Acetylenedicarboxylate-based Zirconium Metal-Organic Framework with UiO-type Structure

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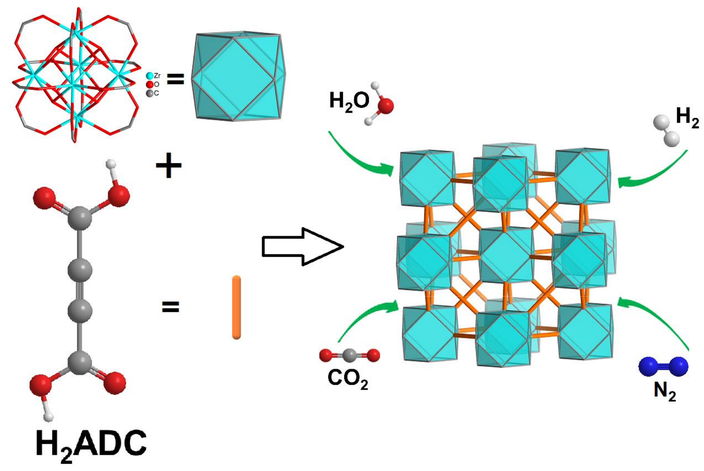
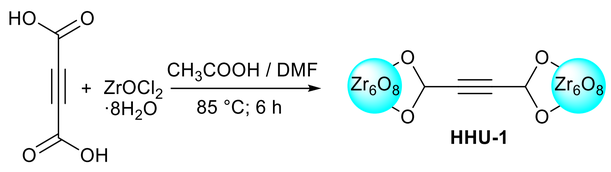
ABSTRACT

Acetylenedicarboxylate (ADC) is the shortest straight linear dicarboxylate linker that can be used to construct isoreticular members of MOF families. However, no porous metal-organic framework (MOF) based on this linker was yet successfully obtained. We have synthesized the first experimentally porous ADC-based Zr(IV)-MOF (**HHU-1**) having the same structure as UiO-66. Its microporosity was proven by nitrogen adsorption and its usefulness was investigated for hydrogen storage and carbon dioxide capture. The nature of this linker results in high hydrophilicity, as well as high H_2 and CO_2 adsorption affinities.



Synthesis and characterization



Modulated synthesis using acetic as modulator within short reaction time and mild temperature

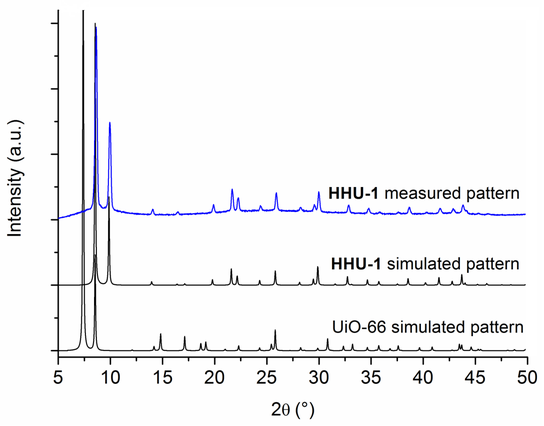


Fig. 1. PXRD pattern of **HHU-1** compared to UiO-66.

