Water stable Cu(II)-based porous Metal-Organic materials for CO_2 capture and environmentally application

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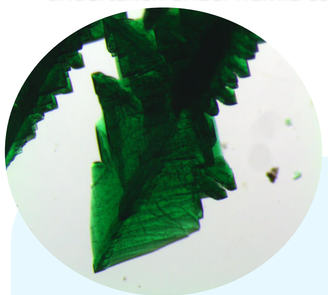
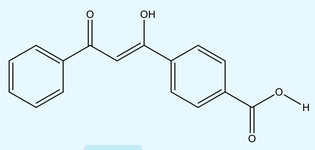
In the context of the ongoing climate emergency, the study of porous materials takes on a crucial role in addressing environmental challenges. In this respect, the storage and release of different molecules in a controlled manner could be considered one of the most important applications of metal-organic porous materials.[1], [2] In our attempt to obtain new Cu(II)-based porous metal-organic materials, we exploited the use of β-diketone ligands featuring functional groups with N- and O-donor atoms. In particular, reacting the asymmetric β-diketone/carboxylic ligand 1-(4-carboxyphenyl)-3-phenyl-1,3-propanedione) (H_2**^{1}L**) [3] with copper acetate we obtained three isostructural Metal-Organic Cages (MOCs) of general formula $[Cu_{16}(^1L)_{16}(A)_n(B)_8](S)_x$ [A= THF (tetrahydrofuran), n=8, B=H_2O (**1**); A=diox (dioxane), n=4, B=H_2O (**2**); A = B = dme (dimethoxyethane), n=8 (**3**). Interestingly, the cages demonstrated remarkable stability in water, and preliminary investigations of their host-guest chemistry indicate that coordinated tetrahydrofuran (THF) molecules in compound **1** can be completely replaced by organic ether molecules. This intriguing behavior is currently being studied for its potential in removing organic pollutants from water. Furthermore, we present findings on the water and CO2 adsorption capabilities of the third-generation water-stable metal-organic framework (MOF) $[Cu(^2L)(H_2O)_2]_2\cdot(X_n)$ (**4**) (H²L = 1,3-Bis(4-pyridyl)-1,3-propanedione; X=F^-, Cl^-, Br^-, NO_3^-, BF_4^-, $SO_3CF_3^-$, n=2; X=SO_4^{2-}, n=1). The structure boasts a remarkable 70% of unoccupied space. Notably, it has been observed that the desolvated-amorphous phase of compound **4** can reversibly adsorb significant quantities of water over multiple cycles (at least five). Moreover, CO_2 adsorption experiments have unveiled that while minimal gas uptake occurs under dry conditions, the uptake of CO2 experiences a substantial increase when undertaken under humid conditions.



Metal-Organic Cages (MOCs)

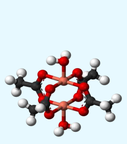
$[Cu_{16}(L)_{16}(A)_n(B)_8](S)_x$

The ligand

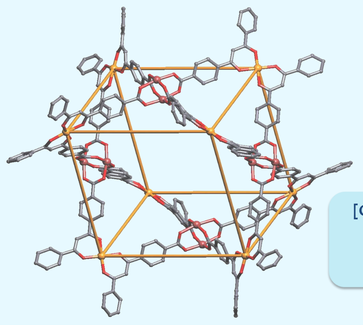


$H_2{}^1L$

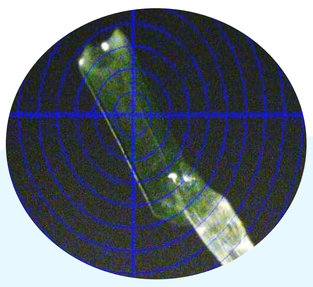
Synthesis and crystallization by slow diffusion



$Cu(OAc)_2\cdot 2H_2O$ + H_2L



$[Cu_{16}(L)_{16}(A)_n(B)_8](S)_x$
A= THF, n=8, B=H_2O (1)
A=diox, n=4, B=H_2O (2)
A = B = dme, n=8 (3)
S=CH_3CN

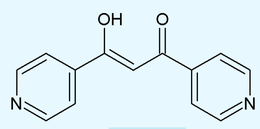


Metal-Organic Frameworks (MOFs)

$[Cu(L_2)(H_2O)_2]_2X_n$ (X=F, Cl, Br, NO_3, BF_4, SO_3CF_3 n=2; X=SO_4, n=1)

A new family of porous copper 3D networks

The ligand



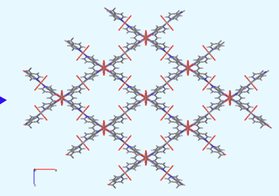
H^2L

Synthesis and crystallization

CuX_n + H^2L

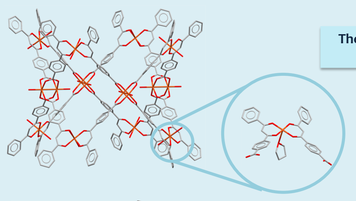
Crystallization by slow diffusion

Bulk synthesis in water (heterogeneous phases)



