

## Unexpected reversal of reactivity in organic functionalities when immobilized together in a metal-organic framework (MOF)

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## MATERIALS

All chemicals were used as received from commercial sources unless otherwise noted. Isopropyl isocyanate (98%), ethyl isocyanate (98%), *n*-propyl isocyanate (99%), allyl isocyanate (98%), phenyl isocyanate ( $\geq 98\%$ ), 2-aminoterephthalic acid (**BDC-NH<sub>2</sub>**, 99%), terephthalic acid (benzene dicarboxylic acid, **BDC**, 98%), and chloroform were purchased from Sigma Aldrich. Meso- $\alpha,\beta$ -di(4-pyridyl) glycol (**DPG**, 98.0+%), 4,4'-bipyridine (**BIPY**, 98%), 3,5-bis(trifluoromethyl)phenyl isocyanate (98.0+%), triethylamine (99%), and diisopropylethylamine (99%) were purchased from TCI. Sulfuric acid-*d*<sub>2</sub> (D<sub>2</sub>SO<sub>4</sub>, 98 wt.% in D<sub>2</sub>O, 99.5+% atom D) was purchased from Acros Organics. *N,N*-dimethylformamide (DMF), acetonitrile, chloroform, and toluene was purchased from Fisher Scientific (ACS certified). Zinc nitrate hexahydrate was purchased from Strem Chemicals, and 3-isocyanatopyridyl (95%) from Enamine. 1,4-Diazabicyclo[2.2.2]octane (DABCO) (95%) was purchased from Oakwood Products. Dimethyl sulfoxide-*d*<sub>6</sub> (*d*<sub>6</sub>-DMSO, 99.9 atom % D) was purchased from Cambridge Isotopes Laboratories.

## SYNTHETIC PROCEDURES

**Synthesis of KSU-1000.** Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (940 mg; 3.16 mmol), **BIPY** (624 mg; 4.00 mmol), and DMF (100 mL) were combined in a 500 mL Florence flask. A solution of **BDC-NH<sub>2</sub>** (181 mg, 1.00 mmol) in DMF (20 mL) was added, and the flask incubated at 60 °C. After 1 h, the flask was removed from the heating block and left at room temperature for a month. Yellow-orange crystals (135 mg, 27 % yield) of the product were collected by filtration after several ~30 min washings with DMF.

**Synthesis of KSU-3.** Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (223 mg; 0.75 mmol), **DPG** (182 mg; 0.84 mmol), deionized water (2 mL) and DMF (180 mL) were combined in a 500 mL Florence flask. The flask was heated at 60 °C in an oven until all solids dissolved and the solution became clear. A solution of **BDC** (140 mg; 0.84 mmol) in DMF (20 mL) was added, and the flask incubated at 60 °C. After 24 h, the flask was removed from the oven and left at room temperature for 48 h. Colorless transparent crystals (142 mg, 28 % yield) of the product were collected by filtration and washed several times with warm DMF (~60 °C).

### General procedure for the reaction of MOF materials with isocyanates.

At least three replicates were performed for all experiments. In a typical experiment, the as-synthesized MOF in DMF was filtered and ~15 mg was transferred to a 1-dram vial containing fresh acetonitrile and mixed for ~30 min. The supernatant was exchanged with fresh acetonitrile and mixed for ~30 min. 3 more times. After the final rinsing, 2 mL of a 0.2 M solution of the isocyanate (0.4 mmol) in acetonitrile were added to the vial. The reaction was left at 80 °C with continuous mixing on a Corning LSE Low Speed Orbital Shaker. Samples of the reacted MOF were taken at appropriate intervals, filtered, and digested for analysis.

**Table S1. Approximate amounts of MOF in reactions with isocyanate solutions (2 mL, 0.2 M).**

| MOF             | Weight (mg) | Moles (mmol) | -OH (mmol) | -NH <sub>2</sub> (mmol) |
|-----------------|-------------|--------------|------------|-------------------------|
| <b>KSU-1</b>    | 15 mg       | 0.021        | 0.043      | 0.043                   |
| <b>KSU-1000</b> | 15 mg       | 0.037        | -          | 0.037                   |
| <b>KSU-3</b>    | 15 mg       | 0.022        | 0.044      | -                       |

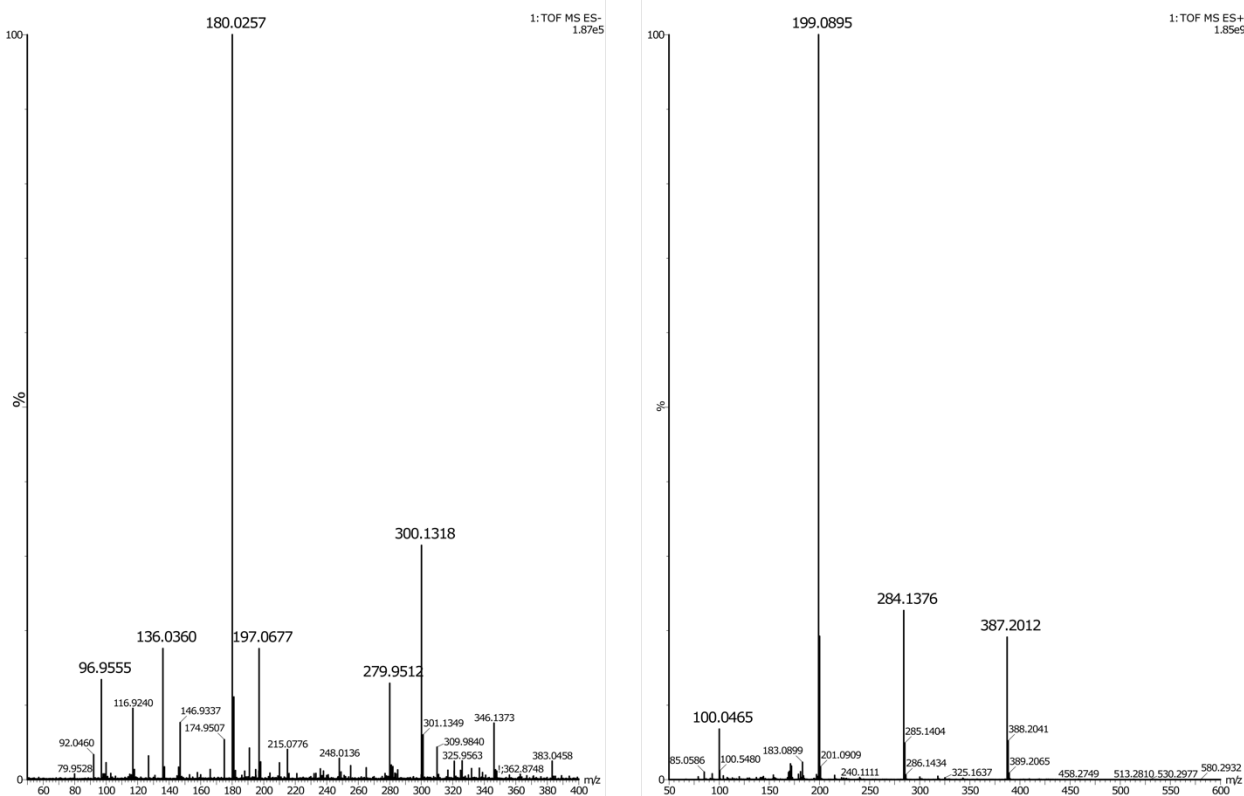
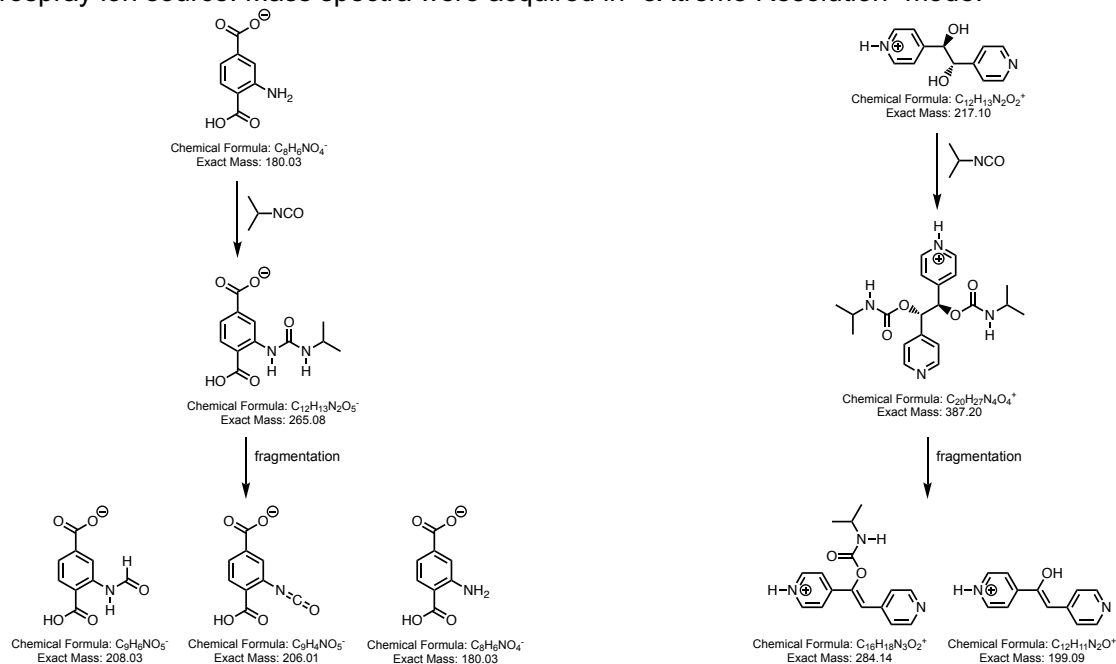
**Table S2. Reactions of KSU-1 -NH<sub>2</sub> and -OH with isopropyl isocyanate under different conditions.**

