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Supplementary Information

A mechanochemical strategy for IRMOFs assembly based on predesigned oxo-zinc precursors

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Experimental Section

All manipulations were conducted under a nitrogen atmosphere by using standard Schlenk techniques. All reagents were purchased from commercial vendors. Solvents were dried and distilled prior to use. Redistilled water was degassed carefully by six freeze-pump-thaw cycles before use. NMR spectra were acquired on Varian Mercury 400 Spectrometer. Elemental analyses were performed on a Vario EL apparatus (Elementar Analysensysteme GmbH). The infrared spectra were recorded on a FT-IR Perkin-Elmer System 2000 spectrometer. TG experiments were performed under argon with a heating rate of 2°C min⁻¹ using a TA Instruments Q600 apparatus. Powder XRD data were collected on a Siemens D5005 diffractometer (Bruker AXS). SEM measurements were performed on scanning electron microscope (SEM Zeiss ULTRA Plus) with field emission gun.

Synthesis of 2: Et₂Zn (0.492 g, 4.00 mmol) was added to a suspension of benzamide (0.726 g, 6.00 mmol) in THF (10 mL) at -78°C and then the reaction mixture was allowed to warm to 20°C. After 4 h, degassed H₂O (18 μ L, 1.00 mmol) was added, and the solution was stirred for an additional 20 h. Colourless plate crystals were obtained after crystallization from dilute THF solution at 20°C; isolated yield ca. 87%. Elemental analysis (%) calculated for C₄₂H₃₆O₇N₆Zn₄ (998.33 g mol⁻¹): C 50.50, H 3.60, N 8.41; found: C 50.62, H 3.77; N 8.44 ¹H NMR (CDCl₃, 400.10 MHz, 298 K): δ = 2.40 (s, 1H; -CONH), 7.45 - 8.13 ppm (m, 5H; Ar). IR: v = 403w, 418w, 439m, 488s, 521s, 605w, 661s, 673s, 770vw, 804w, 829vw, 896w, 930w, 1001w, 1027m, 1054w, 1131m, 1184w, 1223m, 1234m, 1303w, 1450vs, 1500m, 1535m, 1559s, 1598s, 1624w, 1658w, 2857w, 2971w, 3061vw, 3179w, 3369w.

Mechanochemical synthesis of MOF-5₁: The reaction was performed at 0.1 mmol scale, by placing a mixture of 1 (0.100 g; 0.1 mmol) and H₂bdc (0.049 g; 0.3 mmol) in the presence of 150 μ L DEF into a 10 mL stainless steel jar with two 7 mm diameter stainless steel balls. The mixture was ground for 60 min in a Retsch MM200 mill at 30 Hz. The as-synthesized grinded material was activated by immersion in anhydrous THF for 1 day, during which time the activation solvent was replenished twice. Complete activation was monitored by ¹H NMR (d₆-DMSO, DCl, 25°C). The sample was subsequently placed under a vacuum of 10⁻⁵ Torr with heating at 100°C. The yield of MOF-5₁ was found to be 72%.

Mechanochemical synthesis of MOF-5₂: The reaction was performed at 0.1mmol scale, by placing a mixture of **2** (0.100 g; 0.1 mmol) and H_2bdc (0.049 g; 0.3 mmol) into a 10 mL stainless steel jar with two 7 mm diameter stainless steel balls. The mixture was ground for 30 min in a Retsch MM200 mill at 30 Hz. The as-synthesized grinded material was activated by immersion in anhydrous THF for 1 day, during which time the activation solvent was replenished twice. Complete activation was monitored by ¹H NMR (d₆-DMSO, DCl, 25°C). The sample was subsequently placed under a vacuum of 10⁻⁵ Torr with heating at 100°C. The yield was found to be 92%.

X-Ray Crystallography

Single-crystal X-Ray Diffraction

Data were collected using the 'oil drop technique' to mount crystals on a Nonius Kappa-CCD equipped with an Oxford Cryostream low-temperature device. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data for **2**, $C_{42}H_{36}O_7N_6Zn_4$: M = 998.33, crystal dimensions $0.40 \times 0.34 \times 0.12 \text{ mm}^3$, trigonal, space group P -3 c 1 (no. 165), a = 14.5525(3) Å, b = 14.5525(3) Å, c = 24.7573(6) Å, U = 4540.6(3) Å³, Z = 4, F(000) = 2024, $D_c = 1.460 \text{ g m}^3$, T = 100(2)K, $\mu(\text{Mo-K}\alpha) = 2.140 \text{ mm}^{-1}$, Nonius Kappa-CCD diffractometer, $\theta_{\text{max}} = 23.25 \text{ °}$, 1904 unique reflections. The structure was solved by direct methods using the SHELXS97 ^[1] program and was refined by full matrix least–squares on F² using the program SHELXL97.^[2] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at geometrically idealized coordinates with a fixed isotropic displacement parameters (R1 = 0.0539, wR2 = 0.1134 for 2532 reflections with $I_o > 2\sigma(I_o)$). The goodness-of-fit on F² was equal 1.086. A weighting scheme $w = [\sigma^2(F_o^2 + (0.0418P)^2 + 3.1964P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the final stage of refinement. The residual electron density = $+ 0.36 / - 0.34 \text{ eÅ}^{-3}$. CCDC-972578.



