[Supporting Information (SI) to accompany:]

A mixed dicarboxylate strut approach to enhance catalytic activity of a *de novo* urea derivative of metal-organic framework UiO-67

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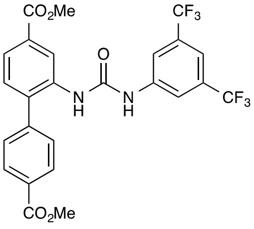
Supporting Information

General Procedures

All reactions were carried out under a nitrogen atmosphere in flame-dried glassware with magnetic stirring unless otherwise stated. THF was purified by passage through a bed of activated alumina.[1] All reagents were purchased from Aldrich and used as received unless otherwise stated. Benzaldehyde, *p*-methoxybenzaldehyde, ${}^{i}Pr_2EtN$, nitromethane and mesitylene were were purified prior to use following the guidelines of Perrin and Armarego.[2] Dimethyl 2-aminobiphenyl-4,4′-dicarboxylate was prepared according to literature procedure.[3] ${}^{1}H$ NMR spectra were recorded on a Bruker AVANCE III 500 (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm, DMSO-d_6 at 2.50 ppm). Data are reported as (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constant(s) in Hz; integration). Proton-decoupled ${}^{13}C$ NMR spectra were recorded on a Bruker AVANCE III 500 (126 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.16 ppm and DMSO-d_6 at 39.52 ppm). ${}^{19}F$ NMR spectra were recorded on an Agilent DDR2-400 (376 MHz) spectrometer and are reported in ppm referenced to $CFCl_3$ at 0.00 ppm. Mass spectra data were obtained on a Waters Acquity Single Quadrupole ESI Spectrometer and Micromass Quadro II Spectrometer.

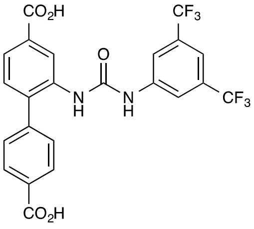
Powder X-ray diffraction (PXRD) patterns were collected on a Bruker AXS APEX2 diffractometer equipped with a CCD detector and a CuKα IμS microfocus source with MX optics. Samples were mounted in nylon cryoloops on a goniometer head. Data was collected with an area detector as rotation frames over 180° in φ at 2θ values of 12°, 24°, 36°, 48° and exposed for 10 min for each frame. At a distance of 150 mm, the detector area covers 24° in 2θ. Powder pattern data were treated for amorphous background scatter (EVA 16, Copyright Bruker-AXS 1996-2010).

Supercritical CO_2 drying was performed using a Tousimis™ Samdri® PVT-30 critical point dryer. N_2 adsorption and desorption isotherm measurements were performed on a Micromeritics Tristar II 3020 (Micromeritics, Norcross, GA) at 77K. Thermogravimetric analysis (TGA) experiments were performed on a Mettler Toledo TGA/DSC 1 Star^{e} System (Schwerzenbach, Switzerland) interfaced with a PC using Stare software (version 9.10). Samples were placed in alumina pans and heated at a rate of 7 °C/min from 25-800°C under a nitrogen atmosphere.



Me_2-Urea

Synthesis of Me_2-Urea: To a stirred solution of dimethyl 2-aminobiphenyl-4,4′-dicarboxylate (0.471 g, 1.7 mmol) in THF (17 mL) at 0 °C was added 3,5-bis(trifluoromethyl)phenyl isocyanate (0.43 ml, 2.5 mmol). The reaction was slowly warmed up to room temperature and stirred overnight. The mixture was concentrated under reduced pressure, washed with Et_2O and dried under high vacuum to yield a white solid. Yield = 0.711 g (80%). ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 9.65 (s, 1H), 8.53 (s, 1H), 8.16 (s, 1H), 8.08 (d, *J* = 7.9 Hz, 2H), 8.00 (s, 2H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.72 – 7.54 (m, 3H), 7.45 (d, *J* = 8.0 Hz, 1H), 3.90 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 166.0, 165.9, 152.5, 142.3, 141.6, 136.9, 135.7, 130.8, 130.7 (q, *J* = 32.8 Hz), 129.7, 129.5, 129.2, 124.7, 123.8, 123.3 (q, *J* = 272.6 Hz), 117.9, 114.6, 52.4, 52.3; ^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -61.8; LRMS (ESI): Mass calcd for $C_{25}H_{19}F_6N_2O_5$ $[M+H]^+$, 541.12. Found 541.4.



