Preparation and characterisation of new metal-organic frameworks

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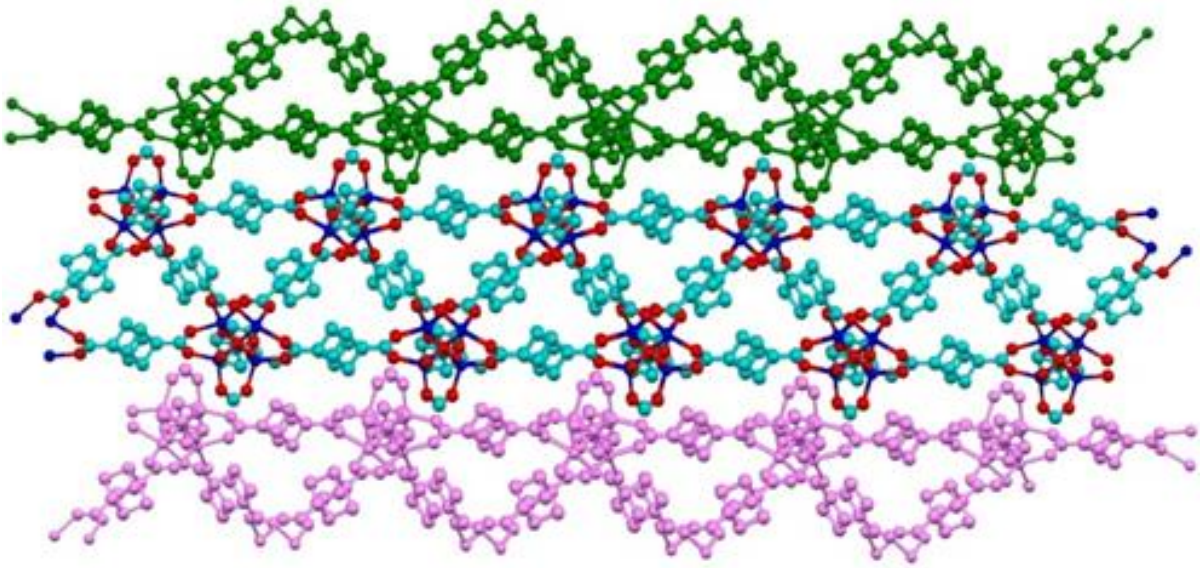
Outline

- Metal-Organic Frameworks
- Terms of reticular chemistry
- Results of the recent 3 years
- Discussion of new MOF-5 analogue structure with cubane
- Future plans



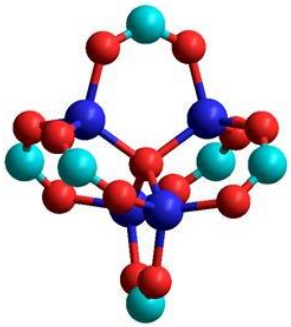
Metal-organic frameworks (MOFs)

- Porous coordination polymers with crosslinks (2D and 3D polymers)
- Microporous materials with exceptional high porosity → high surface area
- Gas storage, heterogenous catalysis, molecular sensing, separation...
- Crystalline frameworks with two unique structural units:

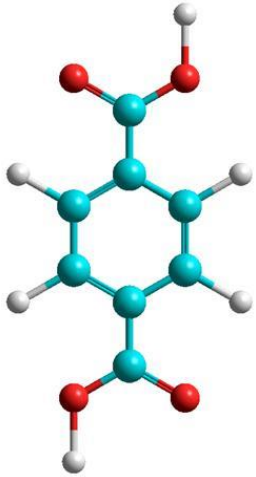
  Rigid, inorganic metal-containing clusters at the nodes (Inorganic Secondary Building Units, SBUs)

  Organic linkers join the SBUs

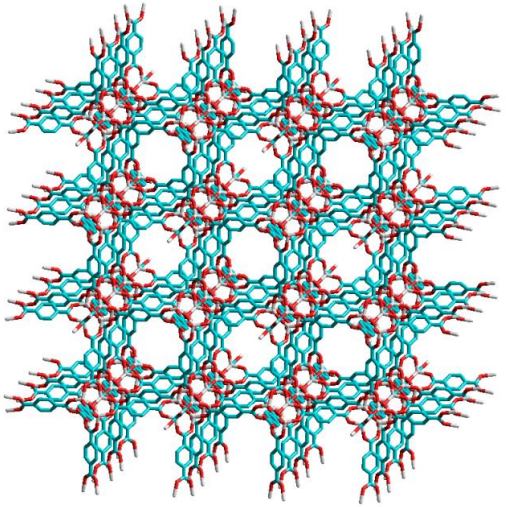
- Strong metal-ligand bonding → high thermal stability → easy-to-activate structures



