

## Electronic Supplementary Information

### Quest for High-Connected Robust Porous Metal-Organic Framework on the Basis of a Bifunctional Linear Linker and a Rare Heptanuclear Zinc Cluster

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## General methods

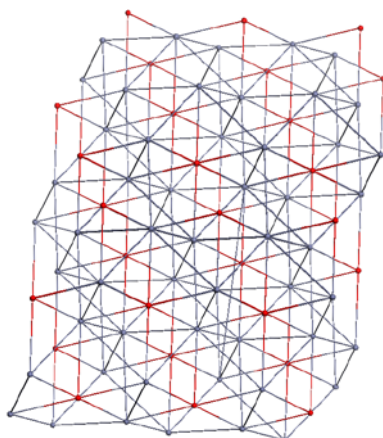
Commercially available reagents were purchased as high purity from Fisher Scientific and used without further purification. Thermogravimetric analysis (TGA) was performed under nitrogen on a TA Instrument TGA 2950 Hi-Res from 25°C to 700 °C at the speed of 10 °C/min. Powder x-ray powder diffraction (PXRD) data was recorded on a Bruker D8 Advance X-ray diffractometer at 40 kV, 40 mA for CuK $\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ), with a scan speed of 0.5 s/step (6°/min) and a step size of 0.05° in 2 $\theta$  at room temperature.

## Gas Adsorption Experiments

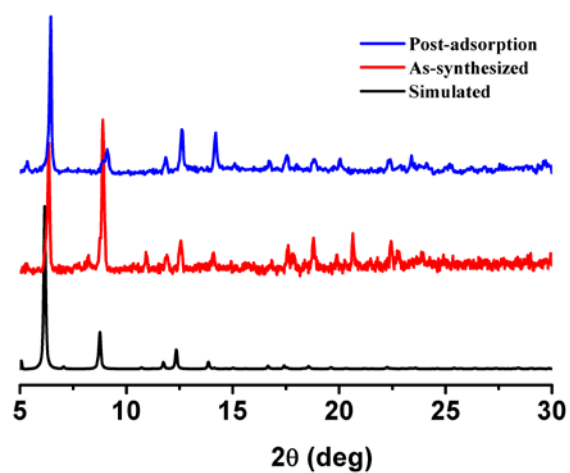
Low pressure gas adsorption isotherms of MTAF-4 were collected using the surface area analyzer ASAP 2020. Before the measurements, the freshly prepared sample was exchanged with methanol for 3 days. The sample was dried on the Schlenk line for overnight at room temperature and then degassed by using the “outgas” functional of ASAP 2020 for 3 hours at 150 °C. N<sub>2</sub> sorption isotherms were measured at 77 K using a liquid N<sub>2</sub> bath. Ar sorption isotherms were measured at 87 K using a liquid Ar bath. High pressure gas sorption isotherms were measured using a computer controlled Sieverts-type apparatus, details of which have been published elsewhere.<sup>1</sup>

## Preparation of MTAF-4

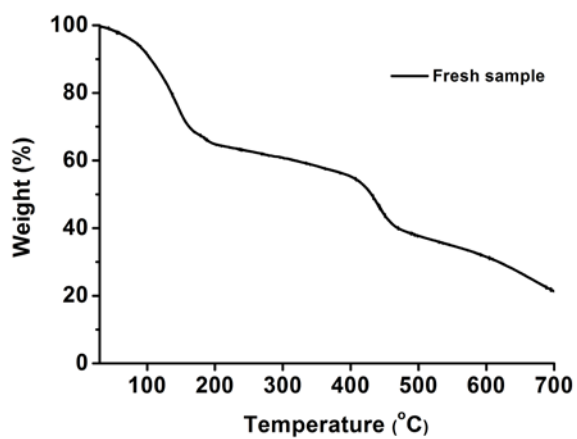
A mixture of 4-(1,2,3-triazol-4-yl)-benzoate (tab) (50 mg), Zn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (190 mg), and fresh N,N'-dimethylformamide (DMF) (10.0 mL) was sealed in a 20 mL vial and heat to 135 °C for 72 hours. The resulting colorless pyramid-shaped crystals of MTAF-4 were obtained. (yield: 70% based on tab ligand).



