ELECTRONIC SUPPLEMENTARY INFORMATION FOR

A Single-Crystalline Microporous Coordination Polymer with Mixed Parallel and Diagonal Interpenetrating α-Po Networks

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Section 1: Methods

Single-crystal X-ray diffraction data were collected on a BRUKER SMART-APEX CCD diffractometer using Mo Kα radiation (λ= 0.71073 Å). The structure was solved by direct methods and refined by full-matrix least-squares refinement with anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms were generated geometrically and included in the refinement with fixed position and thermal parameters. Powder X-ray diffraction (XRPD) data were recorded on a Bruker AXS D8 diffractometer operated at 1600W power (40 kV, 40 mA) for Cu Kα (λ=1.5418Å) with a scan speed of 2 sec/step and a step size 0.01^o in 2θ at room temperature. The XRPD is in reflection mode. The samples were manually ground into fine powder and were spread into uniform thin film on a quartz slide.

NMR experiments were recorded on either a Bruker DRX-300 with a z-gradient BBI probe or a Bruker DPX-400 with a z-gradient BBO probe operating at 300.13 MHz and 400.13 MHz for ^1H observation, respectively.

Thermogravimetric analysis was performed under nitrogen on TA instruments TGA Q500 Hi-Res.

N_2 adsorption isotherms were obtained with a Quantachrome Autosorb instrument between 0 and 1 partial pressure of nitrogen. Samples were outgassed at 70℃ under vacuum to remove any adsorbed solvent or moisture.

Section 2: Materials and Synthesis

Fresh solvents were taken directly from the Solvent Dispensing System. All the commercially available chemicals were used as received without further purification.

Synthesis of H_2L1

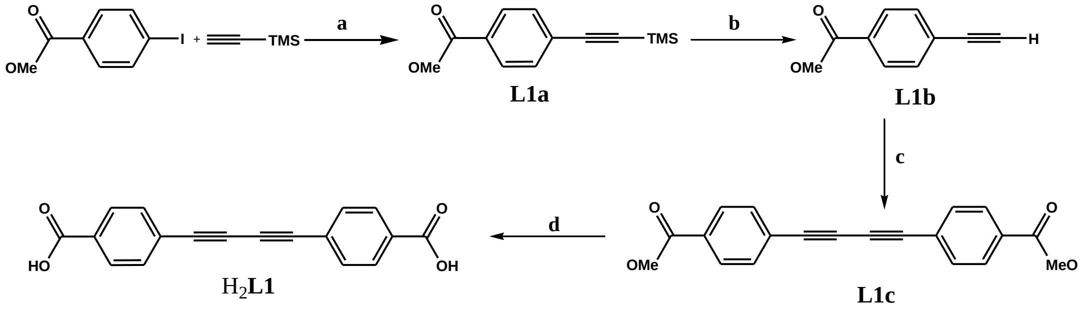

Figure S1. Synthesis of organic ligand H_2**L1**. a. $PdCl_2(PPh_3)_2$, CuI, THF, reflux, under Argon, 24 hours; b. Tetrabutylammonium fluoride hydrate (TBAF), THF, room temperature, 1hour; c. $PdCl_2(PPh_3)_2$, CuI, I_2, THF, room temperature, 24hours; d. (1) $LiOH \cdot H_2O$, THF, room temperature, 3days, (2) 3M HCl.

Methyl-4-ethynyl trimethylsilane benzoate (L1a): Methyl-4-iodobenzoate (5mmol, 1.31g), $PdCl_2(PPh_3)_2$ (0.15mmol, 105mg), CuI (0.3mmol, 57mg) were added into a flamed two-neck round flask under Argon. The flask was attached to a Schlenk line, then evacuated and flushed with Argon three times. Fresh Et_3N (9ml), THF (30ml) and degassed ethyny trimethylsilane (6mmol, 831μL) were added to the flask. The reaction mixture was evacuated and flushed with Argon twice. The reaction mixture was then refluxed for 24 hours. The solvent was removed *in vacuo***,** the residue was dissolved in CH_2Cl_2 and purified by passing through a silica gel column to get **1a**. The yield of **1a** is ca. 96%. ^1H NMR ($CDCl_3$, 400MHz): δ 7.94 (d, *J*=8Hz), 7.48 (d, *J*=8Hz), 3.89, 0.23 ppm.

