

Supporting Information for:

Structure-Directing Factors when Introducing Hydrogen Bond Functionality to Metal-Organic Frameworks

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Table of Contents

S1. Experimental Summary	S2
S2. Ligand and Pillar Synthesis	S3
S3. MOF Synthesis	S5
S4. Topological Analysis	S7
S5. Hypothetical Structures Preparation	S7
S6. Cambridge Structural Database Searching	S9
S7. Gas Adsorption Simulations and Computational Structural Characterisation	S9
S8. References	S11

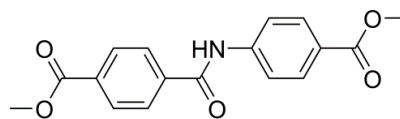
S1. Experimental Summary

All chemicals and solvents, including **L1** and **P1**, were used as received from Sigma Aldrich, Fisher and/or Acros. The remaining ligands and pillars were synthesised as described. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer at 298 K, and chemical shifts are reported in ppm relative to residual solvent peaks (multiplicities are given as s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, with coupling constants reported in Hz). Single crystal diffraction experiments on compounds **1**, **3** and **4** were performed on a Bruker Apex II diffractometer using a Quasar (CCD) detector (λ (MoK α) = 0.71073 Å) at 150(2) K, where the data reduction was performed using the Apex2 software package. Corrections for incident and diffracted beam absorption effects were applied using empirical absorption correction. Single crystal diffraction analysis on compound **2** was carried out on an Oxford Gemini S Ultra A diffractometer; (λ (MoK α) = 0.71073 Å) at 150(2) K, with absorption effects corrected via an analytical method using a multifaceted crystal model.^[S1] Refinement was carried out with SHELXS-2008^[S2] and SHELXL-2014/7^[S2] using WinGX^[S3] via a full matrix least-squares on F^2 method. All non-hydrogen atoms were refined anisotropically unless otherwise stated. Topological analysis was carried out using Topos 4.0.^[S4]

The obtained crystals for the four different compounds presented poor diffraction quality, while crystals of **3** and **4** were twinned, so determining their structures presented some difficulties. The solvent employed was pure *N,N'*-dimethylformamide (DMF), therefore disordered solvent molecules were modelled as such. Disordered DMF solvent molecules were modelled as fully as possible using sensible electron density peaks. Subsequently, the SQUEEZE procedure was applied to all four datasets, including the twin data for **3** and **4**. Large spacial voids were evident from the SQUEEZE analysis, comprising 35% (for **1**), 54% (for **2**), 6% (for **3**) and 41% (for **4**) of the crystal volumes, respectively. Reported formulae were determined by including the SQUEEZE results and therefore there were big molecular weight differences between the calculated and reported formulae.

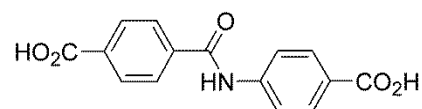
S2. Ligand and Pillar Synthesis

L2 bis-Me ester



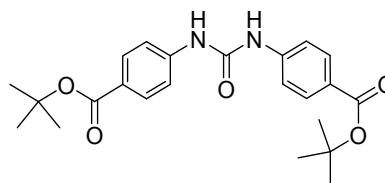
Methyl 4-Aminobenzoate (3.00 g, 19.9 mmol, 1 eq) and potassium carbonate (6.86 g, 49.7 mmol) were dissolved in 90 ml acetone with stirring. Methyl 4-(chloroformyl)benzoate (3.94 g, 19.9 mmol, 1eq) was dissolved separately in 30 ml acetone by sonication and added drop-wise to the stirring reaction mixture. The reaction mixture was sealed and allowed to stir overnight, after which a white solid was collected by filtration. The solid was stirred with water and collected by filtration. The white solid was then suspended in 250 ml THF and hot filtered. The THF filtrate was then subject to rotary evaporation yielding a white solid. The white solid was stirred with hexane, collected by filtration and dried under vacuum (4.37g, 13.9 mmol, 70%). ^1H NMR (DMSO): δ /ppm 3.84 (s, 3H), 3.90 (s, 3H), 7.97 (m, 4H), 8.10 (m, 4H), 10.76 (s, 1H). ^{13}C NMR (DMSO): δ /ppm 51.90 (CH_3), 52.42 (CH_3), 119.69 (CH), 124.58 (C), 128.20 (CH), 129.19(CH), 130.11 (CH), 132.27 (C), 138.61 (C), 143.34 (C), 165.15 (C), 165.62 (C), 165.79 (C). HRESIMS calculated for $\text{C}_{17}\text{H}_{15}\text{NNaO}_5$ ($\text{M}+\text{Na}$) $^+$ 336.0848, found m/z 336.0813.

