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Supporting Information

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A family of nanoporous materials based on an amino acid backbone

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Experimental procedures

1. Synthesis of Ni(L-asp)(H_2O)2.H2O (Ni(Asp))

$NiCO_3$ (1mmol) was added to a hot solution of aspartic acid (1mmol) in water (100 ^oC) and this solution was concentrated till a pale blue precipitate of $Ni(C_4O_4H_5N)(H_2O)_2.H_2O$ (NiAsp) started to form. The solution was then cooled to room temperature and left at 5^oC for 12hrs. Yield = ~85%. (Micro analysis(%): C=19.82(19.79); H=4.76(4.55); N=5.72(5.76); ICP(%):Ni=24.21(24.17)). Bulk chirality (GC,ee) =100%.

Synthesis of $[Ni_2(L\text{-}asp)_2(bpy)].CH_3OH.H_2O$ (I):

0.219gm NiAsp (0.9mmol) was dispersed in a mixture containing 3mL of water (167mmol) and 3mL of methanol (94mmol) and 0.3124gm of 4,4'-bipyridyl (2mmol) was added to this mixture. The final mixture of the composition NiAsp: 2.2 (4,4'-bipyridyl): 185 H_2O: 104 CH_3OH was sealed into an autoclave and heated at 150^oC for 48hrs. I.pH=6.5; F.pH=6.8; Yield = ~40 This product, $[Ni_2(L\text{-}Asp)_2(bpy)].CH_3OH.H_2O$, was filtered and washed with copious amounts of water and methanol. (Micro analysis(%): C=38.94(38.96); H=4.11(4.13); N=9.64(9.56); ICP(%):Ni=20.12(20.04)). Bulk chirality (GC,ee)=100%.

Synthesis of single crystals of $[Ni_2(L\text{-}asp)_2(bpy)].CH_3OH.H_2O$ (I):

0.0891gm of $NiCO_3$ (0.75mmol) and 0.1gm (0.75mmol) of L-aspartic acid were dispersed in a mixture containing 2mL of methanol (62.4mmol) and 0.2mL of water (11.1mmol). To this solution, 0.0586gm of 4,4'-bipyridyl ((0.375mmol) was added and stirred for ~1 hr. The final mixture of the composition $NiCO_3$: L-Asp: 0.5(4,4'-bipyridyl): 15 H_2O: 83 CH_3OH was sealed into an autoclave and heated at 150^oC for 48hrs. I.pH=5.8; F.pH=6.2; Yield = ~50%. The product a mixture of large blue-green single crystals of $[Ni_2(L\text{-}Asp)_2(bpy)].CH_3OH.H_2O$, **I**, with rod-like morphology and blue crystals of $Ni(C_4O_4H_5N)(H_2O)_2.H_2O$ was washed with water and methanol. These crystals of **I** were suitable for single crystal X-ray diffraction.

Synthesis of the achiral polymorph [Ni_2(L,D-asp)$_2$(bpy)]. $2H_2O$ (II):

0.0891gm of $NiCO_3$ (0.75mmol) and 0.1gm (0.75mmol) of L-aspartic acid were dispersed in a mixture containing 2mL of water (111mmol) and 0.2mL of methanol (6.2mmol). To this solution, 0.0586gm of 4,4'-bipyridyl ((0.375mmol) was added and stirred for ~1 hr. The final mixture of the composition $NiCO_3$: L-Asp: 0.5(4,4'-bipyridyl): 148 H_2O: 8.3 CH_3OH was sealed into an autoclave and heated at 150^oC for 48hrs. I.pH=5.8; F.pH=6.2; Yield = ~50%. The product, blue-green single crystals of [Ni_2(asp)$_2$(bpy)].$2H_2O$, with truncated polyhedral morphology was washed with water and methanol. Bulk chirality (GC,ee)=38%.

Alternative procedure for the synthesis of achiral polymorph (II):

0.05gm of Ni(asp) (0.21mmol) and 0.0644gm of 4,4'-bipyridyl (0.42mmol) were dispersed in a mixture containing 3mL of water and 2mL of methanol. Contents were stirred for ~1hr and the final mixture of the composition Ni(asp): L-asp: 2.0 (4,4'-bipyridyl): 812 H_2O: 305 CH_3OH was sealed into an autoclave and heated at 150^oC for 48hrs. I.pH= 6.0; F.pH=6.2; Yield = ~30%. The product, **II**, blue-green single crystals with truncated polyhedral morphology was washed with water and methanol. Bulk chirality (GC,ee)=42%.