| Entry | Temp. | Additive (0.2 M)  | % Conversion 3 h (stdev) |         | % Conversion 24 h (stdev) |     |
|-------|-------|-------------------|--------------------------|---------|---------------------------|-----|
|       |       |                   | -NH <sub>2</sub>         | -OH     | -NH <sub>2</sub>          | -OH |
| 1     | 25 °C | -                 | 1                        | 4       | 3                         | 32  |
| 2     | 80 °C | Proton Sponge     | 8 (6)                    | 96 (4)  | -                         | -   |
| 3     | 80 °C | Et <sub>3</sub> N | 38 (11)                  | 82 (15) | -                         | -   |

0.2M in acetonitrile.

## HIGH-RESOLUTION MASS SPECTROMETRY (HRMS)

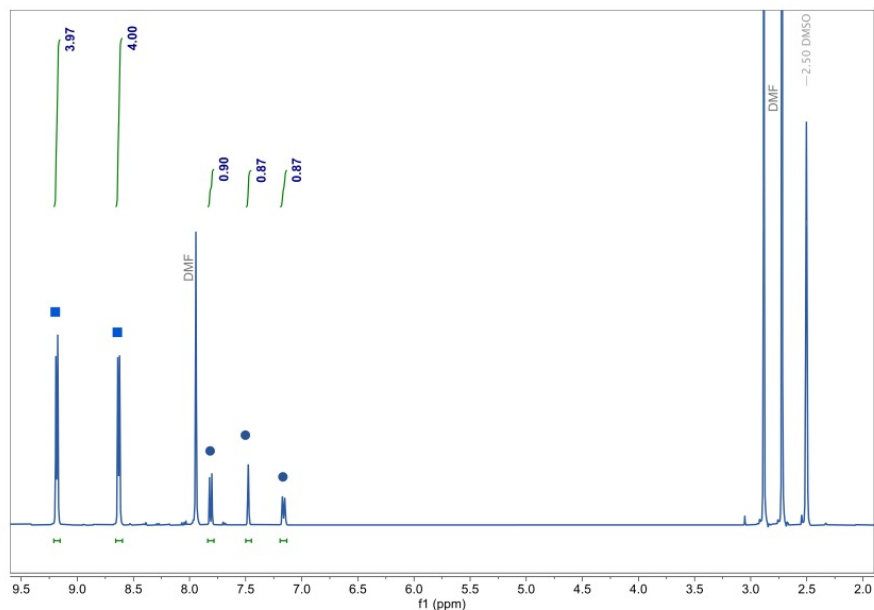
MOF samples (~5mg) were placed in a solution of DABCO (10 mg) and 0.25ml of DMSO in a 2-dram vial. The vial was sonicated for ~ 1 min then heated at 80 °C overnight. A small amount of residue was filtered out and the resulting solution was analyzed using a Xevo G2-XS QToF quadrupole time-of-flight mass spectrometer coupled with an ACQUITY M-class UPLC and a NanoLockSpray dual electrospray ion source. Mass spectra were acquired in “eXtreme Resolution” mode.



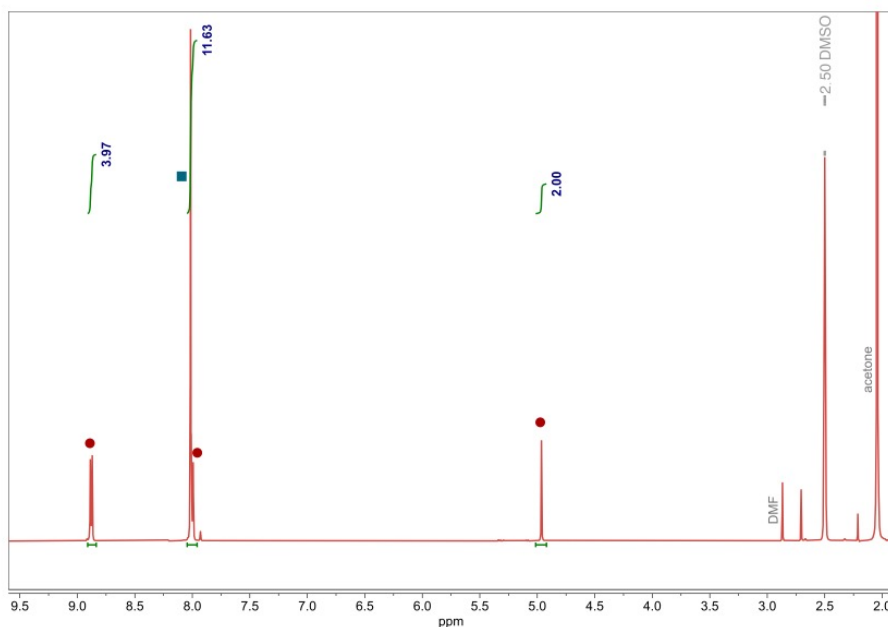
**FIGURE S1.** HRMS of KSU-1 after reacting with *i*-PrNCO (2 h). Left: the negative mode has no indication of the BDC urea product, though the [BDC-NH<sub>2</sub>-H<sup>+</sup>] starting material peak could also be a fragmentation product. Right: the positive mode has *m/z* peaks corresponding to DPG dicarbamate and its fragments, with no indication of starting DPG.