L2



A solution containing **L2 bis-Me ester** (4.37 g, 13.9 mmol), NaOH (1.13 g, 28.3 mmol), ethanol (125 ml) and H_2O (125 ml) was prepared and subject to reflux overnight. The resulting transparent solution was cooled to room temperature and acidified with a 75 ml 2 M HCl/75 ml H_2O mixture, forming a white suspension. The reaction mixture was sealed and allowed to stir for 3 hours. The product was collected by filtration and washed copiously with water until washings were neutral. The white powder was added to a sample vial which was dried under vacuum (3.88 g, 13.73 mmol, 98%). ^1H NMR (DMSO): δ /ppm 7.94 (m, 4H), 8.07 (m, 4H), 10.69 (s, 1H), 13.04 (s, 2H). ^{13}C NMR (DMSO): δ /ppm 119.57 (CH), 125.76 (C), 128.03 (CH), 129.30 (CH), 130.22 (CH), 133.52 (C), 138.34 (C), 143.00 (C), 165.26 (C), 166.68 (C), 166.88 (C). HRESIMS calculated for $\text{C}_{15}\text{H}_{10}\text{NO}_5$ ($\text{M}-\text{H}$) $^-$ 284.0564, found m/z 284.0611.

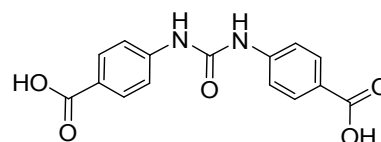
L3 bis-^tBu ester



Procedure adapted from reference [S5]:

Tert-Butyl 4-aminobenzoate (2.00 g, 10.4 mmol, 1 eq) was dissolved in 22 ml THF with stirring. To this stirred solution *N,N'*-carbonyldiimidazole (1.00 g, 6.20 mmol, 0.6 eq) was added, resulting in a pale yellow solution which was refluxed overnight. After 24 hours a further portion of *N,N'*-carbonyldiimidazole (1.00 g, 6.20 mmol, 0.6 eq) was added. The reaction mixture was refluxed overnight. The THF was removed by rotary evaporation, resulting in a thick yellow paste, which was dissolved in 120 ml ethyl acetate with stirring. The resulting solution was washed with 1M HCl (2 x 60 ml), brine (1 x 40 ml) and dried over MgSO₄. The resulting solution was filtered and then subject to rotary evaporation to yield a white solid. The resulting solid was stirred with acetonitrile for 1 hour. The white solid was collected by filtration, added to a sample vial and dried under vacuum (1.35 g, 3.27 mmol, 63%). ¹H NMR (DMSO): δ/ppm 1.54 (s, 18H), 7.57 (d, 4H, J=8.8 Hz), 7.83 (d, 4H, J=8.8 Hz), 9.16 (s, 2H); ¹³C NMR (DMSO): δ/ppm 27.83 (CH₃), 80.07 (C), 117.34 (CH), 124.56 (C), 130.17 (CH), 143.56 (C), 151.84 (C), 164.63 (C); HRESIMS calculated for C₂₃H₂₈N₂NaO₆ (M+Na)⁺ 435.1890, found *m/z* 435.1871.

L3

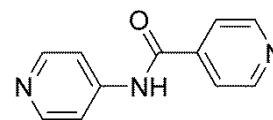


Procedure adapted from reference [S5]

L3 bis-^tBu ester (0.50 g, 1.20 mmol) and TFA (5 ml) were stirred at room temperature for 3 hours. Reactant mixture was diluted with H₂O, filtered and a white solid collected. The white solid was washed copiously with water until washings were neutral. The solid was added to a sample vial and dried under vacuum (0.36 g, 1.20 mmol, 100%). ¹H NMR (DMSO): δ/ppm 7.57 (d, 4H, J=8.8 Hz), 7.88 (d, 4H, J=8.7 Hz), 9.14 (s, 2H), 12.59 (s, 2H); ¹³C NMR (DMSO): δ/ppm 117.39 (CH), 123.96 (C), 130.47 (CH), 143.58 (C), 151.89 (C), 166.91 (C); HRESIMS calculated for C₁₅H₁₁N₂O₅ (M-H)⁻ 299.0673, found *m/z* 299.0666.