Methyl-4-ethyny benzoate (L1b): To a solution of L1a (4.5mmol,1.0g) in 90 ml THF was added Tetrabutylammonium fluoride hydrate (TBAF) solution (7.5mmol TBAF in 30ml THF) dropwise with stirring. The reaction mixture was kept stirring at room temperature for about 1 hour after TBAF addition. The solvent was removed *in* *vacuo* and the residue was dissolved in CH_2Cl_2 and purified by passing through a silica gel column to get **L1b**. The yield of **L1b** is ca. 90%. ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.76 (d, *J*=8Hz), 7.51 (d, *J*=8Hz), 3.89, 3.2 ppm.

1, 4-Bis(4-carbomethoxyphenyl)butadiyne (L1c): To a solution of L1b (4mmol, 0.64g) in 40 ml diisopropylamine under Argon were added $PdCl_2(PPh_3)_2$ (0.1mmol, 70mg), CuI (0.25mmol, 95mg) and I_2(3mmol, 0.76g) while stirring. The reaction mixture was stirred at room temperature for 24 hours.The solvent was removed *in vacuo* and the residue was dissolved in CH_2Cl_2 and purified by passage through a silica gel column to get **L1c**. Yield of **L1c** is 85%. ^{1}H NMR($CDCl_3$, 300MHz): δ 8 (d, *J*=9), 7.57 (d, *J*=8), 3.91.

1,4-(4-carboxylic-phenyl) butydiyne (H_2**L1):** To the solution of $LiOH{\cdot}H_2O$ (16mmol, 0.67g) in a small amount of water was added **L1c** (1.57 mmol, 0.5g) in 30ml THF while stirring. The reaction mixture was stirring for 3 days. 3M HCl was added to adjust the PH of the reaction mixture to 2 ~ 3 and a white precipitate formed in the solution. H_2**L1** was obtained by filtration after washing with cool water and hexanes. The yield of **L1**-H_2 is ca. 89%. ^{1}H NMR (DMSO-d6, 400MHz): δ 13.28, 7.98 (d, *J*=8Hz), 7.75 (d, *J*=8Hz).

Synthesis of 1

$\{[Zn_4O(L1)_3]$ $[Zn_4O(L1)_3(DMF)_2]$ $(DMF)_2$ $(H_2O)_{16}\}$ (1): 4,4'-(1,3-butadiyne-1,4-diyl)bis-benzoic acid (0.1mmol, 29mg) and $Zn(NO_3)_2{\cdot}6H_2O$ (0.2mmol, 60mg) in 10ml fresh DMF were added into a 23ml Teflon linear bomb. The reaction mixture was slowly heated up to 100°C and held at this temperature for 48 hours. Upon cooling down to room temperature, pale yellow crystal formed, which were collected by filtration, and washed with fresh DMF and MeOH. The yield was *ca.* 85%.

