Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Converting 3D Rigid Metal-Organic Frameworks (MOFs) to 2D Flexible Networks via Ligand Exchange for Enhanced CO_2/N_2 and CH_4/N_2 Separation

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1. General Information

Chemicals: All reagents were purchased from commercial sources (Sigma Aldrich and Merck) and were used without further purification. Specifically, Zinc acetate dehydrate $Zn(CH_3COO)_2 \cdot 2H_2O$, 4,4′-biphenyldicarboxylic acid (BPDC), 4,4′-Dipyridyl (BiPY) (98%), 1,3-Bis(4-pyridyl)propane (BPP) (98%), Dimethyl sulfoxide-d_6 (DMSO- d_6)(99.9 atom %D), Sulfuric acid-d2 solution (D_2SO_4/D_2O)(96-98 wt. % in D_2O) were purchased from Sigma-Aldrich. Glacial Acetic acid AR(CH3COOH)(100%), and Ethanol (C_2H_5OH) (100%) were purchased from chem-supply. N,N-dimethylformamide (DMF) (99.9%) was purchased from PROLABO CHEMICALS.

2. Materials synthesis

Parent material **1**: A mixture of Zinc (II) acetate dehydrate (1 mmol, 0.2195 g), 4′-biphenyldicarboxylic acid (1 mmol, 0.242 g) and 4,4′-Dipyridyl (0.5 mmol, 0.0788 g) in 20 mL DMF was stirring for 3 hours and then transferred to a 40ml Teflon-lined stainless steel autoclave. The autoclave was transferred to pre-heated oven at 120 °C for 72 hours before it was cooled down slowly. The colourless crystals of **1** were filtered and washed with DMF (15 ml) three times and dried in a vacuum oven for 2 hours (86% yield based on zinc acetate).

Daughter material **2**: Based on the single crystal of **1** as precursor, the daughter material **2** was synthesized by Solvent-Assisted Ligands Exchange (SALE). To be specific, a concentrated 1,3-Bis(4-pyridyl)propane (BPP) solution was prepared: 1 mmol (0.1983 g) BPP was dissolved in 8 ml DMF by ultrasound for 5 minutes, then 2 ml Ethanol and 200 μl acetic acid were added. Approximately 200 mg of parent crystals of **1** were soaked in the BPP solution and transferred to a 20 ml Teflon lined autoclave. The reaction was undertaken at 105 ℃, and every 3 days, the product was washed thoroughly with hot DMF (3*20ml) and the BPP solution was refreshed. The above procedure was repeated 4 times (12 days reaction time in total). Elemental analysis calcd(%)for desolvated **2** Zn(BPDC)(BPP), ($ZnC_{27}O_4N_2H_{22}$) C 64.41, H 4.37, N 5.56; found: 62.60, H 4.38, N 5.23.

3. Characterization measurements

NMR: ^{1}H NMR experiment were conducted on a Bruker AvanceIII 400 spectrometer, operating at 400 MHz. The samples for ^{1}H spectral measurements were prepared by the following procedure: around 5 mg of a sample was washed thoroughly by DMF and dried at 60 °C in a vacuum oven. The sample was digested by 10 min sonication in deuterated dimethyl sulfoxide (DMSO) solution mixed with 3 drops of D_2SO_4. The digestion solution was used directly for ^{1}H-NMR.

SEM: The morphology of the products was investigated on a JEOL 7001F FEG scanning electron microscope (SEM), operating at 15 kV. The sample was crushed and sprinkled on carbon tape mounted on a metal stub and coated with a 1 nm layer of platinum metal.

TGA: Thermogravimetric (TG) analyses were conducted using a Mettler Toledo TGA-SDTA851 analyser (Switzerland) from 30 to 800 °C with ramping rate of 2 °C/min, under nitrogen (40 mL/min) to investigate thermal stability and composition of the sample **1** and **2**.

CHN elemental analysis: The determination of carbon, hydrogen, and nitrogen (%CHN analysis) for the sample **2** was conducted by Carlo Erba Flash 2000 Elemental Analyser at the London Metropolitan University.

Synchrotron Powder X-ray Diffraction: High-resolution synchrotron powder X-ray diffraction (PXRD) data was collected on both parent and daughter samples by a Mythen-II detector on powder diffraction beamline, Australian synchrotron. The wavelength was calibrated by NIST LaB_6 660b standard of 0.7742 Å. For phase identification and structure determination, the synthesized samples were dried at 60 °C in vacuum oven and directly loaded into 0.7 mm glass capillaries sealed with waxfor PXRD measurements. An Oxford cryostream instrument was used to control the sample temperature in the range of 100K – 500K.