P2

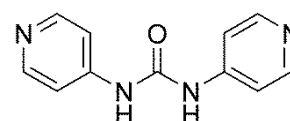
Procedure adopted from reference [S6]:



Isonicotinic acid (2.00 g, 16.24 mmol) and triethylamine (2.2ml, 16.24 mmol) were dissolved in 160 ml THF. To this stirring solution, Ethyl-Chloroformate (1.8ml 18.00 mmol) was added dropwise. A thick white suspension remained, to which 4-Aminopyridine (1.26 g, 13.52 mmol) in 40ml THF, was added dropwise. The reaction mixture was left to stir overnight. The reaction solvent was then evaporated under reduced pressure, yielding an off-white solid. The obtained product was washed with potassium carbonate solution (10% wt)(100 ml), H₂O (2 x 20ml) and diethyl ether (20ml). The product was added to a sample vial which was dried under vacuum (2.39 g, 12.03 mmol, 89%). ¹H NMR (DMSO): δ/ppm 7.77 (dd, 2H, J=1.5, 4.8 Hz), 7.86 (dd, 2H, J=1.8, 4.5 Hz), 8.51 (dd, 2H, J=1.5, 4.8 Hz), 8.81 (dd, 2H, J=1.8, 4.5 Hz); ¹³C NMR (DMSO): δ/ppm 114.14 (CH), 121.60 (CH), 141.24 (C), 145.42 (C), 150.35 (CH), 150.38 (CH), 165.05 (C); HRESIMS calculated for C₁₁H₁₀N₃O (M+H)⁺ 200.0824, found *m/z* 200.0817.

P3

Procedure adopted from reference [S7]:



1,1'-Carbonyldiimidazole (1.44 g, 8.90 mmol, 1 eq) and 4-Aminopyridine (1.50 g, 15.9 mmol, 1.79 eq) were dissolved in 240 ml toluene. The solution was left to reflux at 80°C for 3 hours. The heat source was then removed from the reaction and the reaction mixture was left to stir overnight at room temperature. The resulting white powder was obtained by filtration, washed with Toluene (100 ml), DCM (50 ml), water (10 ml) and finally with diethyl ether (60 ml). The product was added to a sample vial which was dried under vacuum (0.90 g, 4.22 mmol, 47%). ¹H NMR (DMSO): δ/ppm 7.45 (dd, 4H, J=1.6, 4.8 Hz), 8.38 (dd, 4H, J=1.6, 4.8 Hz), 9.31 (s, 2H); ¹³C NMR (DMSO): δ/ppm 112.50 (CH), 145.95 (C), 150.22 (CH), 151.76 (C); HRESIMS calculated for C₁₁H₁₀N₄NaO (M+Na)⁺ 237.0752, found *m/z* 237.0741.

S3. MOF Synthesis

The general syntheses of the MOFs presented involve combining the ligand, pillar and [Zn(NO₃)₂][·]6H₂O in *N,N'*-dimethylformamide (DMF), and then heating in a sealed vessel. A

variety of ratios, temperatures, concentrations and reaction times were analysed, with compounds **1-4** being the only species isolated for their particular mixtures of ligands and pillars across a range of metal:ligand:pillar starting ratios. The following conditions were found to be optimal for synthesis:

Compound 1: $[\text{Zn}_2(\text{L1})_2(\text{P2})]_n$. $[\text{Zn}(\text{NO}_3)_2] \cdot 6\text{H}_2\text{O}$ (50 mg, 0.17 mmol), **L1** (40 mg, 0.17 mmol) and **P2** (50 mg, 0.25 mmol) were each dissolved in DMF (5 ml) by sonication. The solutions were combined in a 50 ml Pyrex screw top jar. A further 10 ml of DMF was added and the resultant MOF solution was sonicated before being placed in the oven at 65 °C for 2 days. Upon removal from the oven the mother solution was exchanged for fresh DMF. The crystals were left to stand before being analysed by single crystal X-ray diffraction.

Compound 2: $[\text{Zn}_2(\text{L2})_2(\text{P1})]_n$. $[\text{Zn}(\text{NO}_3)_2] \cdot 6\text{H}_2\text{O}$ (21 mg, 0.07 mmol), **L2** (20 mg, 0.07 mmol) and **P1** (5.5 mg, 0.035 mmol) were combined in a 20 ml scintillation vial and DMF (2 ml) was added. The reactant components were dissolved by sonication before being placed in the oven at 80 °C for 2 days. Upon removal from the oven the mother solution was exchanged for fresh DMF. The crystals were left to stand before being analysed by single crystal X-ray diffraction.

