

# Urea containing metal–organic frameworks as heterogeneous organocatalysts

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## Supporting Information

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## Experimental Section

### Apparatus and Reagents

All starting materials, including 1,1'-Carbonyldiimidazole, 4-Aminobenzoic acid were purchased from commercial suppliers (Sigma-Aldrich, Merck) and used as received. The infrared spectra were recorded on a Nicolet Fourier Transform IR, Nicolet 100 spectrometer in the range 500-4000  $\text{cm}^{-1}$  using the KBr disk technique. Elemental analyses (carbon, hydrogen, and nitrogen) were performed using an ECS 4010 CHN made in Costech, Italy. Melting points were obtained by a Bamstead Electrothermal type 9200 melting point apparatus and corrected. Thermogravimetric analyses (TGA) of the compounds were performed on a computer-controlled PL-STA 1500 apparatus. The  $^1\text{H-NMR}$  spectrum was recorded on a Bruker AC-250 MHz spectrometer at ambient temperature in  $d_6$ -DMSO and  $\text{CDCl}_3$ . X-ray powder diffraction (XRPD) measurements were performed using a Philips Xpert diffractometer with monochromated Cu-K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). The samples were also characterized by field emission scanning electron microscope (FE-SEM) SIGMA ZEISS and TESCAN MIRA (Czech) with gold coating.

### Single-Crystal Diffraction.

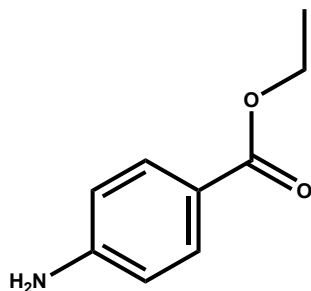
X-ray crystal structure determinations: Crystals in viscous paraffin oil were mounted on cryoloops and intensity data were collected on the Australian Synchrotron MX1 beamline at 100 K with wavelength ( $\lambda = 0.71073 \text{ \AA}$ ). The data were collected using the BlueIce<sup>[1]</sup> GUI and processed with the XDS<sup>[2]</sup> software package. The structures were solved by conventional methods and refined by full-matrix least-squares on all  $F^2$  data using SHELX97<sup>[3]</sup> or SHELX2014 in conjunction with the X-Seed<sup>[4]</sup> or Olex2<sup>[5]</sup> graphical user interface. Anisotropic thermal parameters were refined for non-hydrogen atoms and hydrogen atoms were calculated and refined with a riding model.

Crystallographic data: TMU-18:  $\text{C}_{83}\text{H}_{63}\text{N}_{13}\text{O}_{21}\text{Zn}_4$ ,  $M = 1839.94 \text{ g mol}^{-1}$ , Triclinic,  $P\bar{1}$ ,  $a = 21.179(4) \text{ \AA}$ ,  $b = 22.560(5) \text{ \AA}$ ,  $c = 23.138(5) \text{ \AA}$ ,  $\alpha = 105.30(3)^\circ$ ,  $\beta = 114.19(3)^\circ$ ,  $\gamma = 102.88(3)^\circ$ ,  $V = 9013(4) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calc}} = 0.678 \text{ g cm}^{-3}$ ,  $\lambda = 0.71073$ ,  $T = 100 \text{ K}$ ,  $R_I = 0.0688$ ,  $wR_2 = 0.1817$ ,  $S = 0.897$ ,  $\text{ccdc} = 1041981$ ; TMU-19:  $\text{C}_{21}\text{H}_{16}\text{N}_3\text{O}_5\text{Zn}$ ,  $M = 455.74 \text{ g mol}^{-1}$ , orthorhombic,  $Pnna$ ,  $a = 21.035(4) \text{ \AA}$ ,  $b = 16.064(3) \text{ \AA}$ ,  $c = 29.891(6) \text{ \AA}$ ,  $V = 10100(3) \text{ \AA}^3$ ,  $Z = 8$ ,  $\rho_{\text{calc}} = 0.599 \text{ g cm}^{-3}$ ,  $\lambda = 0.71073$ ,  $T = 100 \text{ K}$ ,  $R_I = 0.0786$ ,  $wR_2 = 0.2428$ ,  $S = 1.103$ ,  $\text{ccdc} = 1041982$ .