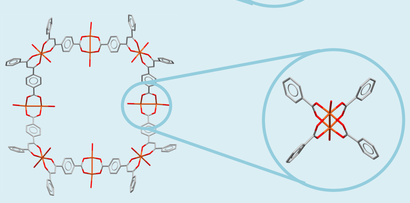
Single 3D network of lvt topology

Structural analysis



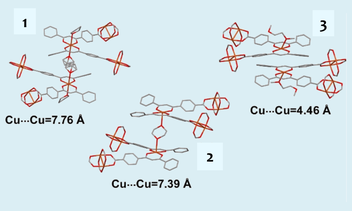
The cube vertices
$[Cu(L)_2(A)]$

The bis-chelate Cu(II) centers coordinate a solvent molecule (THF or diox or dme).



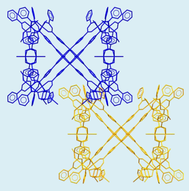
Four faces are centered by paddle-wheels
$[Cu_2(\mu_2\text{-}L)_4(B)_2]$

Two water molecules (in 1 and 2) or two dme molecules (in 3) are coordinated on the paddle-wheel units

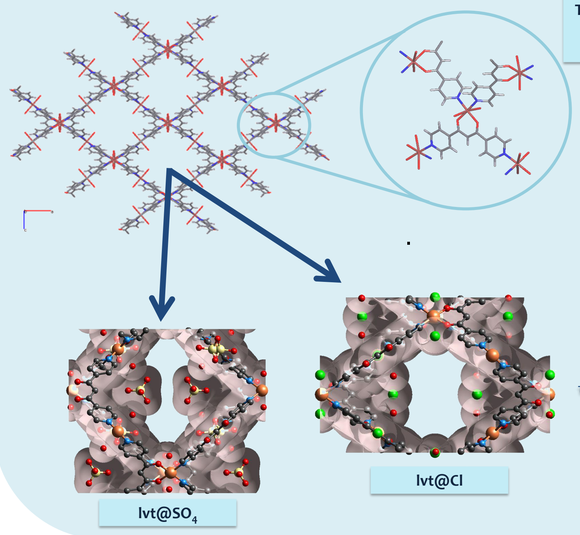


The different solvent molecules affect the packing by controlling the distance between adjacent cages

Packing

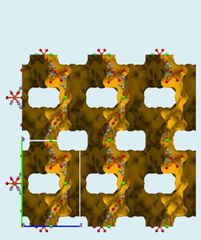


Structural analysis



The 4-conn node of lvt network

lvt@SO_4
VOID 66,7 %
Tetragonal (I-42d)
a = *b* = 21.391 Å
c = 17.812 Å
V= 8150.32 Å³



The different nature of counterions affect the channel shape

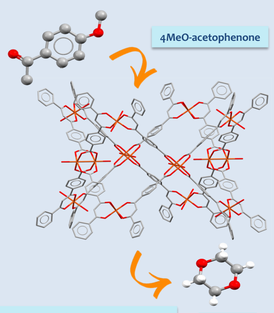
lvt@Cl
VOID 62,5 %
Tetragonal (I-42d)
a = *b* = 22.435 Å
c = 15.154 Å
V= 7627.45 Å³

lvt@SO_4

lvt@Cl

NMR experiment

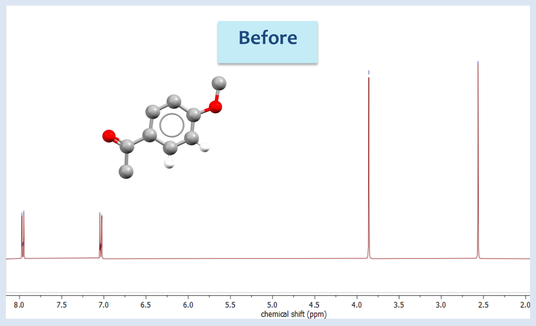
Host-Guest Chemistry



4MeO-acetophenone

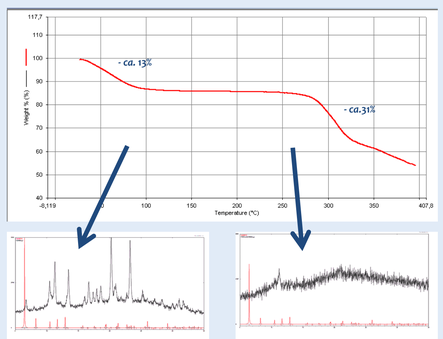
Compound **2** in water interacting with 4MeO-acetophenone