## PROTON NUCLEAR MAGNETIC RESONANCE ( $^1\text{H}$ NMR)

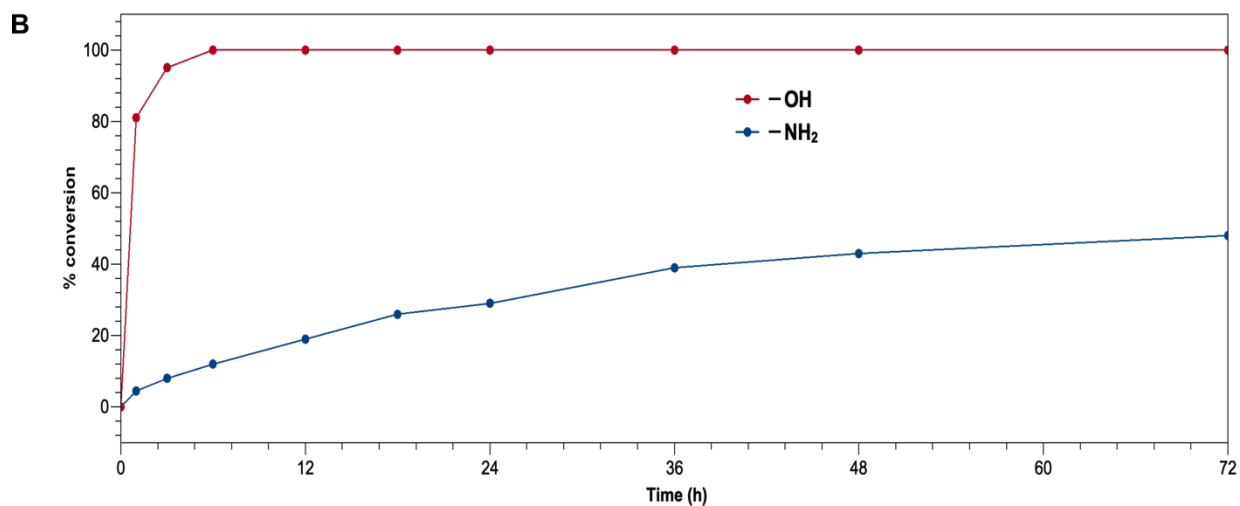
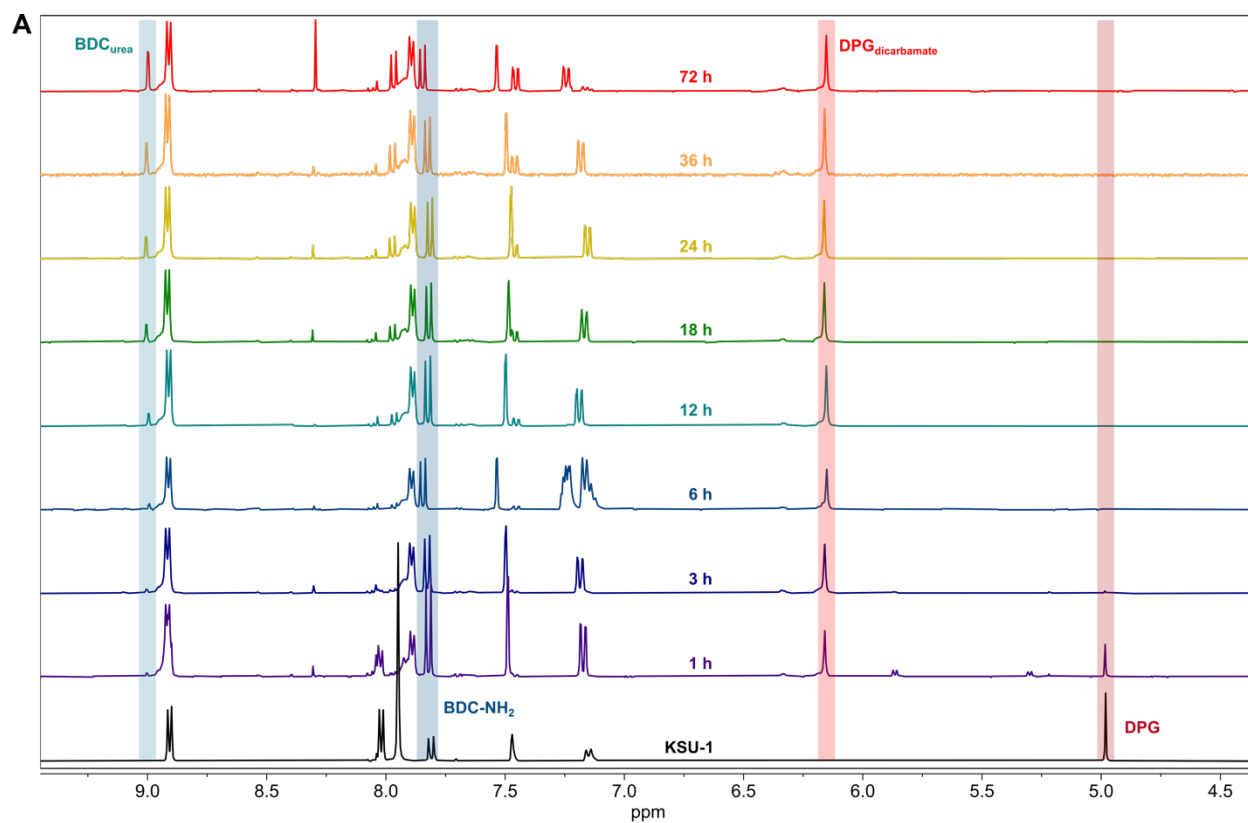
Spectra were recorded on a Bruker Avance NEO spectrometer (400 MHz for  $^1\text{H}$ , Bruker BioSpin, Billerica, MA, USA). NMR chemical shifts are reported in ppm against a residual solvent resonance as the internal standard ( $\delta(d_6\text{-DMSO}) = 2.5$  ppm). In a typical analysis, MOF materials stored in DMF were solvent exchanged with  $\text{CHCl}_3$ , isolated by vacuum filtration, and then evacuated in a vacuum oven at  $80^\circ\text{C}$  overnight. Evacuated MOF samples (5-6 mg) were transferred into an NMR tube and  $d_6\text{-DMSO}$  (0.55 mL) was added. Subsequently,  $\text{D}_2\text{SO}_4$  (0.09 mL, 98% w/w in  $\text{D}_2\text{O}$ ) was also added. The tubes were capped and sonicated until all the solid was dissolved ( $\sim 1$  min).



