

Supporting Information

Assembly of Super-Supertetrahedral Metal-Organic Clusters into Hierarchical Porous Cubic Framework

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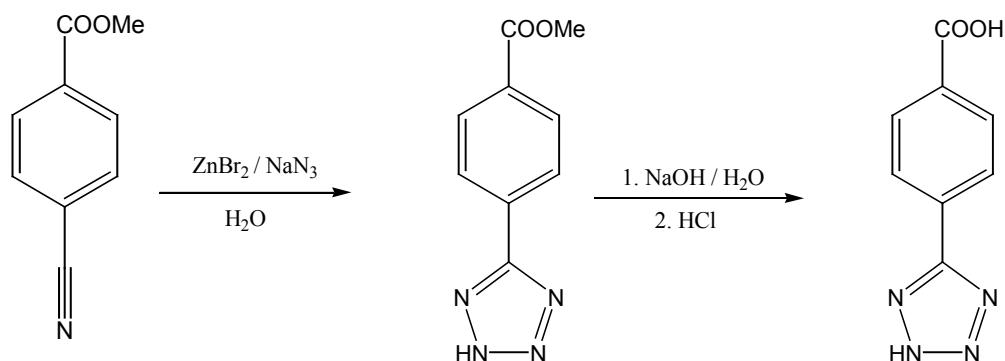
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1. Synthetic procedures and general characterization:

Methyl 4- cyanobenzoate (TCI), Sodium azide (Aldrich), Zinc bromide (Alfa Aeser), Manganese Dichloride (Aldrich), and Ammonium formate (Aldrich), were used as purchased without any further purification.

The synthesis of 4-tetrazol benzoic acid is conducted according to methodology reported by literature¹. Click reaction with starting material of methyl 4- cyanobenzoate (3.225 g, 20 mmol), and sodium azide with 10% excess (1.433 g, 22 mmol) are refluxed in 40 g of water with 4.5 g ZnBr₂ as Lewis acid for 8 hrs. When reaction completed, white precipitate was extracted with ethylacetate followed by rotovaporation. Further hydrolysis of the ester de-protection was carried in 200ml of 2 M NaOH (aq) under 90 °C overnight. Final product was precipitated around pH value of 2 adjusted by 4M hydrochloric acid.



The CPF-5 reported in this study is synthesized under solvothermal conditions. By reacting a mixture of MnCl₂ powder (100mg), 4- tetrazole benzoic acid (80 mg), ammonium formate (15 mg), in a solution of 1.8 g DMF and 200 mg water under 120°C for 3 days in a 23ml glass vial, colorless cubic crystal beautifully formed of 76% yield based on 4- tetrazole benzoic acid. Elemental analysis of the fresh sample indicates C 30.0%, H 2.585% and N 16.6%, these values are very close to the theoretical value calculated from the formula given by crystal data (C 33.3%, H 2.68% and N 16.6%). The crystalline sample was collected after washing with dichloromethane. Data of the single crystal X-ray structure analysis, powder-XRD pattern, and TGA information, are all obtained from the as-synthesized sample. Gas adsorption measurements were performed on the samples with solvent exchange treatment in dichloromethane for 24 hours.

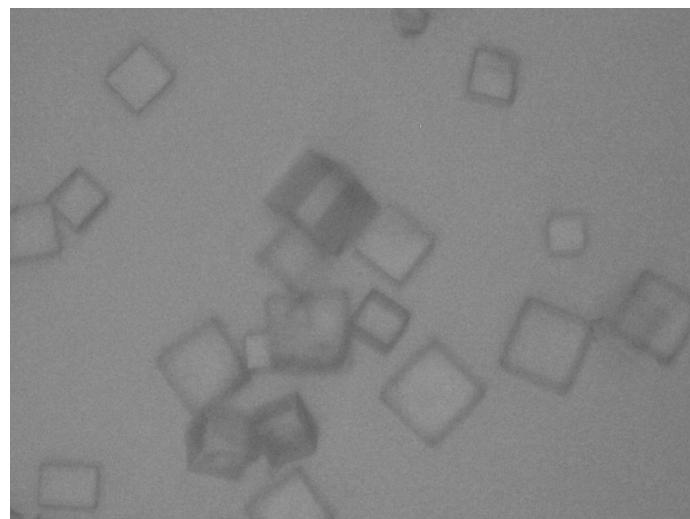


Figure S1 An optical image of crystals synthesized.