## Synthesis & catalytic reaction

The urea ditopic ligand was synthesized in three steps, starting from commercially available 4-aminobenzoic acid. The synthetic procedure is as follows.

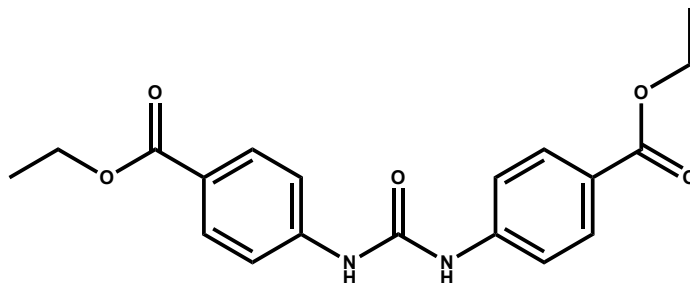
### Synthesis of ethyl 4-aminobenzoate (1)



4-aminobenzoic acid (1.37 g, 10 mmol) was dissolved in a minimum amount of absolute ethanol (15 mL). As 1 mL of concentrated sulphuric acid was added, a white suspension formed which was vigorously stirred and refluxed for 3 h to give a clear solution. The reaction mixture was cooled to 40 °C and poured into a saturated solution of sodium bicarbonate in water (100 mL). Vigorous effervescence was observed with the precipitation of a white solid. The precipitate was filtered and dried in air at room temperature.

(M.p. 88-90°C), FT-IR (KBr pellet, cm<sup>-1</sup>): 3421, 3342, 3223, 2978, 1685, 1597, 1512, 1280, 1169, 1119, 1023, 847, 772, 698. Anal. calcd for C<sub>9</sub>H<sub>11</sub>NO<sub>2</sub>: C, 65.44; H, 6.71; N: 8.48, Found: C, 65.36; H, 6.59, N: 8.14. MS (m/z): 165.1 (M<sup>+</sup>, base peak), 137.1.

### Synthesis of diethyl 4,4'-(carbonylbis(azanediyl))dibenzoate (2)

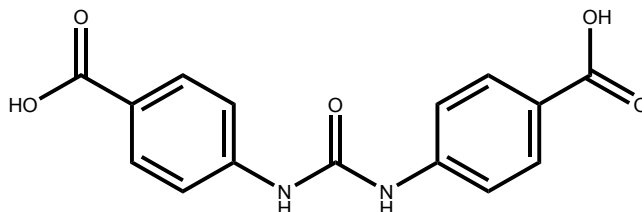


Ethyl 4-aminobenzoate (1.65 g, 10 mmol) was dissolved in 25 mL of dry THF with stirring. To this solution, 1,1'-Carbonyldiimidazole (0.97 g 6 mmol) was added. The mixture was refluxed under argon atmosphere overnight. The mixture was cooled to room temperature and the solvent was removed in vacuo. The resulting residue was taken

up in ethyl acetate, washed with 1M HCl and brine (3 times), dried over MgSO<sub>4</sub> and concentrated to afford 1.33 g (75%) of **2** as a white powder.

