Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Uniform and Simultaneous Orthogonal Functionalization of a Metal-Organic Framework Material

Kanchana P. Samarakoon,[a] Mohammad S. Yazdanparast,[a] Victor W. Day[b] and Tendai Gadzikwa*[a]

Department of Chemistry, Kansas State University, Manhattan, Kansas 66506, USA.

Email: gadzikwa@ksu.edu

MATERIALS

All chemicals were used as received from commercial sources unless otherwise noted. Meso-*α*,*β*-di(4-pyridyl) glycol (**DPG**) was purchased from TCI. Sulfuric acid-*d*$_2$ (D_2SO_4, 98 wt.% in D_2O, 99.5+% atom D), Copper bromide (98%) were purchased from Acros Organics. *N*,*N*-dimethylformamide (DMF), tetrahydrofuran (THF), Acetonitrile (MeCN), *tert*-butyl nitrite (90 %) and phenyl acetylene (98%) were purchased from Fisher Scientific, and zinc nitrate hexahydrate from Strem Chemicals. Chloroform ($CHCl_3$), 2-aminoterephthalic acid (**BDC-NH$_2$**), and isopropyl isocyanate (98%) were purchased from Sigma Aldrich. 1,4-Diazabicyclo[2.2.2]octane (DABCO) and trimethylsilyl azide (95%) were purchased from Oakwood Products. Dimethyl sulfoxide-*d*$_6$ (*d*$_6$-DMSO, 99.9 atom % D) was purchased from Cambridge Isotopes Laboratories.

SYNTHETIC PROCEDURES

Synthesis of BDC-N$_3$. Followed a modified literature procedure.[1] 2-aminoterephthalic acid (**BDC-NH$_2$**) (0.20 g, 1.10 mmol, 1 equiv.) was dissolved in dry THF (20 ml) and *tert*-butyl nitrite (0.39 ml, 3.3. mmol, 3 equiv.) was added at 0 °C. After stirring for 15 min trimethylsilyl azide (0.38 ml, 2.20 mmol, 2 equiv.) was added at 0 °C, the reaction mixture was slowly warmed-up to room temperature and stirred for 48 h. The reaction mixture was evaporated under reduced pressure, the solid was washed with cold THF, filtered and dried under vacuum to give **BDC-N$_3$** as a yellow solid (0.24 g ,94%).

Synthesis of KSU-2. $Zn(NO_3)_2{\cdot}6H_2O$ (297.0 mg, 0.10 mmol), **DPG** (246.0 mg. 1.13 mmol), and DMF (80 mL) were combined in a 500 mL Florence flask. The flask was heated at 60 °C in a 500 mL heating block until the solution became clear. A solution of **BDC-N$_3$** (104.5 mg, 0.50 mmol) in DMF (20 mL) was added, and the flask incubated at 60 °C. After 24 h, the flask was removed from the heating block and left at room temperature for 24 h. Yellow crystals (142.7 mg, 21% yield) of the product were collected by filtration after several ~30 min washings with DMF.

General Procedure for the CuAAC reaction of MOF materials with phenyl acetylene.
Following a modified literature procedure,[2] the azide-bearing MOF (1 equiv) was transferred into a 10 mm diameter glass exchange thimble with a glass frit that was placed into a 20 mL scintillation vial. The vial was charged with phenyl acetylene (16 equiv) and enough DMF to make a 100 mM solution. This solution was degassed with bubbling N_2 gas for 60 minutes, before CuBr (10 mol%) was added. The mixture was left under N_2, at 60 °C for 72 h with continuous mixing on a Corning LSE Low Speed Orbital Shaker. The thimble containing the MOF material was then transferred to a new scintillation vial containing fresh DMF and mixed for ~30 min. The DMF was exchanged with fresh DMF, with ~30 min. mixing, 3 more times. Product crystals were isolated from the frit and stored under DMF.

CuAAC of KSU-2 (Synthesis of KSU-2$_{\text{triazole}}$). **KSU-2** (50 mg, 0.066 mmol, ca. 0.132 mmol of $-N_3$), phenyl acetylene (214 µL, 1.0 mmol), DMF (10 mL), and CuBr (14.3 mg, 0.1 mmol). Green crystals were isolated from the frit (98% yield) and stored under DMF.

CuAAC of KSU-2$_{\text{dicarbamate}}$ (Synthesis of KSU-2$_{\text{bi-Path1}}$). **KSU-2 $_{\text{dicarbamate}}$** (50 mg, 0.054 mmol, ca. 0.108 mmol of $-N_3$), phenyl acetylene (214 µL, ~1.0 mmol), DMF (10 mL), and CuBr (14.3 mg, 0.1 mmol). Brownish-green crystals were isolated from the frit (93% yield) and stored under DMF.

