Harvesting Water from Air with High-Capacity, Stable Furan-Based Metal-Organic Frameworks

Ali H. Alawadhi,^{1,2,3} Saumil Chheda,⁴ Gautam D. Stroscio,⁵ Zichao Rong,^{1,2,3} Daria Kurandina,^{1,2,3} Ha L. Nguyen,^{1,2,3} Nakul Rampal,^{1,2,3} Zhiling Zheng,^{1,2,3} Laura Gagliardi,^{5*} and Omar M. Yaghi^{1,2,3,6*}

¹Department of Chemistry, University of California, Berkeley, CA 94720, United States

²Kavli Energy Nanoscience Institute, University of California, Berkeley, CA 94720, United States

³Bakar Institute of Digital Materials for the Planet, College of Computing, Data Science, and Society, University of California, Berkeley, CA 94720, United States

⁴Department of Chemical Engineering and Materials Science, Department of Chemistry, and Chemical Theory Center, University of Minnesota-Twin Cities, Minneapolis, MN 55455, United States

⁵Department of Chemistry, Pritzker School of Molecular Engineering, and Chicago Center for Theoretical Chemistry, University of Chicago, Chicago, IL 60637, United States

⁶KACST–UC Berkeley Center of Excellence for Nanomaterials for Clean Energy Applications, King Abdulaziz City for Science and Technology, Riyadh 11442, Saudi Arabia

*Corresponding authors. Email: lgagliardi@uchicago.edu; yaghi@berkeley.edu

Table of Contents

Section S1. General Methods and Materials	1
Section S2. Synthetic Procedures	1
Section S3. Nuclear Magnetic Resonance (NMR)	6
Section S4. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectro	oscopy
(EDS)	12
Section S5. Single-Crystal X-ray Diffraction Analysis (SCXRD)	15
Section S6. Computational Study of MOF-LA2-1(furan) and MOF-LA2-2(furan):	20
Section S7. Powder X-ray Diffraction Analysis (PXRD)	22
Section S8. Nitrogen Sorption Analysis	24
Section S9. Water Sorption Analysis	30
Section S10. References	

Section S1. General Methods and Materials

All chemicals were purchased commercially and used without any further purification. 5formylfuran-2-carboxylic acid, Furan-2,5-dicarbaldehyde, and Aluminum Sulfate Octadecahydrate were purchased from Fisher Scientific with \geq 98.0%, \geq 98.0%, and 99.999% purity respectively. Pyridine, *N*,*N*-Dimethylformamide, Methanol, HCl, NaOH, Dimethyl sulfoxide-d₆, D₂O, and NaOD (40 wt. % in D₂O) were purchased from Sigma Aldrich. Argon, Helium, and Nitrogen gases were purchased from Linde Air with ultra-high purity (99.999% pure). Microwave reactions were conducted using the CEM Discover® Microwave Synthesizer. Elemental analysis measurements were performed using the Perkin Elmer CHNS 2400 Series II Analyzer.

Section S2. Synthetic Procedures

Synthesis of (*E*)-5-(2-carboxyvinyl)furan-2-carboxylic acid (H₂FVDC):



Step 1: In a 25 mL round bottomed flask with a stirrer bar and under a N_2 atmosphere, 2.228 g of malonic acid (21.41 mmol, 3 equiv.) was dissolved in 4.800 mL of *N*,*N*-Dimethylformamide. Next, 1.000 g of 5-formylfuran-2-carboxylic acid (7.138 mmol, 1 equiv.) was added to the solution and stirred until it fully dissolved. Following that, 0.600 mL of pyridine (7.42 mmol, 1.04 equiv.)

was added to the solution dropwise. The prepared solution was then heated by immersing the round-bottomed flask in a 90 $^{\circ}$ C oil bath with a water-cooled condenser connected on top of the flask. The reaction was left to run for 24 hours while being under a N₂ atmosphere.

Step 2: The solution was allowed to cool down to room temperature, and then was added to a 100 mL beaker with a stirrer bar. To the solution, 8.490 mL of deionized H_2O was added while stirring. Next, 1.770 mL (21.41 mmol, 3 equiv.) of 12.1 M aqueous HCl was added to the solution dropwise while stirring. The precipitate collected was then filtered.