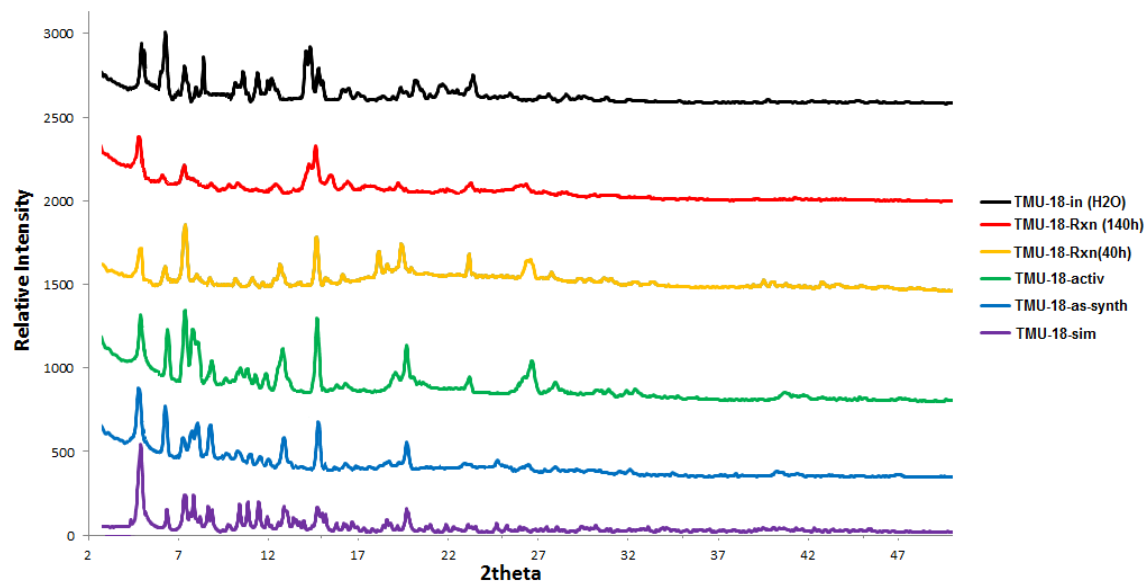
FT-IR (KBr pellet, cm<sup>-1</sup>): 3322 (s), 2979 (w), 1711 (vs), 1652 (s), 1600 (s), 1553 (s), 1405 (w), 1280 (s), 1170 (m), 1021(m), 767 (m), 637 (m). Anal. calcd for C<sub>19</sub>H<sub>20</sub>N<sub>2</sub>O<sub>5</sub>: C, 64.04; H, 5.66; N: 7.86, Found: C, 63.94; H, 5.52, N: 7.80. MS (m/z): 356.5 (M<sup>+</sup>, base peak), 311.4, 191.3.

### Synthesis of 4,4'-(carbonylbis(azanediy))dibenzoic acid (**3**)

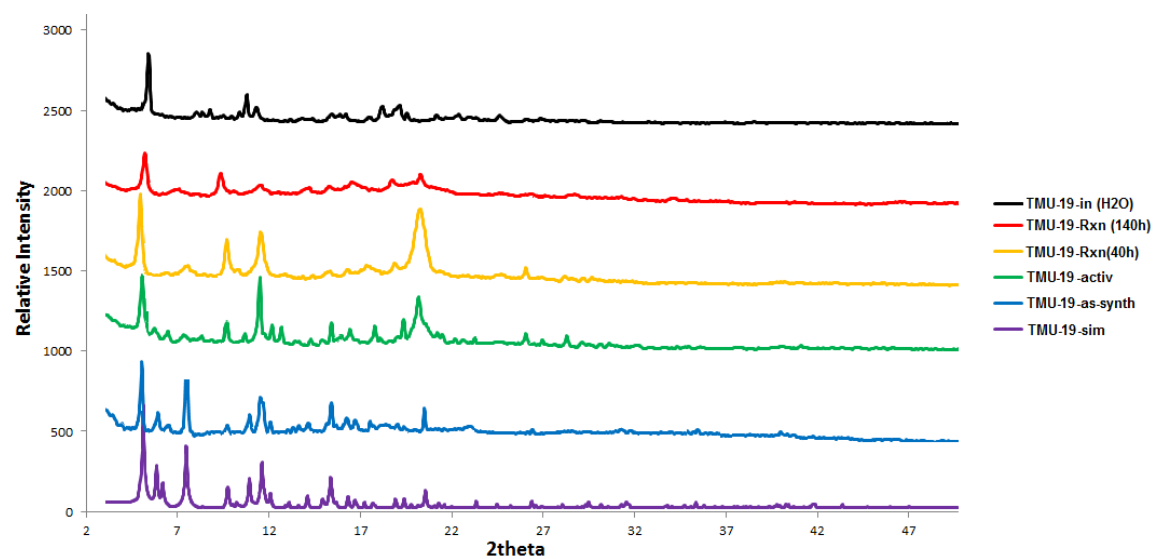


To a 100 mL round-bottom flask was added **2** (3.56 g, 10 mmol) and potassium hydroxide (4.0 g, 0.072 mol) in methanol (30 mL). The mixture was stirred vigorously and refluxed. A white precipitate appeared after about an hour, and this mixture was refluxed for an additional 5 h. The precipitate was filtered and washed several times with distilled water and dried in vacuo to give **3** (2.4 g, 82% yield).