H_2-Urea

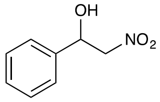
Synthesis of H_2-Urea: To a stirred mixture of **Me_2-Urea** (0.476 g, 0.88 mmol) in MeOH (13 mL) and water (4.5 mL) was added in one portion lithium hydroxide monohydrate (0.739 g, 17.6 mmol). The mixture was stirred at room temperature overnight. The reaction was concentrated under reduced pressure and acidified to ~pH 1with conc. HCl. The resulting precipitate was isolated by filtration and washed with water, MeOH, CH_2Cl_2 and dried under high vacuum. Yield = 0.410 g (91%). ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 13.11 (s, 2H), 9.67 (s, 1H), 8.52 (s, 1H), 8.12 (s, 1H), 8.06 (d, *J* = 7.9 Hz, 2H), 8.01 (s, 2H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.63 (s, 1H), 7.59 (d, *J* = 7.9 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 167.1, 167.0, 152.6, 142.0, 141.6, 136.7, 135.5, 130.7 (q, *J* = 32.8 Hz), 130.7, 130.3, 129.9, 129.3, 124.9, 124.1, 123.3 (q, J = 272.7 Hz), 117.8, 114.5; ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.8; LRMS (ESI): Mass calcd for $C_{23}H_{15}F_6N_2O_5$ $[M+H]^+$, 513.09. Found 513.4.

Synthesis of UiO-67-Urea: To a 20 mL scintillation vial containing zirconium(IV) chloride (0.045 g, 0.20 mmol) was added DMF (2.5 mL) and conc. HCl (0.25 mL). The resulting mixture was sonicated for 20 min until fully dissolved. The reaction was diluted with DMF (5 mL) and **H_2-Urea** (0.100 g, 0.20 mmol) was added. The mixture was heated in an oven at 80 °C overnight. The resulting white solid was isolated by filtration, washed with DMF (2 x 15 mL) and dried in air over a fine frit.

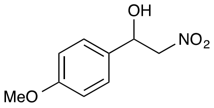
Synthesis of UiO-67-Urea/bpdc: To a 20 mL scintillation vial containing zirconium(IV) chloride (0.091 g, 0.390 mmol) was added DMF (5 mL) and conc. HCl (0.5 mL). The resulting mixture was sonicated for 20 min until fully dissolved. The reaction was diluted with DMF (10 mL), followed by the addition of **H_2-Urea** (0.100 g, 0.20 mmol) and 4,4'-biphenyldicarboxylic acid (0.047 g, 0.20 mmol). The mixture was heated in an oven at 80 °C overnight. The resulting white solid was isolated by filtration, washed with DMF (2 x 15 mL) and dried in air over a fine frit.

Preparation of UiO-67 derivatives for catalysis and supercritical CO_2 activation: To a 2 dram vial containing **UiO-67-Urea** or **UiO-67-Urea/bpdc** was added THF (5 mL). The sample mixtures were heated at 50 °C for 2 days, exchanging the solvent with fresh THF several times a day. The supernatant was decanted off and the exchanged material was dried over a flow of air over several hours. A small amount of the solid was digested with a few drops of D_2SO_4, diluted with DMSO-d_6 and then analyzed by ^{1}H NMR spectroscopy on a Bruker AVANCE III 500 MHz with a DMSO-d_6 solvent setting.

General Procedure for Catalysis Reactions: A stock solution (corresponding to 0.5 mmol of aldehyde, 0.5 mL of THF and 8 μL of mesitylene) was added to a 1 dram vial containing the catalyst (0.025 mmol, 5 mol%). To the resulting mixture was added ^{i}Pr$_2$EtN (0.017 ml, 0.10 mmol) and lastly nitromethane (0.27 ml, 5.0 mmol). The vial was placed in a KEM-Labs Vortex mixer and shook for 24 h. Aliquots of the reaction were taken at 2, 5, 8, 21 and 24 h, diluted with $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy. Mesitylene was used as the internal standard to determine % yield.