General Procedure for the reaction of MOF materials with isopropyl isocyanate
Following a modified literature procedure,[3] the DPG-containing MOF (1 equiv) was transferred into a 10 mm diameter glass exchange thimble with glass frit, that was placed into a 20 mL scintillation vial that had been charged with isopropyl isocyanate (12 equiv) and enough MeCN to make a 0.2 M solution. The mixture was left at 80 °C for 48 h with continuous mixing on a Corning LSE Low Speed Orbital Shaker. The thimble containing the MOF material was then transferred to a new scintillation vial containing fresh MeCN and mixed for ~30 min. The MeCN was exchanged with fresh MeCN, and shaken for ~30 min., 3 more times. The solvent was exchanged with fresh DMF, and shaken, a further 3 times. MOF crystals were isolated from the frit and stored under DMF.

Reaction of KSU-2 with isopropyl isocyanate (Synthesis of KSU-2$_{\text{dicarbamate}}$). **KSU-2** (50 mg, 0.066 mmol, ca. 0.132 mmol of −OH), isopropyl isocyanate (78 µL, 0.80 mmol), and MeCN (4 mL). Reddish-brown crystals were isolated from the frit (67% yield) and stored under DMF.

Reaction of KSU-2$_{\text{triazole}}$ with isopropyl isocyanate (Synthesis of KSU-2$_{\text{bi-Path2}}$). **KSU-2$_{\text{triazole}}$** (50 mg, 0.052mmol, ca. 0.104 mmol of −OH), isopropyl isocyanate (61µL, 0.62 mmol), and MeCN (4 mL). Green crystals were isolated from the frit (87% yield) and stored under DMF.

Procedure for the simultaneous reaction of KSU-2 with phenyl acetylene and isopropyl isocyanate (Synthesis of KSU-2$_{\text{bi-Sim}}$).

KSU-2 (50 mg, 0.066 mmol, ca. 0.132 mmol of $-N_3$, ca. 0.132 mmol of −OH) was transferred into a 10 mm diameter glass exchange thimble with a glass frit that was placed into a 20 mL scintillation vial. The vial was charged with phenyl acetylene (214 µL, 1.0 mmol), isopropyl isocyanate (196 µL, 2.0 mmol), and 10 mL of MeCN:DMF (50:50 v/v). This solution was degassed with bubbling N_2 gas for 60 minutes, before CuBr (14.3 mg, 0.1 mmol, 10 mol %) was added. The mixture was left under N_2, at 60 °C for 6 days with continuous mixing on a Corning LSE Low Speed Orbital Shaker. The thimble containing the MOF material was then transferred to a new scintillation vial containing fresh DMF:MeCN and mixed for ~30 min. The DMF was exchanged with fresh DMF, with ~30 min. mixing, 3 more times. Product crystals were isolated from the frit and stored under DMF.

POWDER X-RAY DIFFRACTION (PXRD)

Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker AXS D8 Advance Phaser diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) with Cu Kα radiation (λ = 1.5418 Å) over a range of 4° < 2θ < 40° in 0.02° steps with a 0.5 s counting time per step. Samples were collected from the bottom of the reaction vial as a thick suspension in DMF and spread on a Si-Einkristalle plate immediately before PXRD measurements.