***In situ* Synchrotron Powder X-ray Diffraction depending on CO_2 pressure**: The samples were activated at 120 °C under high vacuum over night before being loaded in 0.01mm wall thickness capillaries purchased from Hilgenberg. The sample containing capillary was fitted with an in-house designed flow cell connected to CO_2 gas line and vacuum by selective valves. CO_2 was introduced to each pressure point. Equilibrium was assumed by exposing the sample for 30 mins.

The single crystal XRD:

A suitable crystal of **1** was taken directly from the mixture and coated in protective oil. The crystal was held at 130 K for the data collection. The X-ray data on a crystal of solvated **1** were collected using an Oxford Xcalibur diffractometer fitted with a CuKα X-ray source. The crystal parameters of material **1** based on single XRD data are provided in Table S1.

Single crystal data of daughter sample **2** was also collected by the above procedures but the data quality is too poor for a single-crystal structural determination.

Table S1: Structure information of 1 and 2:

Sample name	Space group	a(Å)	b(Å)	c(Å)	α (deg)	β (deg)	γ (deg)
1	Orthorhombic *Pbcn*	25.052	18.160	14.511	90	90	90
2	Monoclinic $P2_1/c$	29.3482	11.7160	15.7311	90.000	90.126	90.000

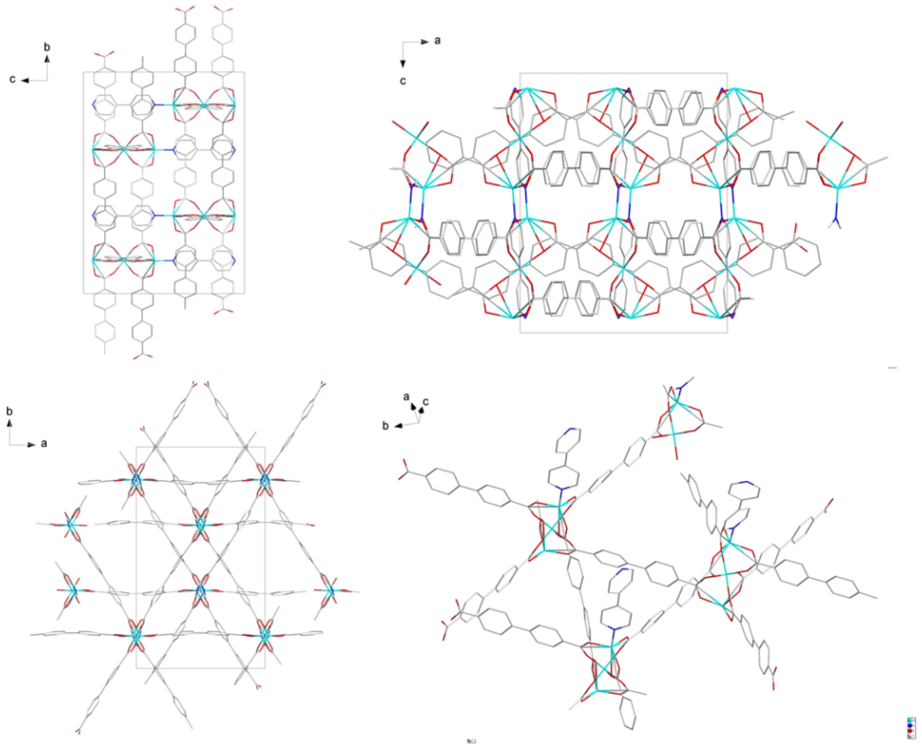


Fig. S1 Crystal structure of parent sample **1**. [1]

Structure determination of daughter material 2: The PXRD pattern can be indexed with a monoclinic unit cell using DICVOL06.[2] The structure solution was started using the charge-flipping algorithm implemented in the program TOPAS v4.2.[3] Two Zn atoms were easily located in the electron density maps. However, it was difficult to locate the BPDC and BPP molecules directly. The structure was subsequently solved in the space group of $P2_1/c$ (No. 14) by global optimization in direct space with 8 BPDC and 8 BPP molecules with combined PXRD and single crystal data (trimmed above 2.25 Å) using the program FOX[4]. During the structure determination, the BPDC and BPP molecules were constructed as rigid bodies with relaxed restraints. Rietveld refinement was performed using TOPAS v4.2, and the refined lattice parameters are a = 11.7126(1) Å, b = 15.7432(1) Å, c = 29.3424(1) Å, V = 5410.54(1) Å^3. The diffraction profile fit by Rietveld refinement using these parameters is shown in Fig. S1, with the agreement factors of R_{wp} = 8.2%, R_B = 6.5%, and *Go*F =1.84. The details of the structure determination and crystallographic data are presented in Table S2.

Table S2: Experimental and crystallographic data of $Zn_8(BPDC)_8(BPP)_8$.