$Zn_4O(CO_2)_6$

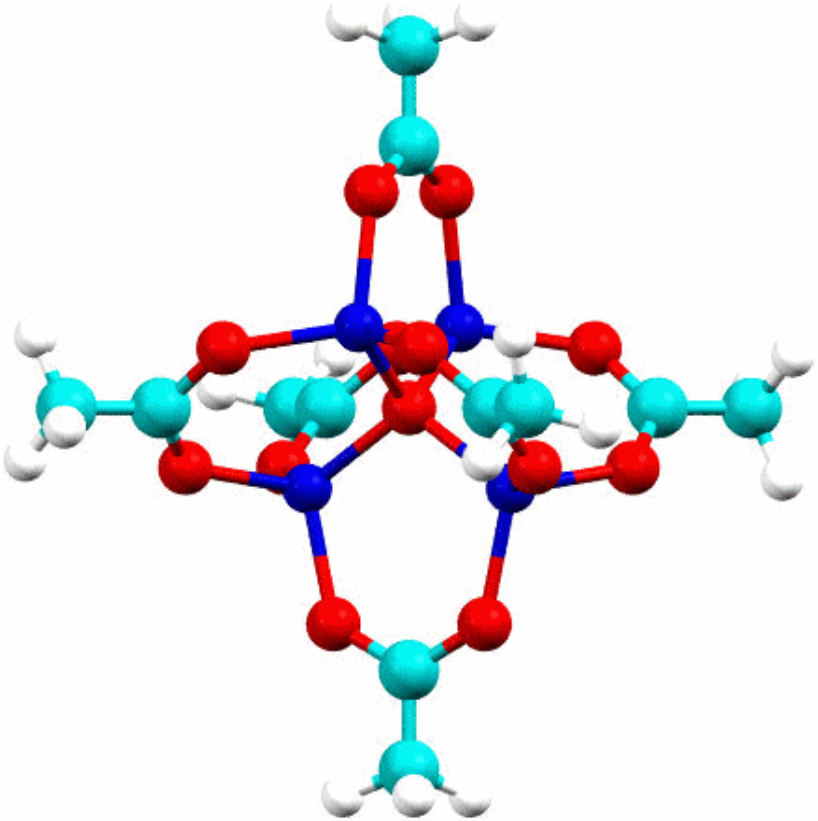


Terephtalic acid

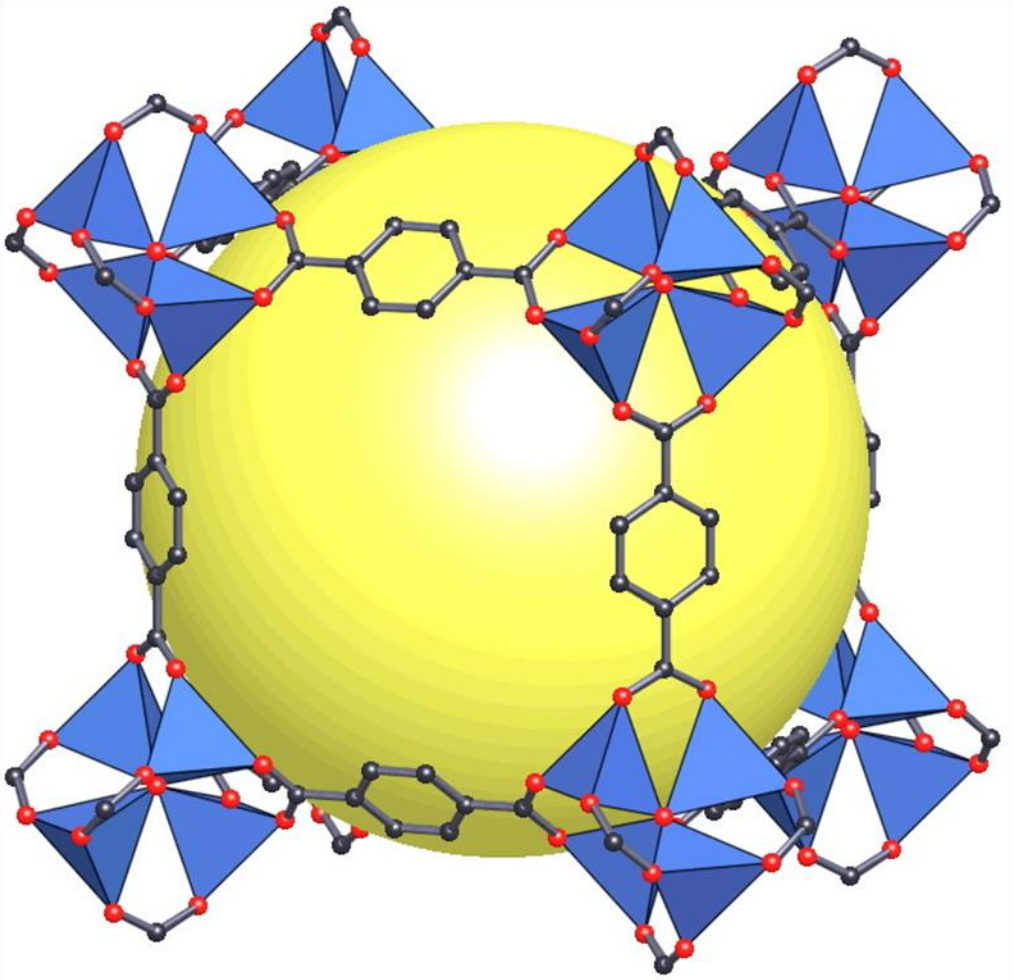


Porous structure of MOF-5

Basic zinc acetate



The structure of MOF-5



79 % void volume → H_2 storage (10 wt. % on 77 K and 100 bars)