Section 3: Results

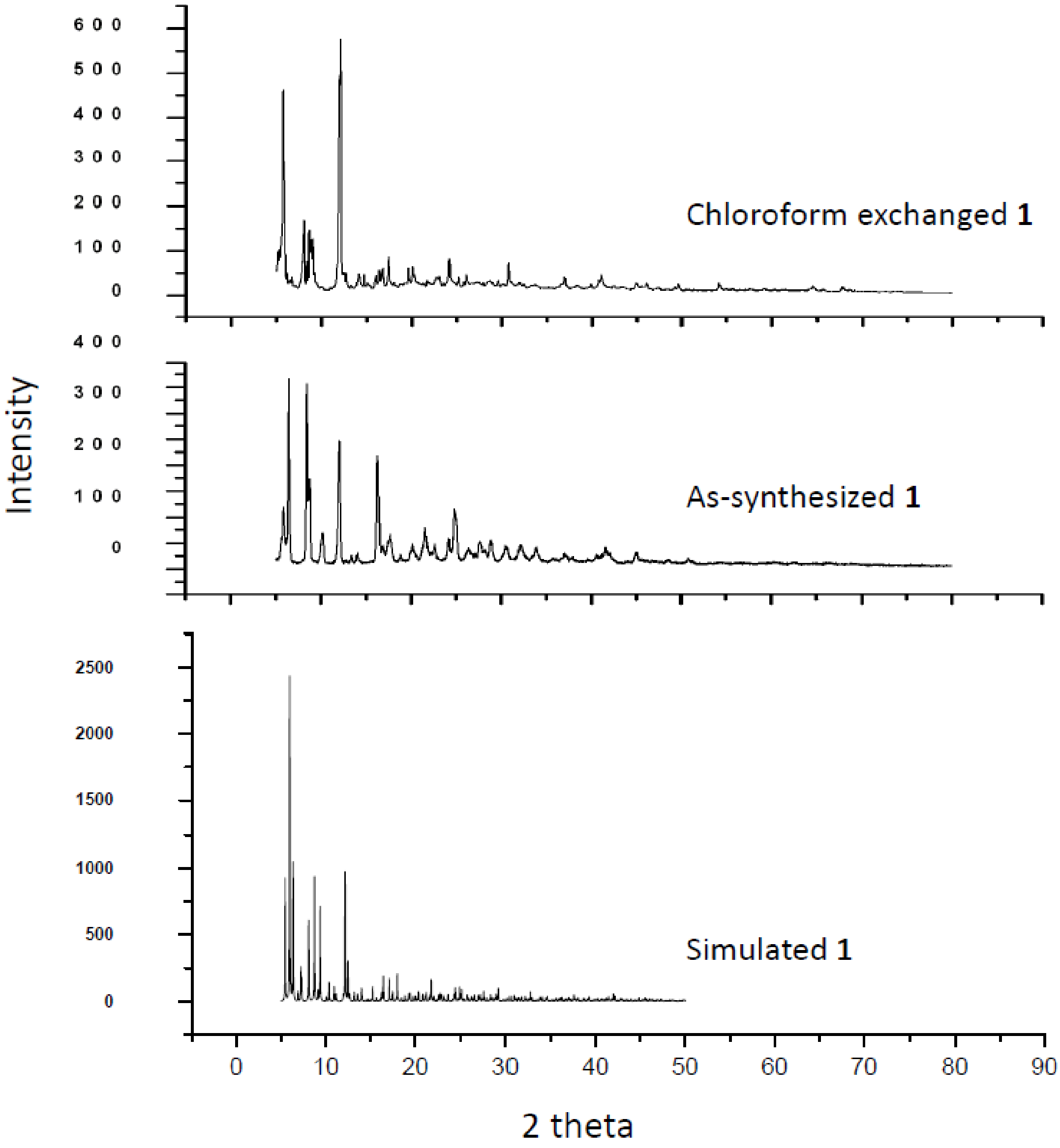

Figure S2. Experimental and simulated XRPD pattern of as-synthesized **1** and chloroform exchanged **1** [note: Peak positions on the experimental XRPD pattern match those on the simulated XRPD pattern. Peak intensity variations between simulated and experimental XRPD patterns of **1** may be attributed to temperature difference for the powder and single crystal data collections, and to the solvent molecules not located by the single crystal method. The guest exchange experiment caused notable differences in XRPD patterns, possible due to the dynamic nature of the structure, e.g., the entanglement of individual nets is somewhat rearranged due to gas exchange. However, the crystallinity of the coordination polymer **1** was retained**].**