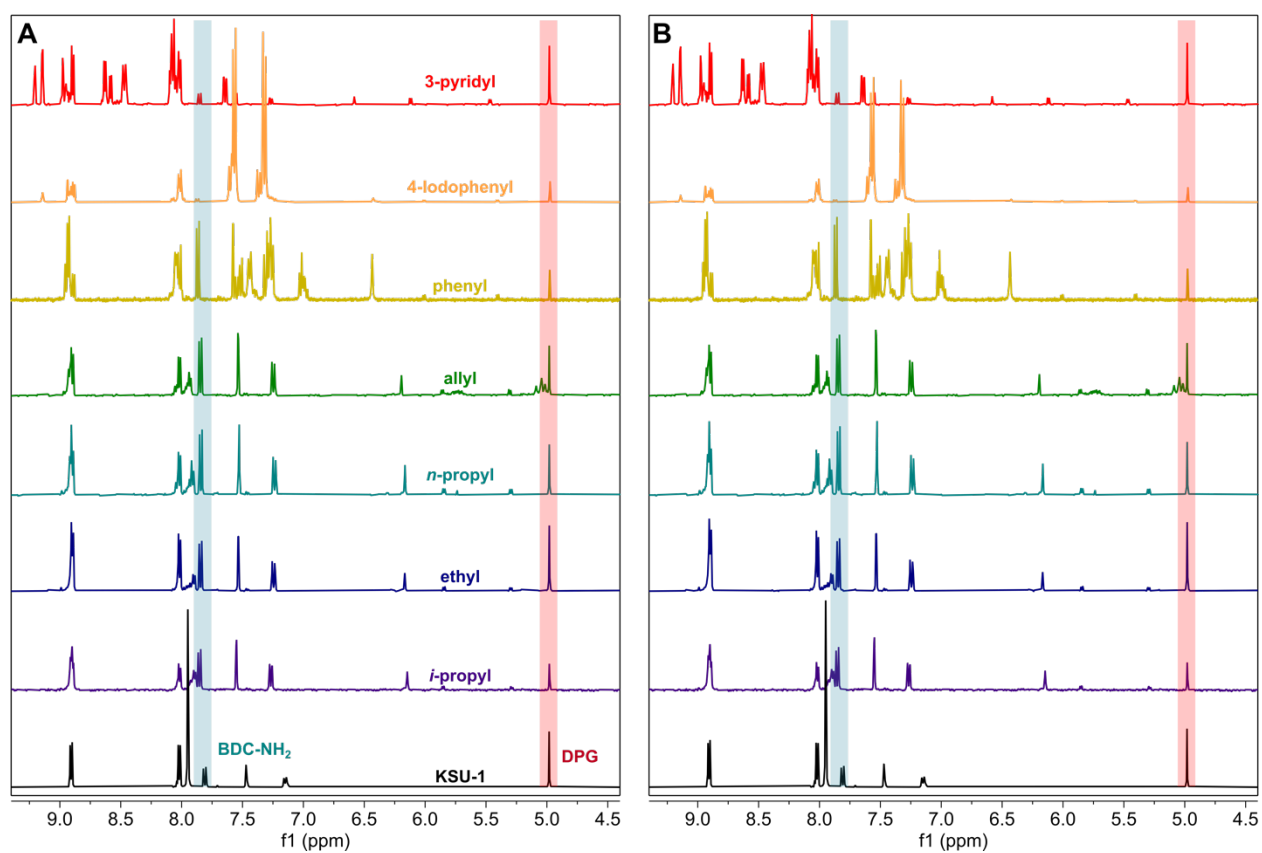
**Figure S2.**  $^1\text{H}$ -NMR (400 MHz,  $d_6\text{-DMSO}/\text{D}_2\text{SO}_4$ ) spectrum of **KSU-1000**. Circles represent 2 molecules of BDC- $\text{NH}_2$  [ $\delta$  7.81 (d, 2H,  $J = 8$  Hz, ArH),  $\delta$  7.48 (s, 2H, ArH),  $\delta$  7.16 (d, 2H,  $J = 8$  Hz, ArH)]. Squares represent one molecule of BIPY [ $\delta$  9.82 (d, 4H,  $J = 6.5$  Hz, ArH),  $\delta$  8.63 (d, 4H,  $J = 6.5$  Hz, ArH)].



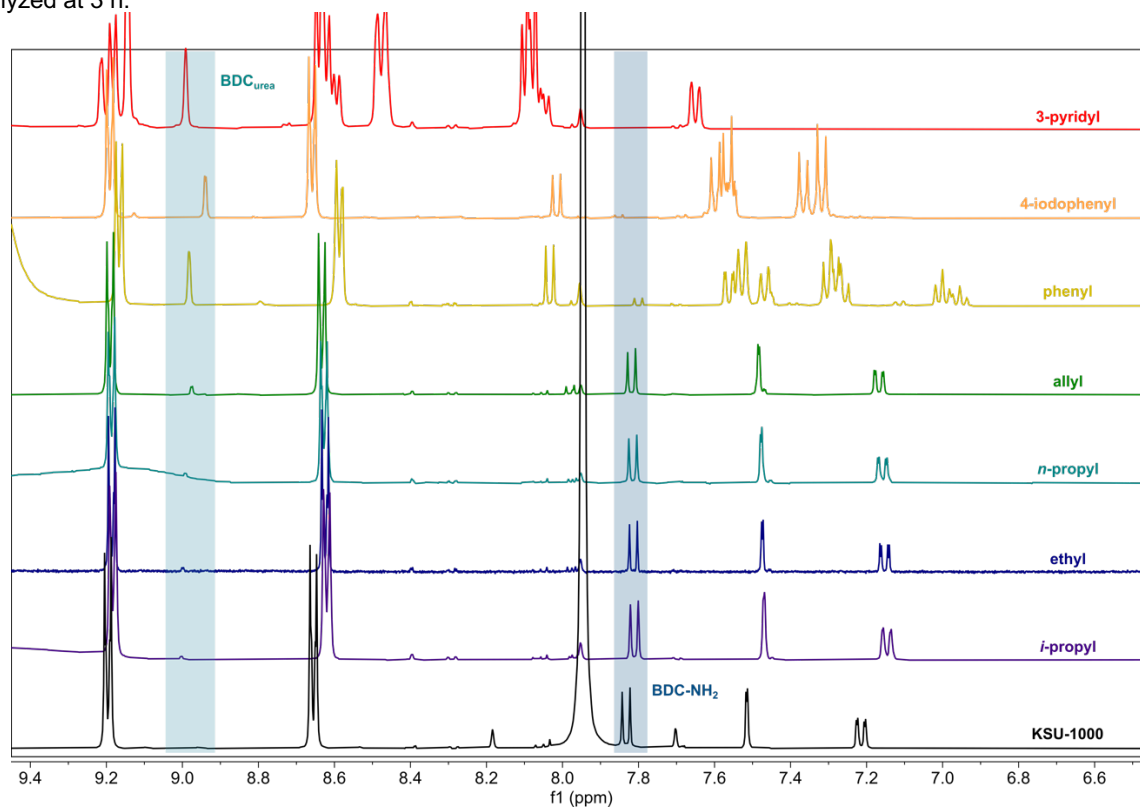
**Figure S3.**  $^1\text{H}$ -NMR (400 MHz,  $d_6\text{-DMSO}/\text{D}_2\text{SO}_4$ ) spectrum of **KSU-3**. Circles represent 1 molecule of DPG [ $\delta$  8.88 (d, 4H,  $J = 6.5$  Hz, ArH),  $\delta$  8.00 (s, 4H,  $J = 6.5$  Hz, ArH),  $\delta$  4.96 (s, 2H,  $-\text{CHOH}$ )]. Square represents two molecules of BDC [ $\delta$  8.02 (s, 8H, ArH)].