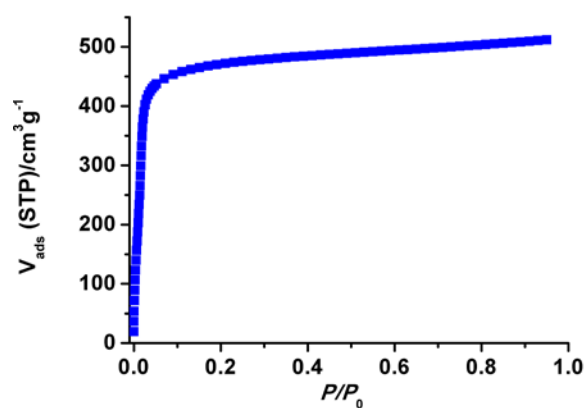
**Fig. S1.** Schematic representation of (6, 9)-connected topological network (red, 6-c nodes; grey, 9-c nodes).



**Fig. S2.** Powder x-ray patterns of MTAF-4.



**Fig. S3.** TGA plot of MTAF-4.



**Fig. S4.** Ar adsorption isotherm of MTAF-4 at 87 K.

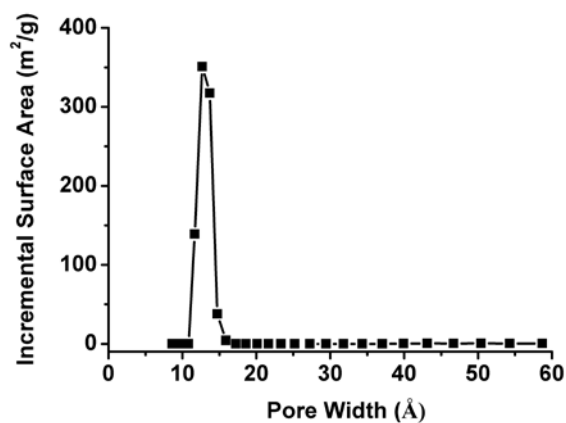


Fig. S5. Pore size distribution based upon Ar isotherm at 87K.

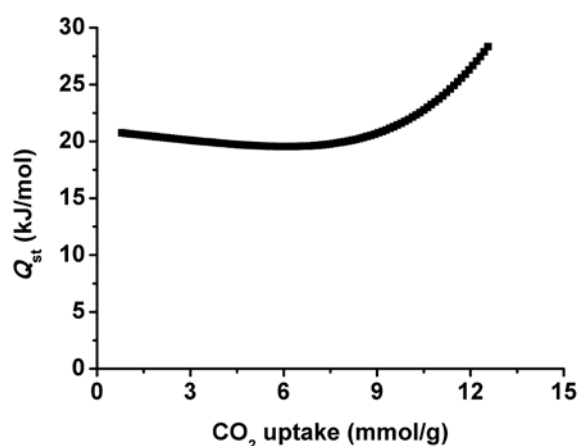


Fig. S6. Heat of adsorption for H<sub>2</sub> high-pressure adsorption.

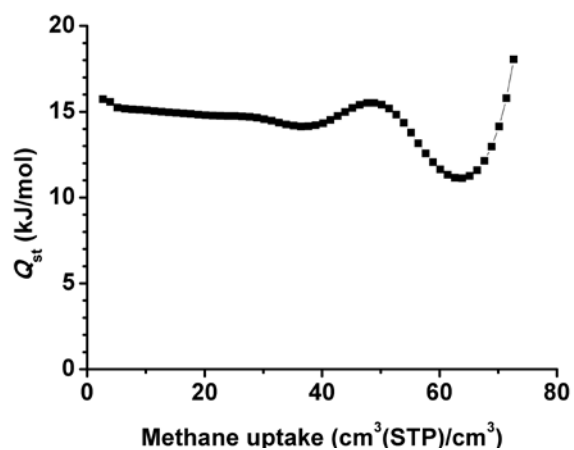
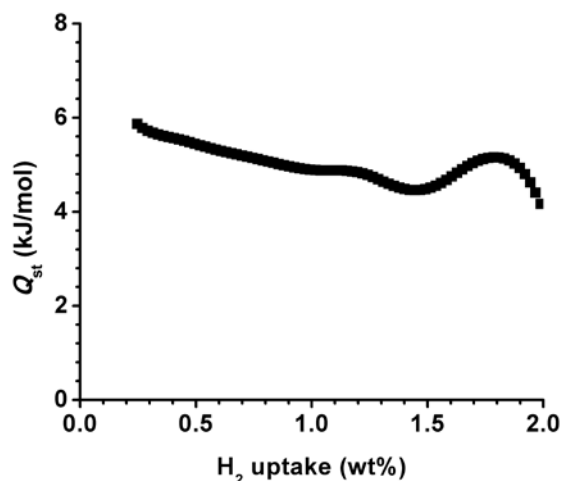


Fig. S7. Heats of adsorption for CH<sub>4</sub> high-pressure adsorption.