Step 3 (optional): The obtained product was further purified using acid-base extraction. First, a solution was prepared by adding 3.295 mL of 5 M aqueous NaOH solution to 30.0 mL of deionized water in a 100 mL beaker. Second, the product obtained in **Step 2** was completely dissolved in the solution using a stirrer bar and then filtered. The filtrate then had 4.500 mL of 12.1 M aqueous HCl added to it dropwise in another 100 mL beaker, reprecipitating the product in the process. The product was then filtered and washed with 3 x 15 mL of deionized water, then dried at 110 °C in vacuo. Yield: 1.116 g, 86%.

¹H NMR (500 MHz, DMSO-*d*₆) δ 13.00 (s, 2H), 7.42 (d, *J* = 15.9 Hz, 1H), 7.28 (d, *J* = 3.6 Hz, 1H), 7.06 (d, *J* = 3.6 Hz, 1H), 6.35 (d, *J* = 15.9 Hz, 1H) (Figure S1). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 166.85, 159.02, 153.05, 145.90, 130.18, 119.78, 119.44, 116.12 (Figure S5). Elemental Analysis of H₂FVDC: Calculated for C₈H₆O₅: C, 52.80; H, 3.32 %. Found: C, 51.32; H, 3.39 %.

Synthesis of (*E*,*E*)-3,3'-(2,5-Furandiyl)bis[2-propenoic acid] (H₂FDP):



Step 1: In a 25 mL round bottomed flask with a stirrer bar and under a N_2 atmosphere, 5.031 g of malonic acid (48.35 mmol, 6 equiv.) was dissolved in 9.600 mL of *N*,*N*-Dimethylformamide. Next, 1.000 g of Furan-2,5-dicarbaldehyde (8.058 mmol, 1 equiv.) was added to the solution and stirred until it fully dissolved. Following that, 1.300 mL of pyridine (16.12 mmol, 2 equiv.) was added to the solution dropwise. The prepared solution was then heated by immersing the round-bottomed flask in a 90 °C oil bath with a water-cooled condenser connected on top of the flask. The reaction was left to run for 24 hours while being under a N_2 atmosphere.

Step 2: The solution was allowed to cool down to room temperature, and then was added to a 100 mL beaker with a stirrer bar. To the solution, 19.200 mL of deionized H_2O was added while stirring. Next, 2.664 mL (32.23 mmol, 4 equiv.) of 12.1 M aqueous HCl was added to the solution dropwise while stirring. The precipitate collected was then filtered.

Step 3 (optional): The obtained product was further purified using acid-base extraction. First, a solution was prepared by adding 2.855 mL of 5 M aqueous NaOH solution to 25.0 mL of deionized water in a 100 mL beaker. Second, the product obtained in **Step 2** was completely dissolved in the solution using a stirrer bar and then filtered. The filtrate then had 1.180 mL of 12.1 M aqueous HCl added to it dropwise in another 100 mL beaker, reprecipitating the product in the process. The

product was then filtered and washed with 3 x 25 mL of deionized water then dried at 110 °C in vacuo. Yield: 1.433 g, 85%.

¹H NMR (500 MHz, DMSO-*d*₆) δ 12.48 (s, 2H), 7.38 (d, *J* = 15.7 Hz, 2H), 7.02 (s, 2H), 6.38 (d, *J* = 15.8 Hz, 2H) (Figure S2). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 167.18, 152.10, 129.99, 118.39, 117.56 (Figure S6). Elemental Analysis of H₂FDP: Calculated for C₁₀H₈O₅: C, 57.69; H, 3.88 %. Found: C, 57.40; H, 3.92 %.

Microwave synthesis of MOF-LA2-1(furan):



Step 1: 100 mg (0.549 mmol, 1 equiv.) of 5-formylfuran-2-carboxylic acid was added to a 35 mL microwave vessel, capped with a silicone type cap. Next, 458 μ L of *N*,*N*-Dimethylformamide was added to the vessel. The mixture was vortexed until the powder is fully dissolved, forming a clear yellow solution. Following that, 730 μ L of deionized water was added to the vessel and vortexed again forming a cream-white suspension until the mixture is fully homogenized. Finally, 1100 μ L (0.275 mmol, 0.5 equiv.) of an aqueous 0.25 molar Al₂(SO₄)₃·18H₂O solution was added to the mixture in the vessel and vortexed again, maintaining the white homogeneous suspension.

Step 2: The vessel was securely capped and placed in the microwave reactor. The reaction was run for 1 hour, at a temperature setting of 135 °C, a maximum power rating of 300 W, and no stirring.