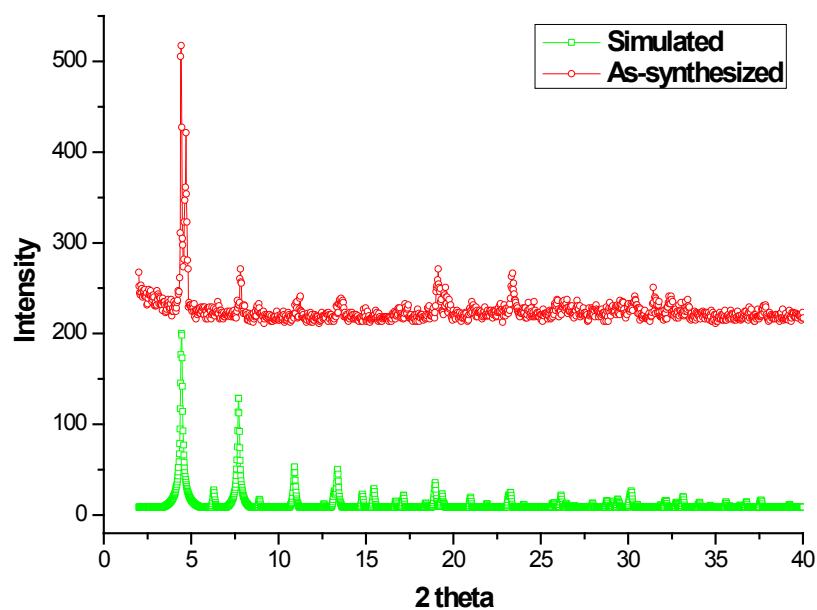


Figure S2 Measured and simulated powder XRD patterns for CPF-5.

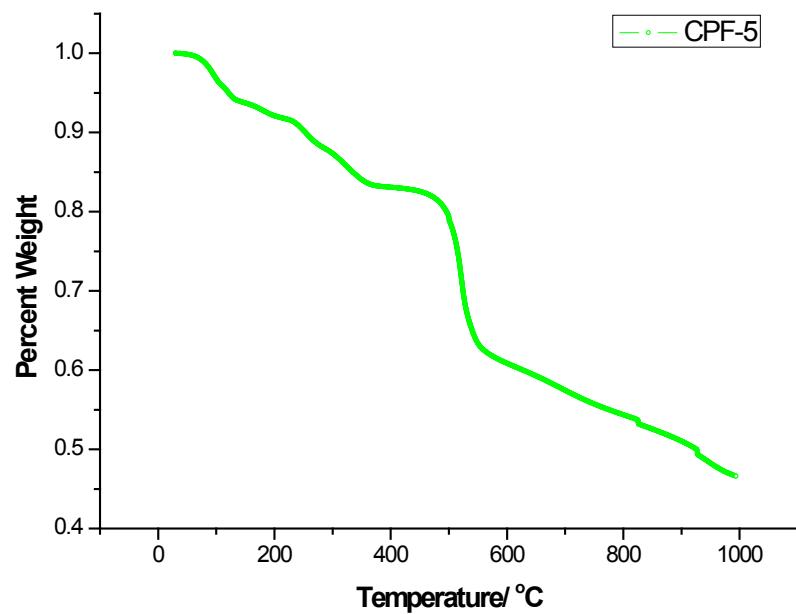


Figure S3. TGA plot of CPF-5 heated under nitrogen atmosphere. TGA experiment was performed on STD-Q600 with initial temperature of 30°C increased to 1000°C with 10K per minute under nitrogen environment with a flow rate of $100 \text{ ml}/\text{minute}$.