2-nitro-1-phenylethanol: Reaction was set up according to the general procedure. A stock solution (0.5 mmol of benzaldehyde, 0.5 mL of THF and 8 μL of mesitylene) was added to a 1 dram vial containing **UiO-67-Urea/bpdc** (0.052 g, corresponding to 0.025 mmol of urea strut). To the resulting mixture was added ^{i}Pr$_2$EtN (0.017 ml, 0.10 mmol) and lastly nitromethane (0.27 ml, 5.0 mmol). After the vial was shook for 24 h, analysis by ^{1}H NMR spectroscopy showed a 67% yield. The reaction was filtered through a Celite plug and purified by preparative HPLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.30 (m, 6H), 5.48 (dt, J = 9.7, 3.3 Hz, 1H), 4.62 (dd, J = 13.4, 9.7 Hz, 1H), 4.52 (dd, J = 13.4, 2.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.2, 129.2, 129.2, 126.1, 81.3, 71.1.



1-(4-methoxyphenyl)-2-nitroethanol: Reaction was set up according to the general procedure. A stock solution (0.5 mmol of *p*-methoxybenzaldehyde, 0.5 mL of THF and 8 μL of mesitylene) was added to a 1 dram vial containing **UiO-67-Urea/bpdc** (0.052 g, corresponding to 0.025 mmol of urea strut). To the resulting mixture was added $^{i}Pr_2EtN$ (0.017 ml, 0.10 mmol) and lastly nitromethane (0.27 ml, 5.0 mmol). After the vial was shook for 24 h, analysis by ^1H NMR spectroscopy showed a 48% yield. The reaction was filtered through a Celite plug and purified by preparative HPLC. ^1H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 2H), 6.98 – 6.87 (m, 2H), 5.42 (dt, *J* = 9.7, 3.2 Hz, 1H), 4.61 (dd, *J* = 13.3, 9.7 Hz, 1H), 4.48 (dd, *J* = 13.3, 3.0 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.2, 130.3, 127.4, 114.5, 81.38, 70.8, 55.5.

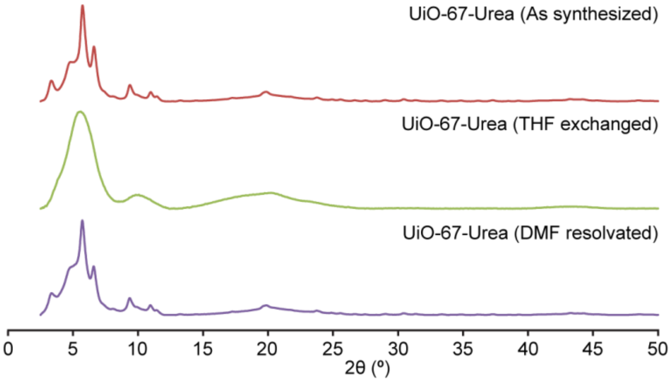


Fig. S1 PXRD patterns of the as synthesized, THF exchanged and DMF resolvated **UiO-67-Urea** framework. Although the THF exchanged **UiO-67-Urea** showed broad peaks in its PXRD pattern, we do not believe this is an indication of a lost in structural integrity since subsequent resolvation with DMF results in a sharping of the peaks again.