Step 3: After the reaction was complete and the vessel has cooled down to room temperature, a cream-white colored precipitate was observed at the bottom of the reaction mixture. The mixture was then transferred to a 15 mL centrifuge tube and diluted to a total volume of 15 mL using deionized water. The mixture was centrifuged at 4500 RPM for 5 minutes then the supernatant was discarded. The same procedure of dilution, centrifugation, and supernatant discarding was repeated 3 more times with 15 mL of deionized water and then 3 more times with 15 mL of methanol to wash the obtained cream-white product, discarding the supernatant after each washing step. After the last washing step with methanol the supernatant was discarded, and the solid product was dried at room temperature using a Schlenk line forming a white colored dry powder. Yield: 98 mg, 80%.

¹H NMR (500 MHz, D₂O) δ 6.93 (d, J = 15.9 Hz, 1H), 6.79 (d, J = 3.5 Hz, 1H), 6.50 (d, J = 3.5 Hz, 1H), 6.26 (d, J = 15.9 Hz, 1H) (Figure S3).

Microwave synthesis of MOF-LA2-2(furan):



Step 1: 100 mg (0.480 mmol, 1 equiv.) of 2,5-formylfuran was added to a 35 mL microwave vessel, capped with a silicone type cap. Next, 400 μ L of *N*,*N*-Dimethylformamide was added to the vessel. The mixture was vortexed until the powder is fully dissolved, forming a clear brown solution. Following that, 639 μ L of deionized water was added to the vessel and vortexed again forming a yellow suspension until the mixture is fully homogenized. Finally, 961 μ L (0.240 mmol, 0.5 equiv.) of an aqueous 0.25 molar Al₂(SO₄)₃ · 18H₂O solution was added to the mixture in the vessel and vortexed again, maintaining the yellow homogeneous suspension.

Step 2: The vessel was securely capped and placed in the microwave reactor. The reaction was run for 1 hour, at a temperature setting of 135 °C, a maximum power rating of 300 W, and no stirring.

Step 3: After the reaction was complete and the vessel has cooled down to room temperature, a cream-brown colored precipitate was observed at the bottom of the reaction mixture. The mixture was then transferred to a 15 mL centrifuge tube and diluted to a total volume of 15 mL using deionized water. The mixture was centrifuged at 4500 RPM for 5 minutes then the supernatant was discarded. The same procedure of dilution, centrifugation, and supernatant discarding was repeated 3 more times with 15 mL of deionized water and then 3 more times with 15 mL of methanol to wash the obtained cream-brown product, discarding the supernatant after each washing step. After the last washing step with methanol the supernatant was discarded, and the solid product was dried at room temperature using a Schlenk line forming a light brown colored dry powder. Yield: 99 mg, 82%.

¹H NMR (500 MHz, D₂O) δ 6.92 (d, *J* = 15.9 Hz, 2H), 6.51 (s, 2H), 6.20 (d, *J* = 15.9 Hz, 2H) (Figure S4).

Section S3. Nuclear Magnetic Resonance (NMR)

Liquid-state ¹H and ¹³C NMR spectra were collected using a Bruker NEO-500 (500 MHz). For linker sample measurements, ¹H signals were referenced using residual $(CH_3)_2SO$ at 2.50 ppm or H₂O at 4.79 ppm. ¹³C signals were referenced using $(CD_3)_2SO$ at 39.52 ppm. For MOF linker compositions, samples were analyzed by digesting 10 mg of sample in 500 µL of NaOD solution (5 wt. % in D₂O) prior to NMR measurements. ¹H signals were referenced using residual D₂O at 4.79 ppm.



Figure S1. ¹*H NMR spectrum of H*₂*FVDC linker (500 MHz, DMSO-d*₆).



Figure S2. ¹H NMR spectrum of H₂FDP (500 MHz, DMSO-d₆).



Figure S3. ¹*H NMR spectrum of base digested MOF-LA2-1(furan) (500 MHz, D*₂*O).*



Figure S4. ¹*H NMR spectrum of base digested MOF-LA2-2(furan) (500 MHz, D*₂*O).*



Figure S5. ¹³*C NMR* spectrum of H₂*FVDC* linker (126 MHz, DMSO-d₆).



Figure S6. ¹³*C NMR* spectrum of H₂*FDP* linker (126 MHz, DMSO-d₆).