Synthesis of [Ni_2(D/L-asp)$_2$(bipy)](1,2-pd), III:

About 100 mg of **II**, was dispersed in 2 mL of 1,2-propanediol and stirred for 30 mins. The contents were sealed into a stainless steel autoclave and heated at 100 ^oC for 12 hours. The product, a crop of blue-green crystals of **III,** was washed with copious amounts of methanol and water.

Crystallographic details of the structure of **I** at 150K and 373K, and the structure of **III**, have been deposited at CCDC with the following reference numbers:

CCDC-607295 (**III**)

CCDC-607296 (150K, **I**)

CCDC-607297 (373K, **I** desolvated)

Measurement details

Single crystal X-ray diffraction data were collected on station 9.8 of the Synchrotron Radiation Source, Daresbury Laboratory.

X-ray powder diffraction data were collected in transmission geometry using a Stoe Stadi-P diffractometer with Cu $K\alpha_1$ radiation.

CO_2 sorption isotherms were measured using a Hiden IGA gravimetric sorption balance.

TGA data were recorded using a Seiko S-II instrument.

Procedure for the guest loading and their subsequent removal for estimation of the enantio selectivity of the host using GC:

Procedure for the loading and removal of diol guest molecules from homochiral framework, I:

100 mg of **I** is activated by heating to 100 °C under dynamic vacuum for 16 hours in a Schlenk tube. This procedure has been shown to remove all guest molecules from the porous network of the framework. After this time the Schlenk tube is allowed to cool to ambient temperature and purged with Ar. This purge cycle is completed 3 times and then the tube is left under an Ar atmosphere. To this is added 2 ml of the diol via a syringe, and the vessel transferred to a refrigerator at 5 °C. This is typically left for 24 hours to allow equilibration to occur.

The solid framework is removed from the diol by vacuum filtration through a sinter funnel (porosity 4) and the material washed with a small volume of MeOH (1 – 5 ml) to remove surface adsorbed guest molecules. The solid is transferred to a custom-designed micro-distillation apparatus (total volume of this equipment is approx 15 cm^3) and the guest is removed from the framework by distillation under vacuum. Post-distillation, the solid is subject to mass-spectrometry and elemental analysis to confirm complete removal of the guest molecules from the host framework.

Determination of the Enantiomeric excess (ee) of the extracted diols by capillary-GC:

All of the extracted diol guest molecules were derivatised with trifluoroacetic anhydride (TFA) prior to GC analysis. Typically, 1 ml of dichloromethane and an excess of TFA (150 µl) was added to the extract and this was allowed to stir under ambient conditions overnight (~ 18 hrs) in a screw-capped glass vial. After this time the solvent was removed by rotary evaporation, and further portions of DCM added and removed until no further smell of the acid was detected. (Standard samples were prepared in the same way from 50 mg of diol and 500µl of TFA.) Solutions of 0.1 – 0.5 % (w/v) were prepared in DCM for injection into the GC.

GC analysis was carried out using a cyclodextrin-based Lipodex-E capillary-GC column (length 25m, inner diameter 0.25mm, outer diameter 0.40mm) supplied by Machery-Nagel. All enantiomeric separations were carried out using the following conditions: Carrier Gas, 0.5 bar He; Column Temp Program, isothermal; Detector, FID 220°C; Injector, 220°C. The column temperature employed was dependent on the diol under investigation and was typically in the range 70 - 85°C. All diols were separated with baseline resolution under these conditions. (For separation factors, a, of the diols studied see W. A. König, *Jounal of High Resolution Chromatography*, **1993**, *16*, 569)

All determined ee's were verified using a second column (Chiralsil-DEX CB) which gave comparable results. The ee's reported in the manuscript are those based on the Lipodex-E results as the separation of the enantiomers on the Chiralsil-DEX CB column was not as complete.