dioxane



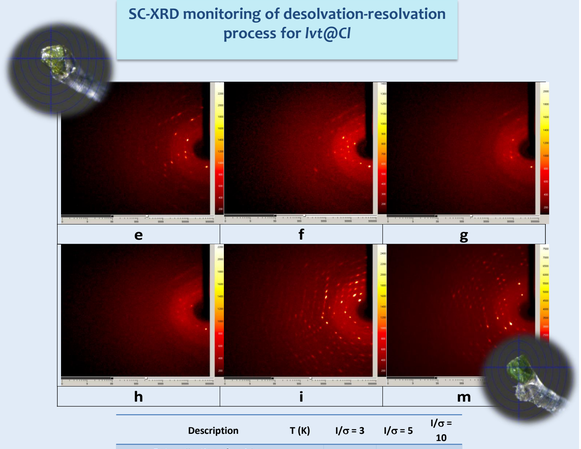
^{1}H-NMR analysis revealed that cage 2 exchange quantitatively 1 mmol of dioxane with 1 mmol of the guest, reaching the equilibrium in four days

Thermal behavior of lvt@SO_4



The monitoring of desolvation process by XRPD shows that the process is accompanied by a loss of crystallinity. The crystallinity is recovered if the amorphous material is re-exposed to water vapours or left in the ambient for a night.

SC-XRD monitoring of desolvation-resolvation process for *lvt@Cl*



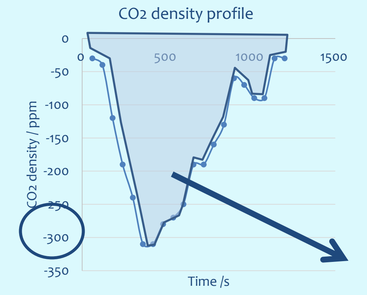
	Description	T (K)	I/σ = 3	I/σ = 5	I/σ = 10
e	Data collection after 1 hour at 303 K	303 K	95	62	23
f	After 30 minutes at 323 K	323 K	44	25	10
g	After another 1 hour at 323 K	323 K	17	6	3
h	After 1 hour at 100 K	100 K	12	6	3
i	After 4,5 days exposure to water vapor	100 K	305	215	115
m	After 1 day at T_{amb}	T_{amb}	112	168	58

CO_2 adsorption under dry and humid conditions for lvt@SO_4

Sample preparation

Cu compound: approximately 2 g
CO_2+ N_2 flow gas (approximately 10 mL/min)
Temperature: r.t.
Pretreatment condition 373 K, 2h under N_2 flow
1. Without H_2O vapor
2. With H_2O vapor (gas bubbling)

CO2 density profile

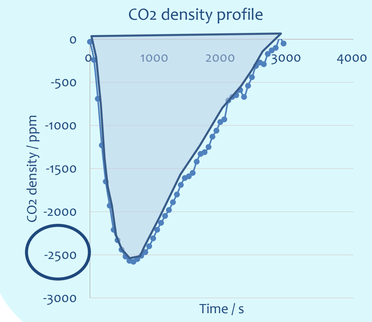


Dry conditions

Tentative adsorbed amount 0.020 mg/g

Adsorbed area

CO2 density profile



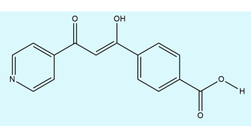
Humid conditions

Tentative adsorbed amount 0.25 mg/g

Future perspective

To improve the crystal structure stability

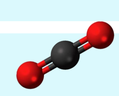
- The crystallization of the cages in the presence of different spacers is under investigation to strenghten their interaction and improve the stability upon desolvation.
- Gel-crystallization
- Design of derivatives of $H_2{}^1L$ in which the phenyl group is substitued by a pyridine or a methyl fragments.
- Explore the reactivity of $H_2{}^1L$ with different metals



To deeply investigate the host-guest chemistry and the porosity of the cages

- ^{1}H NMR and UV-Vis monitoring in water of organic molecules capture (e.g. organic pollutants, drugs, dyes, essential oils)
- Gas adsorption measurements

Future perspective



- Optimization of the bulk synthesis of the lvt MOF with different anions
- Water and CO2 adsorption of other members of the isoreticular series of lvt MOF

References

[1] J. Yu, L. H. Xie, J. R. Li, Y. Ma, J. M. Seminario, and P. B. Balbuena, *Chem Rev*, **2017**, 117, 9674.
[2] S. Rojas and P. Horcajada, *Chem Rev*, **2020**, 120, 8378.
[3] J. Zawadiak, J. Zawadiak, M. Mrzyczek, and T. Piotrowski, *European Journal of Chemistry*, **2011**, 3, 289.

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