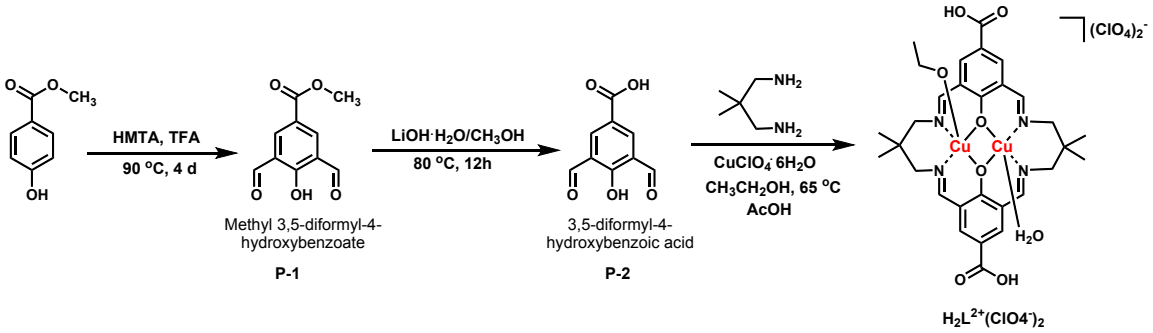
−Supporting Information for the manuscript entitled−

"A rare 4-fold interpenetrated metal-organic framework constructed from an anionic indium-based node and a cationic dicopper linker"

Sreenath Pappuru,[a] Karam B. Idrees, [b] Zhijie Chen, [b] Dina Shpasser [a] and Oz M. Gazit *[a]

ozg@technion.ac.il
Wolfson Department of Chemical Engineering
Technion-Israel Institute of Technology,
Haifa-3200003, Israel

Synthesis of $\mathbf{H_2L^{2+}(ClO_4^-)_2}$:



Scheme S1 Synthetic route for $\mathbf{H_2L^{2+}(ClO_4^-)_2}$

Compounds P-1 and P-2 were synthesized with slight modification to a previously reported procedure.[1,2]

Methyl 3,5-diformyl-4-hydroxybenzoate

A mixture of methyl 4-hydroxybenzoate (12 g, 79 mmol) and hexamethylenetetramine (45.6 g, 325 mmol) was dissolved in anhydrous TFA (90 ml). The obtained yellow solution was heated under reflux for 4 d, to obtain a viscous dark-orange solution. 530 ml H_2O were added and the mixture was heated up to give a homogeneous solution. Upon cooling, the product precipitated slowly from the solution (yield: 12.15g, 74 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.05 (s, 1H), 10.27 (s, 2H), 8.65 (s, 2H), 3.96 (s, 3H).

3,5-diformyl-4-hydroxybenzoic acid:

A mixture of methyl 3,5-diformyl-4-hydroxybenzoate (5 g, 24 mmol) and $LiOH.H_2O$ (8.43 g, 201 mmol) was added to a flask containing 500 mL H_2O and 125 ml methanol. The solution was refluxed at 80 °C overnight to yield a yellow solution. Subsequently, the methanol was evaporated by rotary evaporation and a 6N HCl solution was added until the pH=2. The obtained light-yellow precipitate, was filtered out and dried under vacuum (yield: 4.42 g, 95 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.31 (bs, 1H), 12.12 (bs, 1H), 10.28 (s, 2H), 8.54 (s, 2H).