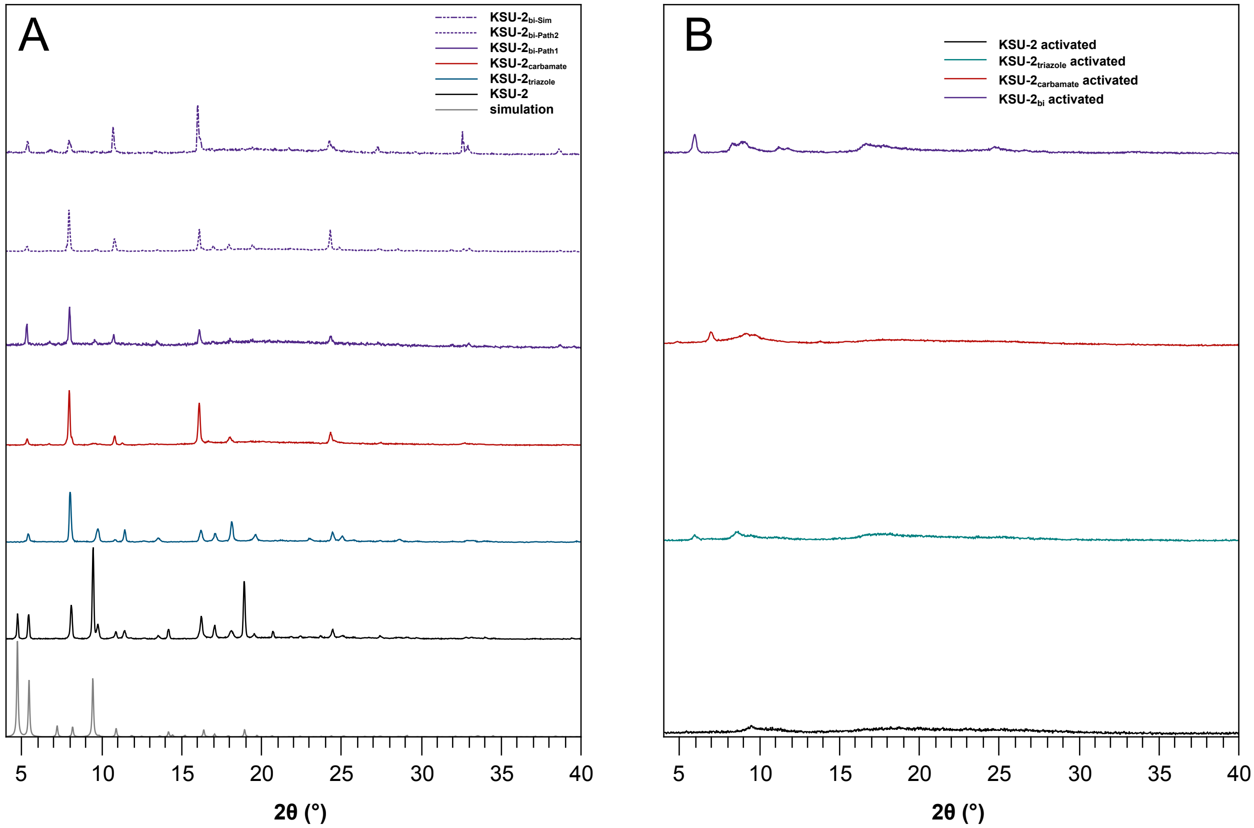

Figure S1. A: The simulated PXRD pattern for **KSU-2**, along with the experimental PXRD data for **KSU-2**, **KSU-2$_{\text{triazole}}$**, **KSU-2$_{\text{bi-Path1}}$**, **KSU-2$_{\text{dicarbamate}}$**, **KSU-2$_{\text{bi-Path2}}$**, and **KSU-2$_{\text{bi-Sim}}$**. B: PXRD patterns for activated samples.

PROTON NUCLEAR MAGNETIC RESONANCE (^{1}H NMR)

Proton NMR spectra were recorded on a Bruker Avance NEO spectrometer (400 MHz for ^{1}H, Bruker BioSpin, Billerica, MA, USA). NMR chemical shifts are reported in ppm against a residual solvent resonance as the internal standard (δ(d_6-DMSO) = 2.5 ppm). In a typical analysis, MOF materials stored in DMF were solvent exchanged with $CHCl_3$, isolated by vacuum filtration, and then evacuated in a vacuum oven at 80 °C overnight. Evacuated MOF samples (5-6 mg) were transferred into an NMR tube and d_6-DMSO (0.55 mL) was added. Subsequently, D_2SO_4 (0.09 mL, 98% w/w in D_2O) was also added. The tubes were capped and sonicated until all the solid was dissolved (~ 1 min).