Determination of the bulk chirality of the framework, I:

Firstly, the aspartic acid needs to be extracted from the bulk material, and is done so by adding 1N NaOH (4 ml) to the framework (~ 30 mg) and removing the resulting precipitate by filtration through a small plug of cotton wool. The addition of NaOH to the framework results in the precipitation of insoluble $Ni(OH)_2$ and the 4,4'-bipyridyl linking ligands which are also insoluble in basic aqueous solution. Removal of the solids leaves disodium-aspartate in the filtrate. The filtrate is neutralised by the addition of 1N HCl and the aqueous solution removed by rotary evaporation. The resulting white solid is a

mixture of aspartic acid (^{1}H NMR) and NaCl (generated by the neutralisation step) as confirmed by elemental analysis.

Once the aspartic acid has been recovered from the bulk framework sample it is necessary to derivatise this prior to GC analysis. The carboxylic acid groups are first converted to methyl esters by heating in MeOH (4ml) and HCl (4N, 1ml) in a 20 ml round-bottom flask equipped with a condenser for 4 hours. The primary amine is transformed into an amide by reaction with TFA (0.5 ml in 5 ml DCM, RT overnight) as outlined for the diol derivatisation. The NaCl present in the mixture does not interfere with either of the two steps of the derivatisation procedure and is not removed until the very end when the Asp(OMe/TFA) derivative is dissolved in DCM and the NaCl is simply filtered off. The solution concentration for GC analysis is 0.5% (w/v) Asp(OMe/TFA) in DCM, and is carried out using a Lipodex-E capillary-GC column (as outlined above) at 120°C.

Other members of the family

It is possible to replace 4,4'-bipy with longer chain bifunctionalised aromatic amines – the 1,2-bis(4-pyridyl)ethylene and 4,4'-azobispyridine ligands with ethene and aza units separating the layers have *c* parameters of 25.463 and 25.536Å respectively, while 2,4,6-tri-pyridin-4-yl-[1,3,5]triazine gives a *c* parameter of 29.57Å and has the potential to provide a free basic function within the channels, thus giving the family chemical diversity. In the case of the triazine ligand, only two of the three potential aromatic nitrogen donors are used in framework formation, and the third extends into the void space to provide a basic reaction site.

Computational procedures

The two enantiomers of pentane-1,2-diol and 2-methylpentane-2,4-diol were subjected to a *in silico* docking procedure using Autodock[1] and associated suite of programs. Autodock uses an empirical function to estimate the free energy of binding. This function contains five terms: a Lennard-Jones 12-6 dispersion/repulsion term; a directional 12-10 hydrogen bonding term; a screened Coulombic electrostatic potential; unfavourable entropy of binding due to restricted conformations and a desolvation energy term. For the calculations, the structure of the chiral framework was rigid and the metal atoms were not considered as the parameters have not been defined for this element. The neutral charge was maintained by adding protons to the carboxylate groups such that they were occupying the space where the nickel atoms had been, minimising the effect on the putative binding site. This is justifiable as the crystal structure of propane-1,2-diol-loaded framework **III** shows that the guest interaction is with asapartate rather than the metal centres. A combination of a Lamarckian genetic algorithm and pseudo-Solis and Wets local search was used to generate docking poses for each alcohol. The parameters used in this 'blind docking' procedure were those that have been shown to reproduce the binding mode of drugs within known structures of drug:crystal complexes with no prior knowledge of the binding site.[2] The most popular docking pose for each diol, as clustered by their RMSD, was subjected to a single point energy calculation using semi-empirical quantum mechanics using PM3 parameters.[3]

[1] Morris, G. M.; Goodsell, D. S.; Halliday, R. S.; Huey, R.; Hart, W. E.; Belew, R. K.; Olson, A. J.; *J. Computational Chemistry*, **1998**, 19, 1936.
[2] Hetényi, C.; Van Der Spoel, D.; *Protein Science*, **2002**, 11, 1729.
[3] Spartan 04, Wavefunction, Inc., 18401 Von Karman Avenue, Suite 370, Irvine, CA 92612 U.S.A.