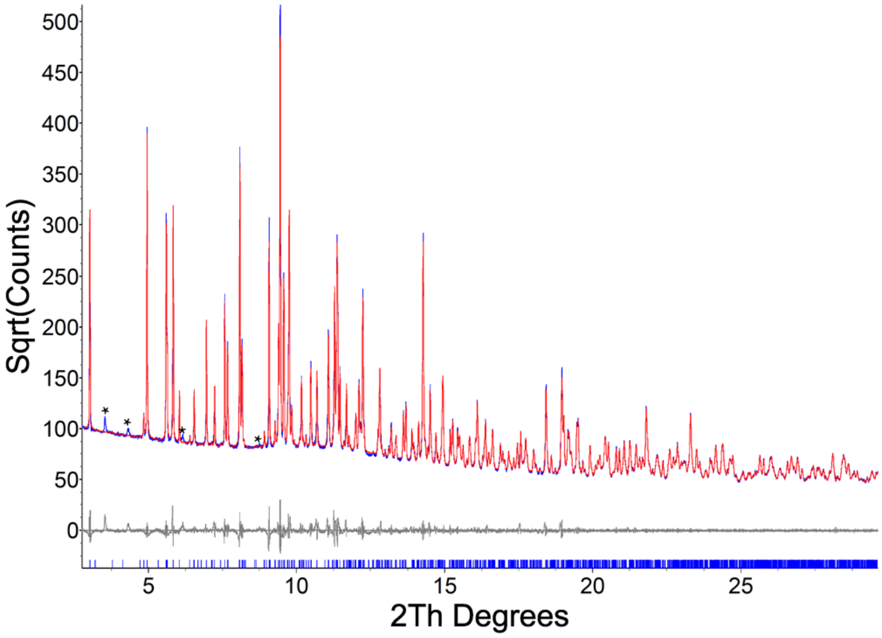
Phase data

Formula sum	Zn_8 C_{216} O_{32} N_{16}
Formula weight	3853.58 g/mol
Crystal system	monoclinic
Space-group	P 1 2_1/c 1 (14)
Cell parameters	a=11.7126(1) Å b=15.7432(1) Å c=29.3424(1) Å β=90.126(1)°
Cell ratio	a/b=0.7440 b/c=0.5365 c/a=2.5052
Cell volume	5410.54(1) Å^3
Z	4
Tempture	100K
Calc. density	1.18263 g/cm^3