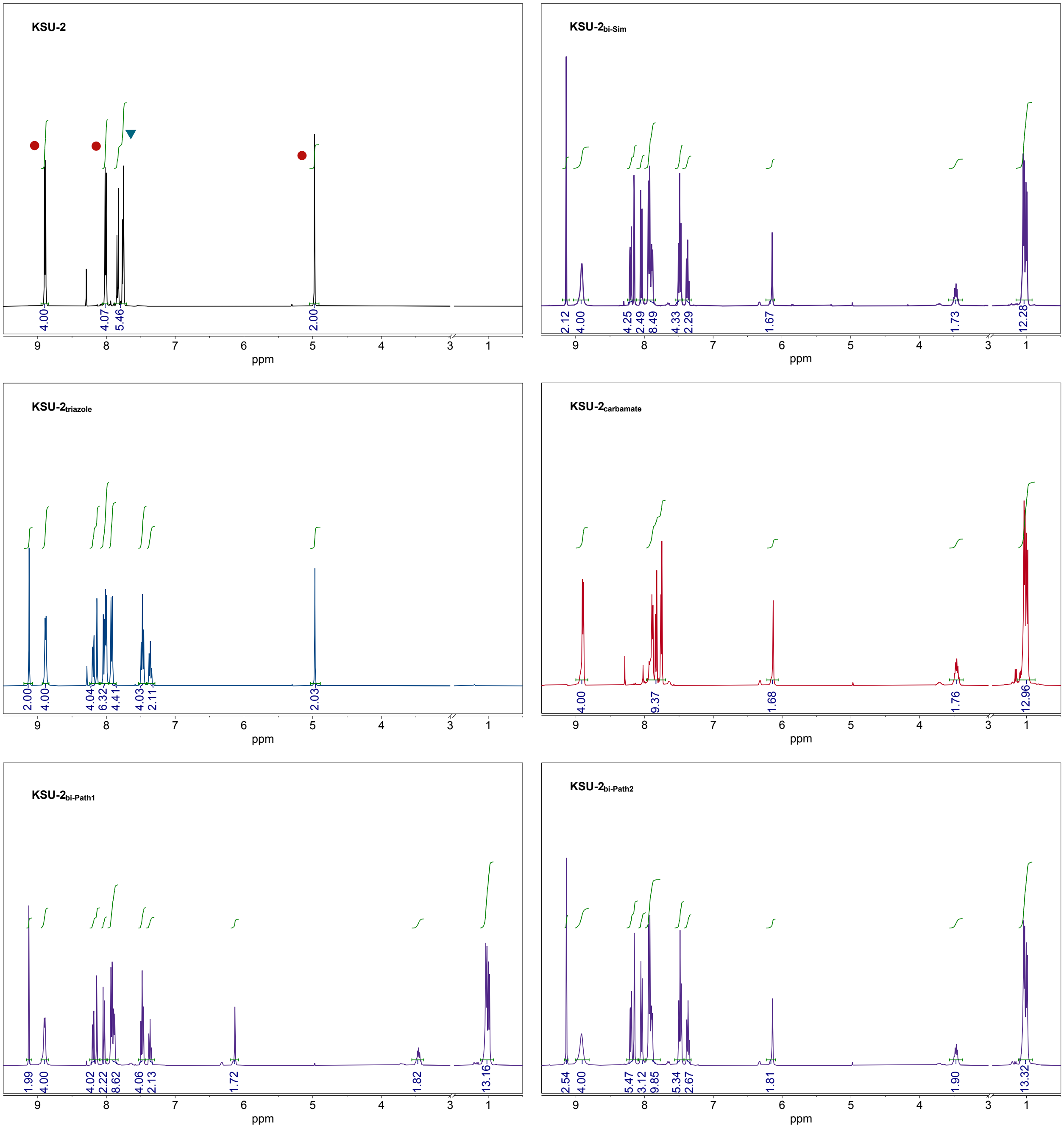

Figure S2. Integrated ^{1}H-NMR spectrum for **KSU-2**, **KSU-2$_{triazole}$**, **KSU-2$_{bi\text{-}Path1}$**, **KSU-2$_{bi\text{-}Sim}$**, **KSU-2$_{dicarbamate}$**, and **KSU-2$_{bi\text{-}Path2}$** digested in D_2SO_4/d_6-DMSO. For **KSU-2**, red circles mark the DPG protons and cyan triangles mark the BDC-N_3 protons.

NITROGEN GAS ADSORPTION/DESORPTION

Measurements were performed on an Autosorb iQMP (Quantachrome Instruments, Anton Paar USA, Ashland VA) at 77 K. Samples were prepared in the following manner: MOF materials that had undergone DMF to hexanes solvent exchanges were again solvent exchanged with chloroform by two quick washes. Finally, the sample was washed with dichloromethane and dried under vacuum (< 10-3 torr) at 60 °C for 5 h. Using the "outgas" function of the surface area analyzer, the sample was dried again for 360 min at 80 °C to remove all residual solvent.