Synthesis of $\mathbf{H_2L^{2+}(ClO_4^-)_2}$:

The dicopper Robson-type ligand $\mathbf{H_2L^{2+}(ClO_4^-)_2}$ was synthesized with slight modification to a previously reported procedure.[2] In a 20 ml vial, 3,5-diformyl-4-hydroxybenzoic acid (40 mg, 0.2 mmol) was dissolved in 6 ml hot ethanol. 100 mg $Cu(ClO_4^-)_2{\cdot}6H_2O$ (0.27 mmol), 23μL CH_3COOH (0.4 mmol) and 21 mg 2,2-dimethyl-1,3-propanediamine (0.2 mmol) in 4 ml ethanol were added to the aldehyde solution. After addition, the vial was sealed and heated to 65 °C for 3 days. Prism like dark green crystals were collected and dried. (Yield: 0.147 g, 81 %). ATR IR (cm^{-1}): ν(amine C–H), 2967-2865; ν(COOH), 1679; ν(C=N), 1638; ν(ClO_4^-), 1072 and 621. MS (ESI): m/z 745 [$H_2L^{2+}ClO_4^-$].

Synthesis of TIF-1:

27 mg ligand, 2 mg $In(NO_3)_3{\cdot}xH_2O$, DMF(3 ml), CH_3CN(2 ml) and HNO_3 (0.2 ml, 2.7M in DMF) were added to a 20 ml vial and the vial was sealed and placed in an 80 °C oven for 5 d, green prism like crystals of **TIF-1** were collected and air dried, 72 % Yield. ATR IR (cm^{-1}): ν (H_2O),

3385; ν (amine C–H), 2961-2871; ν (C=N), 1642; ν (COO), 1578, 1316; ν (NO_3^-), 1402. In addition, we note that during MOF synthesis optimization, we have also tried different temperatures (80, 90, 100 and 110 ^oC), several metal ions (ligand: $In(NO_3)_3$ = 1:1, 1:2, 1:2.5, 1:3, 1:4, 1.5:1, 2:1, 3:1, 4:1 and 5:1) and modulator concentrations (0.5M, 1M, 1.5M, 2M and 2.7M HNO_3, Acetic acid in DMF) to synthesize heterometallic MOF's. Only the above mentioned optimal temperature (80 ^oC) and ideal ratio of starting materials (ligand: $In(NO_3)_3$ =5.6:1) yielded **TIF-1** product. The other ratio of starting materials and temperature yielded amorphous products, which was confirmed from PXRD analysis.

X-ray crystallographic measurements:

The single-crystal material was immersed in Paratone–N oil and mounted on a APEX II Bruker diffractometer at 200K. Data collection was performed using monochromated Mo Kα radiation, λ = 0.71073 Å, using ϕ and ω scans to cover the Ewald sphere. Accurate cell parameters were obtained with the amount of indicated reflections. the structure was solved with the Olex2[3] software using the olex2.solve[4] structure solution program, applying charge flipping, and refined with the ShelXL[5] refinement package using Least Squares minimization. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Mercury 3.10.1 software was used for molecular graphics.[6]
The X-ray crystallographic coordinates for structures $\mathbf{H_2L^{2+}(ClO_4^-)_2}$ and **TIF-1** reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number CCDC 2039820-2039821.

Supercritical drying procedure[7]:

TIF-1 was evacuated with supercritical CO_2 in a Tousimis™ Samdri® PVT-30 critical point dryer. prior to drying, the DMF dispersed MOF sample was soaked in absolute ethanol (EtOH), replacing the soaking solution every 24 h for 72 h, to exchange the occluded solvent to EtOH. After the 72 h the exchange process was completed, the ethanol-containing samples were placed inside the dryer and the ethanol was exchanged with $CO_{2(L)}$ over a period of 6 h. During this time the liquid CO_2 was vented under positive pressure for 5 minutes each hour. The rate of venting of $CO_{2(L)}$ was always kept below the rate of filling so as to maintain a full drying chamber. After 6 hr of venting and soaking with $CO_{2(L)}$ the chamber was sealed and the temperature was raised to 40ºC. This brought the chamber pressure to around 1300 psi above the critical point of CO_2. The chamber was held above the critical point for 1 h at which point the chamber was slowly vented over the course of 15-18 h. The dried samples were placed in sealed containers and stored in a desiccator or immediately tested in CO_2 physisorption.