Figure S1. ORTEP diagram of molecular structure of **2** with thermal ellipsoids set at 40% probability; Operators for generating equivalent atoms: -y+1, x-y+1, z; -x+y, -x+1, z

$[Zn_4(\mu_4-O)(HNOCPh)_6]$ (2)					
Zn1-O1	1.952(6)	Zn1 - O1 - Zn2	100.45(12)		
Zn2 - O1	1.939(6)	Zn1 - O1 - Zn3	109.50(12)		
Zn3 - O1	1.950(6)	Zn1 - O1 - Zn4	109.43(12)		
Zn4 - O1	1.942(6)	Zn2 - O1 - Zn3	109.44(12)		
Zn2 - O2	1.950(8)	Zn2 - O1 - Zn4	109.53(12)		
Zn1 - N1	1.925(8)	Zn3 - O1 - Zn4	109.46(12)		
C1 – O2	1.292(8)	O1 - Zn2 - O2	112.04(12)		
C1 – N1	1.240(8)	O1 – Zn1 – N1	106.78(11)		

Table S1. Selected Bond Lengths (Å) and Angles (deg) for 2.

Powder X-ray Diffraction Analysis (PXRD)

Powder XRD data were collected on a Siemens D5005 diffractometer (Bruker AXS). Measurements employed Ni-filtered Cu K α radiation of a copper sealed tube charged with 40kV voltage and 40mA current and Bragg-Brentano geometry with beam divergence of 1 deg. in the scattering plane. Diffraction patterns were measured in the range of 4-40 degrees of scattering angle by step scanning with step of 0.02 degree.



Figure S2. Comparison of experimental and simulated PXRD patterns of: a) simulated zinc terephthalate [Znbdc]_n (DIKQET); b) LAG of ZnO and H₂bdc using H₂O; c) LAG of ZnO and H₂bdc using DMF; d) neat grinding of ZnO and H₂bdc; e) simulated H₂bdc; f) simulated ZnO.



Figure S3. a) simulated pattern of PhCONH₂ (BZAMID01); b) simulated pattern for MOF-5 (EDUSIF); LAG of **2** with H₂bdc using c) 25μ L and d) 100 μ L of THF.

Fourier-transform infrared spectroscopy (FTIR)

a) IR data for **2**: v = 403w, 418w, 439m, 488s, 521s, 605w, 661s, 673s, 770vw, 804w, 829vw, 896w, 930w, 1001w, 1027m, 1054w, 1131m, 1184w, 1223m, 1234m, 1303w, 1450vs, 1500m, 1535m, 1559s, 1598s, 1624w, 1658w, 2857w, 2971w, 3061vw, 3179w, 3369w



Figure S4. IR spectrum for 2.

b) IR data for H₂bdc: v = 418m, 447m, 499m, 523s, 559m, 668m, 688m, 725vs, 780m, 878s, 923s, 985m, 997m, 1018m, 1112s, 1135m, 1280s, 1315m, 1389m, 1406m, 1422s, 1509m, 1540m, 1559m, 1573m, 1652s, 1674vs, 1683s, 2540w, 2663vw, 2817w, 2968w, 3063w, 3102w.



Figure S5. IR spectrum for H₂bdc.

c) IR data for post-reaction mixture after milling **2** with 3 equivalents of H₂bdc: v = 458m, 527s, 615s, 634s, 684s, 747s, 790w, 811m, 825w, 884.20w, 925wv, 1017w, 1026w, 1122w, 1144w, 1186w, 1299m, 1378vs, 1449m, 1503m, 1577s, 1658s, 3065w, 3170m, 3367m.



Figure S6. IR spectrum for post-reaction mixture after milling 2 with 3 equivalents of H_2bdc .

d) IR spectrum for post-reaction mixture after treatment of THF: v = 657m, 746s, 823m, 1018w, 1392vs, 1504m, 1598s.



Figure S7. IR spectrum for post-reaction mixture after treatment of THF.