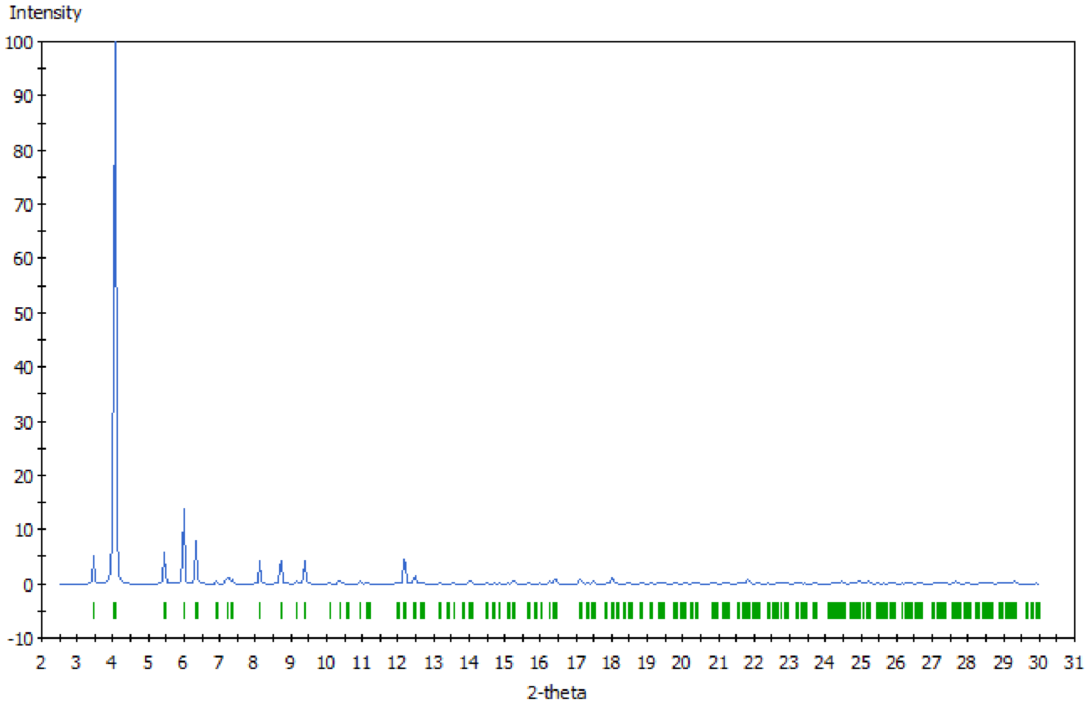

Figure S3. Simulated XRPD pattern of **1** with 2theta range from 2.5 to 30 (note: It should be highlighted that the simulated XRPD pattern of **1** has the strongest peak with 2theta around 4.0. For safety reasons, we could not scan the sample below 5.0 in a XRPD experiment.).