Atomic parameters

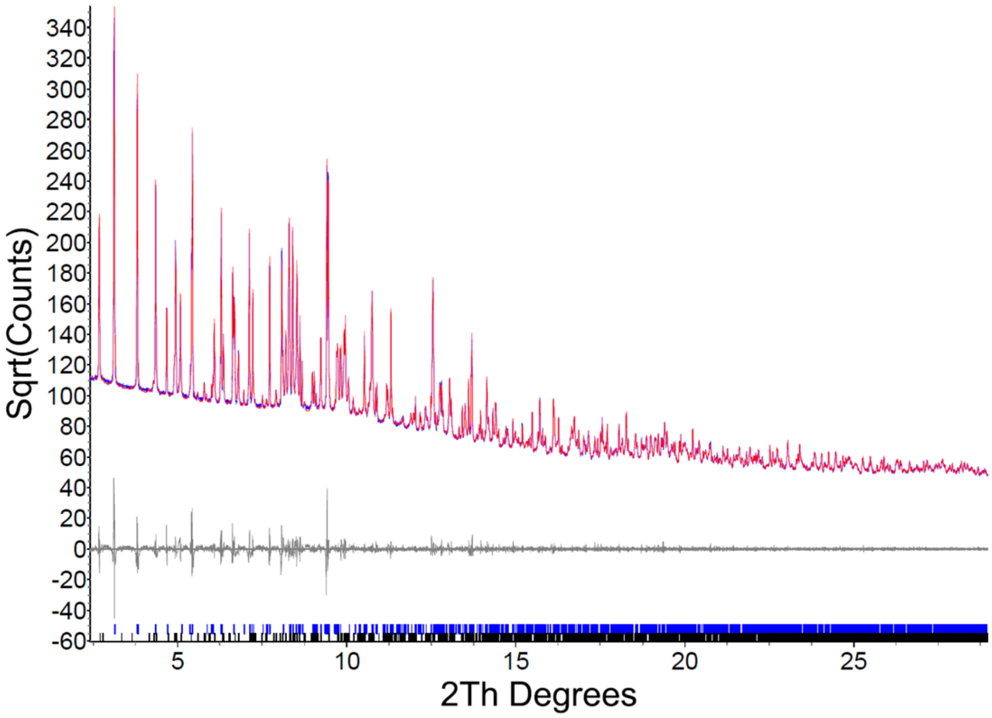
Atom	Wyck.	S.O.F.	x/a	y/b	z/c
Zn01	4e	1	0.47450	0.63260	0.40840
C1C	4e	1	0.27490	0.11480	0.41530
Zn02	4e	1	0.02540	0.13290	0.40850
C2C	4e	1	0.18160	-0.02670	0.42180
C5C	4e	1	0.39290	-0.01870	0.43180
C4C	4e	1	0.37320	0.07300	0.42250
C3C	4e	1	0.29820	-0.05860	0.42900
C9C	4e	1	0.75080	-0.07770	0.42130
C8C	4e	1	0.67490	-0.11920	0.42300
C7C	4e	1	0.58020	-0.09580	0.41920
C6C	4e	1	0.50620	-0.06660	0.44280
C10C	4e	1	0.77020	-0.03780	0.46320
C13C	4e	1	0.86820	0.01910	0.45690
C12C	4e	1	0.86340	0.00970	0.37280
C11C	4e	1	0.77650	-0.05940	0.37780
O1A	4e	1	-0.02030	0.32730	0.84750
C1A	4e	1	0.06020	0.30000	0.83020
C1B	4e	1	0.43310	0.80040	0.82970
O1B	4e	1	0.34920	0.77120	0.84830
N1D	4e	1	0.60040	0.53650	0.41350
C1D	4e	1	0.63250	0.51230	0.45520
N1C	4e	1	0.17350	0.06820	0.41510
O2A	4e	1	0.15160	0.27260	0.84760
C2A	4e	1	0.04670	0.28840	0.77740
O3A	4e	1	-0.00680	0.18200	0.46630
C2D	4e	1	0.65000	0.49740	0.38000
N2D	4e	1	0.32470	0.56690	0.41600
N2C	4e	1	0.90040	0.03460	0.41420
C3A	4e	1	-0.03800	0.30720	0.75320
O2B	4e	1	0.52180	0.82570	0.84680
C2B	4e	1	0.45350	0.78860	0.77710
O4A	4e	1	0.15900	0.24830	0.46530
C3D	4e	1	0.73460	0.42970	0.38250
C4A	4e	1	0.14450	0.26320	0.75660
O4B	4e	1	0.50540	0.68090	0.46520
C4B	4e	1	0.53470	0.81000	0.75190
C5A	4e	1	-0.05240	0.29980	0.70470
C4D	4e	1	0.72780	0.44230	0.46370
C6A	4e	1	0.13010	0.24800	0.70170
C5D	4e	1	0.76310	0.41850	0.42370
C5B	4e	1	0.36800	0.74980	0.70390
C7A	4e	1	0.03920	0.28250	0.68310
C6D	4e	1	0.86280	0.37370	0.42110
C6B	4e	1	0.55010	0.80160	0.70530
C8A	4e	1	0.05440	0.26930	0.63190
C7D	4e	1	0.96110	0.40650	0.39950
C7B	4e	1	0.46460	0.78130	0.68320
C9A	4e	1	-0.03490	0.22850	0.60480
C8D	4e	1	0.99340	0.43070	0.44800
C8B	4e	1	0.45250	0.76640	0.63150
C10A	4e	1	0.15090	0.29520	0.60580
C9D	4e	1	0.11400	0.48210	0.43000
C9B	4e	1	0.35170	0.79240	0.60410
C11A	4e	1	-0.03770	0.21940	0.55650
C10D	4e	1	0.12570	0.57220	0.41870
C10B	4e	1	0.53290	0.72780	0.60400
C12A	4e	1	0.16540	0.28650	0.55970
C11D	4e	1	0.22410	0.60850	0.41410

C11B	4e	1	0.33130	0.78400	0.55940
C14A	4e	1	0.06790	0.22790	0.48640
C13D	4e	1	0.21720	0.42730	0.42740
C14B	4e	1	0.43280	0.72680	0.48800
C13B	4e	1	0.42570	0.74840	0.53670
C13A	4e	1	0.07570	0.24600	0.53610
C12D	4e	1	0.31680	0.47430	0.42540
C12B	4e	1	0.53130	0.71980	0.55550
O3B	4e	1	0.34280	0.74630	0.46530
C3B	4e	1	0.35680	0.76540	0.75620



Plot S1: Experimental (blue), fitted (red), and difference (grey line below observed and calculated patterns) synchrotron PXRD profiles for the sample **2**. Small impurity peaks estimated <1 wt.% are marked as *.