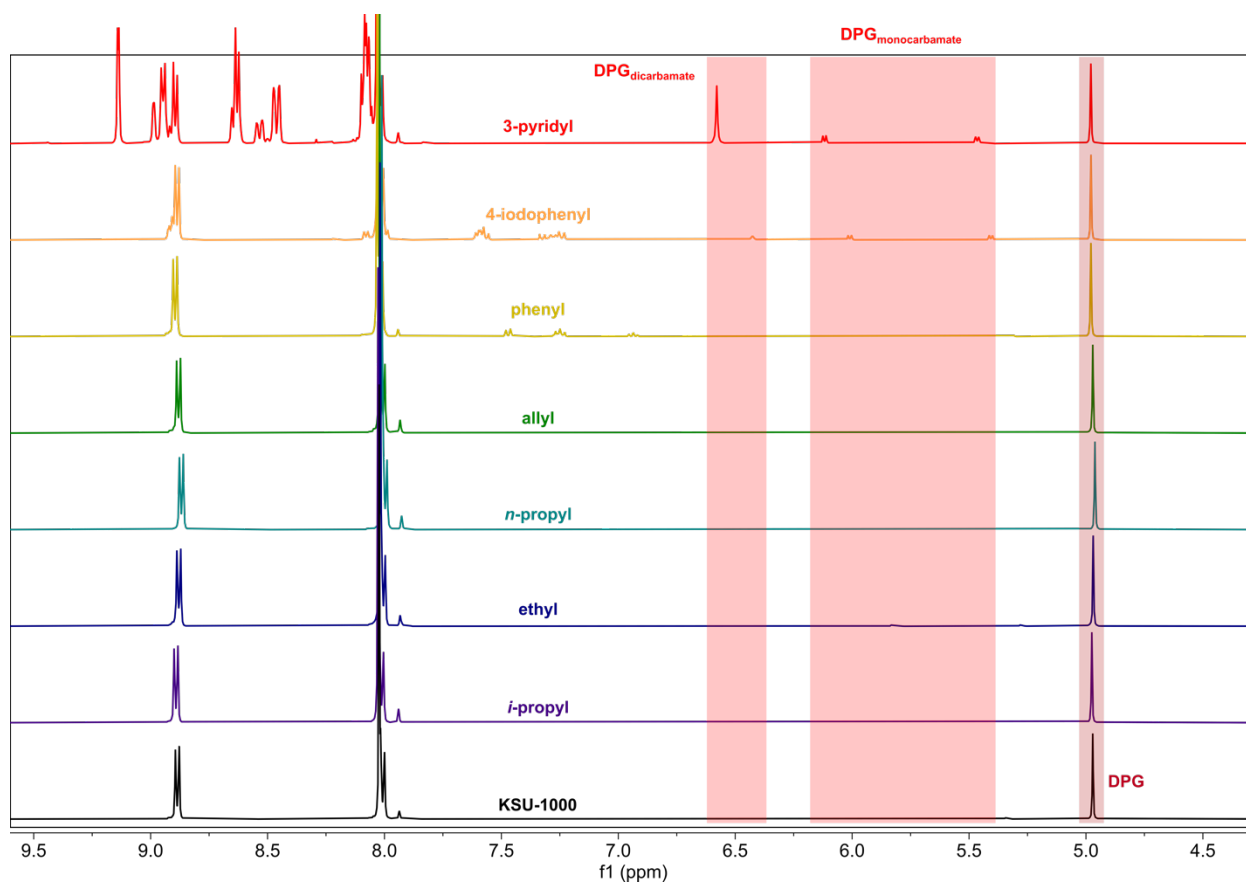
**Figure S4.** A: Representative <sup>1</sup>H-NMR spectra of reactions of **KSU-1** with isopropyl isocyanate over a 72 h period. B: Plot of conversions over time.



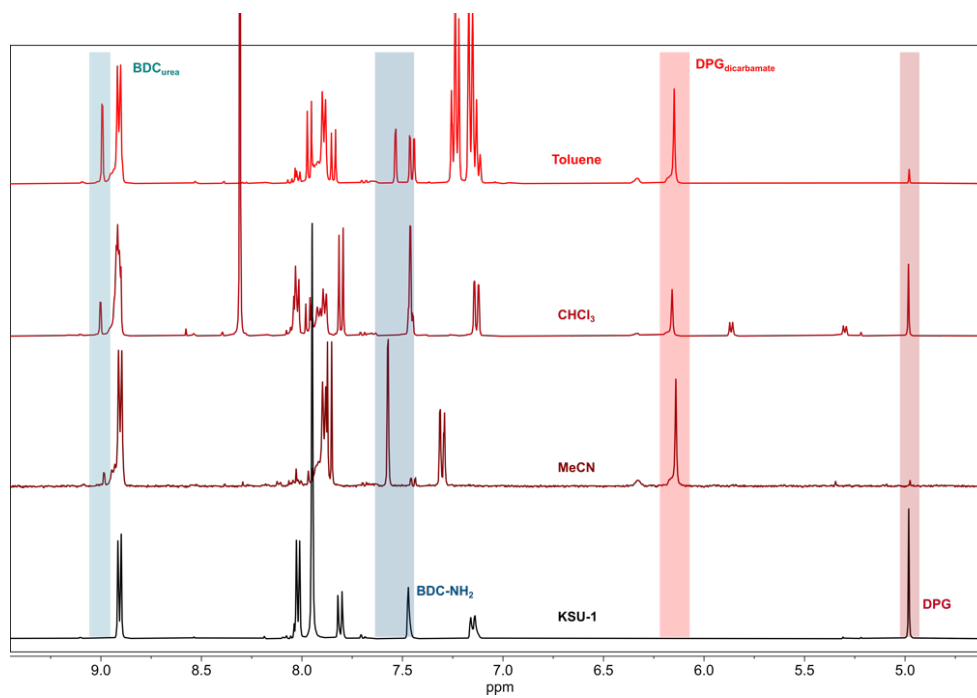
**Figure S5.** Representative  $^1\text{H-NMR}$  spectra of reactions of **KSU-1** with different isocyanates. A: Analyzed at 1 h. B: Analyzed at 3 h.



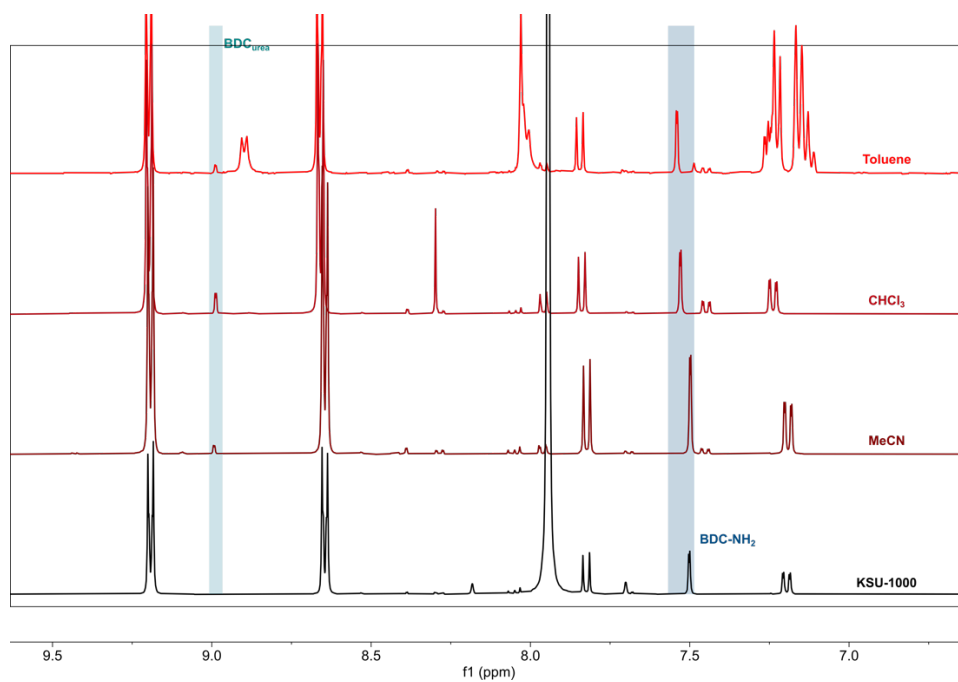
**Figure S6.** Representative  $^1\text{H-NMR}$  spectra of reactions of **KSU-1000** with different isocyanates (1 h).