Thermogravimetric Analysis (TGA)

TGA studies revealed that MOF-5_{1a} (Figure S8) and MOF-5_{2a} (Figure S9) are stable up to approximately 400°C. Thermogravimetric (TG) curve for the MOF-5₂ without any pretreatment procedure (black curve) shows that the weight loss of 49.6% in the range of 110 - 250°C corresponds to the removal of the benzamide molecules generated during milling (the calculated theoretical value for 6 molecules of benzamide *pro* one $\{Zn_4O\}^{6+}$ center of the resulting MOF-5 lattice equals 50.5%).



Figure S8. Thermogravimetric analysis traces for the MOF-5_{1a}.



Figure S9. Thermogravimetric analysis traces for the MOF- 5_2 (black curve), MOF- 5_{2a} (red curve) in an inert (Ar) atmosphere.

SEM measurements

Samples investigated under microscope were evaporated on SEM standard table (Agar Scientific). Samples were not coated by any means. Prepared samples were examined by scanning electron microscope (SEM Zeiss ULTRA Plus) with field emission gun. A wide variety of magnifications (from x1000 up to x250000), working distances (from 1.9mm up to 3.0mm) and accelerating voltage (from 0.9kV up to 2kV) were used to match ideal imaging conditions for different samples.



Figure S10. SEM image of post-reaction mixture for neat grinding reaction of 2 and H₂bdc.



Figure S11. SEM image of post-reaction mixture for neat grinding reaction of 2 and H₂bdc after washing with THF.

Gas Adsorption Analysis

Volumetric gas sorption studies were undertaken using a Micromeritics Instrument Corporation (Norcross, Georgia, USA) ASAP 2020 system. Approximately 100-300 mg of the corresponding solid product was transferred to a preweighed sample tube and evacuated under vacuum at 100°C on the gas adsorption apparatus until the outgas rate was $<5 \mu$ mHg. All gases used were of 99.999% purity. Helium was used for the free space determination after sorption analysis. Adsorption isotherms were measured at 77 K in a liquid nitrogen. The surface area (m²g⁻¹) was determined by fitting the N₂ gas isotherm at 77 K to the BET equation.



Figure S12. Nitrogen adsorption isotherms at 77K for MOF-5_{1a} (white) and MOF-5_{2a} (black).



Figure S13. Hydrogen adsorption isotherm for MOF-5_{1a} material at 77K.



Figure S14. Hydrogen adsorption isotherm for MOF-5_{2a} material at 77K.

Gas adsorption simulation

The adsorption of N_2 was investigated using grand canonical Monte Carlo $(GCMC)^{[3]}$ simulations implemented in RASPA.^[4] We used an atomistic model for the MOF structures, in which the framework atoms were kept fixed at the crystallographic positions. We used the standard Lennard-Jones (LJ) 12-6 potential to model the interactions between the framework and N₂. Apart from the LJ, we included a Coulomb potential between N2 molecules. The parameters for the framework atoms were obtained from the UFF force field. N2 was modeled using the TraPPE potential with charges placed on each atom and at the center of mass.^[5] Partial atomic charges of the MOF were derived from the charge equilibration method (QEq). The Lorentz-Berthelot mixing rules were employed to calculate fluid-solid parameters. Interactions beyond 18 Å were neglected. 10⁷ Monte Carlo steps were performed, the first 50% of which were used for equilibration, and the remaining steps were used to calculate the ensemble averages. To calculate the gas-phase fugacity we used the Peng-Robinson equation of state.^[6] After equilibration, density distributions were obtained by storing the center of mass positions of all the adsorbed molecules at regular intervals during the simulation. These density distributions provide valuable information about the preferential adsorption sites and the local spatial disorder of the adsorbed molecules. Snapshots represent one single molecular configuration during the simulation.

Table S2. Lennard-Jones parameters for framework atoms and the N₂ molecule.

	σ [Å]	ε/k [K]	q [e]
Zn	2.624	62.397	
С	3.431	52.838	
Ν	3.261	34.722	

Н	2.571	22.142	
F	2.998	25.160	
N_N_2	3.310	36.000	-0.482
N_com	0	0	0.964



Figure S15. *(left)* Adsorption isotherms of N₂ on MOF-5 at 77 K. Experiment MOF-5_{1a}, blue squares; experiment MOF-5_{2a}, green triangles; GCMC, red circles; scaled GCMC ($\phi = 0.739$) and *(right)* low pressure detail.



Figure S16. *(left)* Snapshots and *(right)* density distributions of N_2 adsorption on MOF-5 at 77 K at low and high loadings obtained by GCMC simulations. Black points and blue spheres represent the N_2 molecules in the density distributions and snapshots, respectively. Note the preferential adsorption of the N_2 molecules close to the metal clusters at low loadings.

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