Section S4. Scanning Electron Microscopy (SEM) and Energy

Dispersive X-ray Spectroscopy (EDS)

Scanning electron microscopy (SEM) images were obtained on a Zeiss XB 550 high resolution SEM with an accelerating voltage of 1.0 kV. The samples were dispersed on conductive carbon tape, mounted on stubs, and sputter coated (Pd/Au) with a Tousimis sputter coater on top of a Bio-Rad E5400 controller. For Energy Dispersive X-Ray Spectroscopy (EDS), the Oxford X-Max EDS system was used. An accelerating voltage of 15 kV was used as well.



Figure S7. Scanning Electron Microscope (SEM) imagery combined with Energy Dispersive Xray Spectroscopy (EDS) expressing the elemental composition of a MOF-LA2-1(furan) sample crystal representative of the bulk material.



Figure S8. Scanning Electron Microscope (SEM) imagery combined with Energy Dispersive Xray Spectroscopy (EDS) expressing the elemental composition of a MOF-LA2-2(furan) sample crystal representative of the bulk material.

Section S5. Single-Crystal X-ray Diffraction Analysis (SCXRD)

SCXRD measurements were conducted at the Advanced Light Source, Lawrence Berkeley National Laboratory, beamline 12.2.1, utilizing a wavelength of 0.7288 Å and employing combined phi and omega scans. The beamline instrumentation included a PHOTON-II CMOS detector operating in shutterless mode and a Si(111) monochromator. For the measurement, a clear rod crystal of 50 x 15 x 15 μ m was mounted on a Kapton® MiTeGen MicroMountTM, minimally coated with Paratone® N oil, and placed within a cold gas stream maintained at 100(2) K, generated by an Oxford Cryosystems 800 Series Cryostream.

The acquired raw data underwent processing using Bruker APEX4 software.¹ Data integration was initially performed using the SAINT program, followed by absorption correction through the SADABS program.^{2,3} Structural solutions were achieved through SHELXT intrinsic phasing, and subsequent refinement was accomplished by full-matrix least squares on *F*² using SHELXL within the Olex2 software package.^{4–6} The Olex2 Solvent masking procedure was applied to structures with notably disordered co-crystallized solvents.⁷ Additionally, Olex2 was used for the visualization of the obtained crystal structure.⁶

Refinement details for MOF-LA2-2(furan)

The resolution of the entire dataset (PRP file) was cut off to 0.93 Å based on intensity statistics, leading to an R_{int} value of 10.93%. Anisotropic refinement was applied to all non-hydrogen atoms, and hydrogen atom positions were determined through calculations.

The MOF-LA2-2(furan) framework was accurately resolved and subjected to anisotropic refinement. Each aluminum atom exhibited a 6-coordinated environment: two μ_2 -OH groups and four carboxylate groups derived from four FDP²⁻ linkers, arranged in a *trans* configuration. Notably, the carboxylate groups within the FDP²⁻ linker acted as bridging ligands, connecting to two adjacent aluminum atoms in a single rod SBU, thus allowing each FDP²⁻ linker, with two carboxylate groups, to link two rod SBUs.

During refinement, hydrogen bonding was observed between μ_2 -OH and a water molecule, with the water molecule forming additional hydrogen bonds with an oxygen atom from a DMF molecule. Initially, hydrogen atoms associated with the DMF molecule's methyl groups were included in the model but were later removed due to instability during position refinement. The RIGU method was applied to stabilize the entire DMF molecule and a subset of atoms within the MOF framework. Bad Reflections that are affected by the beamstop or having $(I_{obs}-I_{calc})/\sigma > 10$ were omitted. Furthermore, to address inversion twinning, a twin law of [-1 0 0, 0 -1 0, 0 0 -1] was taken into consideration.

Upon convergence of the refinement process, it was observed that the goodness-of-fit (GooF) value remained notably high at 1.403. To address this, supplementary solvent masking was employed using the BYPASS method within Olex2, with default parameters set at a solvent radius of 1.2 Å and a truncation radius of 1.2 Å. As a result of the solvent masking procedure, the GooF value decreased to 1.074, accompanied by a reduction in the R₁ factor from 9.33% to 4.57%. This solvent masking unveiled a void volume of 149 Å³, characterized by 36 masked electrons in accordance with the empirical chemical formula. Taking into consideration the synthetic

conditions of MOF-LA2-2(furan), the remaining electron densities are attributed to unresolved water or DMF molecules residing within the void, owing to the absence of stabilization factors such as hydrogen bonding. Furthermore, the weighting scheme was refined, yielding refined parameters of a = 0.090 and b = 7.24.