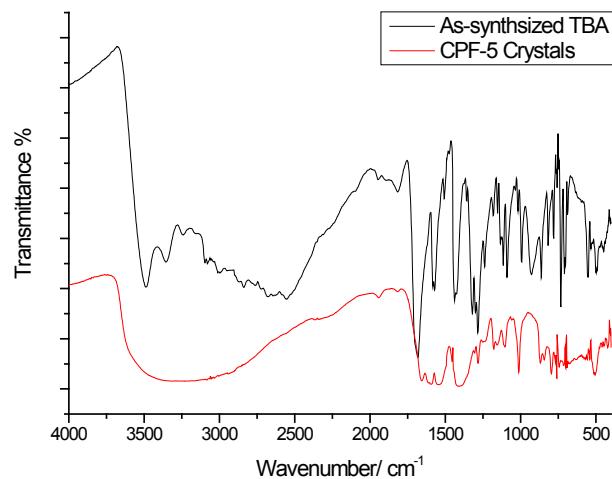


Figure S4. FT-IR of as-synthesized TBA ligand and CPF-5 crystal samples.

For the as-synthesized TBA ligand, the several strong and well separated IR bands were assigned to ν -NH at 3485 cm⁻¹, ν -OH at 3360 cm⁻¹, ν -CO at 1687 cm⁻¹, and different stretching mode for NN and CN bond on the tetrazole five member ring at 1575, 1436, 1323 and 1286 cm⁻¹, as well as ν -CH at 1091 cm⁻¹ and ν -NH at 995 cm⁻¹ according to literature report.²

For the crystallized CPF-5 sample, the framework bonded H₂O covers a very large range from 3600 to 3000 cm⁻¹, the rest of the absorption peaks are widened but still carry some obvious identities from the ligands such as characteristic absorption for ν -CO around 1700 and NCN, CNN, and NNN stretches at around 1630, 1550, and 1430 wavenumbers.

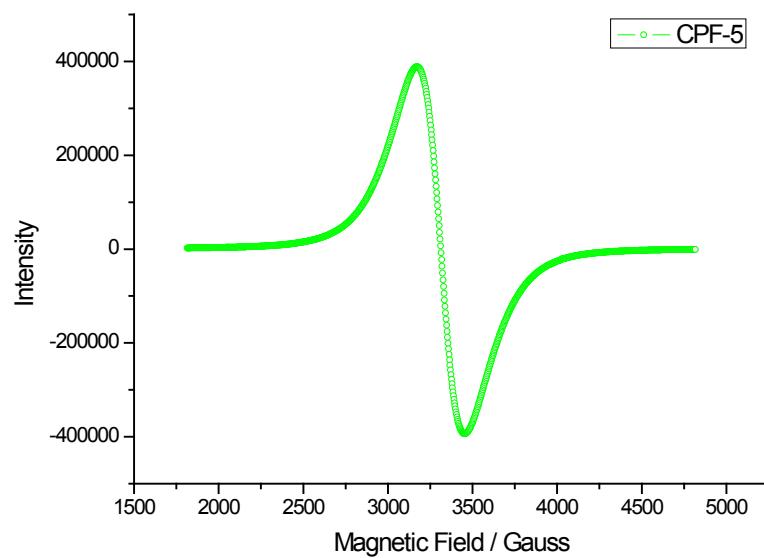


Figure S5. EPR spectra of CPF-5 crystals at 100K.

Since the Mn sites within the crystal is mixed with 6-coordinated and 5-coordinated geometry and experiencing 3 types of different chemical environment, a hyperfine structure with multi peak resolution was not obtained, and the EPR spectra shows a very broad band under the experiment condition of 100 K with frequency of 9.363 GHz.