Procedure for MOF treatment in solvents:

MOF sample was soaked in various organic solvents (DMF, acetone, ethanol, methanol and dichloromethane) for 12 h to evaluate the chemical stability. For PXRD measurements the solvent was decanted and the MOF sample was dried at 80 ^oC under vacuum. As shown by

PXRD results (Fig. S5), the MOF maintained the PXRD patterns and excellent crystallinity in all these solvents.

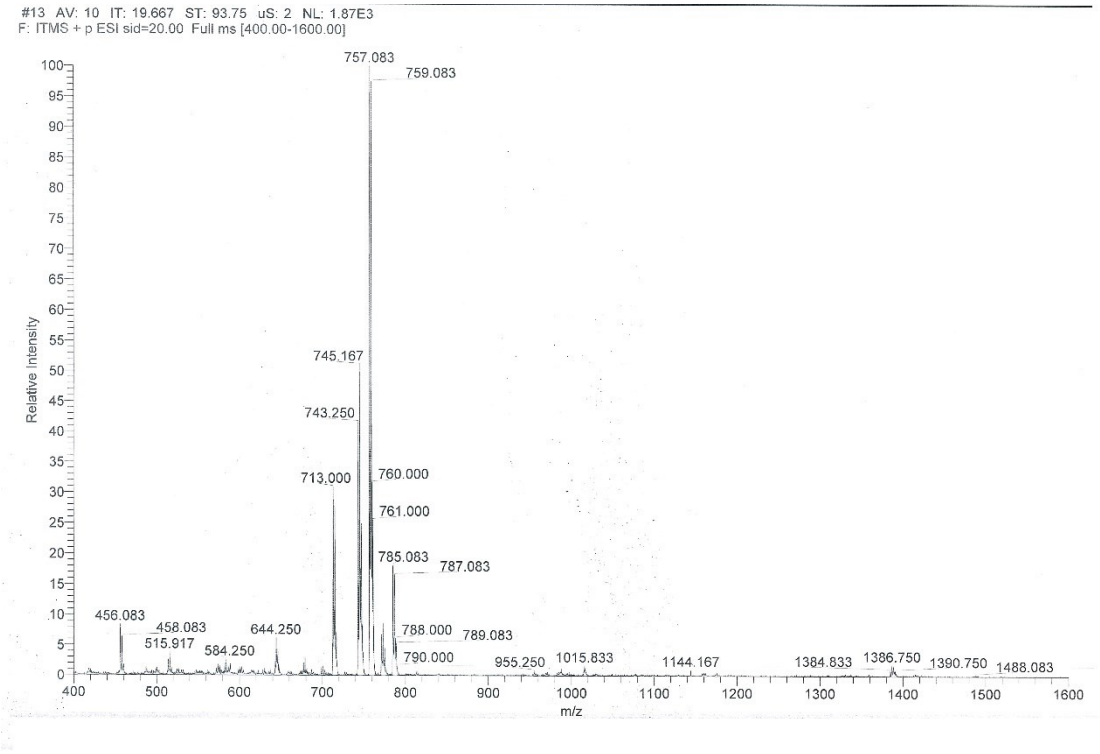


Figure S1. ESI-Mass Spectrum of linker $\mathbf{H_2L^{2+}(ClO_4^-)_2}$.