Synchrotron powder X-ray diffraction analysis reveals that the 2D interpenetrated sheets of the solvated structure 2 are stacked in A-B-A-B-A. Zn-O bond length are approximately 1.969(4) Å, and longer interaction between Zn and O can be 2.757(3) Å. Zn-N bond length ranges from 2.049(3) Å to 2.137(1) Å. The 2D network can mainly be stabilized by van der Waals interactions, evidenced by the typical step isotherms of CO_2, CH_4 adsorption/desorption. It is well-known that van der Waals forces are responsible for the structural robustness of 2D MOFs among literature reports.[5-7]



Plot S2: Synchrotron PXRD profiles for the 6 days exchange sample. The black tick line is daughter structure **2** phase, the blue tick line is parent structure **1** phase. Experimental (blue), fitted (red), and difference (grey line below observed and calculated patterns)

4. Gas adsorption experiment

Adsorption properties were studied by volumetric apparatus ASAP 2010 and ASAP 2050 (Micromeritics, USA). High purity N_2 (99.999%), H_2 (99.999%), CO_2 (99.995%) and CH_4 (99.95%) were used. Around 200 mg of the as-synthesized samples were filtered and washed with DMF. The samples were dried at 60°C in a vacuum oven. Then, the sample was heated up to 120 °C (1 °C /min) under high vacuum (below10^{-2} Pa) and holding at 120 °C for 12 h to obtain desolvated samples.