2. Bond valence calculation for Mn atoms based on crystal data³

Table S1 Bond Valence Calculation for Different Mn Sites

Mn1, corner	Mn-O	Mn-O	Mn-O	Mn-N	Mn-N	Mn-N	
	2.254	2.254	2.254	2.284	2.284	2.284	
Valence Assumed	Valence Contribution						Valence SUM
Mn II	0.285346	0.285346	0.285346	0.326633	0.326633	0.326633	1.835935
Mn III	0.263123	0.263123	0.263123	0.326633	0.326633	0.326633	1.769266
Mn IV	0.258191	0.258191	0.258191	0.326633	0.326633	0.326633	1.754472
Mn2, core	Mn-O	Mn-O	Mn-O	Mn-N	Mn-N	Mn-N	
	2.144	2.144	2.144	2.304	2.304	2.304	
Valence Assumed	Valence Contribution						Valence SUM
Mn II	0.384137	0.384137	0.384137	0.309446	0.309446	0.309446	2.080747
Mn III	0.35422	0.35422	0.35422	0.309446	0.309446	0.309446	1.990996
Mn IV	0.347581	0.347581	0.347581	0.309446	0.309446	0.309446	1.971081
Mn3, bridge	Mn-N	Mn-N	Mn-N	Mn-O	Mn-O	Mn-O	
	2.255	2.122	2.159	2.122	2.235	2.367	
Valence Assumed	Valence Contribution						Valence SUM
Mn II	0.284575	0.40767	0.368875	0.40767	0.300381	0.260998	2.03017
Mn III	0.262412	0.37592	0.340147	0.37592	0.276987	0.260998	1.892385
Mn IV	0.257495	0.368875	0.333772	0.368875	0.271796	0.260998	1.861811