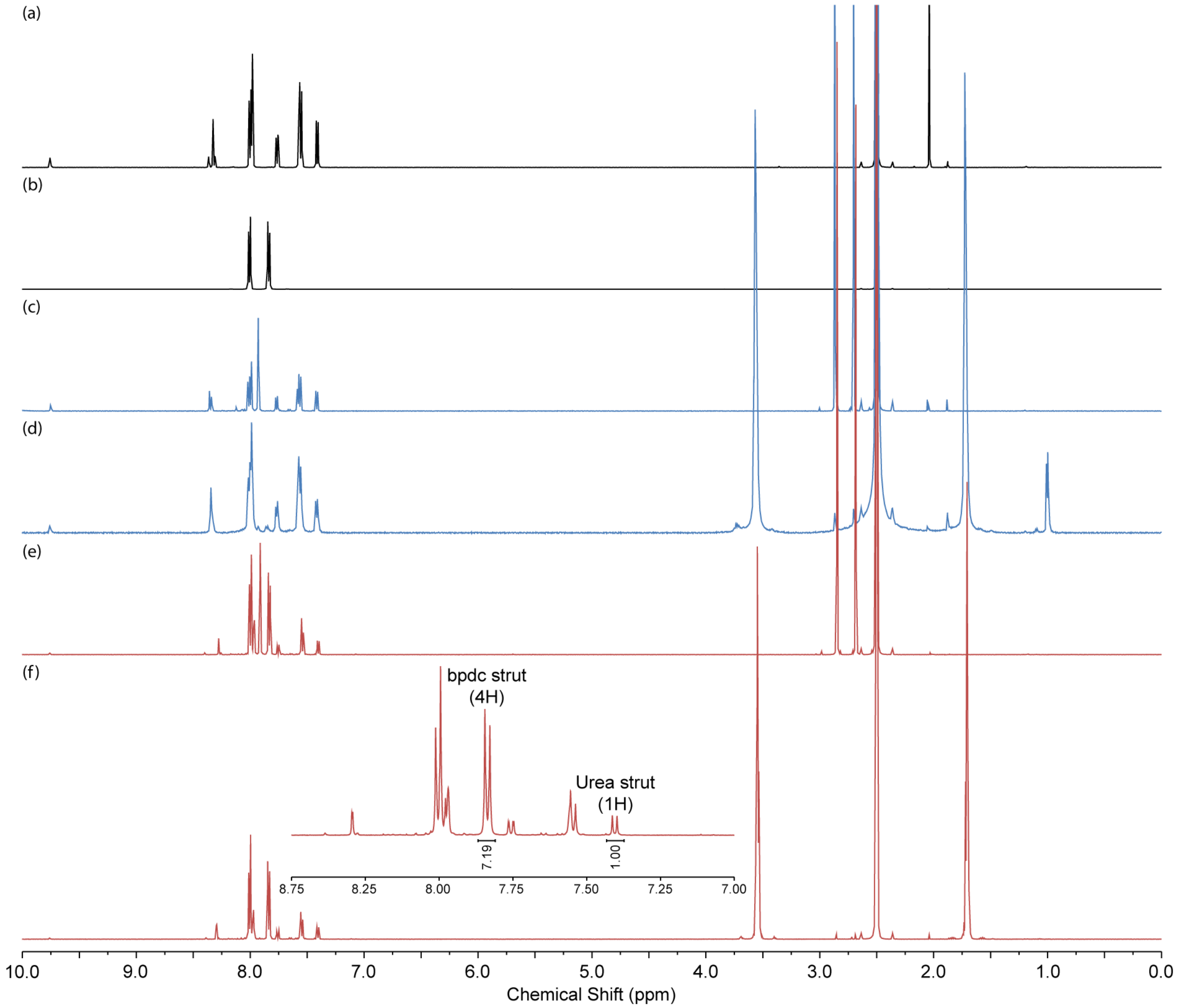


Fig. S2 ^{1}H NMR (500 MHz) spectra of (a) **H_2-Urea** strut, (b) **H_2-bpdc** strut, (c) as synthesized **UiO-67-Urea**, (d) THF exchanged **UiO-67-Urea**, (e) as synthesized **UiO-67-Urea/bpdc**, and (f) THF exchanged **UiO-67-Urea/bpdc** (inset shows relevant integrations for determining %**Urea** strut incorporation). Samples were prepared in DMSO-d_6 with a few drops of D_2SO_4.