Supplementary Figures

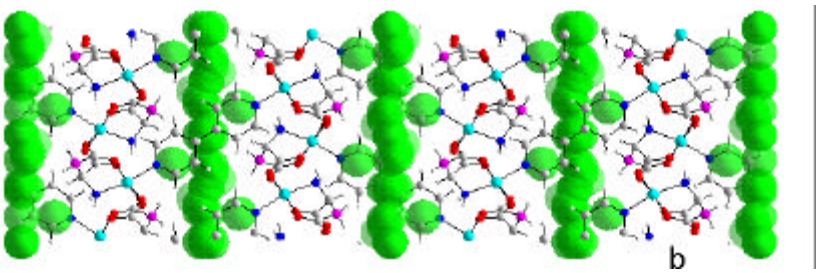

Figure S1. The one-dimensional channels in chiral porous **I,** marked by green spheres. The β-carbon atoms from the aspartate amino acid are highlighted in purple to illustrate how their projection into the channels controls the dimensions of the porosity.

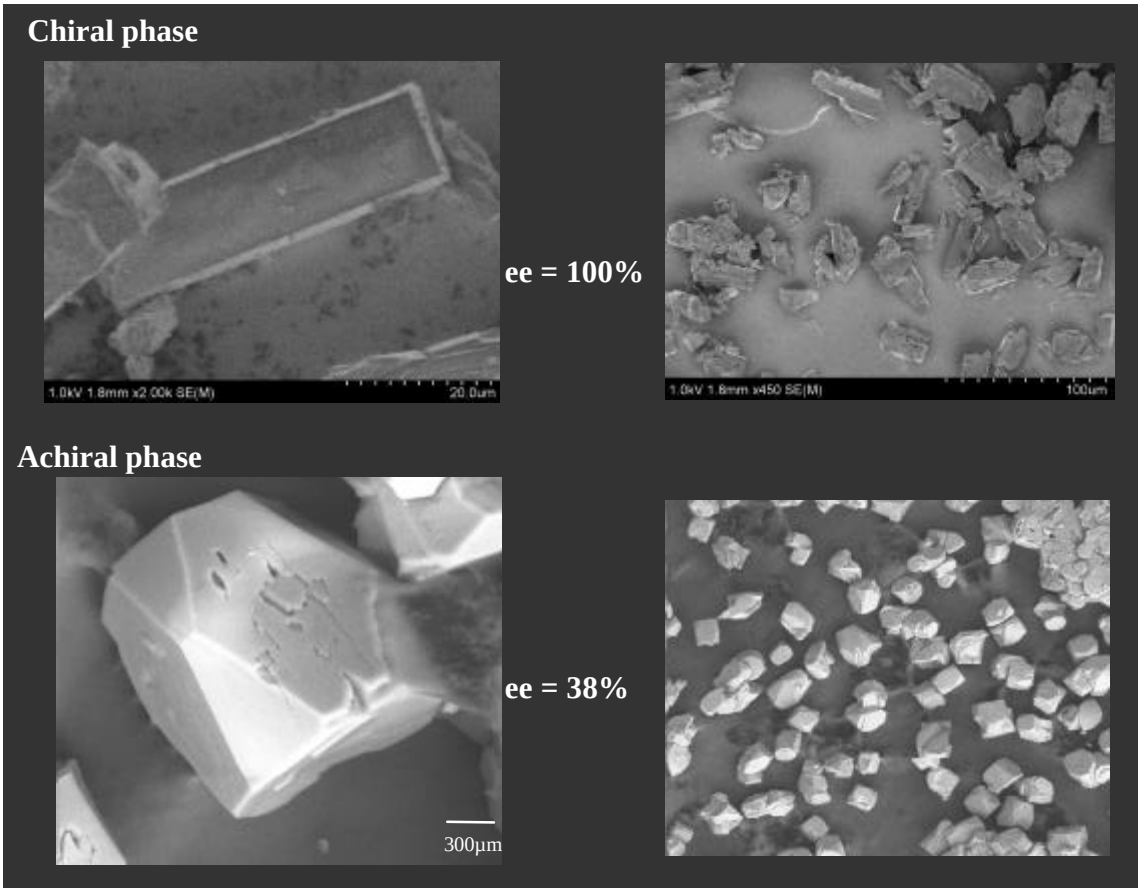

Figure S2. SEM images of the achiral (**II**) and chiral (**I**) polymorphs of Ni_2asp_2bipy. The morphology of the chiral phase reflects the orthorhombic habitat of the crystals whilst the crystals of the achiral phase has a truncated polyhedral morphology and crystallize in the monoclinic setting, $P2_1/n$.