Figure S9. Single crystal structure of MOF-LA2-2(furan). One asymmetric unit including part of the MOF framework, one water molecule and one DMF molecule is shown. Ellipsoids are plotted with 50% probability. Color code: Al, cyan; N, blue; C, grey; H, white; O, red.

	Before solvent masking	After solvent masking
Empirical formula	C ₁₃ H ₁₀ AlNO ₈	C ₁₃ H ₁₀ AlNO ₈
Formula weight	335.20	335.20
Temperature (K)	100.00	100.00
Crystal system	tetragonal	tetragonal
Space group	I4 ₁ md	I4 ₁ md
<i>a</i> (Å)	26.982(2)	26.982(2)
b (Å)	26.982(2)	26.982(2)
c (Å)	10.6514(12)	10.6514(12)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
Volume (Å ³)	7754.6(14)	7754.6(14)
Z	16	16

Table S1. Crystal data and structure refinement for MOF-LA2-2(furan).

ρ_{calc} (g/cm ³)	1.148	1.148	
μ (mm ⁻¹)	0.145	0.145	
F(000)	2752.0	2752.0	
Crystal size (mm ³)	$0.05\times 0.015\times 0.015$	$0.05\times0.015\times0.015$	
Radiation	synchrotron ($\lambda = 0.7288$)	synchrotron ($\lambda = 0.7288$)	
20 range for data collection (°)	4.216 to 46.136	4.216 to 46.136	
	$-28 \le h \le 28, -28 \le k \le 28, -11$	$-28 \le h \le 28, -28 \le k \le 28, -11$	
Index ranges	≤1≤11	≤1≤11	
Reflections collected	60491	60491	
Indexed out unfloations	2646 [$R_{int} = 0.1093$, $R_{sigma} =$	$2646 [R_{int} = 0.1093, R_{sigma} =$	
Independent reflections	0.0267]	0.0267]	
Data/restraints/parameters	2646/51/197	2646/51/197	
Goodness-of-fit on F ²	1.403	1.074	
Final R indexes [I>=2σ (I)]	$R_1 = 0.0933, wR_2 = 0.2809$	$R_1 = 0.0457, wR_2 = 0.1264$	
Final R indexes [all data]	$R_1 = 0.0966, wR_2 = 0.2869$	$R_1 = 0.0485, wR_2 = 0.1292$	
Largest diff. peak/hole / e Å ⁻³	1.34/-0.55	0.32/-0.23	
Flack parameter	0.5(7)	0.5(4)	

Section S6. Computational Study of MOF-LA2-1(furan) and MOF-LA2-2(furan):

Initial periodic density functional theory (DFT) calculations were performed in the *Vienna Ab Initio Simulation* software^{8–10} (VASP version 6.2.1) to identify the most stable linker configurations of MOF-LA2-1(furan). A single unit cell of the MOF containing sixteen Al(μ_2 -OH)(FVDC) formula units was used for the structure optimizations. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation density functional^{11,12} along with Grimme's D3 dispersion correction with Becke-Johnson damping^{13,14} was employed. A plane-wave basis set with an energy cutoff of 520 eV was used. The structures were optimized until a convergence in the energy and forces up to 10⁻⁶ eV and 0.03 eV/Å was achieved. The unit cell volume and shape were relaxed along with the atomic positions of the MOF framework.

Gaussian 16, Rev. A. 03 was used for the cluster DFT calculations.¹⁵ The M06-L¹⁶ density functional was used. The def2-TZVP basis set was used on aluminum and the def2-SVP basis set was used on hydrogen, carbon, oxygen, and, when present, nitrogen.¹⁷ For the examined MOFs (MOF-303, MIL-160, MOF-LA2-1(pyrazole), and MOF-LA2-1-furan), the cluster models consisted of three dicarboxylate linkers connecting parallel segments of aluminum rods. Each segment consisted of six aluminum-based octahedra and seven truncated formate molecules. The formate carbon atoms were frozen in position to model the rigidity of the MOF framework. To obtain charge neutral models, hydroxyl and aqua ligands on the terminating Al octahedra. The MOF-LA2-1(pyrazole) model was cut from its lowest energy published theoretical structure.¹⁸ All

models were optimized both as a dry framework model and as a hydrated framework model with one water molecule displacing an Al-O(linker) bond.