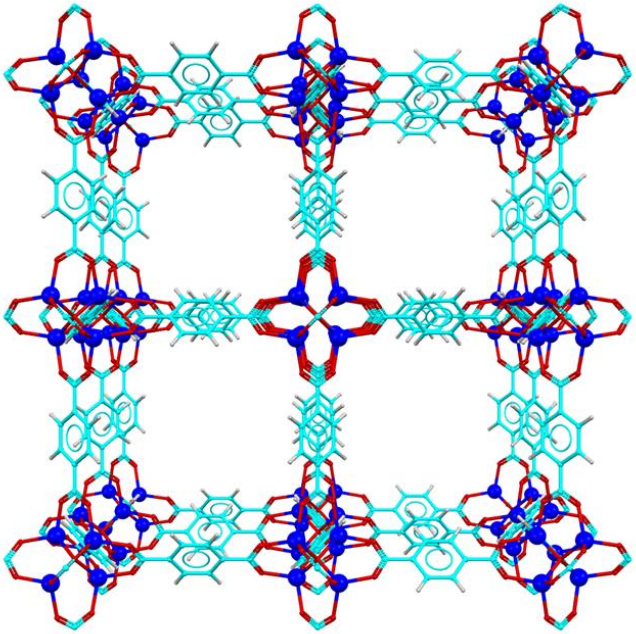
S_{BET}=3800 m^2g^{-1}

H. Li, M. Eddaoudi, M. O'Keeffee, O.M. Yaghi, *Nature*, 402, 276-279 (1999)

Reticular chemistry

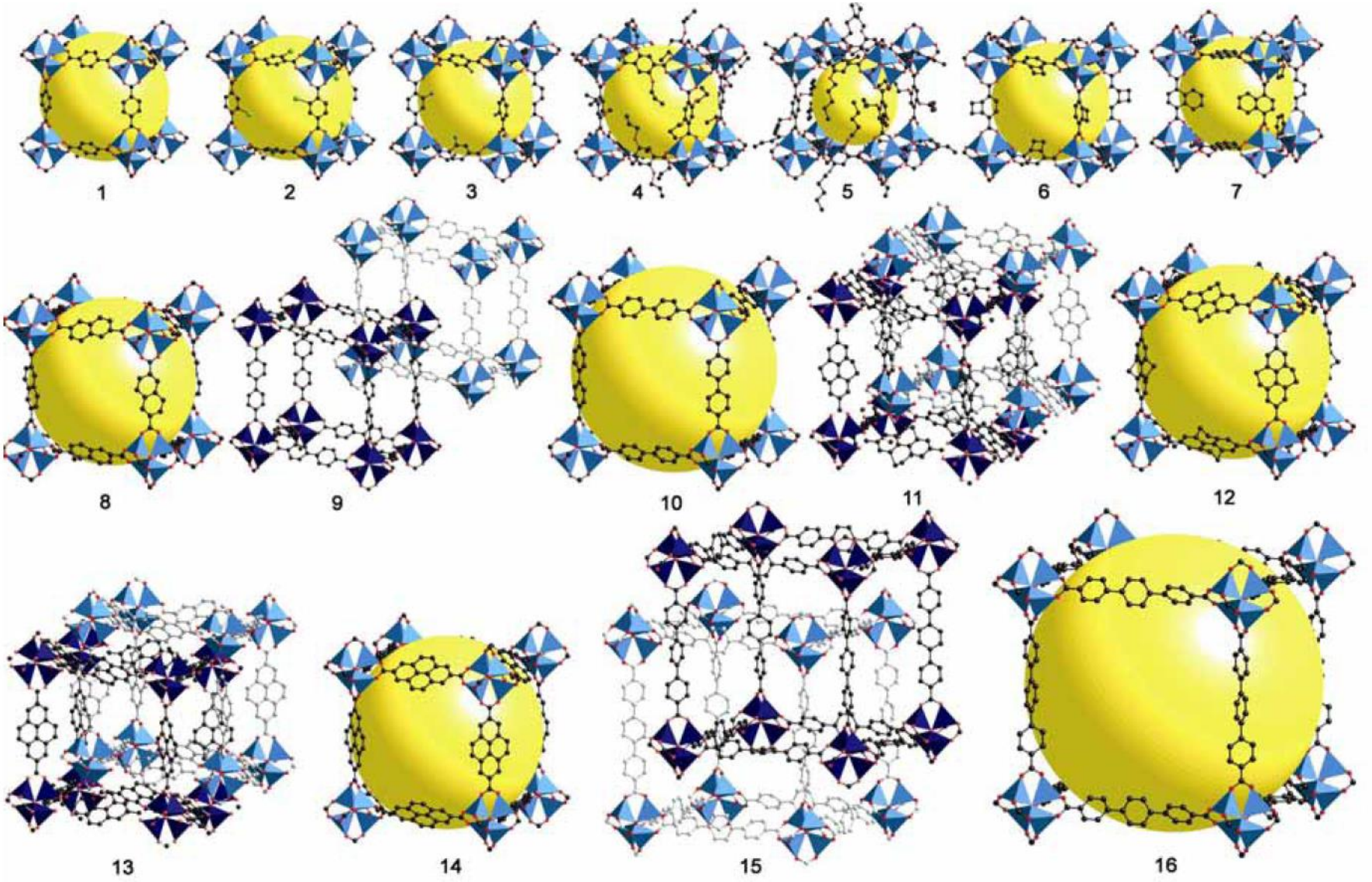
- Based on topology design of new metal-organic frameworks
- Topology is invariant to bending, stretching, squeezing, but not to bond breaking
- Simplified underlying network:
  - ➢ Deconstruction: SBUs with *n* points of extension → *n* coordinated atoms