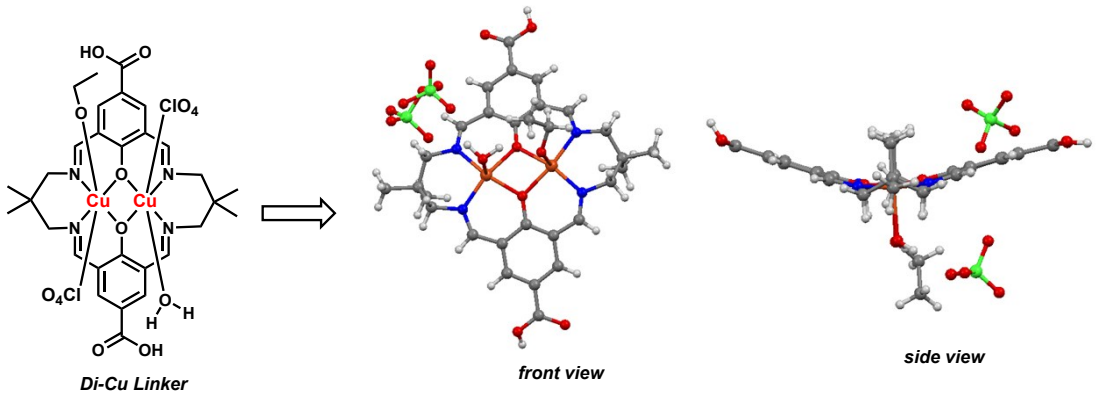
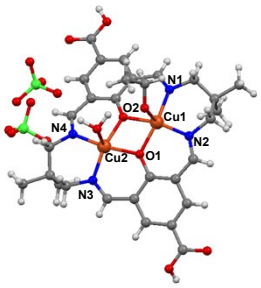
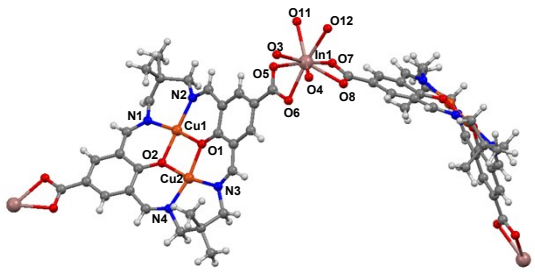


Figure S2. X-ray structure of dicopper Robson-type ligand $\mathbf{H_2L^{2+}(ClO_4^-)_2}$ and representing the bent side view of the linker.

Table S1. The coordination environment of $H_2L^{2+}(ClO_4^-)_2$, **TIF-1** and selected labels for bond lengths (Å) and angles (°) list.



$H_2L^{2+}(ClO_4^-)_2$



In-MOF

Complexes	$H_2L^{2+}(ClO_4^-)_2$	TIF-1
Bond lengths (Å)		
Cu1-O1	1.968(8)	1.964(9)
Cu1-O2	1.987(8)	1.981(9)
Cu1-O7	2.312(8)	-
Cu2-O1	1.985(7)	1.981(9)
Cu2-O2	1.976(8)	1.959(8)
Cu2-O8	2.227(9)	-
Cu1-N1	1.964(10)	1.946(11)
Cu1-N2	1.946(9)	1.926(13)
Cu2-N3	1.961(10)	1.963(11)
Cu2-N4	1.962(10)	1.982(12)
In1-O5	-	2.246(9)
In1-O6	-	2.280(8)
In1-O7	-	2.276(9)
In1-O8	-	2.294(8)
In1-O4	-	2.263(8)
In1-O3	-	2.260(9)
In1-O11	-	2.339(8)
In1-O12	-	2.261(9)
Bond angles (°)		
O1-Cu1-N2	92.00(3)	93.8(4)
N1-Cu1-N2	97.40(4)	94.6(5)
O2-Cu1-N1	93.20(3)	93.6(4)
O1-Cu2-N3	92.80(3)	92.0(4)
N3-Cu2-N4	97.80(4)	96.3(5)
O2-Cu2-N4	91.90(4)	94.1(4)
O2-Cu1-O1	76.3(3)	76.90(3)
O2-Cu2-O1	76.2(3)	77.00(4)
O5-In1-O6	-	57.7(3)
O7-In1-O8	-	58.1(3)
O5-C28-O6	-	119.5(12)
O7-C29-O8	-	121.5(13)