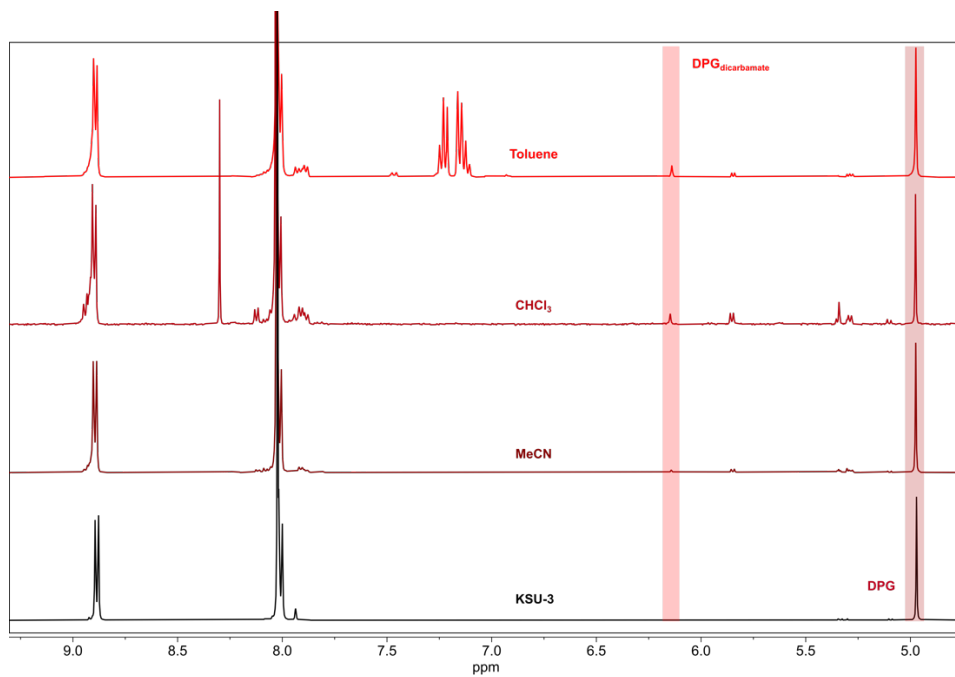
**Figure S7.** Representative  $^1\text{H-NMR}$  spectra of reactions of **KSU-3** with different isocyanates (1 h).



**Figure S8.** Representative  $^1\text{H-NMR}$  spectra of reactions of **KSU-1** with isopropyl isocyanate in different solvents (3 h).

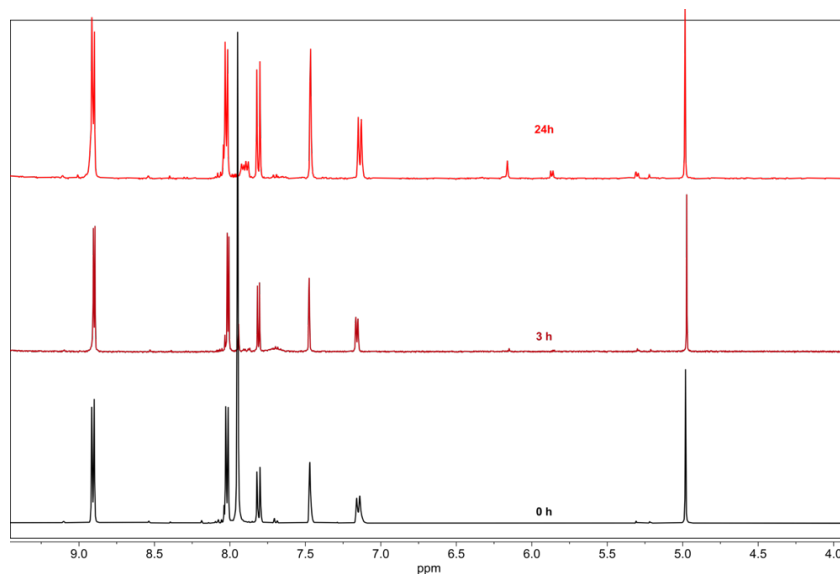


**Figure S9.** Representative <sup>1</sup>H-NMR spectra of reactions of **KSU-1000** with isopropyl isocyanate in different solvents (3 h).



**Figure S10.** Representative <sup>1</sup>H-NMR spectra of reactions of **KSU-3** with isopropyl isocyanate in different solvents (3 h).





**Figure S11.**  $^1\text{H}$ -NMR spectra of room temperature reaction of **KSU-1** with isopropyl isocyanate.

## X-RAY CRYSTALLOGRAPHY

**Single crystal X-ray diffraction (SCXRD)** Single crystal X-ray data for compounds **KSU-1000** and **KSU-3** were collected using a Rigaku XtaLAB Synergy-S diffractometer equipped with a HyPix-6000HE Hybrid Photon Counting (HPC) detector and Cu microfocus sealed X-ray source ( $\lambda = 1.54184 \text{ \AA}$ ). Data collection strategy was calculated within CrysAlisPro [1] to ensure desired data redundancy and percent completeness. Unit cell determination, initial indexing, data collection, frame integration, Lorentz-polarization corrections and final cell parameter calculations were carried out using CrysAlisPro. An absorption correction was performed using the SCALE3 ABSPACK scaling algorithm embedded within CrysAlisPro. The structures were solved using ShelXT [2] structure solution program using Intrinsic Phasing and refined by Least Squares using ShelXL [3] program. All non-hydrogen atoms were refined anisotropically. The solvent mask function of Olex2 [4] was used to calculate and account for the electron density within the solvent accessible voids for **KSU-1000**. For **KSU-3**, SQUEEZE procedure from PLATON program [5] was used for the same purpose. Hydrogen atom positions were calculated geometrically and refined using the riding model. Crystal data and refinement details are summarized in Table S2.

[1] CrysAlisPro Software System, Rigaku Oxford Diffraction, (2020).

[2] Sheldrick, G.M. (2015). *Acta Cryst.* A71, 3-8.

[3] Sheldrick, G.M. (2015). *Acta Cryst.* C71, 3-8.

[4] Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), *J. Appl. Cryst.* 42, 339-341.

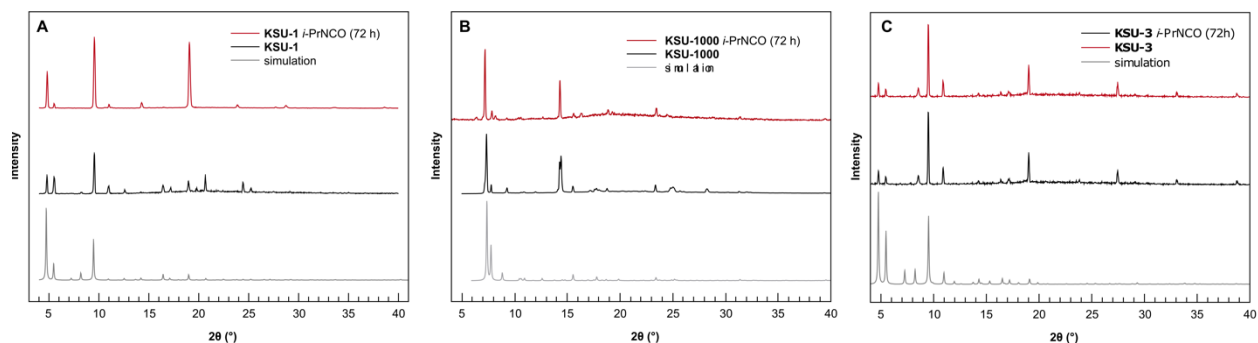
[5] Spek, A. L. (2015). *Acta Cryst.* C71, 9-18.