    Organic spacers → single edges (single bonds)
- Isoreticular structures: framework structures with same underlying network topology



M. O'Keeffee, O.M. Yaghi, *Chem. Rev.,* 112 (2), pp 675–702 (2012)

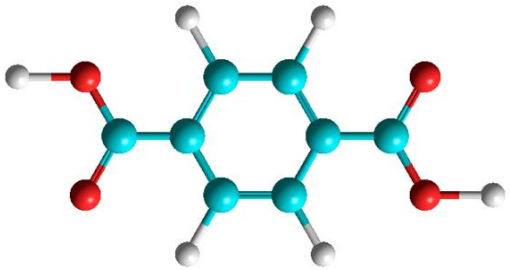
The IRMOF family



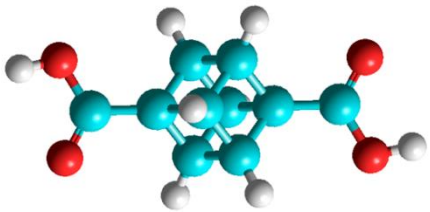
M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science*, 295, 469-472 (2002)

Goal of PhD work

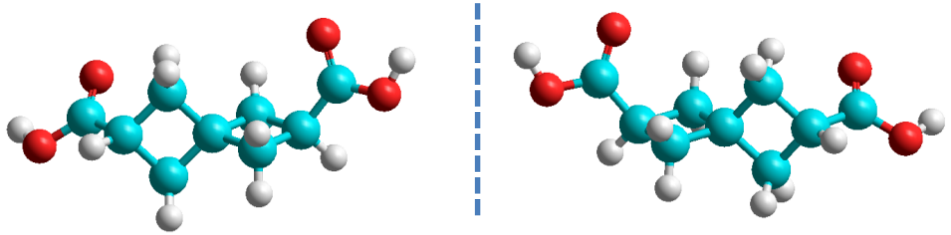
- **Preparation of new MOF structures** by using various organic linkers, and zinc-containing SBUs
- Preparation of new IRMOF structures by using non-aromatic dicarboxylic acids
- Similar size → different gas adsorption?
- Molecular dinamics



Terephtalic acid

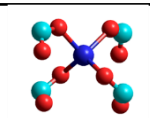
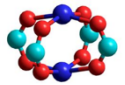
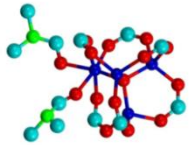
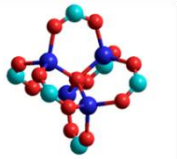
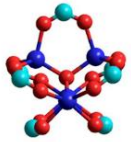
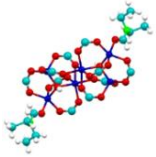


Cubane-1,4-dicarboxylic acid

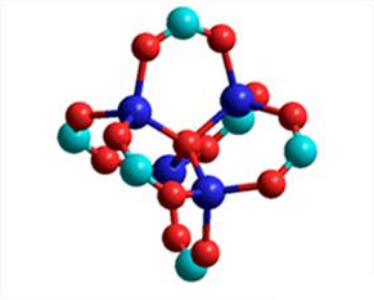


Stereoisomers of spiro[3.3]heptane-2,6-dicarboxylic acid (Fecht's acid)

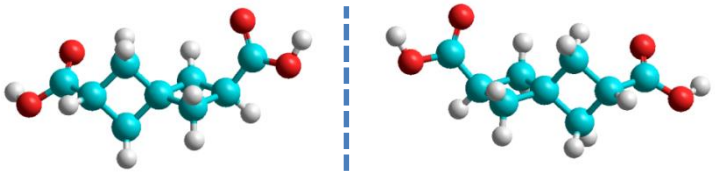
Results I.
New MOF structures with cubane-1,4-dicarboxylic acid

Sample	Solvent	Synthetic conditions	Result	SBU
FD90	DMF	DABCO, 120°C, 2 days	New MOF, mononuclear, interpenetrated anionic framework	
FD80	NMP	105°C, 60 hours	New crystal structure, planar MOF with paddlewheel-like binuclear SBUs	
FD130	DMF	100 °C 60 hours	New MOF, distorted MOF-5 analogue	
FD138	DMF	140 °C, 60 hours		
FD149	DMF	100 °C, 22 hours	New MOF, high simmetry, cubic MOF-5 analogue	
FD137	NMP	105 °C, 60 hours		
FD84	DEF	105 °C, 6 days	New MOF structure, tetranuclear „double-layer” structure	
FD143	DEF	140 °C, 60 hours	New MOF structure, new hexanuclear SBU	