Structure

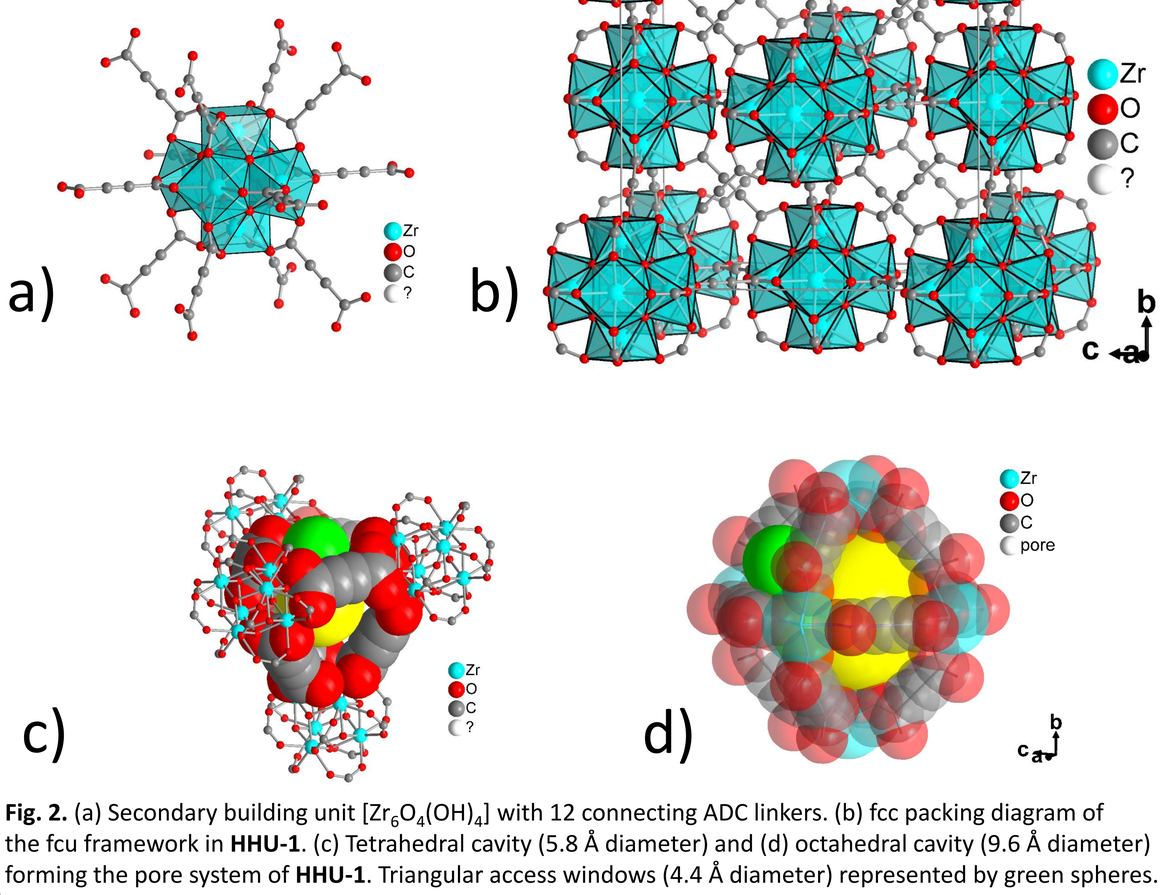


Fig. 2. (a) Secondary building unit $[Zr_6O_4(OH)_4]$ with 12 connecting ADC linkers. (b) fcc packing diagram of the fcu framework in **HHU-1**. (c) Tetrahedral cavity (5.8 Å diameter) and (d) octahedral cavity (9.6 Å diameter) forming the pore system of **HHU-1**. Triangular access windows (4.4 Å diameter) represented by green spheres.

Water and gas sorption properties

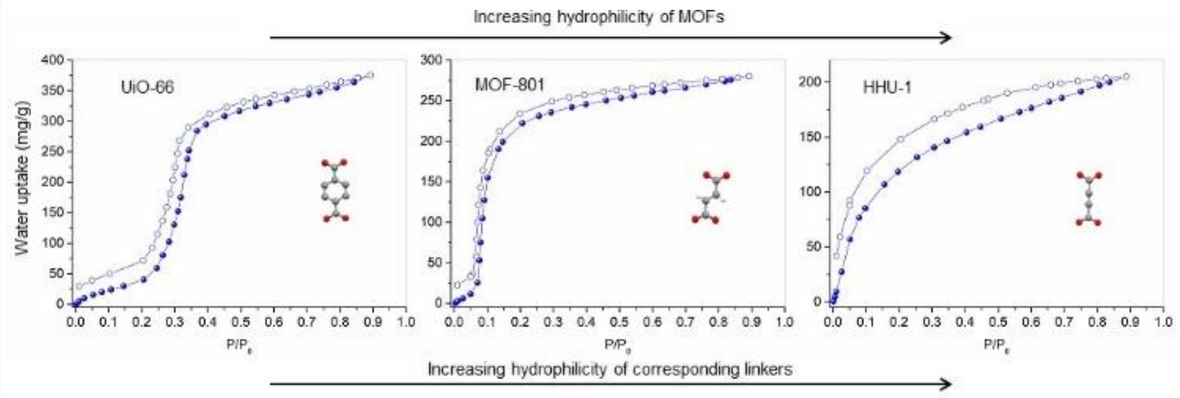


Fig. 3. Water vapor sorption isotherm of **HHU-1** compared to UiO-66 and Zr-fumarate (MOF-801). The very high hydrophilicity of **HHU-1** is due to the C-C triple-bond in ADC.