**Table S3.** Crystal and Refinement Data *KSU-1000* and *KSU-3*.

|  | <i>KSU-1000</i>  | <i>KSU-3</i>  |
|--|--|---|
| Empirical formula                      | C <sub>36</sub> H <sub>26</sub> N <sub>6</sub> O <sub>8</sub> Zn <sub>2</sub> *6C <sub>3</sub> H <sub>7</sub> NO | C <sub>28</sub> H <sub>20</sub> N <sub>2</sub> O <sub>10</sub> Zn <sub>2</sub> *9.667C <sub>3</sub> H <sub>7</sub> NO |
| Formula weight                         | 1239.94  | 1381.89   |
| Temperature                            | 140 K  | 210 K   |
| Crystal system                         | Monoclinic   | Trigonal  |
| Space group                            | P2 <sub>1</sub>  | P312  |
| <i>a</i>                               | 11.4068(2) Å   | 21.4634(7) Å  |
| <i>b</i>                               | 20.0205(3) Å   | 21.4634(7) Å  |
| <i>c</i>                               | 15.0036(3) Å   | 16.1290(7) Å  |
| $\alpha$                               | 90.00°   | 90.00°  |
| $\beta$                                | 93.119(2)°   | 90.00°  |
| $\gamma$                               | 90.00°   | 120.00°   |
| Volume                                 | 3421.29(10) Å <sup>3</sup>   | 6517.9(3) Å <sup>3</sup>  |
| Density                                | 1.204 g/cm <sup>3</sup>  | 1.070 g/cm <sup>3</sup>   |
| Z                                      | 2  | 3   |
| Absorption coefficient                 | 1.392 mm <sup>-1</sup>   | 1.201 mm <sup>-1</sup>  |
| Crystal size                           | 0.28 x 0.23 x 0.19 mm <sup>3</sup>   | 0.44 x 0.27 x 0.22 mm <sup>3</sup>  |
| Theta range                            | 2.95 to 77.85°   | 2.37 to 77.76°  |
| Reflections collected                  | 103778   | 34564   |
| Independent reflections                | 14292 [R <sub>int</sub> = 0.1243]  | 8137 [R <sub>int</sub> = 0.0622]  |
| Completeness to $\theta = 67.68^\circ$ | 99.7 %   | 99.5 %  |
| Data / restraints / parameters         | 14292 / 8 / 480  | 8137 / 55 / 236   |
| Goodness-of-fit on F <sup>2</sup>      | 1.019  | 0.963   |
| Final R indices [ $I > 2\sigma(I)$ ]   | R <sub>1</sub> = 0.0509, wR <sub>2</sub> = 0.1395  | R <sub>1</sub> = 0.0843, wR <sub>2</sub> = 0.2344   |
| R indices (all data)                   | R <sub>1</sub> = 0.0557, wR <sub>2</sub> = 0.1478  | R <sub>1</sub> = 0.1112, wR <sub>2</sub> = 0.2631   |
| Largest diff. peak and hole            | 1.00 and -0.52 e <sup>-</sup> /Å <sup>3</sup>  | 1.92 and -0.66 e <sup>-</sup> /Å <sup>3</sup>   |



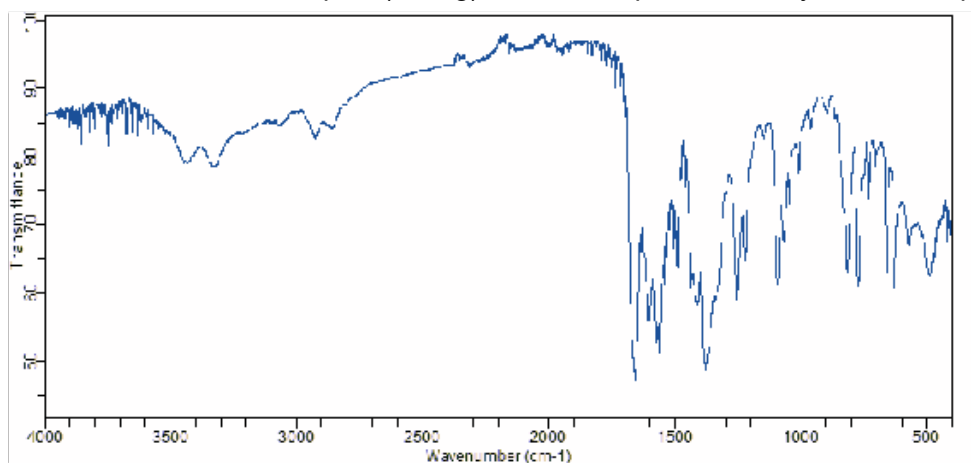
**Powder X-ray diffraction (PXRD)** patterns were recorded on a Bruker AXS D8 Advance Phaser diffractometer (Bruker AXS, Karlsruhe, Germany) with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) over a range of  $4^\circ < 2\theta < 40^\circ$  in  $0.02^\circ$  steps with a 0.5 s counting 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.



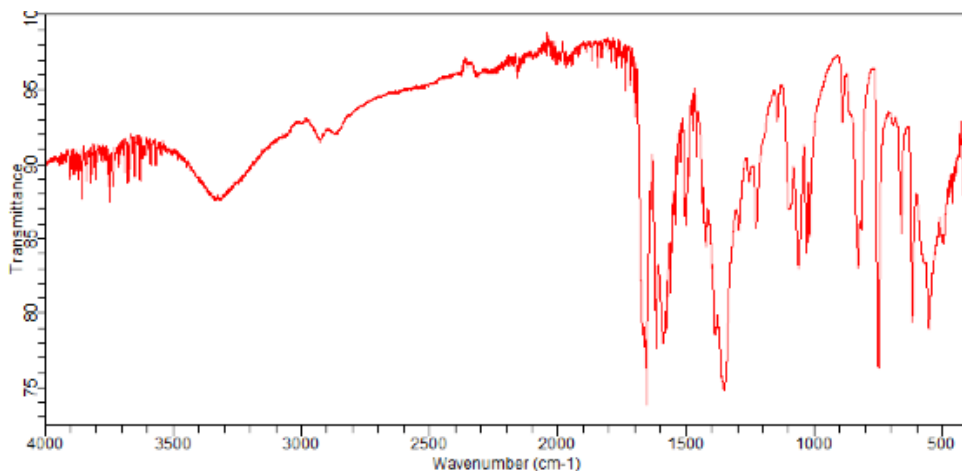
**Figure S12.** The PXRD patterns of the simulated parent MOF, the experimental parent MOF, and the MOF after reacting with isopropyl isocyanate at  $80^\circ \text{C}$  for 72 h. A: **KSU-1**, B: **KSU-1000**, and C: **KSU-3**.

#### FOURIER-TRANSFORM INFRARED SPECTROSCOPY (FTIR)

Spectra were collected on MOF samples ( $\sim 1 \text{ mg}$ ) which were placed directly on the sample holder.



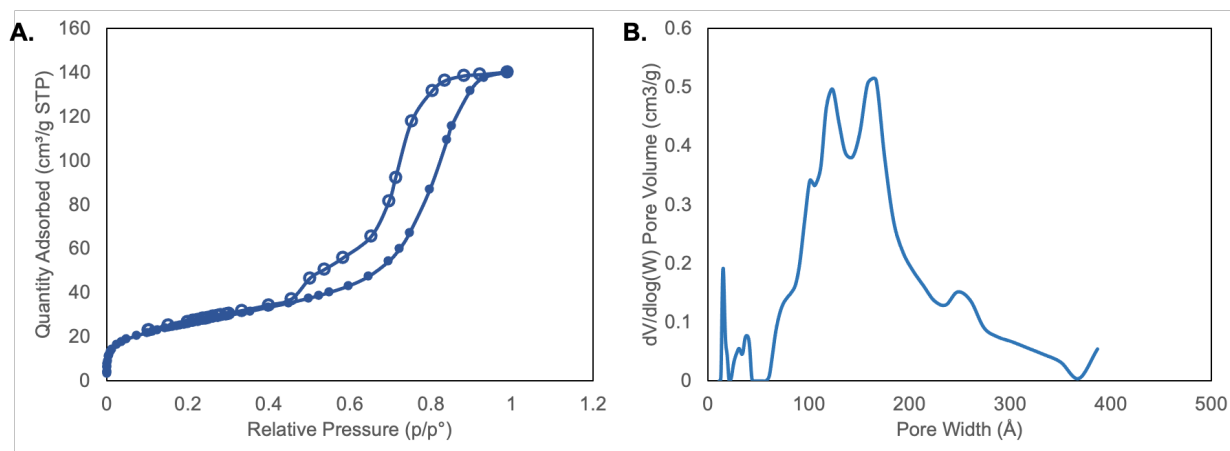
**Figure S15.** IR for **KSU-1000**. The peaks in the  $3300\text{--}3500 \text{ cm}^{-1}$  correspond to the N-H stretches of BDC-NH $_2$ .