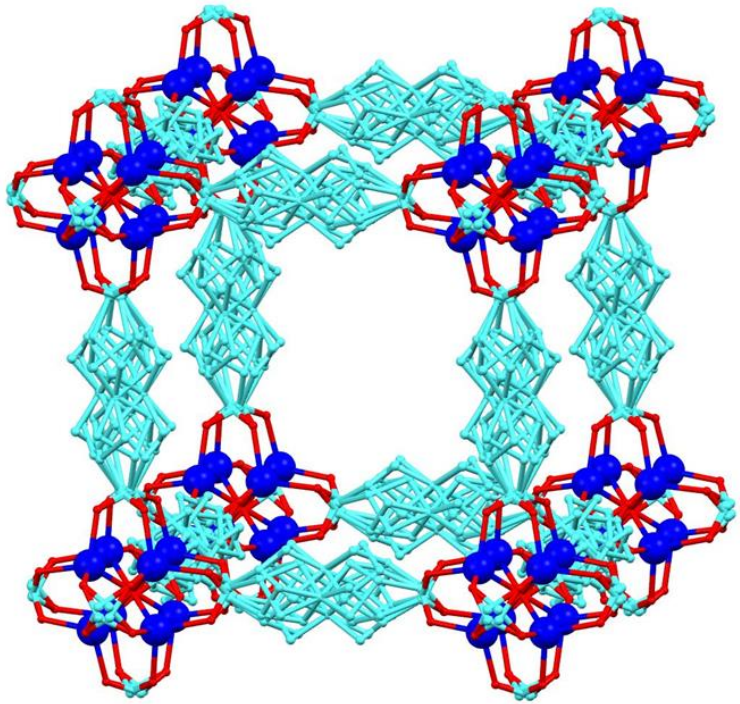
Results II.
MOF-5 structure with Fecht's acid

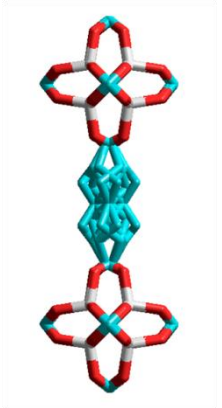


$Zn_4O(CO_2)_6$



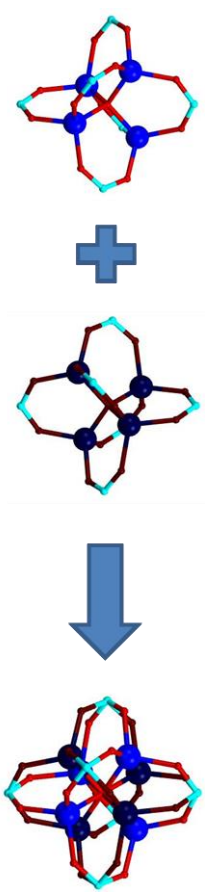
$Zn(NO_3)_2 \cdot 6H_2O$, DMF/toluene (1:1), TEA/toluene (vapour diffusion), R.T.