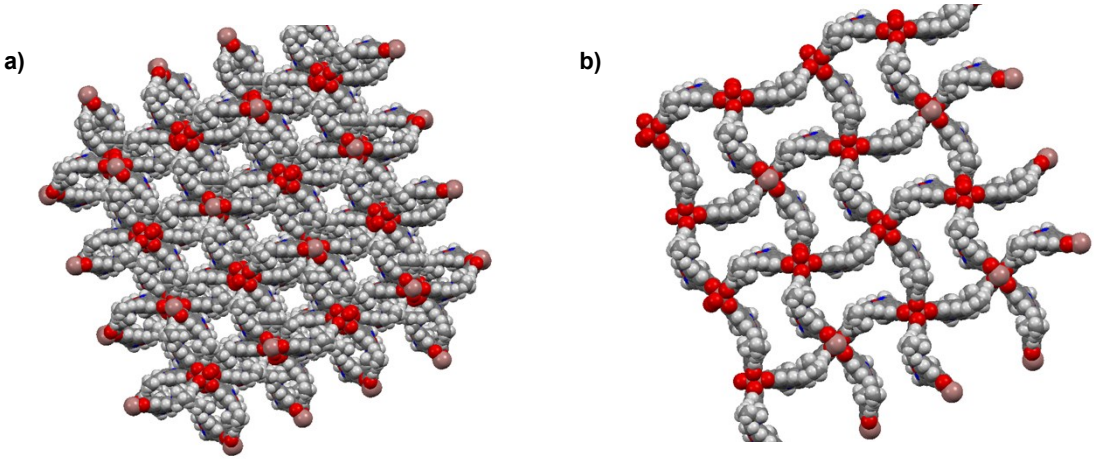


Figure S3. Space-filling diagram of a) 4-fold interpenetrated 3D network and b) single 3D network of **TIF-1**.

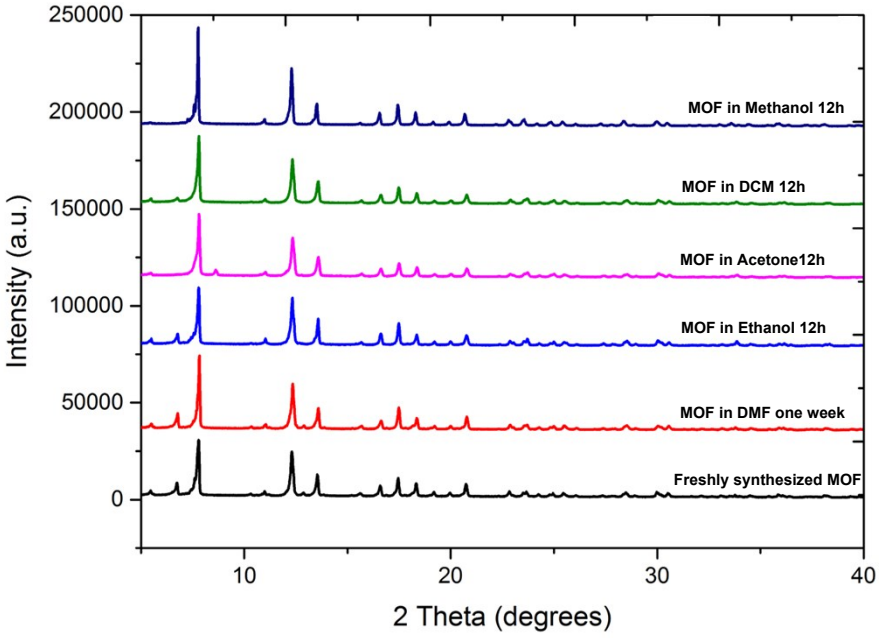


Figure S4. The stability of **TIF-1** in different organic solvents.