5. Experimental results

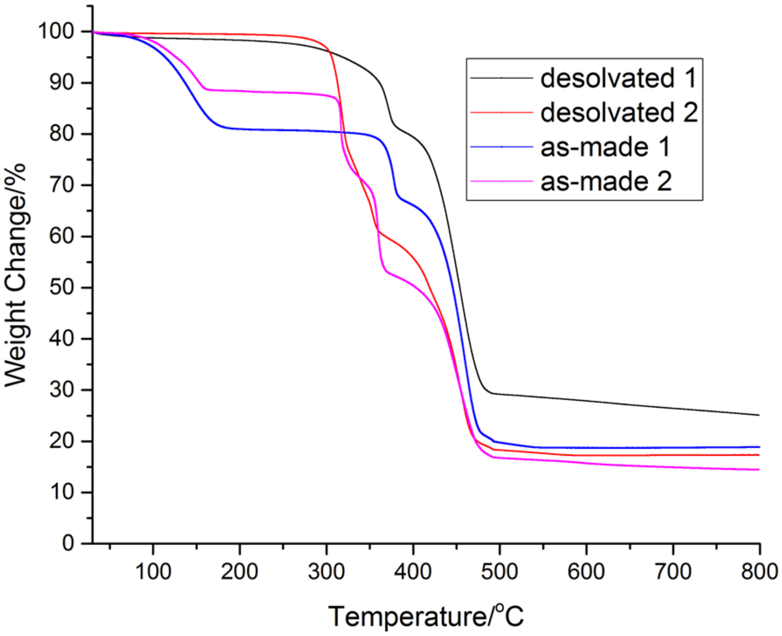


Fig. S2 TGA patterns of sample **1** and **2**

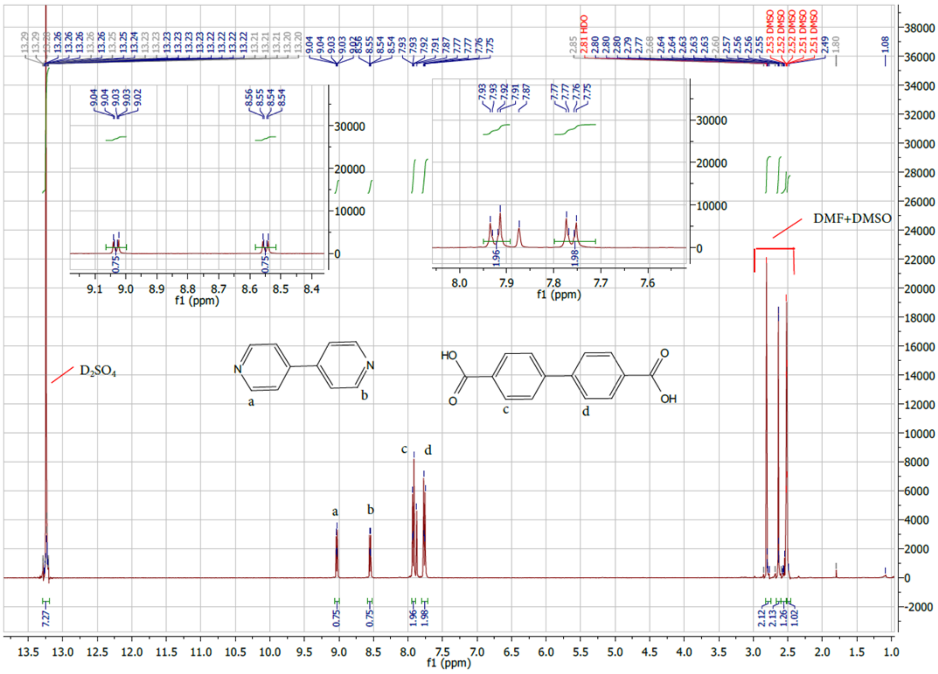


Fig. S3 ^{1}H NMR spectron of parent sample **1**

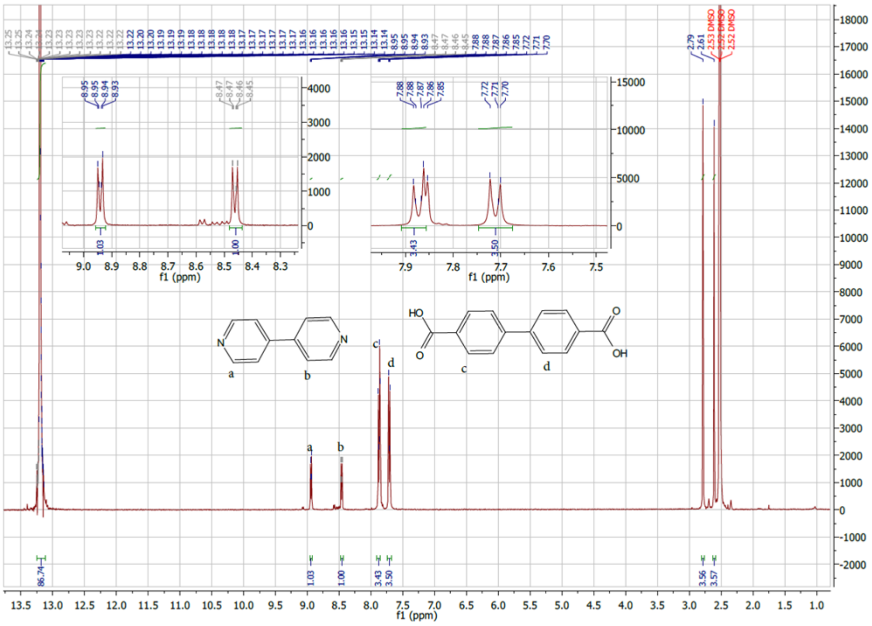


Fig. S4 ^{1}H NMR spectron of sample with 3 days exchange