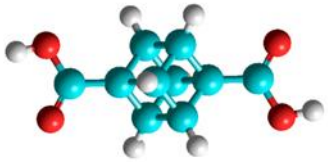


Two enantiomers,
8 position

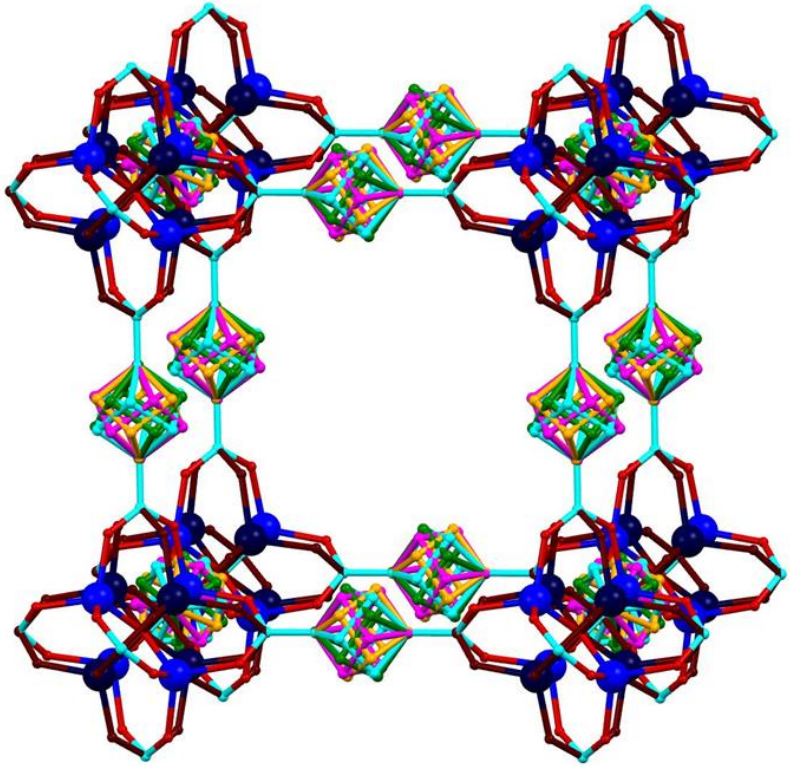
MOF-5 analogue with cubane



Superpostion of perpendicular $Zn_4O(CO_2)_6$ SBUs



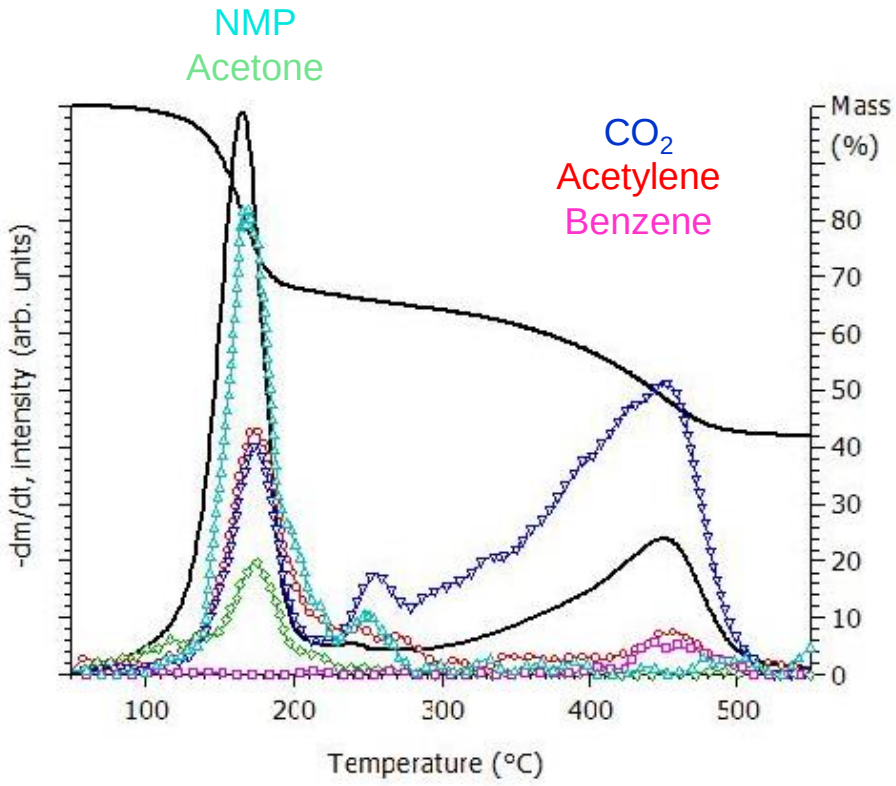
$Zn(NO_3)_2 \cdot 6\ H_2O$
DMF or NMP
100 °C, 22 hours



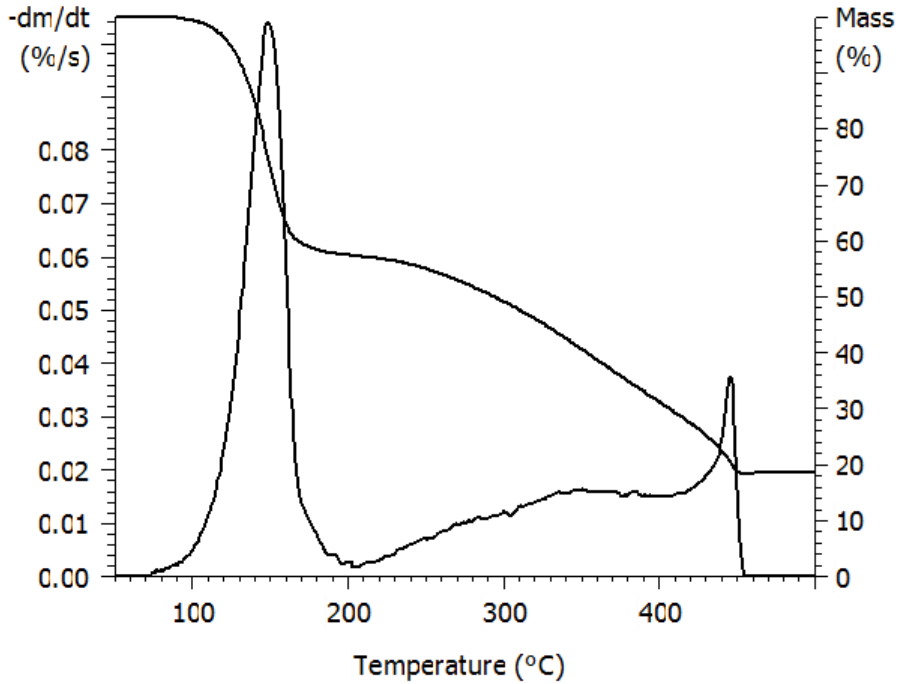
Disordered MOF-5 analogue with cubane-1,4-dicarboxylic acid linkers
$Pm\bar{3}m$, $a = b = c = 12.74$ Å, $\alpha = \beta = \gamma = 90°$, $V = 2068.4$ Å^3.