The energy penalty for linker displacement by a water molecule was estimated as electronic energy difference according to the following equation:

$$\Delta E = E_{MOF \cdot H_2O} - E_{MOF} - E_{H_2O}$$

For MIL-160 and MOF-LA2-1(furan), the linker hydrolysis penalty was found to be 5.3 kcal/mol and 3.4 kcal/mol, respectively while for MOF-303 and MOF-LA2-1(pyrazole), this hydrolysis penalty was computed as 8.4 kcal/mol and 2.8 kcal/mol respectively.

Table	S2.	Relative	stability	(kJ/mol)	per	asymmetric	unit	of	different	linker	configurations	of
MOF-	LA2	2-1(furan)	optimize	d using p	erio	dic density fo	unctio	ona	l theory.			

Linker configuration	Absolute energy (eV)	Relative stability (kJ/mol)
ENT-trans	-2250.074828	34.6
ENT- <i>cis</i>	-2255.815060	0.0
ZUS-trans	-2248.025433	47.0
ZUS- <i>cis</i>	-2252.872055	17.7

Table S3. Absolute energies of cluster models (Hartree)

Structure	E	ΔΕ	
	Hartree	kcal/mol	

Isolated water	-76.350532	-
MIL-160	-9121.877885	5.3
MOF-LA2-1(furan)	-9353.910529	3.4
MOF-303	-9110.444250	8.4
MOF-LA2-1(pyrazole)	-9342.477977	2.8

Section S7. Powder X-ray Diffraction Analysis (PXRD)

Powder X-Ray Diffraction (PXRD) analysis measurements were performed using the Bruker D8 Advance X-ray diffractometer equipped with a Cu anode and a Ni filter (CuK α_1 , $\lambda = 1.54059$ Å) in Bragg-Brentano geometry. The samples were mounted on a zero-background holder and leveled using a glass slide. The PXRD patterns were collected in the range between 3.00° and 50.00° with 2303 steps (0.02° per step) with an acquisition time of 10 seconds per step, thus resulting in ~6.5 hours analysis time.



Figure S10. Pawley refinement of the theoretically determined MOF-LA2-1(furan) structure against the experimentally obtained pattern of MOF-LA2-1(furan).



Figure S11. PXRD pattern of the bulk MOF-LA2-2(furan) powder compared to its simulated pattern.

Section S8. Nitrogen Sorption Analysis

Nitrogen sorption measurements were performed using the Micromeritics ASAP 2420 surface area analyzer. Nitrogen isotherms were measured by immersing sample cells in a liquid Nitrogen bath (77 K) throughout the measurement. Helium gas was used to correct for dead volume.



Figure S12. Nitrogen Sorption Analysis of MOF-LA2-1(furan) and MOF-LA2-2(furan) at 77 K. *P*, nitrogen pressure; $P_0 = 1$ atm; STP, standard temperature and pressure.



Figure S13. Nitrogen Sorption Analysis of MOF-LA2-1(furan) with a logarithmic scale for the x-axis at 77 K. P, nitrogen pressure; $P_0 = 1$ atm; STP, standard temperature and pressure.



Figure S14. Rouquerol plot of Al-LA2-1(furan) to determine appropriate points for BET analysis.



Figure S15. BET plot of MOF-LA2-1(furan) resulting in a BET area of 1,113 m²/g.



Figure S16. Rouquerol plot of Al-LA2-2(furan) to determine appropriate points for BET analysis.



Figure S17. BET plot of MOF-LA2-2(furan) resulting in a BET area of 1,269 m²/g.

Section S9. Water Sorption Analysis

Isothermal water vapor measurements were performed using the Belsorp MAX II high precision gas/vapor adsorption measurement instrument. The vapor source containing deionized water was degassed prior to measurements using 3 cycles of freeze-pump-thaw. The temperature of each respective measurement was maintained by immersing sample cells in an isothermal water bath throughout the measurement. Helium gas was used to correct for dead volume.

Isobaric water vapor measurements were performed using the TA Instruments SDT Q600 Thermogravimetric Analyzer & Differential Scanning Calorimeter. The temperature and relative humidity were monitored using a thermocouple and a humidity sensor positioned downstream of the TGA chamber. To introduce humidity into the TGA chamber, nitrogen gas flowed through a water bubbler apparatus upstream of the TGA chamber. Hence by controlling the ratio of flow rates between the humidified nitrogen feed and another separate dry nitrogen feed, the water vapor partial pressure of the chamber can be controlled. The two gas flows were mixed and fed into the chamber with a total flow rate sum of 200 mL/min and the ratio of the two flow rates were calibrated to maintain the required water vapor partial pressure.