FT-IR (KBr pellet, cm<sup>-1</sup>): 3318 (s), 2845 (w), 2667 (w), 2554 (w), 1668 (vs), 1593 (m), 1537 (vs), 1419 (m), 1303 (s), 1224 (s), 1177 (m), 935 (w), 862(w), 762 (w), 547 (w). Anal. calcd for C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O<sub>5</sub>: C, 60.00; H, 4.03; N: 9.33, Found: C, 59.56; H, 3.92, N: 9.12. MS (m/z): 300.1 (M<sup>+</sup>, base peak), 256.2, 212.2. <sup>1</sup>H-NMR (*d*<sub>6</sub>-DMSO) 9.19 (2H, bs), 7.88-7.92 (4H, d), 7.58-7.61 (4H, d), 3.70 (2H, S).

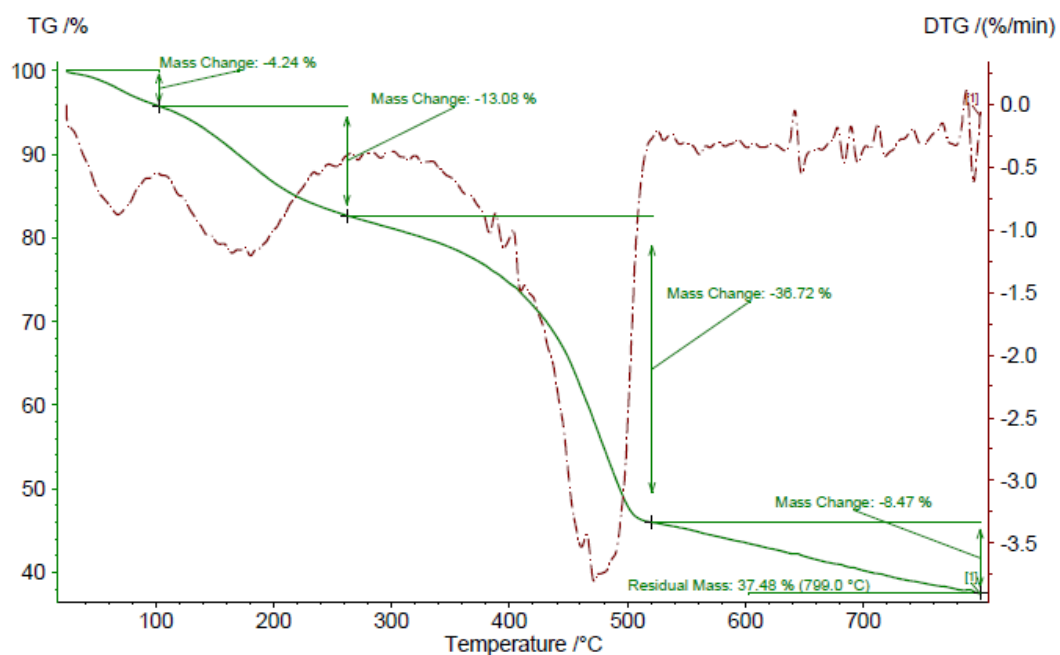


(a)