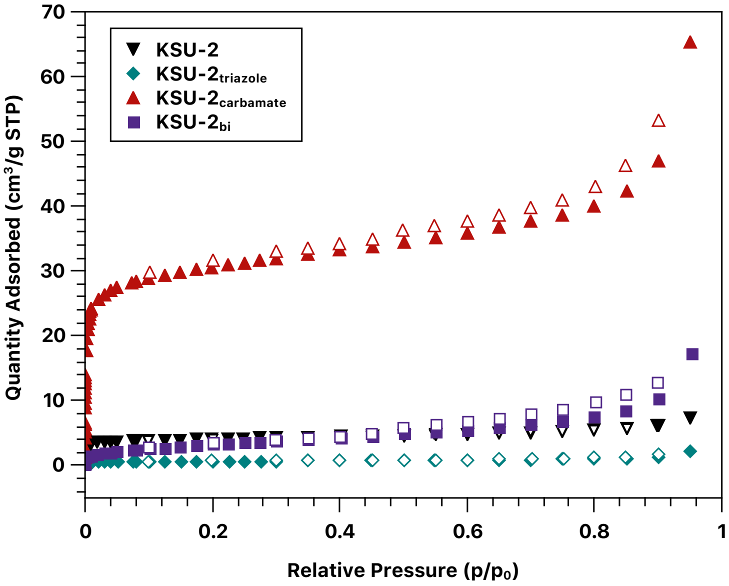

FIGURE S3. N_2 gas adsorption measurements. Closed: adsorption. Open: desorption).

THERMOGRAVIMETRIC ANALYSIS (TGA)

TGA was performed on a TGA-Q50 (TA Instruments, New Castle, DE, USA) interfaced with a PC using TA Universal Analysis software. Samples were heated at a rate of 10 ºC/min under a nitrogen atmosphere. All samples were extensively solvent exchanged with fresh DMF prior to analysis.

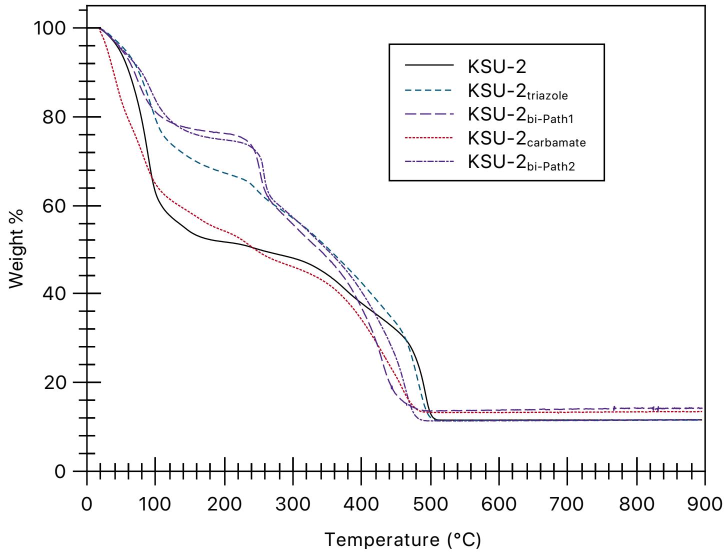

Figure S4. TGA data for **KSU-2**, **KSU-2$_{triazole}$**, **KSU-2$_{bi\text{-}Path1}$**, **KSU-2$_{dicarbamate}$**, and **KSU-2$_{bi\text{-}Path2}$**.

FOURIER-TRANSFORM INFRARED SPECTROSCOPY (FTIR)

Fourier-transform infrared spectroscopy was performed on a Agilent Cary 630 spectrometer (Agilent Technologies, Santa Clara, CA, USA). Spectra were collected on MOF samples (~1 mg) which had combined with 5 mass equivalents (~5 mg) of KBr and ground together to a fine powder.