Figure S18. Isothermal water sorption analysis for MOF-LA2-1(furan) at 25 °C, 35 °C, and 45 °C.



Figure S19. Isothermal water sorption analysis for MOF-LA2-2(furan) at 25 °C, 35 °C, and 45 °C.



Figure S20. The isosteric heat of adsorption (Q_{st}) of MOF-LA2-1(furan) and MOF-LA2-2(furan) plotted as a function of uptake determined using the Clausius-Clapeyron equation.



Figure S21. Isobaric Water Desorption Analysis for MOF-LA2-1(furan) and MOF-LA2-2(furan) at a Water Vapor Pressure of 1.70 kPa.



Figure S22. Isobaric cyclic water sorption measurements performed for MOF-LA2-1(furan) for 173 cycles at a water vapor pressure of 1.70 kPa. A temperature swing mode was used between 30 °C (adsorption) and 65 °C (desorption).



Figure S23. Isobaric cyclic water sorption measurements performed for MOF-LA2-2(furan) for 165 cycles at a water vapor pressure of 1.70 kPa. A temperature swing mode was used between 30 °C (adsorption) and 50 °C (desorption).

Section S10. References

- 1. Bruker AXS Inc. APEX4. Madison, WI 2021.
- 2. Bruker AXS Inc. SAINT. Madison, WI 2020.
- 3. Bruker AXS Inc. SADABS. Madison, WI 2016.
- 4. Sheldrick, G. M. SHELXT Integrated Space-Group and Crystal-Structure Determination. *Acta Cryst.* **2015**, *A71* (1), 3-8. DOI: 10.1107/S2053273314026370.
- Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Cryst.* 2015, *C71* (1), 3 8. DOI: <u>10.1107/S2053229614024218</u>.
- Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.* 2009, *42* (2), 339-341. DOI: <u>10.1107/S0021889808042726</u>.
- Van Der Sluis, P.; Spek, A. L. BYPASS: An Effective Method for the Refinement of Crystal Structures Containing Disordered Solvent Regions. *Acta Cryst.* 1990, *A46* (3), 194-201. DOI: <u>10.1107/S0108767389011189</u>.
- Kresse, G.; Furthmüller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. *Comput. Mater. Sci.* 1996, 6 (1), 15-50. DOI: 10.1016/0927-0256(96)00008-0.
- Kresse, G.; Hafner, J. Ab Initio Molecular Dynamics for Liquid Metals. *Phys. Rev. B* 1993, 47 (1), 558. DOI: <u>10.1103/PhysRevB.47.558</u>.
- Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* 1996, *54* (16), 11169. DOI: 10.1103/PhysRevB.54.11169.
- Perdew, J. P.; Burke, K.; Ernzerhof, M. Perdew, Burke, and Ernzerhof Reply. *Phys. Rev. Lett.* 1998, 80 (4), 891. DOI: <u>10.1103/PhysRevLett.80.891</u>.
- Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, 77 (18), 3865. DOI: <u>10.1103/PhysRevLett.77.3865</u>.
- Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* 2011, *32* (7), 1456-1465. DOI: <u>10.1002/jcc.21759</u>.

- Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. J. Chem. Phys. 2010, 132 (15), 154104. DOI: <u>10.1063/1.3382344</u>.
- 15. Gaussian Inc. Gaussian 16. Wallingford, CT 2016.
- Zhao, Y.; Truhlar, D. G. A New Local Density Functional for Main-Group Thermochemistry, Transition Metal Bonding, Thermochemical Kinetics, and Noncovalent Interactions. J. Chem. Phys. 2006, 125 (19), 194101. DOI: <u>10.1063/1.2370993</u>.
- Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* 2005, 7 (18), 3297-3305. DOI: <u>10.1039/b508541a</u>.
- Hanikel, N.; Kurandina, D.; Chheda, S.; Zheng, Z.; Rong, Z.; Neumann, S. E.; Sauer, J.; Siepmann, J. I.; Gagliardi, L.; Yaghi, O. M. MOF Linker Extension Strategy for Enhanced Atmospheric Water Harvesting. *ACS Cent. Sci.* 2023, 9 (3), 551–557. DOI: <u>10.1021/acscentsci.3c00018</u>.