3. Structure of predicted supertetrahedral metal organic clusters

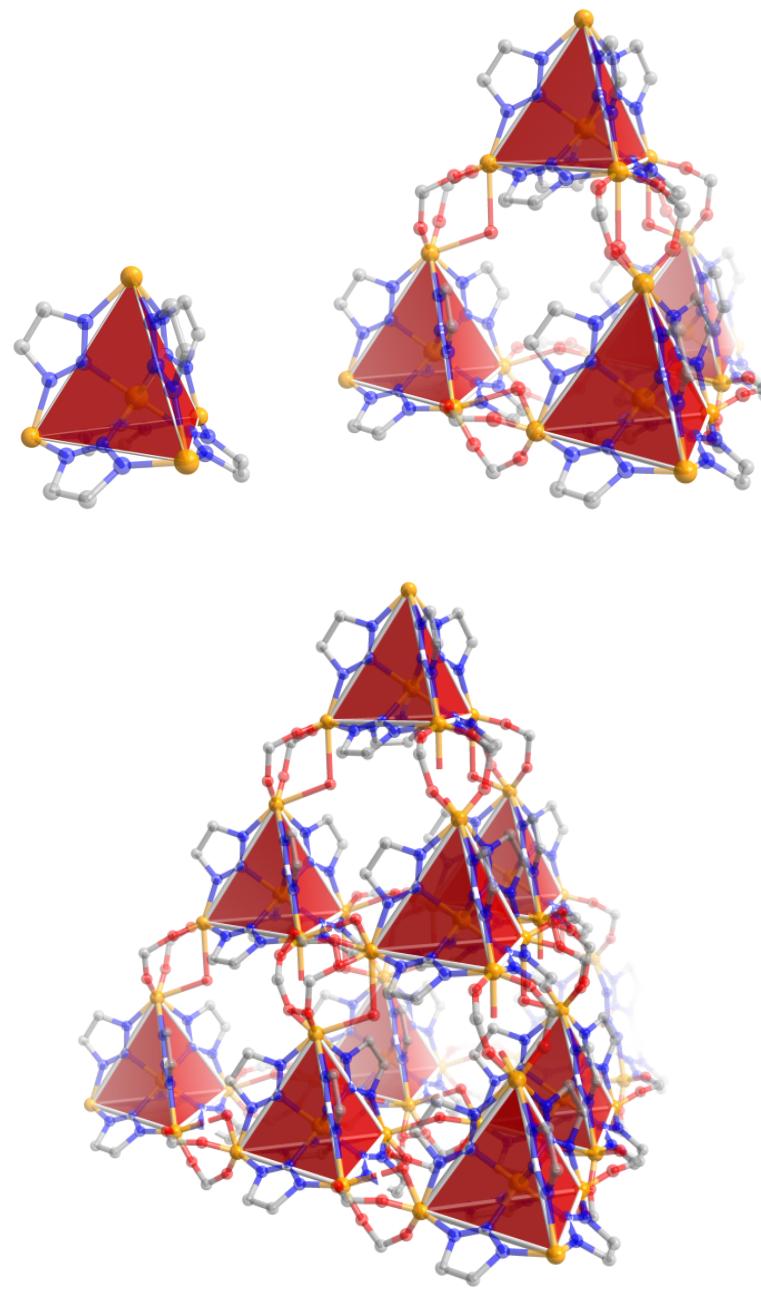


Figure S6. Proposed structure for T1, T2, and T3 tetrahedral metal organic cluster

Table S2 Composition of the Proposed Super-supertetrahedral Metal Organic Clusters

Denotation	T2,1	T2,2	T2,3
Composition	Mn ₅ (ttz) ₆ (OH) ₄ (H ₂ O) ₈	[Mn ₅ (ttz) ₆] ₄ (μ -O) ₆ (CO ₂) ₁₂ (OH) ₄ (H ₂ O) ₈	[Mn ₅ (ttz) ₆] ₁₀ (μ -O) ₁₆ (CO ₂) ₃₆ (OH) ₄ (H ₂ O) ₈
M.W. in Dalton	895	3568	8882
Available Spin Density	25	100	250
Cluster Size	6.36 Å	16.97 Å	29.56 Å

4. Adsorption isotherms for hydrogen and carbon dioxide and BJH pore size distribution graph.

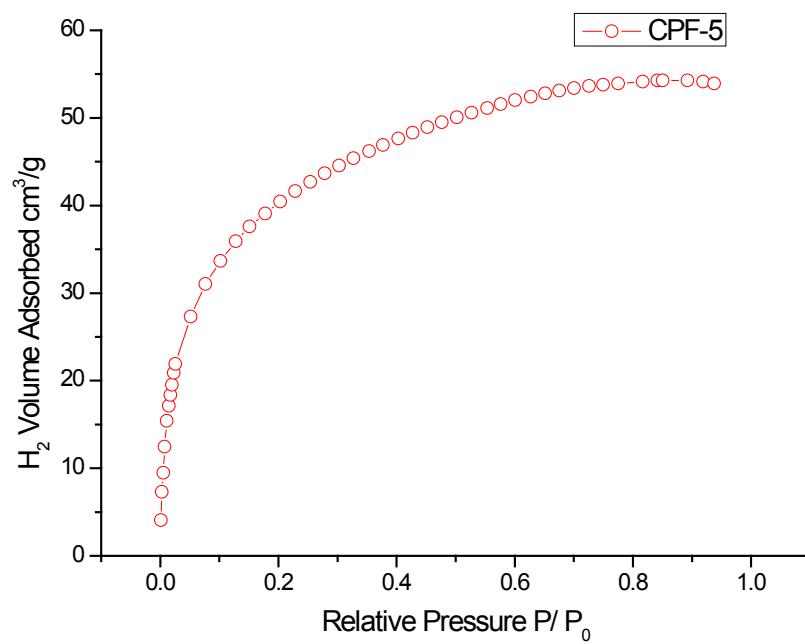


Figure S7. Hydrogen adsorption isotherm under 77K for CPF-5 ($P_0 = 1\text{atm}$).