Compound 3: $[\text{Zn}(\text{L1})(\text{P3})]_n$. $[\text{Zn}(\text{NO}_3)_2] \cdot 6\text{H}_2\text{O}$ (50 mg, 0.17 mmol), **L1** (40 mg, 0.16 mmol) and **P3** (54 mg, 0.25 mmol) were combined in a 50 ml Pyrex screw top jar and DMF (25 ml) was added. The reactant components were dissolved by sonication, and then HCl (2 drops) was added. The resulting solution was placed in the oven at 70 °C for 2 days. Upon removal from the oven the mother solution was exchanged for fresh DMF. The crystals were left to stand before being analysed by single crystal X-ray diffraction.

Compound 4: $[\text{Zn}(\text{L2})(\text{P3})]_n$. $[\text{Zn}(\text{NO}_3)_2] \cdot 6\text{H}_2\text{O}$ (30 mg, 0.10 mmol), **L2** (31 mg, 0.11 mmol) and **P3** (34 mg, 0.16 mmol) were combined in a 50 ml Pyrex screw top jar and DMF (10 ml) was added. The reactant components were dissolved by sonication before being placed in the oven at 80 °C for 2 days. Upon removal from the oven the mother solution was exchanged for fresh DMF. The crystals were left to stand before being analysed by single crystal X-ray diffraction.

All synthetic attempts involving **L3** resulted in the sole synthesis of a framework comprising only Zn^{2+} cations and **L3**, with a structure analogous to that seen for the previously published framework, $[\text{Zn}_4\text{O}(\text{L2})_3(\text{DMF})_2]_n$, referred to as NJU-Bai2.^[S8].

S4. Topological Analysis

The structure of the compounds $[\text{Zn}_2(\mathbf{L1})_2(\mathbf{P2})]_n$ and $[\text{Zn}_2(\mathbf{L2})_2(\mathbf{P1})]_n$, which exhibit paddle-wheel SBUs, were simplified by the cluster simplification method, and the resultant underlying topology is consistent with a uninodal, six-connected **pcu** net. In each case, there are two interpenetrated nets related by an inversion center, being thus classified as IIa type.^[S4b] The structures $[\text{Zn}(\mathbf{L1})(\mathbf{P3})]_n$ and $[\text{Zn}(\mathbf{L2})(\mathbf{P3})]_n$ were studied by the standard simplification procedure, since the secondary building units in these structures are based on isolated hexa-coordinated metal centres that are connected through four different linkers in a distorted tetrahedral geometry. The resultant topology corresponds to a diamond (**dia**) net, and the structures consist of four interpenetrated nets related by an inversion center and by a translation vector, being thus classified as IIIa type.^[S4b]

S5. Hypothetical Structures Preparation

We have built hypothetical new structures corresponding to the synthesised materials with swapped linkers. From the initial 4 structures we built 12 new ones, named as X-(L)(P), where X is the mother structure and **L** and **P** are the ligands and pillars used according to Figure 1. The strategy is similar to the methodology^[S9] we have used previously. We start with the asymmetric unit of every mother structure, maintaining the metal cluster (i.e. Zn paddle wheel or Zn), the **pcu** or **dia** topology as well as the corresponding group symmetry, but swapping the organic linkers. After the asymmetric units are modified, the symmetry operations of the space group allow the construction of the new structures. Since no modification was done in the unit cell size, the lattice parameters were at this point far away from realistic values. The unit cells are then subject to energy minimisation and geometry optimisation based on molecular mechanics, which include van der Waals and electrostatic interactions, modifying the size of the unit cells and the atomic coordinates of the new structures. These calculations were performed with the Forcite module of Materials Studio, using an algorithm which is a cascade of the steepest descent, adjusted basis set Newton-Raphson, and quasi-Newton methods.^[S10] The bonded and the short range (van der Waals) interactions between the atoms were modelled using the Universal Force Field (UFF).^[S11] A cut-off distance of 18.5 Å was used for the van der Waals interactions during the geometry optimization. The long range, electrostatic, interactions, arising from the presence of partial atomic charges, were modeled using a Coulombic term. The Ewald sum method was used to compute the electrostatic interactions. Partial atomic charges were derived from the charge equilibration method (QEq)^[S12] as implemented in Forcite.