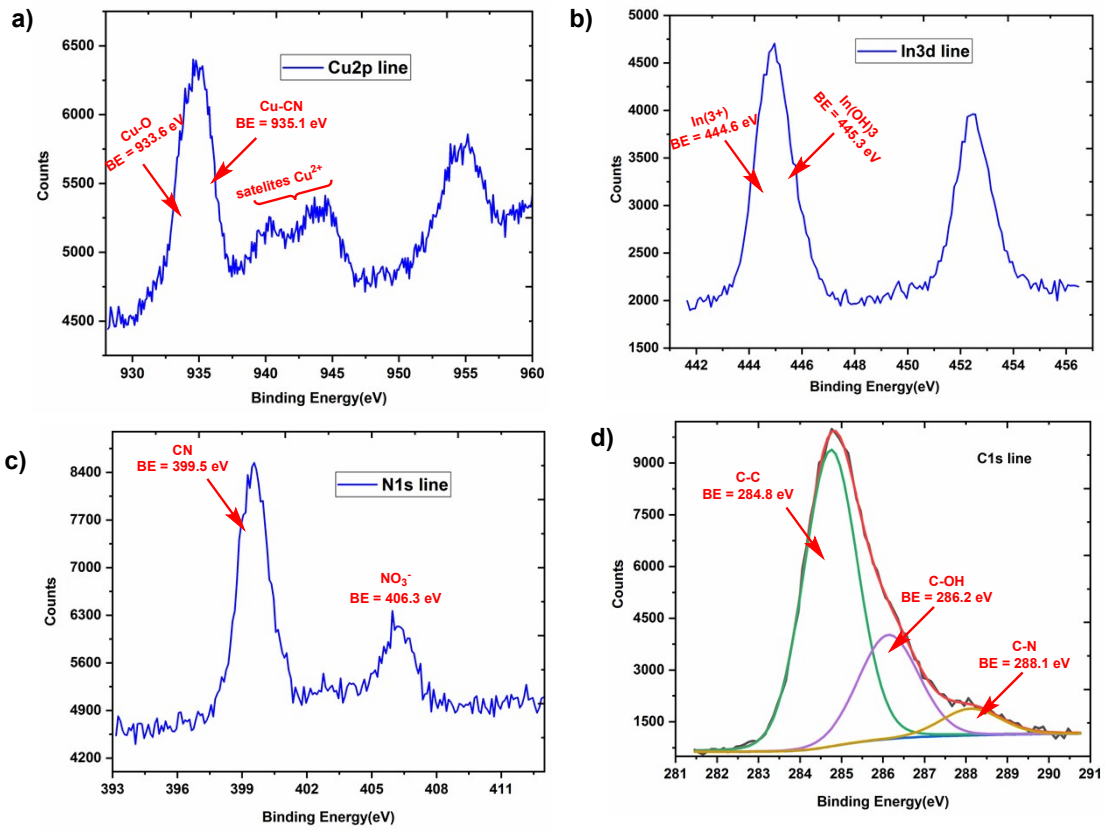


Figure S5. High resolution XPS of (a) Cu2p, (b) In3d, (c) N1s and (d) C1s lines for **TIF-1** MOF.