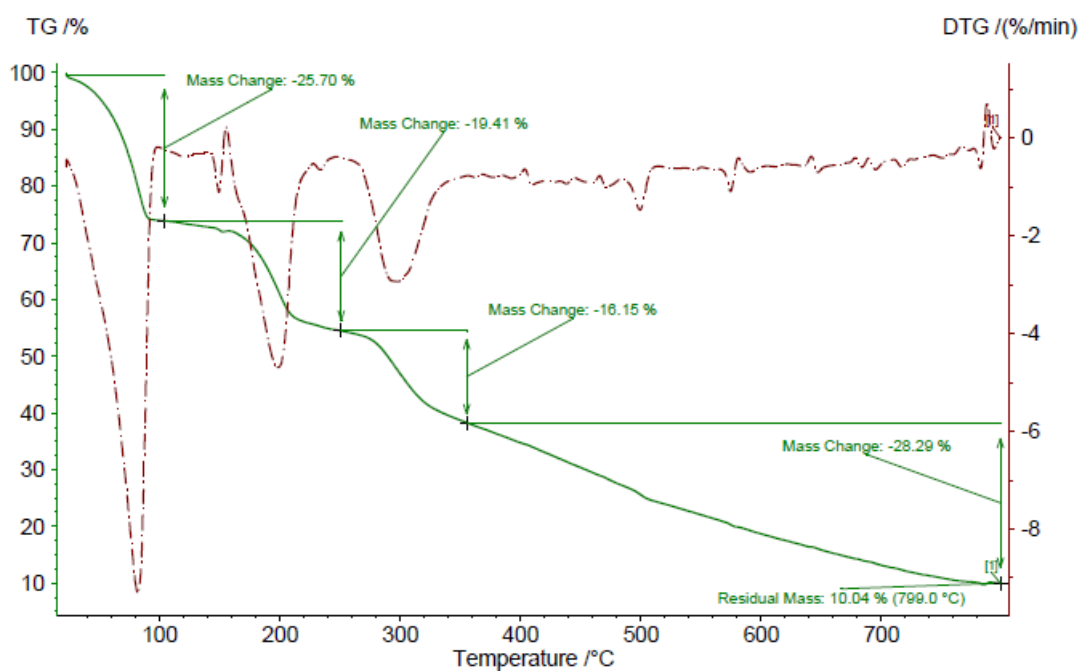


(b)

**Figure S1.** PXRD patterns of TMU-18 (a) and TMU-19 (b), simulated, as synthesized by solvothermal method, after 40 and 140 h of methanolysis reaction of styrene oxide and in deionized water for 48 h.

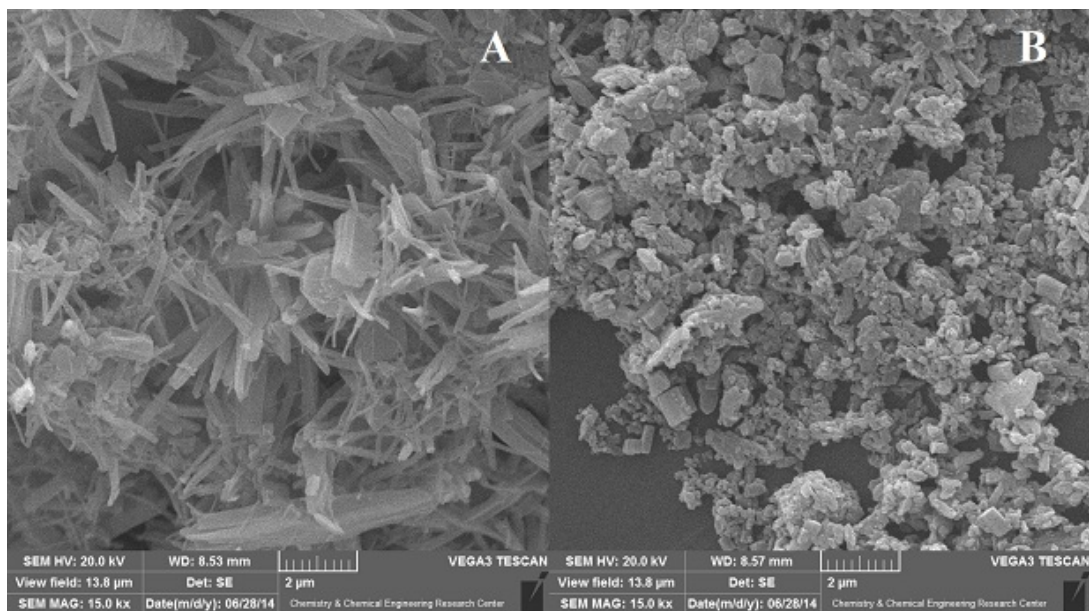


(a)