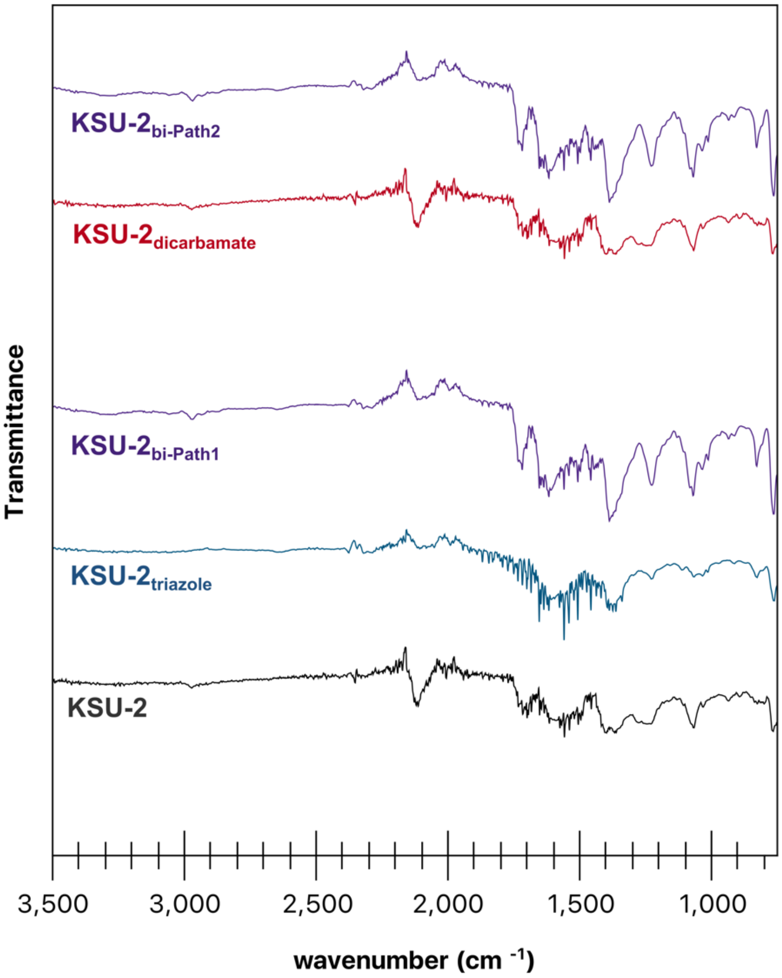

FIGURE S5. Fourier-transform infrared (FTIR) spectroscopy of **KSU-2**, **KSU-2$_{triazole}$**, **KSU-2$_{bi\text{-}Path1}$**, **KSU-2$_{dicarbamate}$**, and **KSU-2$_{bi\text{-}Path2}$**.

ELECTROSPRAY IONIZATION MASS SPECTROMETRY (ESI)

MOF samples (~5mg) were placed in a solution of DABCO (10 mg) and 0.25ml of DMSO in a 2-dram vial. The vial was sonicated for ~ 1 min then heated at 80 °C overnight. A small amount of residue was filtered out and resulting solution was sent for ESI-MS analysis at the Mass Spectrometry Laboratory at the University of Illinois, Urbana-Champaign.

