[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

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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, Pr₂EtN, nitromethane and mesitylene 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 ¹H NMR spectra were recorded on a Bruker AVANCE III 500 (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl₃ at 7.26 ppm, DMSO-d₆ 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 ¹³C NMR spectra were recorded on a Bruker AVANCE III 500 (126 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl₃ at 77.16 ppm and DMSO-d₆ at 39.52 ppm). ¹⁹F NMR spectra were recorded on an Agilent DDR2-400 (376 MHz) spectrometer and are reported in ppm referenced to CFCI₃ at 0.00 ppm. Mass spectra data were obtained on a Waters Acquity Single Quadrupole ESI Spectrometer and Micromass Quadrupol II Spectrometer.

Powder X-ray diffraction (PXRD) patterns were collected on a Bruker AXS APEX2 diffractometer equipped with a CCD detector and a CuKα 1μS 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 20 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 CO₂ drying was performed using a Tousimis™ Samdri® PVT-30 critical point dryer. N₂ 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® 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.

![Chemical Structure](image)

**Synthesis of Me₂-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 Et₂O and dried under high vacuum to yield a white solid. Yield = 0.711 g (80%). ¹H NMR (500 MHz, DMSO-d₆) 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); ¹³C NMR (126 MHz, DMSO-d₆) 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; ¹⁹F NMR (376 MHz, DMSO-d₆) δ -61.8; LRMS (ESI): Mass calcd for C₂₅H₁₉F₆N₂O₅ [M+H]⁺, 541.12. Found 541.4.

![Chemical Structure](image)

**Synthesis of H₂-Urea:** To a stirred mixture of Me₂-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 1 with conc. HCl. The resulting precipitate was isolated by filtration and washed with water, MeOH, CH₂Cl₂ and dried under high vacuum. Yield = 0.410 g (91%). ¹H NMR (500 MHz, DMSO-d₆) 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); ¹³C NMR (126 MHz, DMSO-d₆) 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$_6$N$_2$O$_5$ [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$_2$SO$_4$, 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 $^3$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 $^3$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), 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 iPr2EtN (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, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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 sharpening 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$_2$SO$_4$. 
**Fig. S3** PXRD patterns of the as synthesized, THF exchanged, supercritical CO₂ 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 CO₂ 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