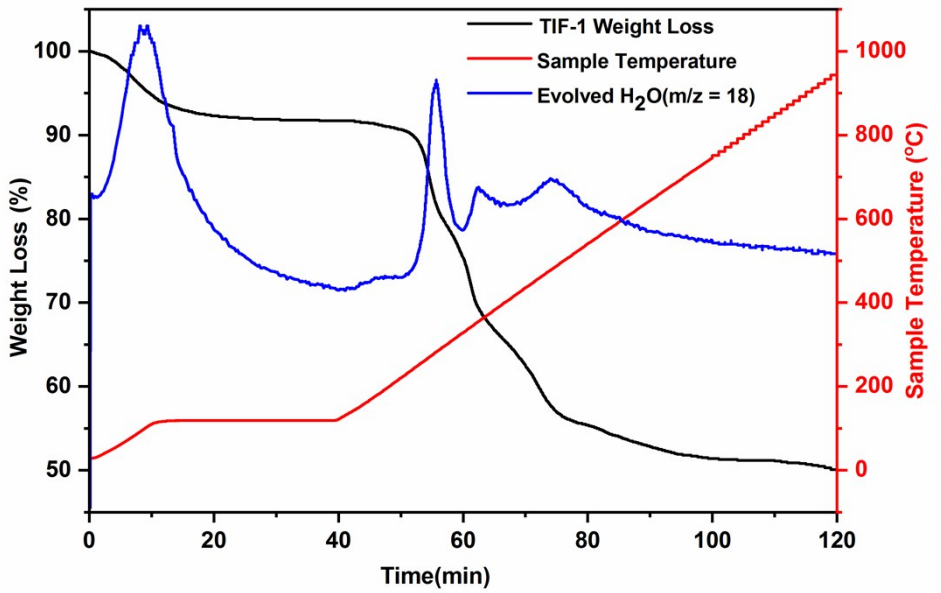


Figure S6. TGA-MS analysis of **TIF-1**.

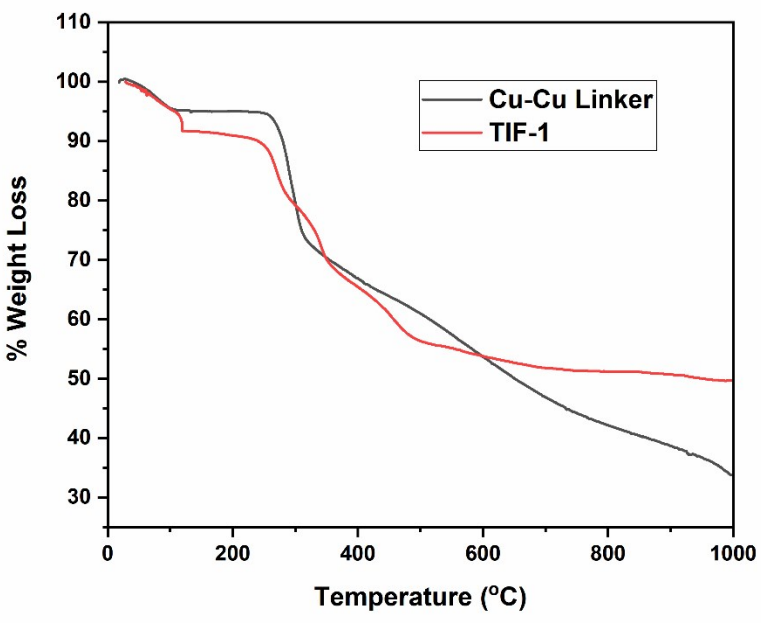


Figure S7. TG curve of linker $H_2L^{2+}(ClO_4^-)_2$ and **TIF-1**.

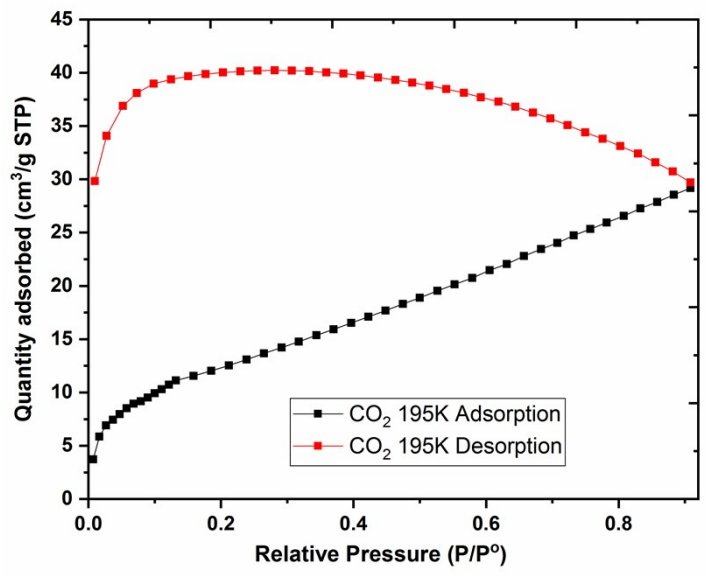


Figure S8. CO_2 adsorption isotherm at 195 K of **TIF-1** after $scCO_2$ activation.

References:

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