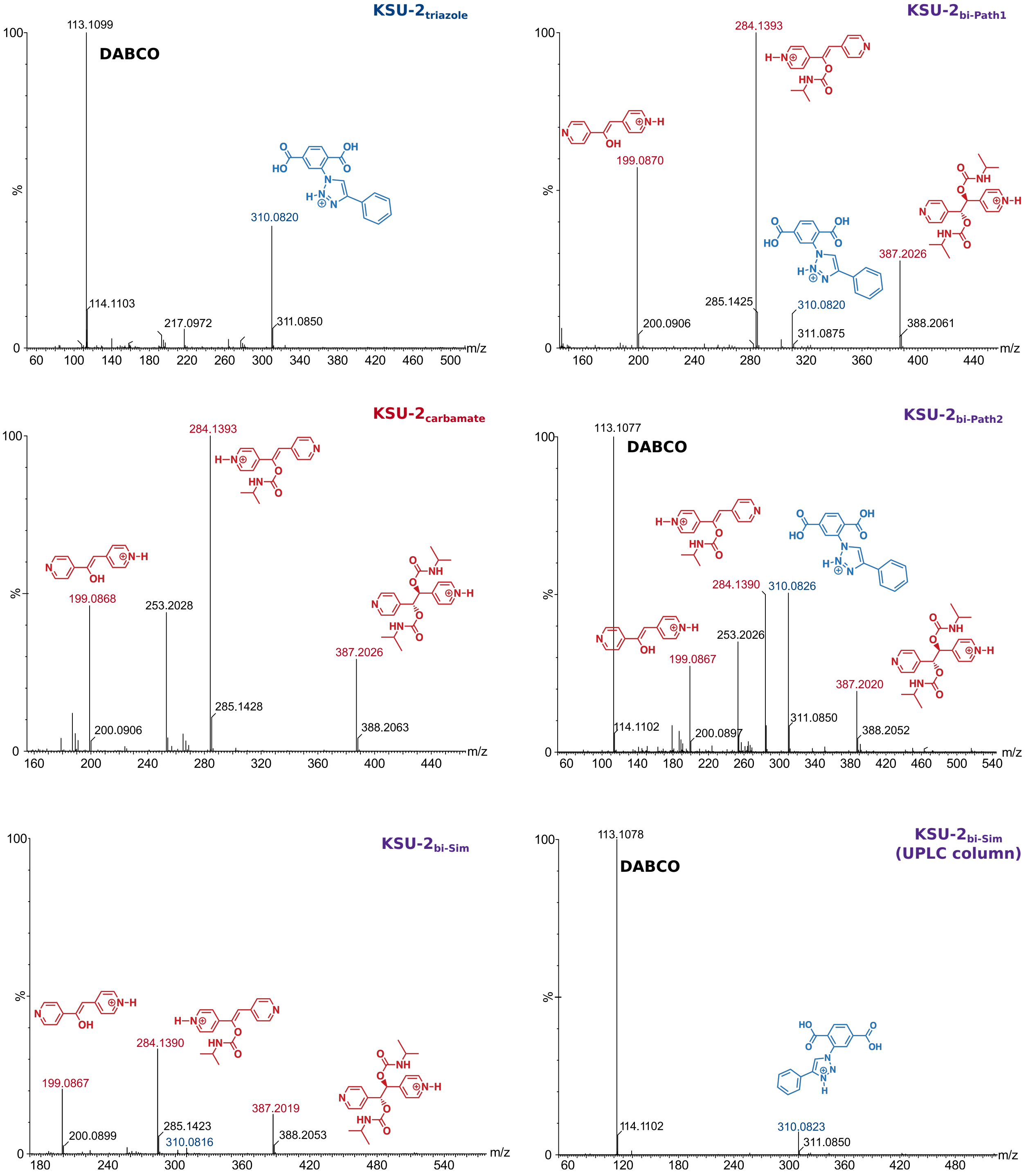

FIGURE S6. High-resolution, positive mode ESI-MS of **KSU-2**$_{\textbf{triazole}}$, **KSU-2**$_{\textbf{bi-Path1}}$, **KSU-2**$_{\textbf{dicarbamate}}$, **KSU-2**$_{\textbf{bi-Path2}}$, **KSU-2**$_{\textbf{bi-Sim}}$, and m/z=310 peak of **KSU-2**$_{\textbf{bi-Sim}}$ isolated on ultra-performance liquid chromatography (UPLC) column.

SINGLE-CRYSTAL X-RAY CRYSTALLOGRAPHY ANALYSIS FOR KSU-2.

A set of diffraction data [38465 reflections using 2290 1º-wide ω- or ϕ-scan frames with scan times of 8-20 seconds] was collected[4] for a single-domain crystal of *KSU-2* using monochromated CuKα radiation (λ = 1.54178 Å) on a Bruker Proteum Single Crystal Diffraction System with dual CCD detectors and associated Helios high-brilliance multilayer optics and a shared Bruker MicroSTAR microfocus Cu rotating anode x-ray source operating at 45kV and 60mA. Data for *KSU-2* was collected with a Platinum 135 CCD detector and a crystal-to-detector distance of 50 mm. The integrated data[5] were corrected empirically for variable absorption effects using equivalent reflections. The Bruker software package SHELXTL was used to solve the structure using "direct methods" techniques. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data with the SHELXTL XL v2018 Version 1 software package.[6] Final crystallographic details are summarized in Table S1.

The asymmetric unit of *KSU-2* contains two Zn^{2+} cations, two 2-azido-1,4-dicarboxylate dianions and one neutral *meso-α,β*-di(4-pyridyl) glycol moiety. Although disorder is common and not unexpected in MOF structures, the bridging ligands in this particular system have additional potential for inherent disorder. While octahedral coordination at the Zn ions will preclude much rotational disorder of the planar terephthalate ligands about the Zn----Zn vector, each "locked" ligand can still bridge the same two Zn metals in four different ways. Since the *meso-α,β*-di(4-pyridyl) glycol ligand coordinates to a Zn atom through a single nitrogen on each end, it could have different rotational orientations about the Zn----Zn vector. The ligand could also bridge the same two metals with its two ends interchanged. Fortunately, both of the terephthalate ligands appear to have only three of the four possible orientations and the di(4-pyridyl) glycol ligands do not appear to be have significant rotational disorder about the Zn----Zn vector.

Fourier maps from the initial structure solution clearly revealed the Zn atoms, all C and O atoms of the terephthalate ligands and the pyridine rings of the di(4-pyridyl) glycol ligand. Non-structured (presumably disordered) electron density was present between the two pyridine moieties. After refining these clearly identified atoms with isotropic thermal parameters, the Zn and terephthalate carbon and oxygen atoms were refined with anisotropic thermal parameters. A difference Fourier revealed low electron density at *sp*^{2}-hybridized positions for four ortho (4- and 7-) carbons of both terephthalate ligands. It also contained a more structured region of electron density between the two coordinated pyridine ligands. The occupancy factors and isotropic thermal parameters for two (one for each terephthalate ligand) of the eight ortho (4- and 7-) nitrogens behaved erratically during refinement cycles and were eventually removed from the structural model. The remaining six nitrogens were included in the final structural model with isotropic thermal parameters and variable occupancy factors that refined to final values ranging from 0.035 to 0.110 for the two terephthalate ligands. Reasonable electron density corresponding to the second and third azide nitrogen atoms did not appear in any difference Fourier.