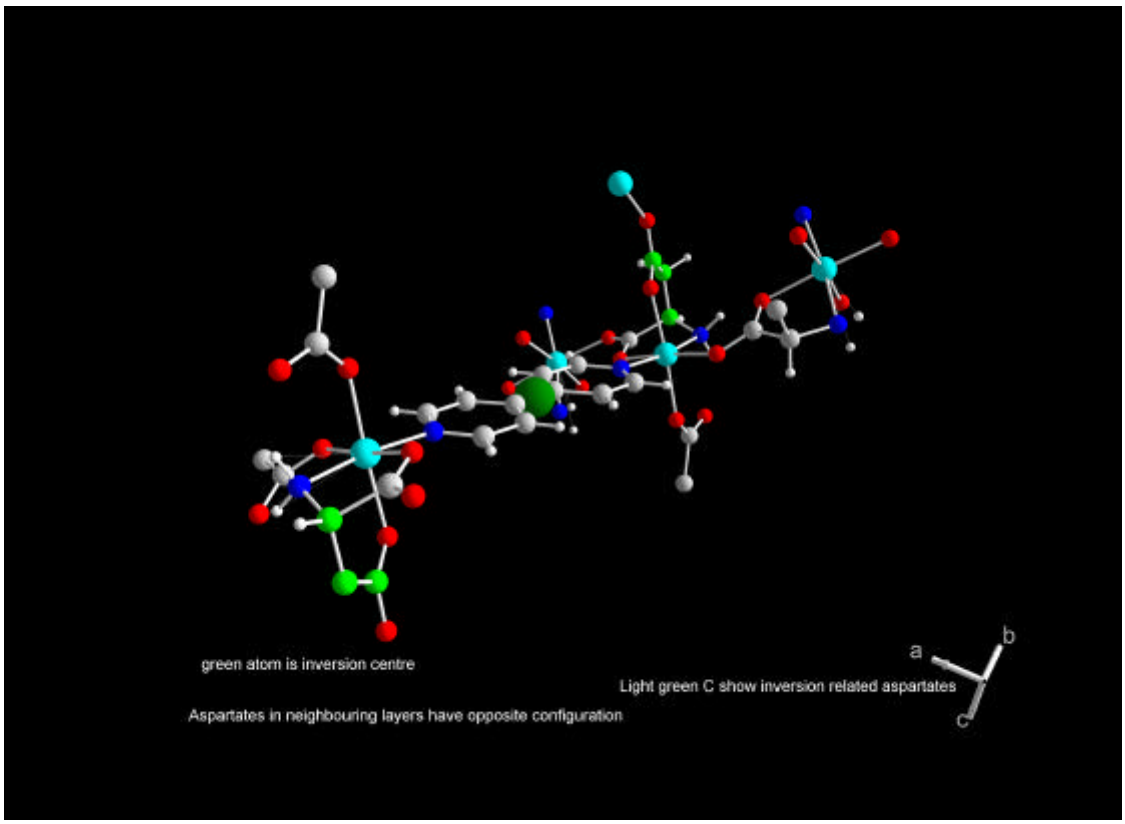

Figure S3. The crystal structure of racemic **II** (and propane-1,2-diol loaded **III**) is very similar to chiral **I** in connectivity, but successive layers are inversion-related and thus contain alternating enantiomers of the aspartate. The green spheres are inversion-related enantiomers, related via the inversion centre (dark green sphere) on which the bipyridyl ligand sits. The layers in racemic **II** differ from those in chiral **I** in that the α-carboxylate of the tridentate aspartate is trans to an α-carboxylate in **II** rather than a β-carboxylate in **I**.