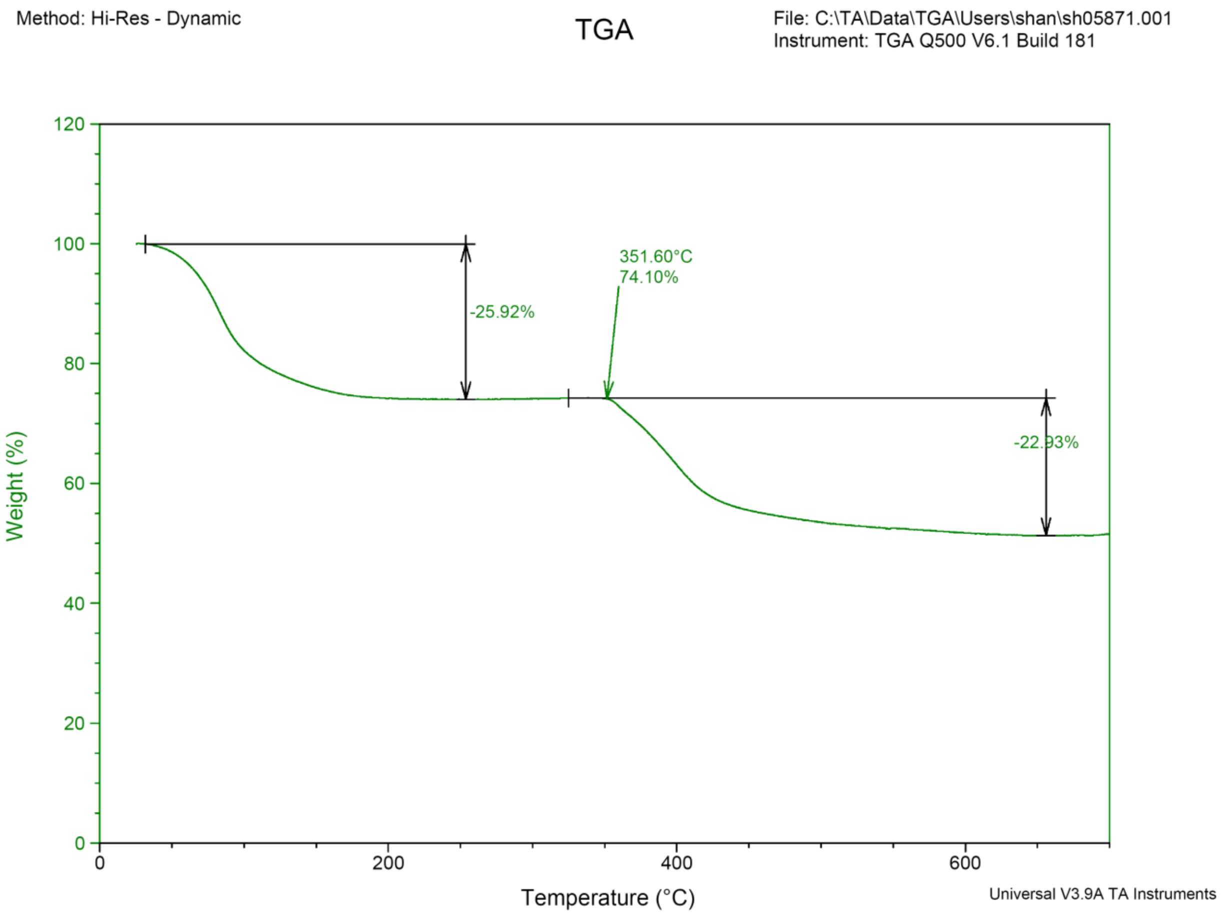

Figure S4. The TGA diagram of as synthesized **1**

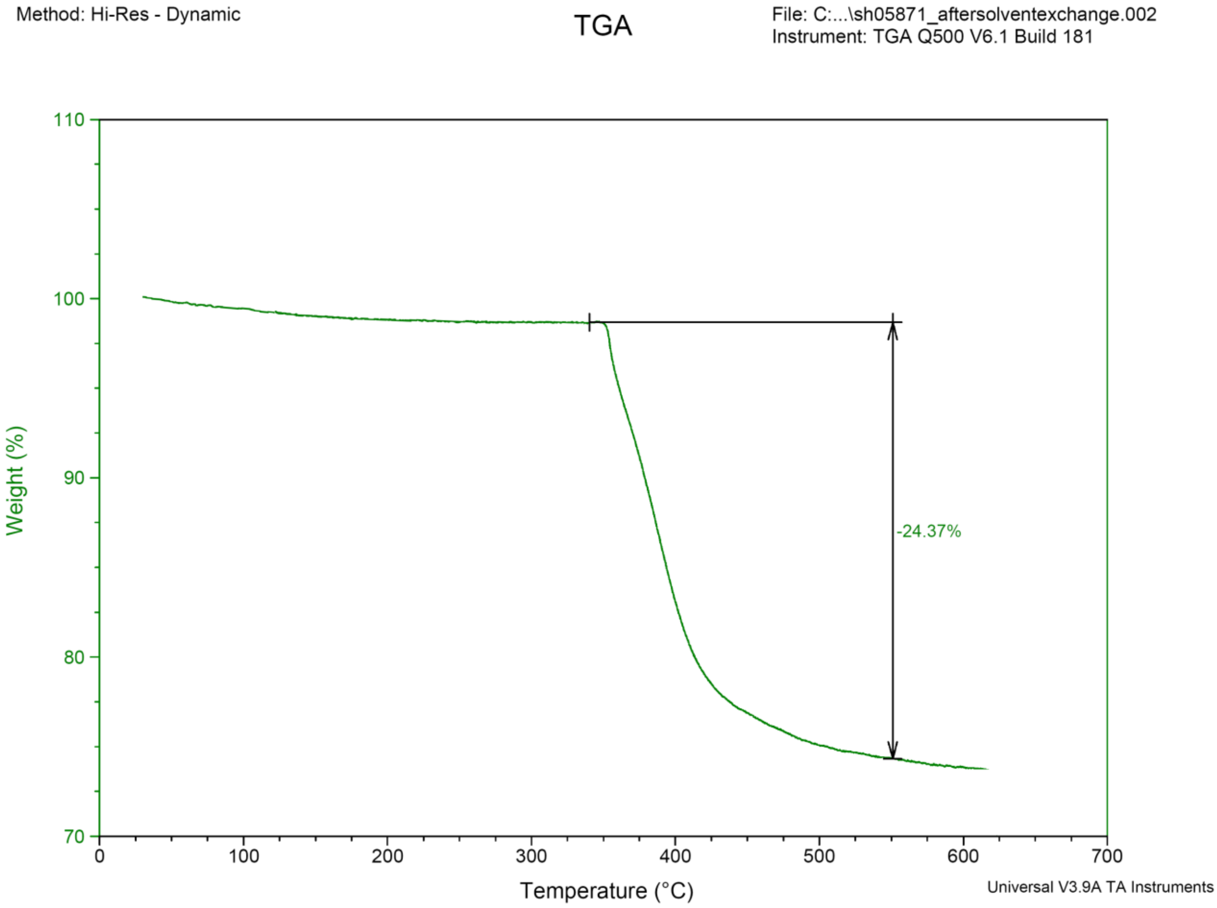

Figure S5. The TGA diagram of **1** after solvent was extracted