The published structure of *meso-α,β*-di(4-pyridyl) glycol was then used with the coordinates of the two pyridine ligands and the disordered electron density between them to derive coordinates for two bridging modes for the *meso-α,β*-di(4-pyridyl) glycol ligand in *KSU-2*. Bond lengths and angles for the atoms of these two *meso-α,β*-di(4-pyridyl) glycol bridging modes were required to have values similar to the published structure. The bond lengths and angles were restrained to idealized sp^2- or sp^3-hybridized multiples of the aromatic C=C bond length that was included in the refinement as a free variable; it refined to a final value of 1.295(2) Å. All four of the 7-atom p-methylpyridine moieties and both 10-atom terephthalate (C21-C27, N24, N26, N27; and C31-C37, N34, N36, N37) moieties were also required to be coplanar. The normalized occupancy factors for the two *meso-α,β*-di(4-pyridyl) glycol bridging modes refined to 52%/48%.

Since the terephthalate atoms were disordered but reasonably well-defined and all of the *meso-α,β*-di(4-pyridyl) glycol nonhydrogen atoms linking the pyridine rings were disordered and not well-defined, the *meso-α,β*-di(4-pyridyl) glycol ligand nonhydrogen atoms were included in the structural model with isotropic thermal parameters. Hydrogen atoms bonded to carbon in all ligands were included in the structural model as idealized riding model atoms (assuming sp^2- or sp^3-hybridization of the carbon atoms and C-H bond lengths of 0.95 Å or 1.00 Å). Hydrogen atoms bonded to hydroxyl oxygen atoms were included as idealized riding model atoms (assuming or sp^3-hybridization of the oxygen atom and an O-H bond length of 0.84 Å) that were free to rotate about their C-O bonds in least-squares refinement cycles. The isotropic thermal parameters of idealized hydrogen atoms in all ligands were fixed at values 1.2 (bonded to C) or 1.5 (bonded to O) times the equivalent isotropic thermal parameter of the carbon or oxygen atom to which they are covalently bonded. The x coordinate of disordered glycol carbon atom C7 was fixed in the final refinement cycles and a DAMP parameter of 400 was used to aid convergence. Low residual difference Fourier electron density appearing at reasonable positions in the MOF channels was included in the structural model as disordered partial-occupancy isotropic oxygen atoms that still did not completely fill the structural voids. Refinement of racemic twinning revealed the crystal was a 69/31 racemic twin.

Table S1. Crystal and Refinement Data *KSU-2*.

	KSU-2
Empirical formula	$C_{28.00}H_{14.00}N_{4.00}O_{16.32}Zn_{2.00}$
Formula weight	299.44
Temperature	200(2) K
Wavelength	1.54178 Å
Crystal system	Trigonal
Space group	$P3 – C_3^1$ (No. 143)
a	21.5814(4) Å
b	21.5814(4) Å
c	16.1592(3) Å
a	90.00°
β	90.00°
γ	120.00°
Volume	6517.9(3)$Å^3$
Z	3
Density (calculated)	0.610 g/cm^3
Absorption coefficient	0.956 mm^{-1}
F(000)	1202
Crystal size	0.050 x 0.050 x 0.040 mm^3
Theta range	2.36 to 70.52°
Index ranges	$-25\leq h\leq 26$, $-24\leq k\leq 26$, $-14\leq l\leq 19$
Reflections collected	85166
Independent reflections	14685 [R_{int} = 0.064]
Completeness to θ = 66°	99.9 %
Absorption correction	Multi-scan
Max. and min. transmission	1.000 and 0.756
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14685 / 107 / 454
Goodness-of-fit on F^2	1.062
Final R indices [I>2σ(I)]	R_1 = 0.108, wR_2 = 0.278
R indices (all data)	R_1 = 0.141, wR_2 = 0.331
Largest diff. peak and hole	1.26 and -1.09 $e^-/Å^3$

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2. X.-C. Yi, F.-G. Xi, Y. Qi and E.-Q. Gao, *RSC Adv.*, 2014, **5**, 893–900.
3. X.-W. Dong, T. Liu, Y.-Z. Hu, X.-Y. Liu and C.-M. Che, *Chem. Commun.*, 2013, **49**, 7681–7683.
4. Data Collection: SMART Software in APEX2 v2014.11-0 Suite. Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711-5373 USA.
5. Data Reduction: SAINT Software in APEX2 v2014.11-0 Suite. Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711-5373 USA.
6. Refinement: SHELXTL Software in APEX2 v2014.11-0 Suite. Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711-5373 USA.