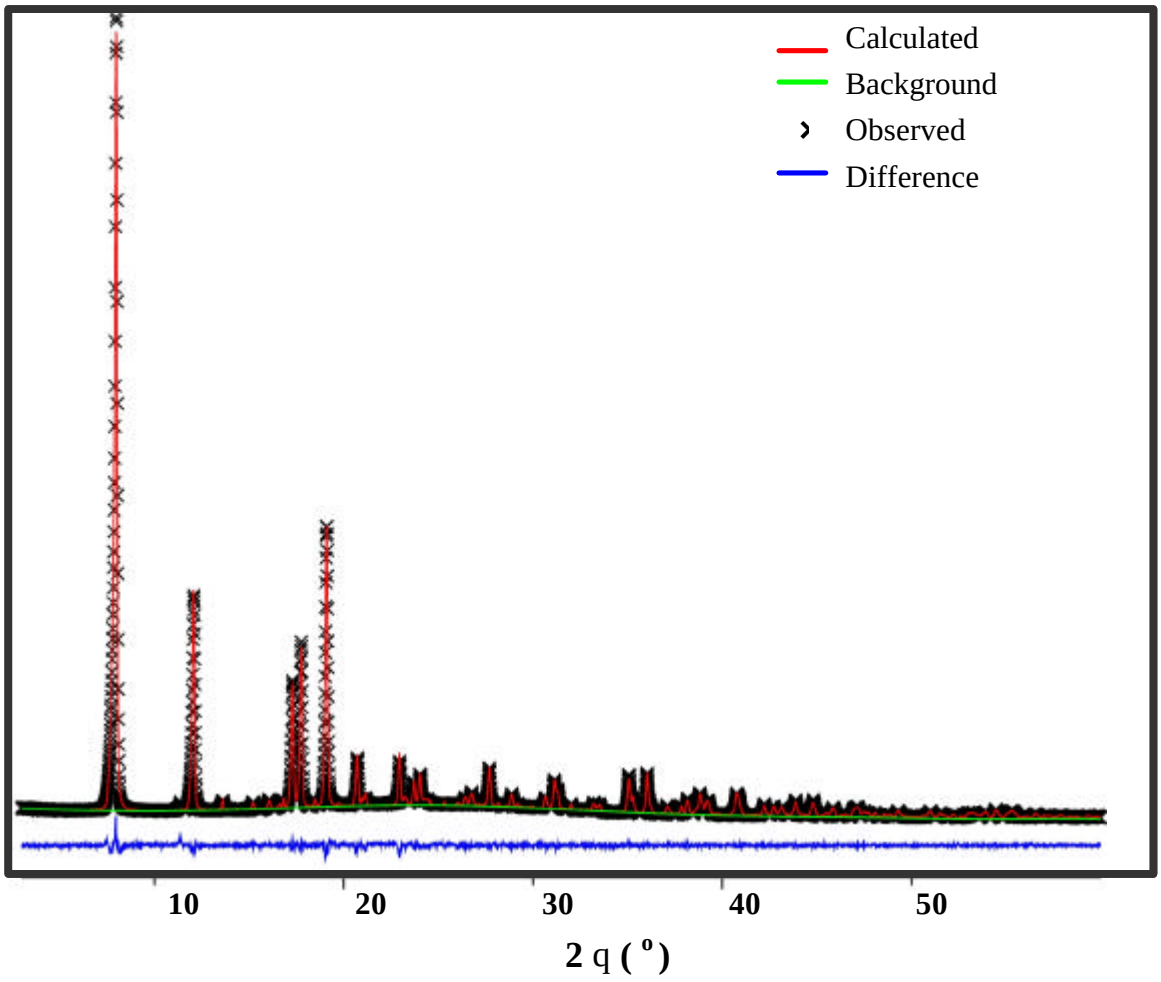

Figure S4. Le Bail fit to the powder X-ray diffraction pattern of **I** measured in transmission geometry with Cu Ka_1 radiation using a 0.5mm capillary.