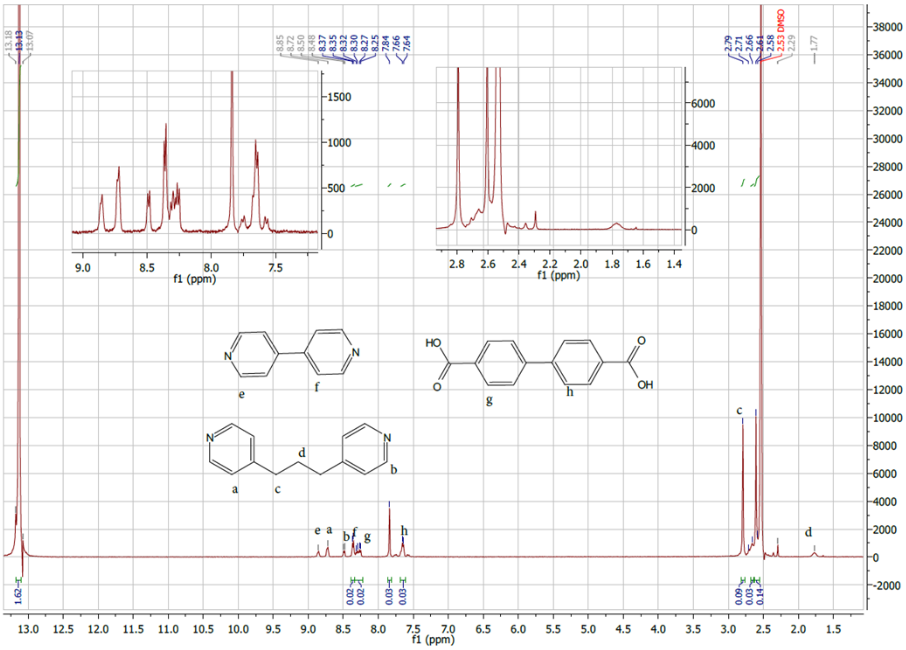


Fig. S5 ^{1}H NMR spectron of sample with 6 days exchange

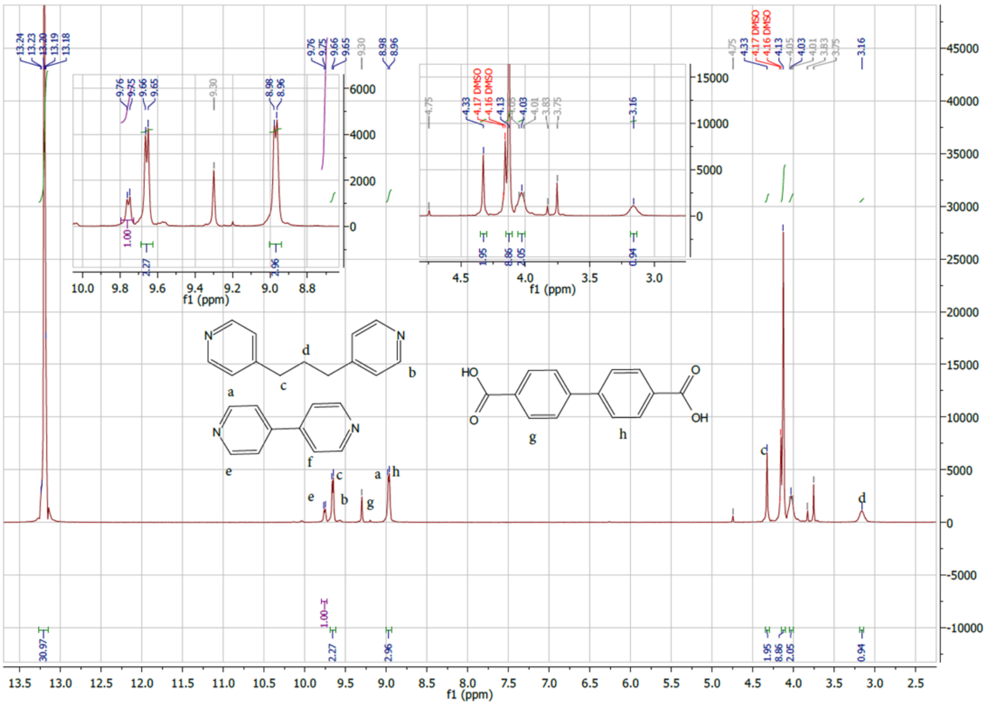


Fig. S6 ^{1}H NMR spectron of sample with 9 days exchange

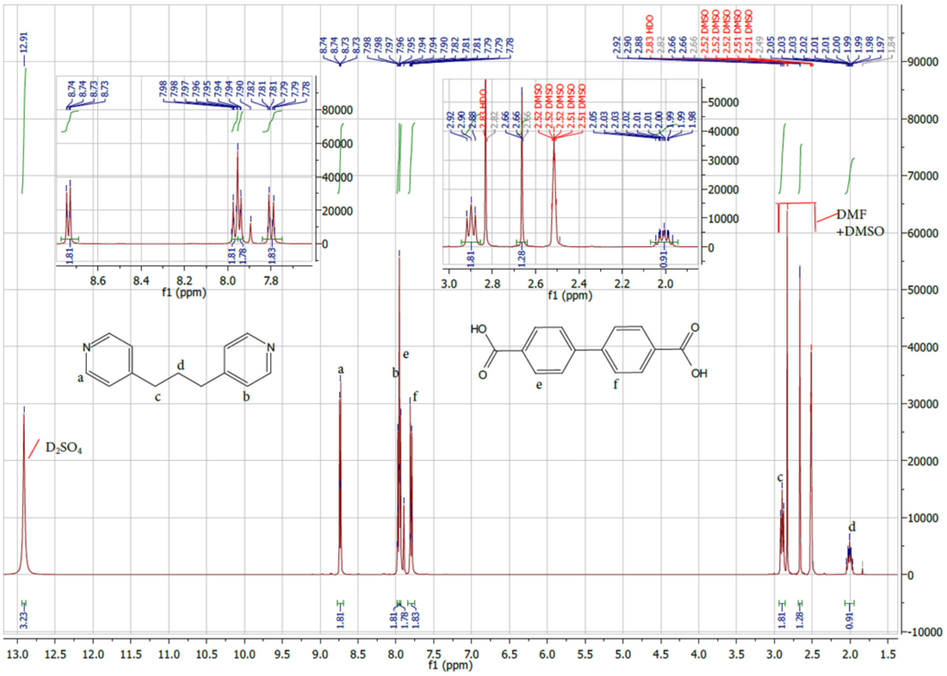


Fig. S7 ^{1}H NMR spectron of daughter sample **2**

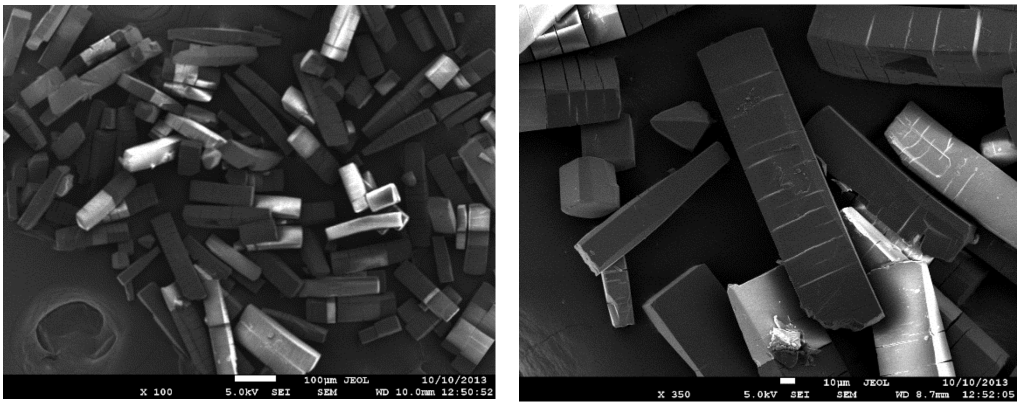