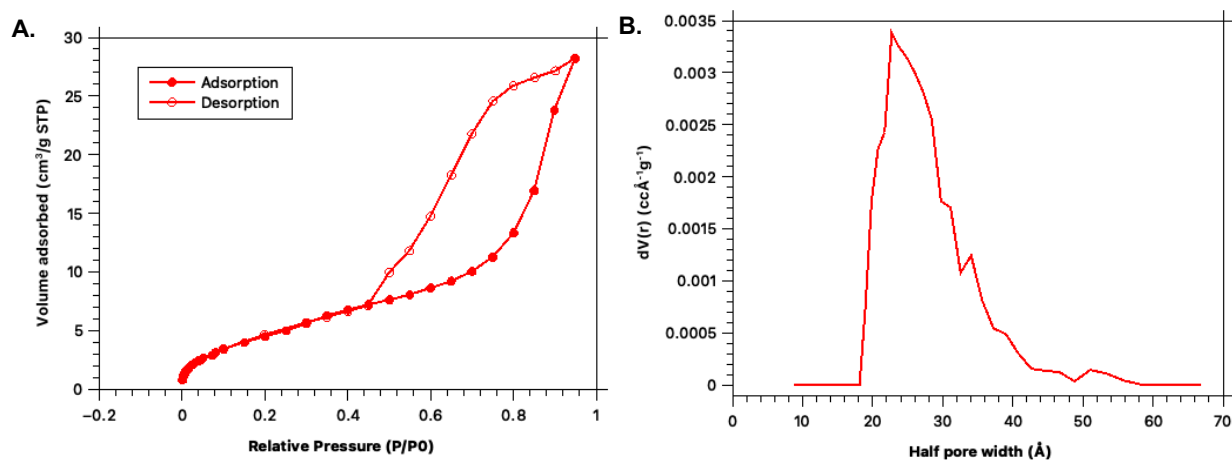
**Figure S16.** IR for **KSU-3**. The broad peaks at  $3400 \text{ cm}^{-1}$  corresponds to the O-H stretch of DPG.

## NITROGEN GAS ADSORPTION/DESORPTION

Measurements for **KSU-1000** were performed on a Micromeritics Tristar II 3020 (Micromeritics, Norcross, GA) at 77 K on samples that underwent supercritical CO<sub>2</sub> drying. Supercritical CO<sub>2</sub> drying was performed using a Tousimis Samdri PVT-30 critical point dryer (Tousimis, Rockville, MD, USA). Supercritically dried samples were prepared in the following manner: MOF materials that had undergone DMF to hexanes solvent exchanges were again solvent exchanged with ethanol by two quick washes. The ethanol-dispersed samples were transferred into the sample holder with a glass pipet and allowed to settle down. Excess EtOH was pipetted out and the sample holder was placed into a Tousimis Samdri-PVT-3D supercritical CO<sub>2</sub> dryer. The temperature was lowered to 0 °C, and the chamber was filled with liquid CO<sub>2</sub> (ultrahigh grade CO<sub>2</sub> with a siphon from Air-Gas Inc). The sample was soaked for 8 hours total, venting for five minutes every two hours. The chamber was then heated to 30 °C, and the supercritical CO<sub>2</sub> was bled off at a rate of 0.25 mL/min until the chamber reached ambient pressure (typically overnight). The chamber was opened and the sample was quickly transferred into a pre-weighed glass sample tube which was sealed and quickly transferred to a system providing 10<sup>-4</sup> torr dynamic vacuum. Measurements for **KSU-3** were performed on an Autosorb iQ MP (Quantachrome Instruments, Anton Paar USA, Ashland VA) at 77K. Samples were prepared in the following manner: **KSU-3** underwent DMF-to-hexanes solvent exchange followed by two quick CHCl<sub>3</sub> washes then dried at 60 °C overnight under vacuum (<10<sup>-3</sup> torr). Using the “outgas” function of the surface analyzer, the sample was dried again for 360 min at 80 °C to remove all residual solvent.



**Figure S17.** A: N<sub>2</sub> gas adsorption measurement for **KSU-1000** (closed circles, adsorption; open circles, desorption). The calculated Brunauer-Emmett-Teller (BET) area is 93 m<sup>2</sup>/g. B: Pore-size distribution (PSD) of **KSU-1000**. The material showed hierarchical porosity composed of various sizes of micro- and mesopores, however, dominant micropores (1.5 nm), mesopores (3.1 and 3.9 nm), and (12.2 and 16.3 nm) are clearly visible from the PSD plot.

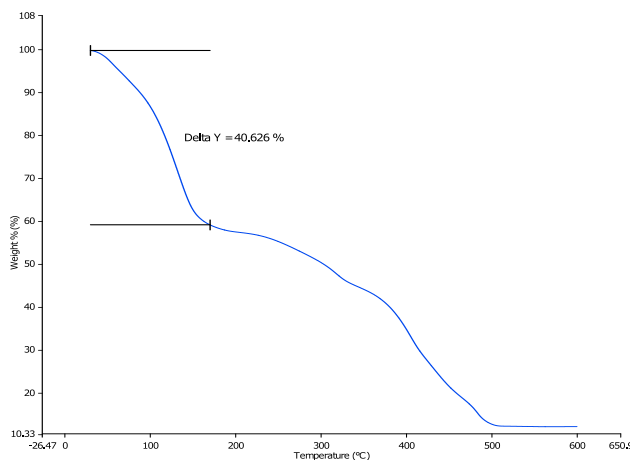


**Figure S18.** A: N<sub>2</sub> gas adsorption measurement for **KSU-3** (closed circles, adsorption; open circles, desorption). The calculated BET area is 10 m<sup>2</sup>/g. B: Pore-size distribution of **KSU-3**. The material displayed predominant mesoporosity, with a mode half pore width of 2.8 nm.

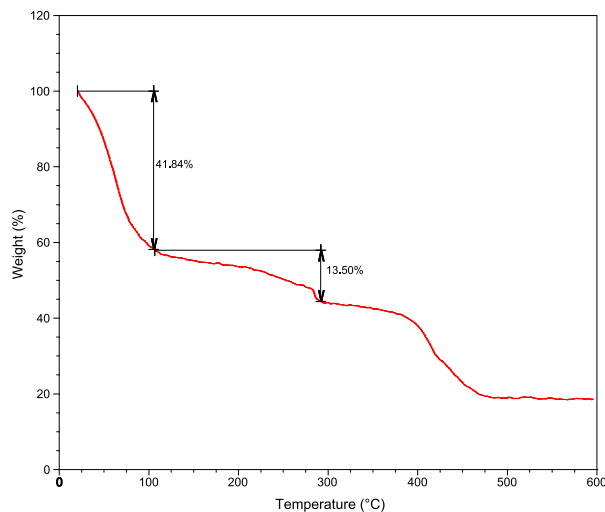
## THERMOGRAVIMETRIC ANALYSIS (TGA)

Thermogravimetric analysis for **KSU-1000** was performed on a TGA 8000 (PerkinElmer Inc., Waltham, MA, USA) interfaced with a PC using Pyris software. For **KSU-3**, the analysis was performed on a TGA-Q50 interfaced with a PC using TA Universal Analysis software. Samples were heated at a rate of 10 °C/min under a nitrogen atmosphere. All samples were extensively solvent exchanged with fresh DMF prior to analysis.

**A.**



**B.**



**Figure S19.** TGA traces for as-synthesized MOFs. **A: KSU-1000.** Calculated solvent loss for  $C_{36}H_{25}N_6O_8Zn_2 \cdot 6[C_3H_7NO]$ : 35.3 %; found: 40.6 %. **B: KSU-3.** Calculated solvent loss for  $C_{28}H_{20}N_2O_{10}Zn_2 \cdot 9\frac{2}{3}[C_3H_7NO]$ : 51.4 %; found: 55.3 %.