(10)	26760.4(1)



Evolution of the XRPD patterns (left) and the particle size (right) of the Zr₆-muconate MOF, depending on the synthesis time

Zr-MOFs with 1-D inorganic sub-network

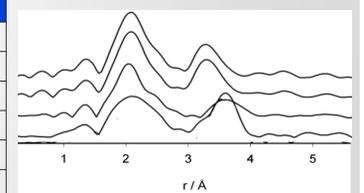


View of the twin chains of zirconium, linked by the terephthalate linkers

View of the 1-D triangular channels of the Zr-BDC-chain based MOF

A new series of isorecticular Zr-MOFs built up from 1D inorganic complex Zr oxide chains and dicarboxylate linkers, has been isolated under solvothermal conditions and their structures either solved from X-ray powder diffraction data or obtained from a combination of experimental cell parameters and computer simulation. The 1D inorganic chains, built up from seven coordinated Zr polyhedra, are related together along the a and b axis via the dicarboxylates which results in a 1D network of triangular pores ($\phi \sim 4\text{-}10\text{Å}$).

linker	Phase type	Zr-Zr distance (Å)
BDC	Zr ₆	3.53*
NDC	Zr ₆	3.48*
BPDC	Zr ₆	3.52 ± 0.04
BDC	Chains	3.30 ± 0.03
NDC	Chains	3.30 ± 0.03
SBU	Zr ₆	3.53 ± 0.04

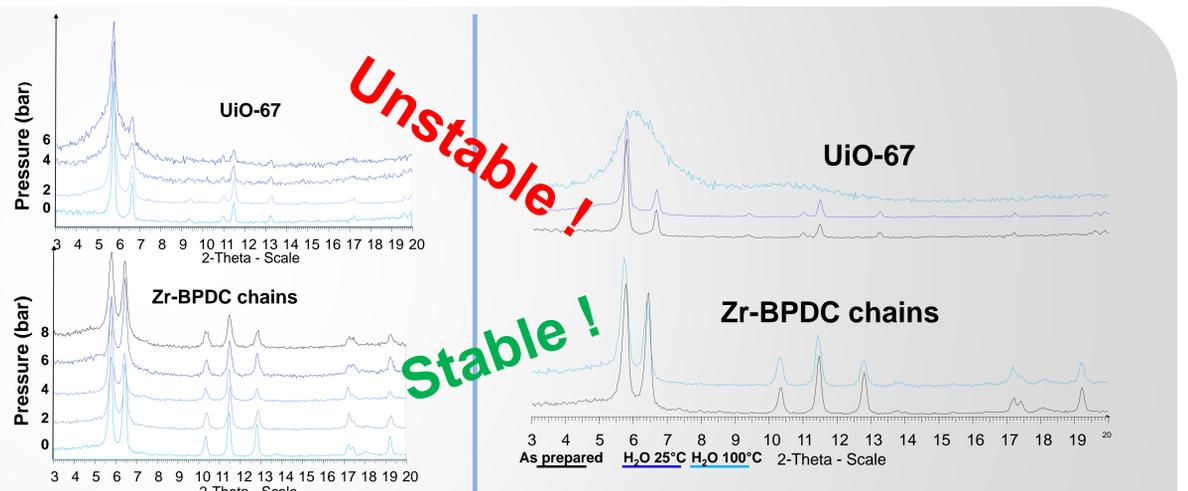


EXAFS data are in agreement with the crystal structures with Zr-Zr distance of ~3.30 Å, different from those observed within the Zr₆ phases (~3.50 Å)

Mechanical and hydrothermal stabilities

Mechanical stability of the two types of Zr solids has been assessed using a IR press. The sample has then analyzed by powder XRPD. It appears clearly that chain-based MOFs, which are denser phases than the Zr₆-based MOFs, exhibit a higher mechanical stability, particularly for the larger analogues.

Hydrothermal tests lead to the same conclusion: If the smaller Zr₆ solid UiO-66, is hydrothermally stable,¹ this is not the case for its larger analogues (UiO-67...) ! On the contrary, all chain-based MOFs are hydrothermally stable, whatever the size of the linker !⁶



References

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Conclusion

We have reported here new Zr carboxylate solids of the UiO-66 topology, a new series of isorecticular zirconium^{IV} dicarboxylates porous solids, as well as the first porous crystalline titanium dicarboxylate. These materials exhibit both high surface areas and a high thermal stability. While the Ti solid exhibits photochromic properties under UV irradiation, some Zr-based solids possess interesting mechanical and hydrothermal stabilities, particularly for the Zr chains based solids. This paves the way for new applications in separation and catalysis.