Table S1. Calculated geometrical surface area for the synthesised and hypothetical materials.

	Compound	Surface Area m ² /g
1	L1P2	2404
2	L2P1	2437
3	L1P3	2039
4	L2P3	2362
	1-L2P1	2332
	1-L2P3	2474
	1-L1P3	2088
	2-L1P2	2214
	2-L2P3	2665
	2-L1P3	2116
	4-L1P2	1461
	4-L2P1	657
	4-L1P3	2109
	3-L1P2	1517
	3-L2P1	1109
	3-L2P3	1179

S6. Cambridge Structural Database Searching

To investigate the propensity for H-bonding between urea groups and carboxylic acid functions in coordination polymers, a search of the Cambridge Structural Database (CSD, November 2013 update) was performed using the search software ConQuest Version 1.16.^[S13] Two fragments were included in the structural search, an N,N'-disubstituted urea function and a carboxylate fragment bound to any metal (Figure S1a).

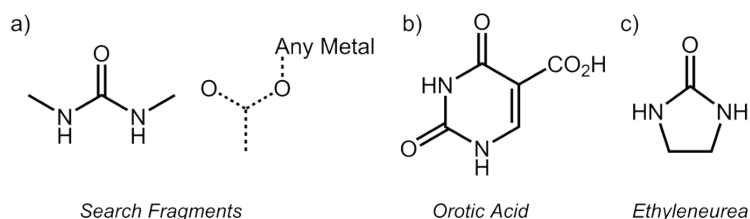


Figure S1. a) Search fragments used to examine solid-state structures containing urea functional groups and metal-carboxylate interactions. Dashed lines represent bonds of any order. b) Orotic acid, and c) ethyleneurea, were common to many hits and structures containing these units were not considered.

This fragment combination yielded 134 hits, many of which contained orotic acid (Figure S1b) or ethyleneurea (Figure S1c), and these structures were not considered. Of the 134 hits, only 16 were found to be coordination polymers with genuine urea functional groups.

S7. Gas Adsorption Simulations and Computational Structural Characterisation

The adsorption of N₂ was investigated using grand canonical Monte Carlo (GCMC) simulations, performed with the in-house multi-purpose code RASPA.^[S14] We used a rigid atomistic model for compounds **1-4**, in which the framework atoms were kept fixed at their crystallographic positions. Solid-fluid and fluid-fluid interactions were calculated using a Lennard-Jones (LJ) + Coulomb potential. LJ parameters for the framework atoms were taken from the Universal Force Field (UFF),^[S11] the N₂, LJ parameters from the TraPPE force field.^[S15] This force field was originally fitted to reproduce the vapour-liquid coexistence of nitrogen. In this force field, nitrogen molecules are modelled using a three-site rigid model (N-N = 1.10 Å), that reproduces the experimental quadrupole moment of nitrogen molecules. Lorentz-Berthelot mixing rules were used for all cross terms, and LJ interactions beyond 12 Å were neglected. Coulombic interactions were modelled by placing partial charges on the framework atoms. The partial charges were calculated using the QEq

method, and the long-range electrostatic interactions were calculated using the Ewald summation method. $6 \cdot 10^4$ Monte Carlo equilibration cycles were performed plus $4 \cdot 10^4$ production cycles to calculate the ensemble averages. In one cycle, an average of N moves were performed, where N is the number of molecules in the system (which fluctuates in GCMC). Monte Carlo moves used with equal probability were translation, rotation, insertion, deletion, and random reinsertion of an existing molecule at a new position. To calculate the gas-phase fugacity, we used the Peng-Robinson (PR) equation of state (EOS).^[S16]

The pore size distributions were calculated using the method of Gelb and Gubbins,^[S17] where the largest sphere that can fit in a random point within a structure without overlapping the van der Waals surface of the framework is recorded for a large number of random points. The geometric surface areas were calculated by rolling a 3.681 Å-diameter sphere, which corresponds to a nitrogen molecule, across the surface of the material.^[S18]

Table S2. Lennard-Jones parameters for framework atoms and the N₂ molecules.

	σ [Å]	ϵ/k [K]	q [e]
C	3.431	52.838	
N	3.261	34.722	
O	3.119	30.192	
H	2.571	22.142	
Zr	2.783	34.751	
N_N ₂	3.310	36.000	-0.482
com_N ₂	0.000	0.000	0.964

S8. References

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