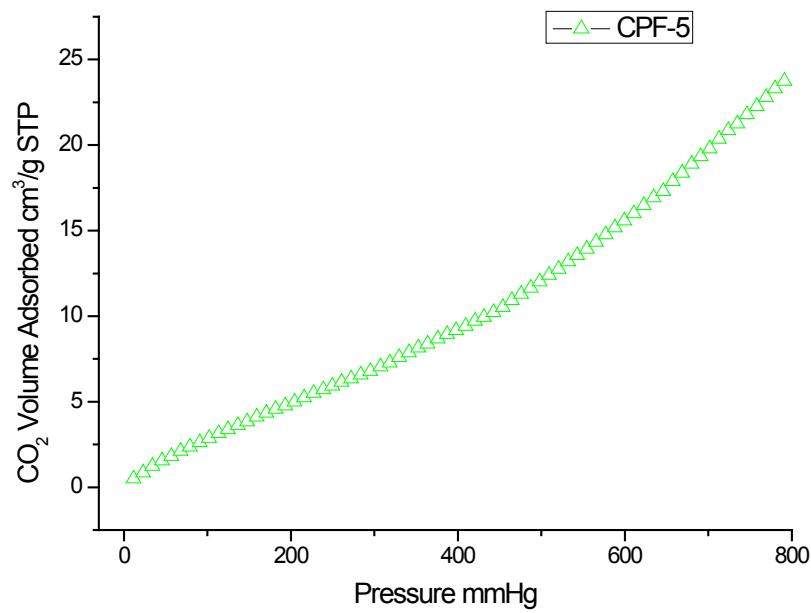


Figure S8. Carbon dioxide adsorption isotherm under 273K for CPF-5.

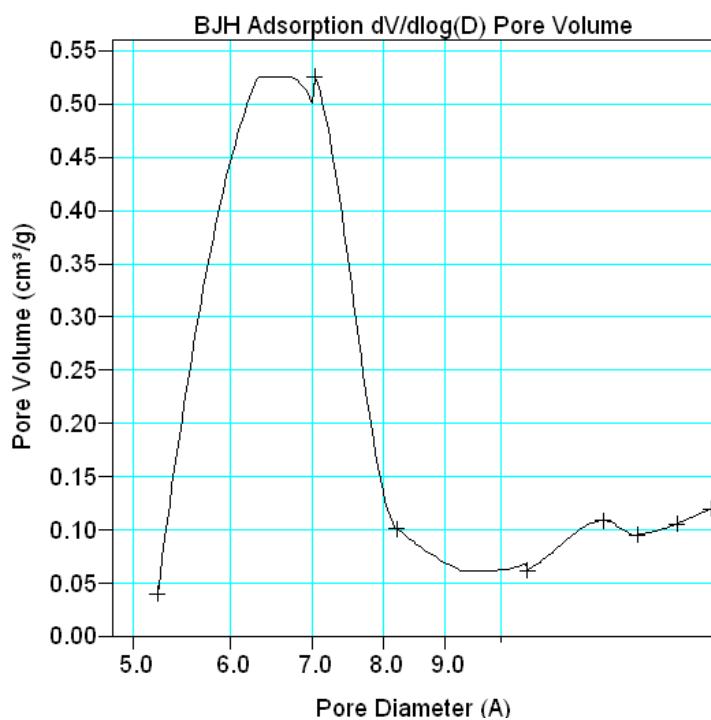


Figure S9. BJH pore size distribution for N_2 adsorption branch of crystal sample of CPF-5.

5. Magnetic property characterizations

Measurements of magnetic properties were conducted using a Quantum Design XL7SQUID magnetometer. Synthesized crystalline samples were first evacuated under 100°C and then incorporated into a diamagnetic eicosane (Alfa Aesar) matrix and loaded into a polycarbonate capsule. The background contribution from the sample mounting (straw, capsule, eicosane) was measured separately and subtracted from the measured sample net magnetic moment. Magnetization was measured in a constant applied magnetic field of 1kOe as the sample was cooled down from 300K to 2K.

References:

1. a) Demko, Z. P.; Sharpless, K. B., *Angew. Chem. Int. Ed.* **2001**, 41, 2010; b) Demko, Z.P.; Sharpless, K. B., *Angew. Chem. Int. Ed.* **2001**, 41, 2013
2. Matveeva, N. A.; Suschko, N. I.; Makarevich, N. I.; Gaponik, P. N.; Ivashkevich, O. A.; Koren, A. O., *J. Appl. Spectrosc.* **1992** (5-6), 57, 845
3. a) Brown, D.; Altermatr, D., *Acta Cryst.*, **1985**, B41, 244; b) Brese, N. E.; O'Keeffe, M., *Acta Cryst.*, **1991**, B47, 192