**Fig. S8.** Heats of adsorption for H<sub>2</sub> high-pressure adsorption.

### Single-Crystal X-Ray Diffraction for MTAF-4

The X-ray diffraction data were collected using Bruker-AXS SMART-APEXII CCD diffractometer using CuK $\alpha$  ( $\lambda = 1.54178 \text{ \AA}$ ). Indexing was performed using *APEX2* (Difference Vectors method).<sup>2</sup> Data integration and reduction were performed using SaintPlus 6.01.<sup>3</sup> Absorption correction was performed by multi-scan method implemented in SADABS.<sup>4</sup> Space groups were determined using XPREP implemented in *APEX2*.<sup>2</sup> MTAF-4 was solved using SHELXS-97 (direct methods) and refined using SHELXL-97 (full-matrix least-squares on  $F^2$ ) contained in WinGX<sup>5,6,7,8</sup> and OLEX2 programs.<sup>9</sup> All non-H atoms were found in the difference Fourier map. And all non-H atoms were refined anisotropically except the coordinated oxygen O6 on heptanuclear zinc cluster which is due to the disorder. Significant disorder is observed in the crystal structure of MTAF-4. As we described in main text, the structure of MTAF-4 can be treated as a (6,9)-connected network with tetra and hepta nuclear zinc clusters as two types of nodes and the ligand as linker. The tetra nuclear zinc cluster is orientationally disordered over two positions, which is due to the disorder of the benzoate part of the ligand. Additional positional disorder of the benzoate part of the ligand, connecting tetra and hepta clusters, imposes that the tetra nuclear zinc cluster occupies only half of available positions at (0,0,0.5) with  $-3m$  site symmetry (regardless of the orientational disorder). In total this ligand is disordered over four positions. The remaining ligand bridging hepta nuclear zinc clusters is positionally disordered over two positions. This is due to the fact that triazolate and carboxylate part of the ligand show similar coordination abilities and therefore can substitute each other at the given site.

Additionally, the disorder of triazolate group is also observed so the carbon and nitrogen atoms share the same crystallographic positions with partial occupancies. The deciphered structure is described in the main text of manuscript. Due to the highly disordered zinc clusters and ligands, particular atoms have been refined using restraints (DFIX, DANG, FLAT, SIMU and ISOR). Hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters:  $U_{iso}(H) = 1.2U_{eq}(-CH)$ . The contribution of disordered guest molecules was treated as diffuse using Squeeze procedure implemented in Platon program.<sup>10,11</sup> Crystal data and refinement conditions are shown in Table S1.

<b>Table S1.</b> Crystal data and structure refinement for MTAF-4	
Identification code	MTAF-4
Empirical formula	$C_{113.46}H_{72.74}N_{37.82}O_{36.82}Zn_{18}$
Formula weight	3731.61
Temperature	228(2) K
Wavelength	1.54178 Å
Crystal system, space group	Hexagonal, <i>P63/mmc</i>
Unit cell dimensions	$a = 20.1753(4)$ Å $\alpha = 90$ deg. $b = 20.1753(4)$ Å $\beta = 90$ deg. $c = 25.0329(6)$ Å $\gamma = 120$ deg.
Volume	8824.3(3) Å <sup>3</sup>
Z, Calculated density	1, 0.702 Mg/m <sup>3</sup>
Absorption coefficient	1.600 mm <sup>-1</sup>
F(000)	1853
Crystal size	0.40 x 0.40 x 0.20 mm
Theta range for data collection	2.53 to 68.36 deg.
Limiting indices	$-22 \leq h \leq 23$ , $-23 \leq k \leq 24$ , $-30 \leq l \leq 28$
Reflections collected / unique	41223 / 2995 [R(int) = 0.0745]
Completeness to theta = 66.60	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7402 and 0.5670
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	2995 / 76 / 177
Goodness-of-fit on F <sup>2</sup>	1.010
Final R indices [I > 2σ(I)]	R1 = 0.0600, wR2 = 0.1759
R indices (all data)	R1 = 0.0770, wR2 = 0.1882
Largest diff. peak and hole	0.533 and -0.538 e. Å <sup>-3</sup>

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