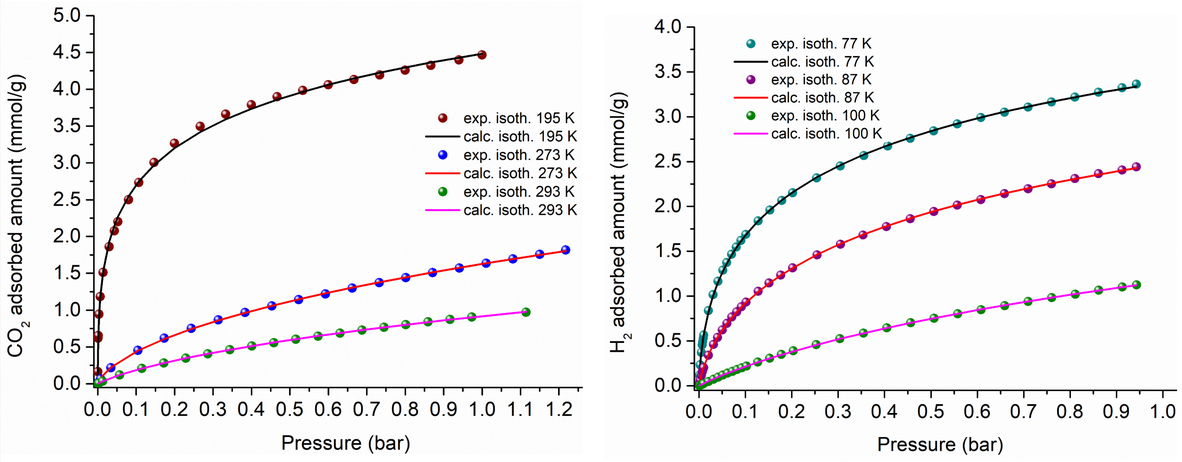


Fig. 4. CO_2 (left) and H_2 (right) adsorption isotherms for **HHU-1** at various temperatures. Symbols represent Experimental isotherms and lines represent the Toth model fits. The type I isotherms obtained attest of the permanent microporosity of guest-free **HHU-1** framework.

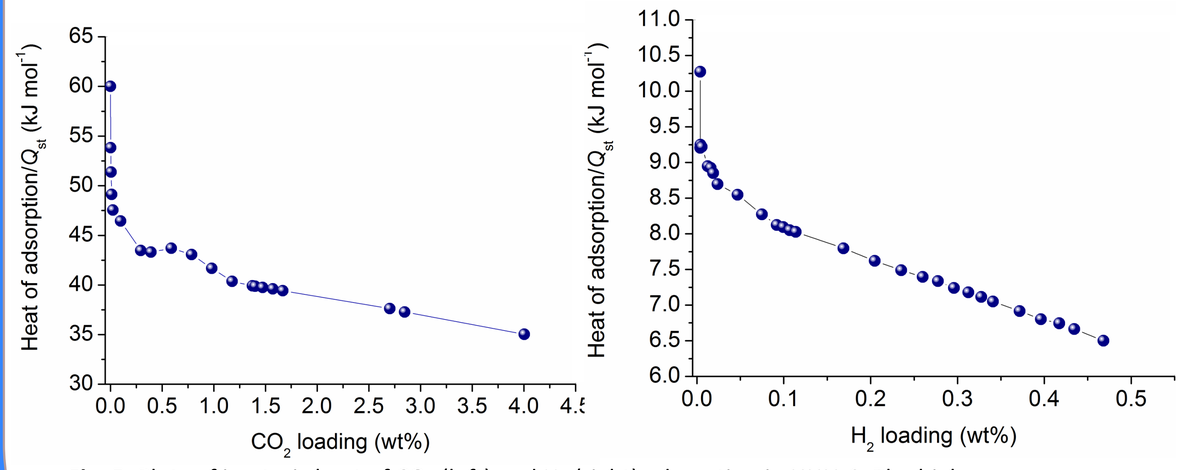


Fig. 5. Plots of isosteric heat of CO_2 (left) and H_2 (right) adsorption in **HHU-1**. The high zero-coverage heat of adsorption indicating strong CO_2/H_2-**HHU-1** affinity is due to synergistic pore confinement and C-C triple-bond of ADC linker.

Conclusion

Using ADC linker yields:

- ✓ small pore sized Zr(IV)-MOF
- ✓ Increased hydrophilicity due to C-C triple-bond
- ✓ Increased CO_2 and H_2 adsorption energetics due to synergistic effects of size reduction and triple-bond

References

T. J. Matemb Ma Ntep, H. Reinsch, B. Moll, E. Hastürk, S. Gökpinar, H. Breitzke, C. Schlüsener, L. Schmolke, G. Buntkowsky and C. Janiak, *Chem. Eur. J*. **2018**, 24, 14048 – 14053.

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