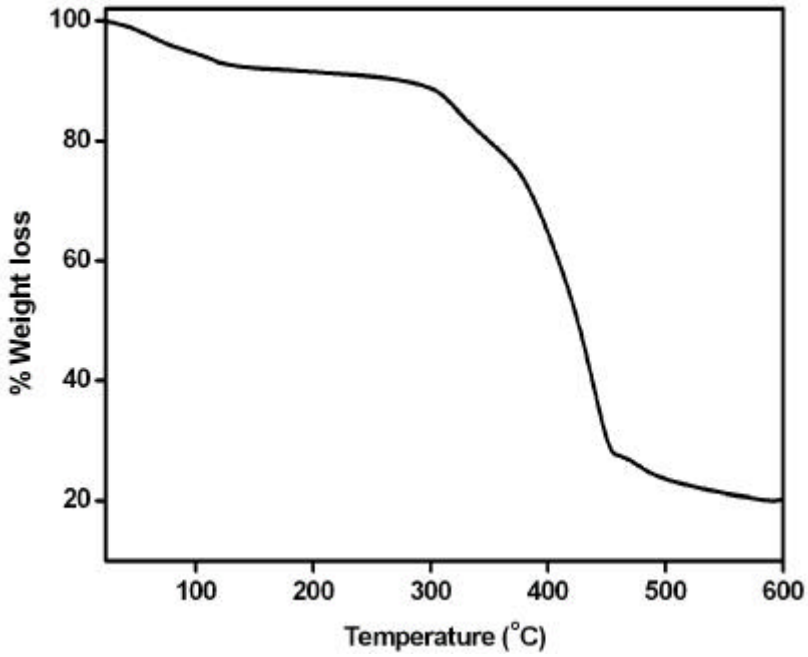

Figure S5. TGA of **I**. A weight loss of approx. 9% (calc. 8.6%) in the temperature range of 25 to 200 ^{o}C corresponds to guest loss accounting for 70% filling of voids by the guest, whilst the weight loss of 71.5% (calc. 71.4%) in the temperature range of 200-600 ^{o}C is in agreement with the weight loss calculated for the decomposition of $Ni_2(Asp)_2(bpy)$ to 2NiO + (organics).The decomposition product was identified to be NiO (JCPDS: 47-1049).