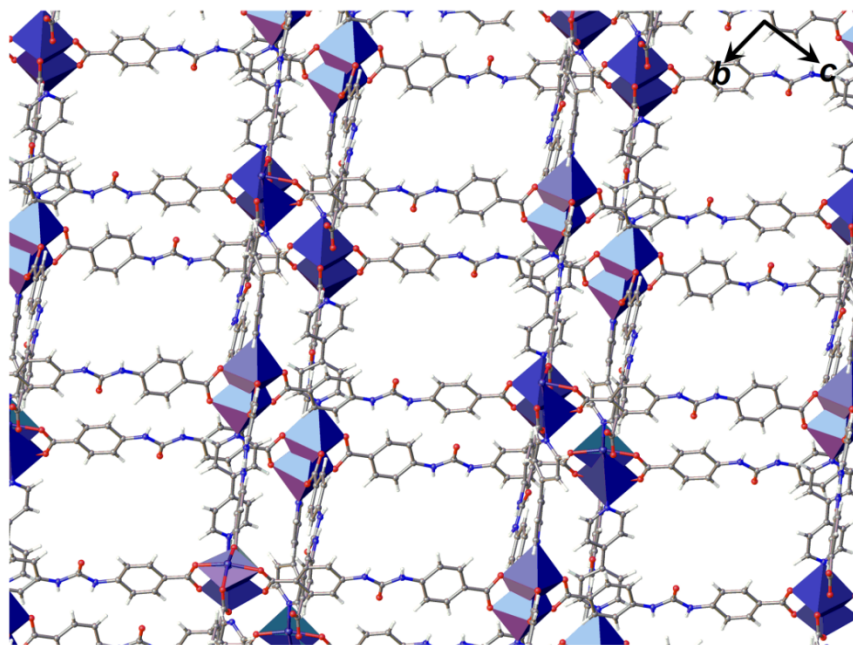


(b)

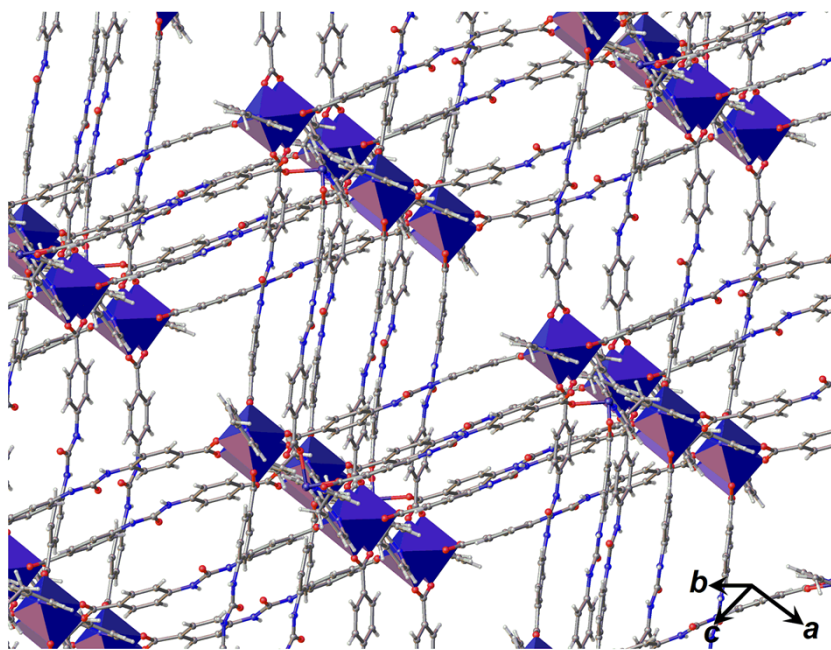
**Figure S2.** Thermogravimetric analysis for **TMU-18** and **TMU-19**, prepared by solvothermal method at 90°C for 120 h