Fig. S8 SEM images of sample **1**

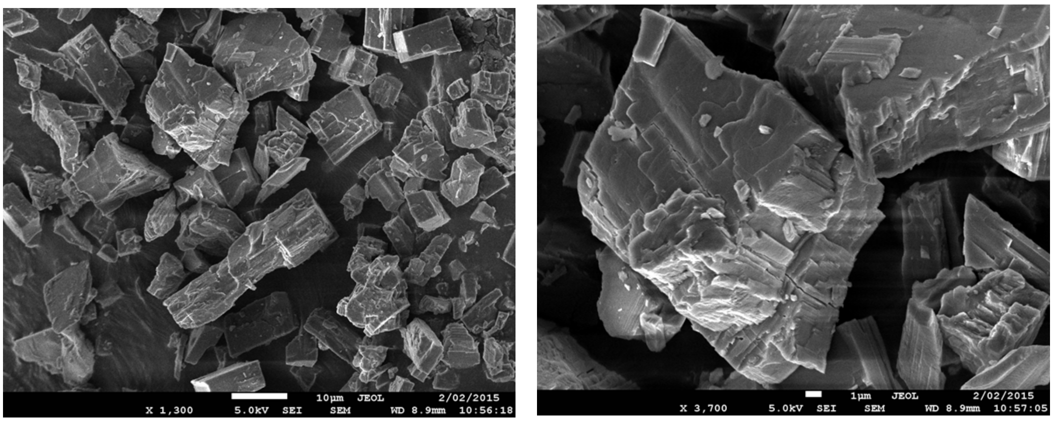


Fig. S9 SEM images of sample **2**

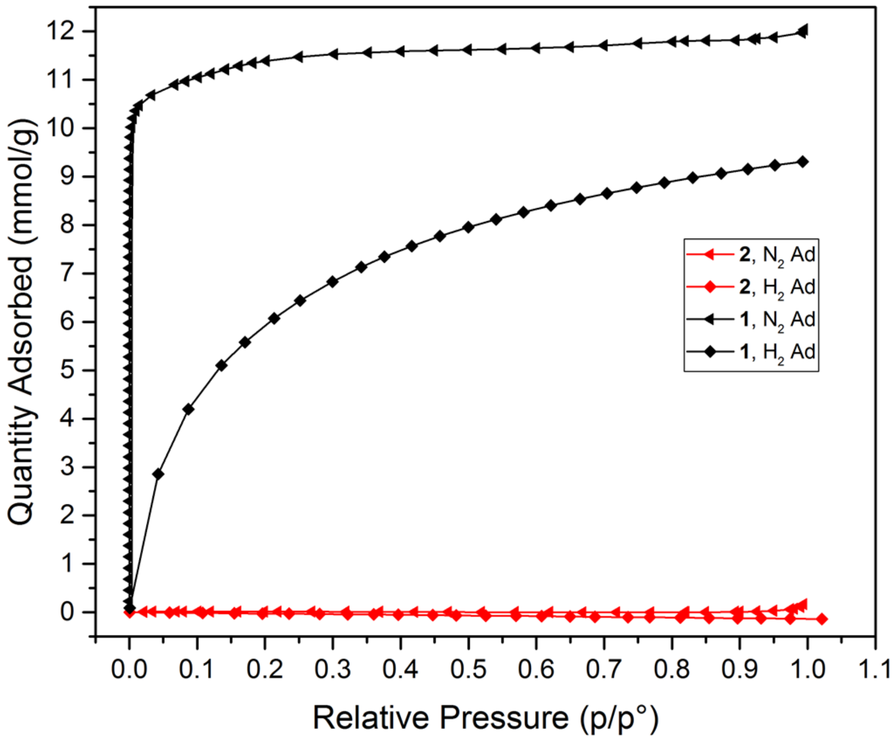


Fig. S10 N_2 and H_2 adsorption isotherms at 77 K of **1** (in black) and **2** (in red).

References

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