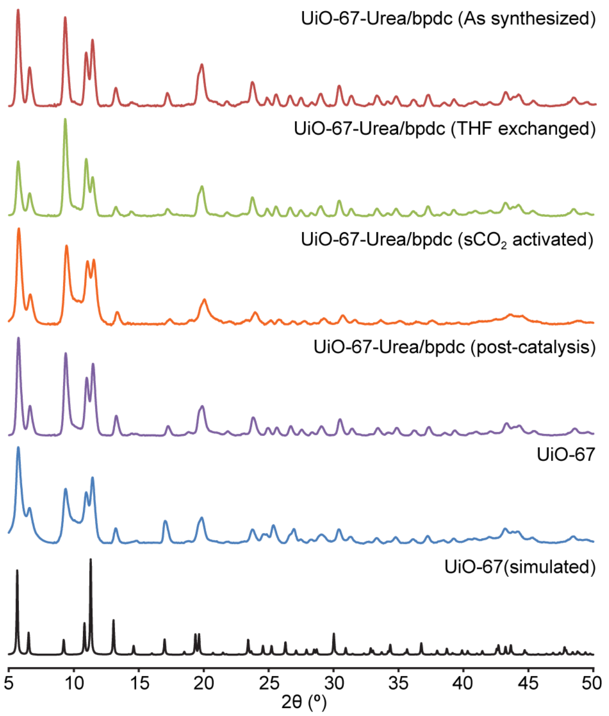


Fig. S3 PXRD patterns of the as synthesized, THF exchanged, supercritical CO_2 activated and post-catalysis **UiO-67-Urea/bpdc** framework in comparison to the parent UiO-67 framework. The PXRD patterns of the THF exchanged, supercritical CO_2 activated and post-catalysis **UiO-67-Urea/bpdc** do not differ significantly from the as synthesized material. Intensity from 8-50° is enhanced 10x for clarity.

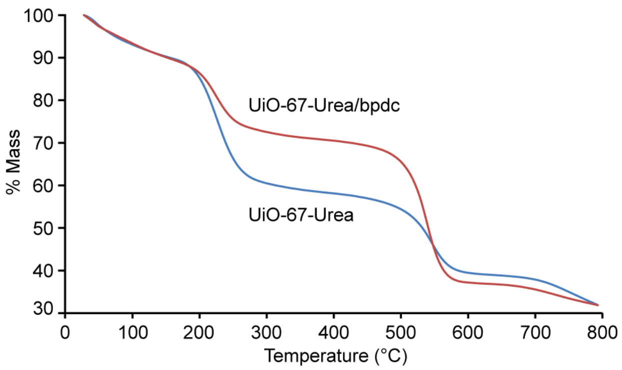


Fig. S4 TGA plots of the mixed strut **UiO-67-Urea/bpdc** and the pure strut **UiO-67-Urea** frameworks.

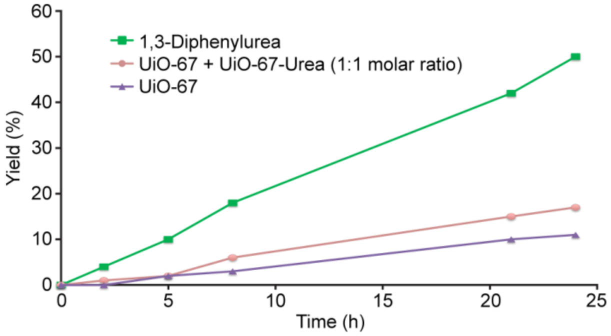


Fig. S5 Catalytic activities of 1,3-diphenylurea, UiO-67 + **UiO-67-Urea** (1:1 molar ratio), and UiO-67 in the Henry reaction between benzaldehyde and nitromethane. All of the reactions were performed for 24 h and monitored by ^{1}H NMR spectroscopy (500 MHz, $CDCl_3$) using mesitylene as an internal standard

References

[1] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics* 1996, **15**, 1518.

[2] D. D. Perrin and W. L. Armarego, Purification of Laboratory Chemicals; 3rd Ed., Pergamon Press, Oxford. 1988.

[3] V. K. Ol'khovik, A. A. Pap, V. A. Vasilevskii, N. A. Galinovskii and S. N. Tereshko, *Russ. J. Org. Chem.*, 2008, **44**, 1172.