**Figure S3.** Represented SEM images for (a) TMU-18, (b) TMU-19 prepared via solvothermal method at 90°C for 120 h



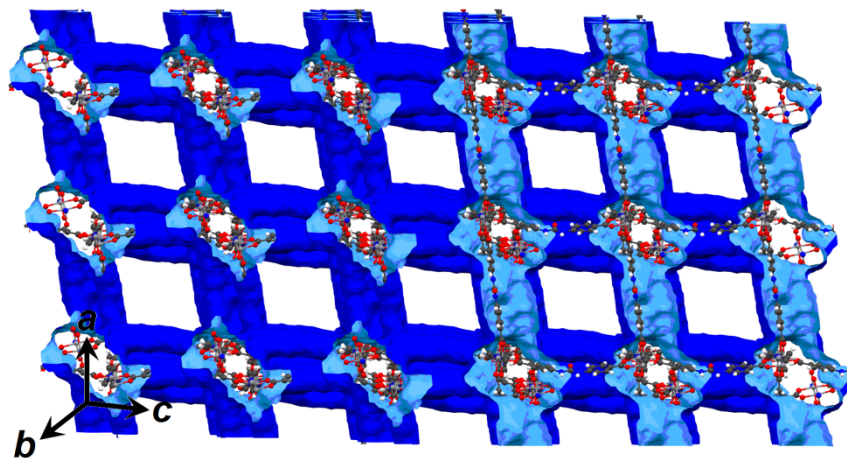
(a)



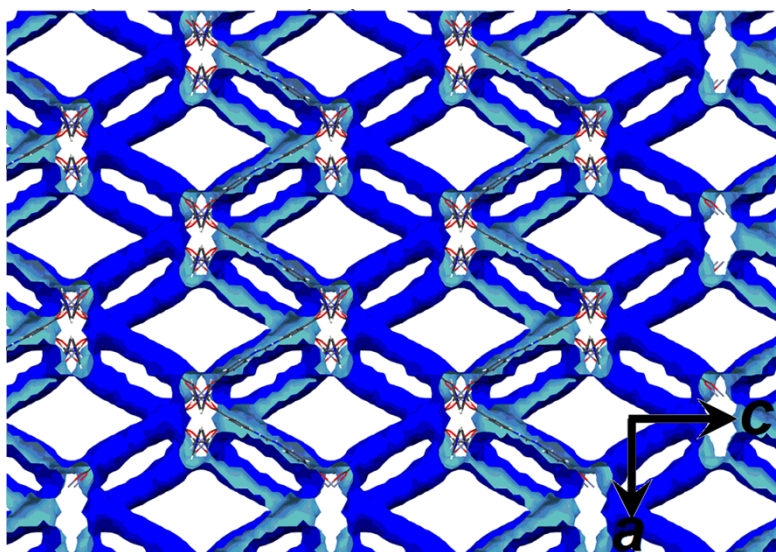
(b)

**Figure S4.** Representation of TMU-18 (a) and TMU-19 (b). Paddle-wheel dinuclear zinc clusters, shown as polyhedron, bridged by the urea struts to form two dimensional square grids. The 2D square grids are further linked to each other by pillaring bipy/bpe forming a 3D framework





(a)



(b)

**Figure S5.** Connolly surface of **TMU-18** (a) and **TMU-19** (b), along the pore channels, with a probe radius of 1.2 Å, solvent molecules were omitted for clarity.

## References

- [1] T. M. McPhillips, S. E. McPhillips, H. J. Chiu, A. E. Cohen, A. M. Deacon, P. J. Ellis, E. Garman, A. Gonzalez, N. K. Sauter, R. P. Phizackerley, S. M. Soltis, P. J. Kuhn, *Synchrotron Rad.* 2002, 9, 401-406.
- [2] W. Kabsch, *J. Appl. Cryst.* 1993, 26, 795-800.
- [3] G. M. Sheldrick, *SHELXL-97* Program for crystal structure refinement, University of Gottingen, Germany, 1997.
- [4] L. J. Barbour, *J. Supramol. Chem.* 2001, 1, 189-191.
- [5] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* 2009, 42, 339-341.