Heat stability, stochiometry

- TG/MS, inert atmosphere → ZnO + C → heat stability up to 200 °C
- TG oxydative atmosphere → ZnO → stochiometry: $Zn_4O[C_8H_6(CO_2)_2]_3(C_5H_9NO)_6$



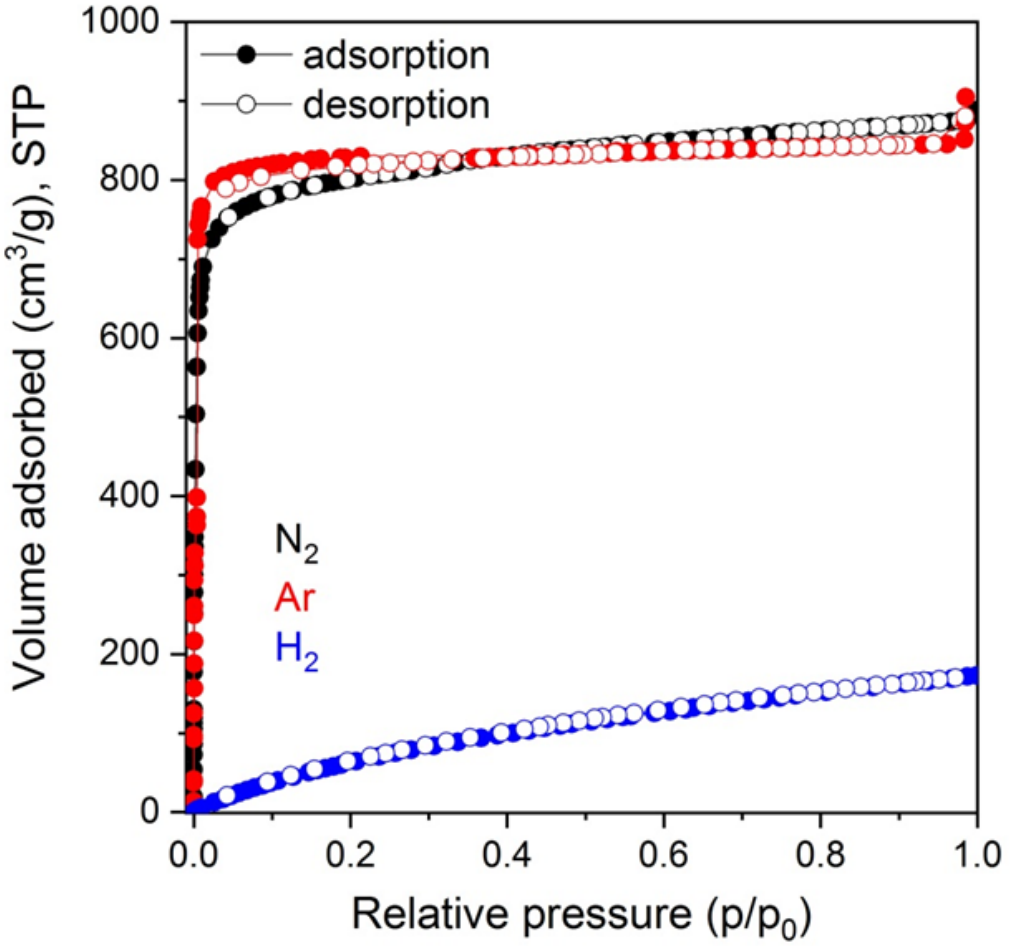
TG/MS inert



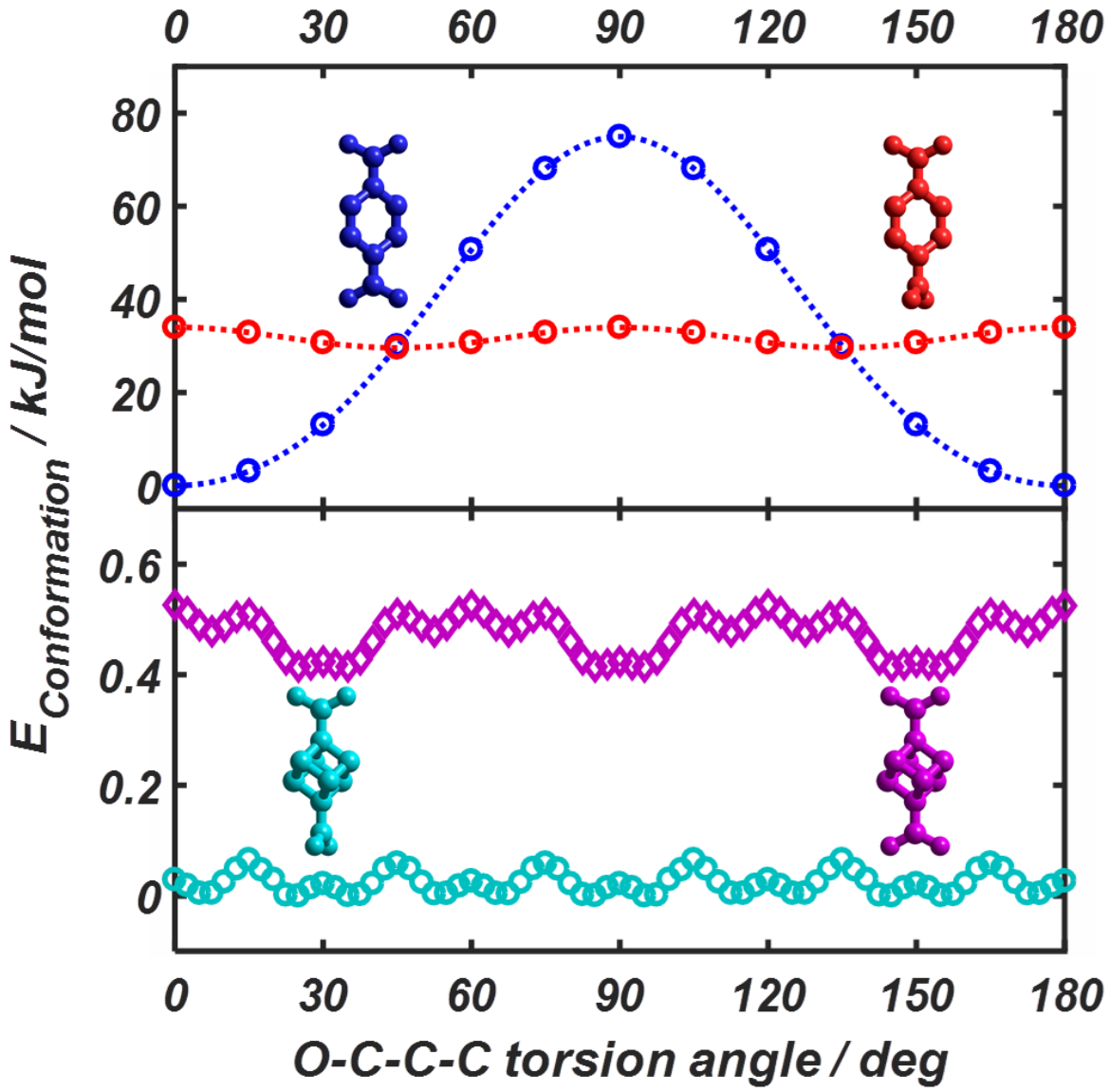
TG oxydative

Activation, gas adsorption

- Solvent exchange activation: DMF → Chloroform → 100 °C, vacuum
- N_2, H_2, Ar isotherms at 77 K: S_{BET} = 3160 m^2g^{-1}; H_2 uptake: 1.5 wt. % and 10.3 g/l

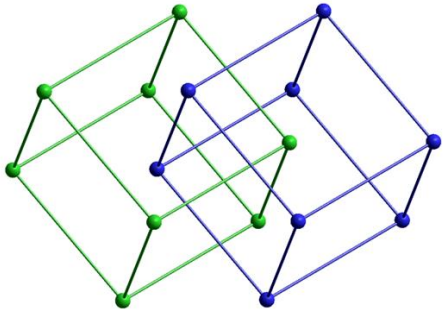


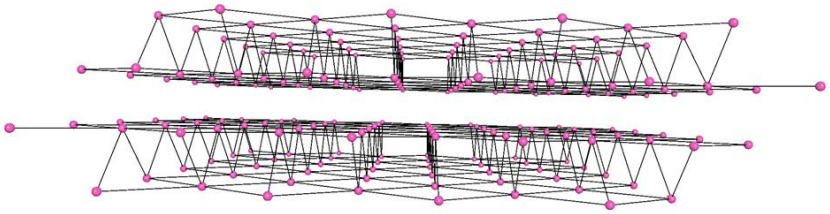
DFT calculation for uniaxial rotation



Future plans

- Publication
- Resolution of *(RS)*-spiro[3.3]heptane-2,6-dicarbocylic acid by chiral HPLC
- Preparation of enantiopure MOFs
- NMR studies of molecular dynamics
- Absolutorium
- Writing PhD dissertation





Courses

- Polimerek kémiája és fizikája (5)
- Természetes- és nem természetes alapú polimerek (5)
- Korszerű elválasztási módszerek az anyagtudományban (5)
- Nanotechnológia (4)
- Pórusos anyagok (5)
- Válogatott fejezetek az anyagvizsgálati módszerekből I. (5)
- Válogatott fejezetek az anyagvizsgálati módszerekből II. (5)
- Szupramolekuláris és koordinációs komplexek (5)

Conferences, publication

Conferences:

- International Joint Conference on Enviromental and Light Industry Technologies, International Symposium on Design and Innovative Technologies, 19th November 2015, poster presentation
- Fiatal Diplomások Fóruma, 24th November, 2015, oral presentation
- Debreceni Röntgendiffrakciós Kerekasztal 20th January 2016, oral presentation
- Műszaki Kémiai Napok 26-28 April, 2016, oral presentation
- 7th Szeged International Workshop on Advances in Nanoscience, 12-15 October 2016, Szeged, poster presentation
- 4th European Crystallography School (ECS4), 2-5 July 2017, poster presentation

Publication:

- Pekker S., Földes D., Kováts É, Bortel G., Jakab E.: Új szerves-fémkoordinációs vázszerkezetek, *Fizikai Szemle,* 2018/1, 11-15.
- Article *in preparation*: Dávid Földes, Éva Kováts, Gábor Bortel, Szilvia Klébert, Emma Jakab, and Sándor Pekker: Basic Zn Cubane-1,4-Dicarboxylate: A new MOF-5 Analogouos with High Porosity and Robust Dynamics

Acknowledgement

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- Éva Kováts
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- Emma Jakab
- Szilvia Klébert

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- István Jalsovszky

Thank you for your attention!