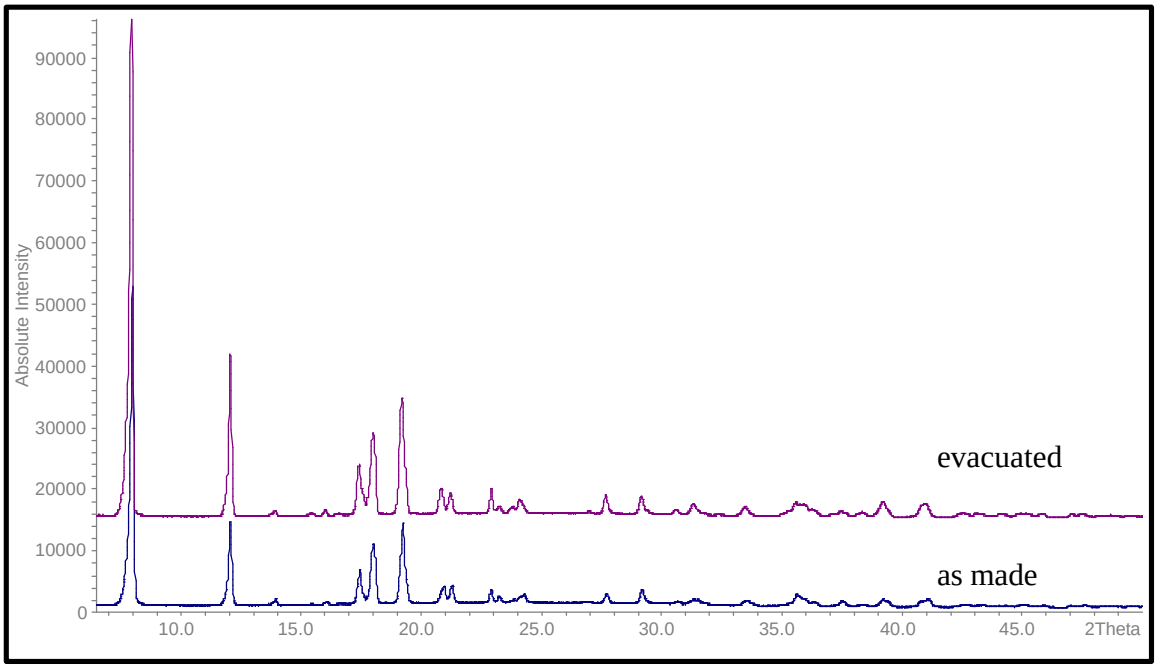

Figure S6. Powder XRD of **I**, before and after activation, (heated on a Schlenk line at 100 ^{o}C for 12 hours). Cell parameters of evacuated sample $P2_12_12$; a = 22.074(18); b=7.762(6); c=6.690(9) Å; V =1146.6(25) Å^3. Note the thermal stability was also determined from powder X-ray diffraction data from a sample heated to 200 ^{o}C on the TGA. The composition of the evacuated sample was shown from the microanalysis to be Ni_2(Asp)(bipy), **II**, % C=40.84(40.35); H=3.38(3.39); N=10.34(10.46), (calc. values in brackets).

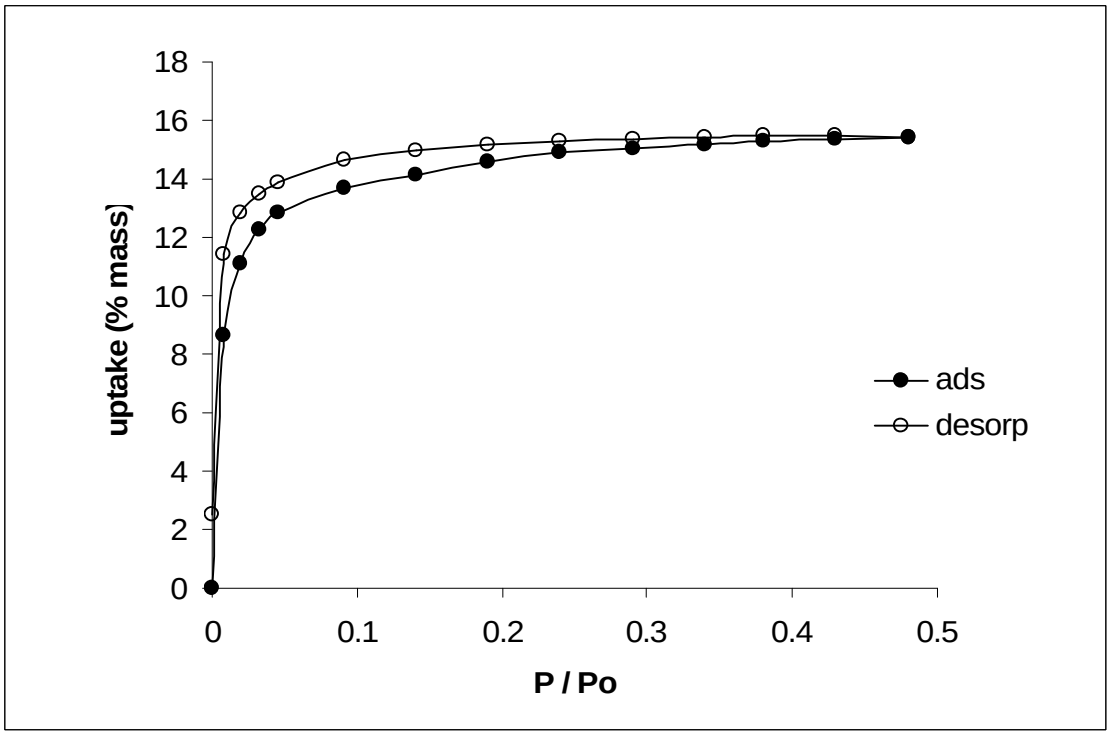

Figure S7. CO_2 sorption isotherm for **I** at 298K. Phase **1** was found to be essentially non-porous to nitrogen at 77K, hence CO_2 was used to determine the BET surface area. This non-porosity toward N_2 under these conditions is not uncommon in metal-organic frameworks prepared from 4,4'-bipyridyl with pore sizes of less than 10 Å. For additional information see A.J. Fletcher, E. J. Cussen, T. J. Prior, M. J. Rosseinsky, C. J. Kepert and K. M. Thomas *J. Am. Chem. Soc.* **2001**, *123*, 10001-10011.