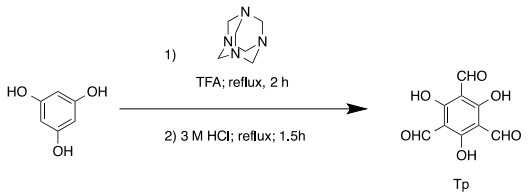
Electronic Supplementary Information (ESI)

Microwave-assisted solvothermal synthesis of crystalline two-dimensional covalent organic frameworks with high CO_2 capacity

Section 1. Materials and Methods

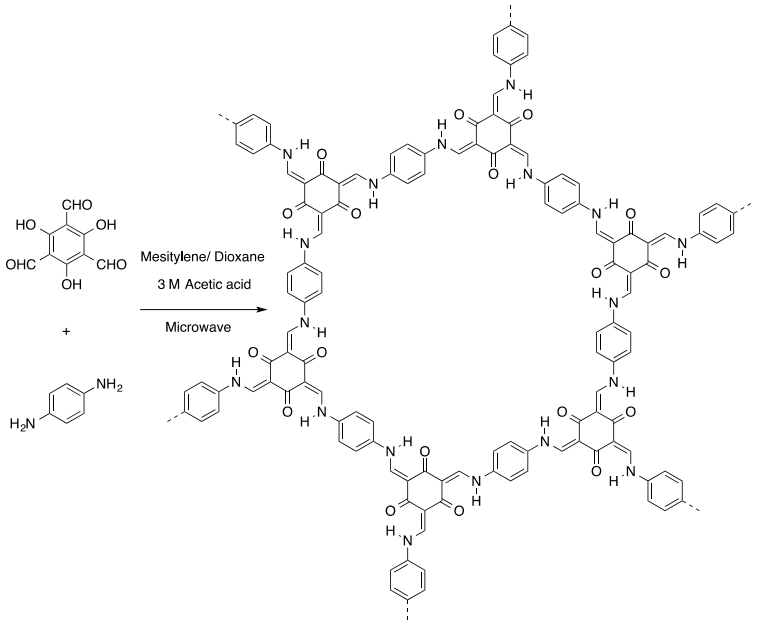
All the reagents were obtained from Aldrich. FT-IR were measured on Perkin-Elmer 70 using KBr pieces. Powder X-ray diffraction (XRD) patterns were obtained with a RIGAKU diffractometer equipped with Cu Ka X-ray radiation. N_2 sorption isotherms were measured on an Accelerated Surface Area & Porosimetry System, ASAP 2010 M+C (Micromeritics Instruments Inc.). Prior to analysis, the materials were solvent exchanged with THF using a Soxhlet washing procedure for 12 h. The powdered solid was loaded into a glass analysis tube and outgassed for 24 h under vacuum at 120 ˚C. N_2 adsorption and desorption isotherms were measured at 77 K and data was analyzed using Brunauer-Emmett-Teller (BET) analysis models to determine the surface area. Scanning Electron Microscopy (SEM). Field-emission SEM (FE-SEM) images were obtained using a Carl Zeiss Ultra 55. High-Resolution Transmission Electron Microscopy(TEM) images were obtained using JEOL 2100F. Thermogravimetric Analysis measurements were carried out on a PerkinElmer Pyris 1. Approximately 5 mg of sample was placed on a platinum pan, which was heated under a flow of N_2 at a rate of 10 ˚C/min up to 1000 ˚C. Elemental analysis (EA) was conducted with Thermo Scientific Flash 2000.

Synthesis of 1,3,5-triformylphloroglucinol (Tp):



Tp was synthesized following previously reported procedure and characterization matched that in the literature.[1]

Synthesis of TpPa-COF (MW):



TpPa-COF(MW) was synthesized under microwave heating conditions by preparing in a 3:2 molar ratio solution of p-phenylenediamine (Pa; 48 mg, 0.45 mmol) and 1,3,5-triformylphloroglucinol (Tp; 63 mg, 0.3 mmol) in a mixture of mesitylene/ 1,4-dioxane/ 3 M acetic acid (7 mL, 3: 3:1). This mixture was sealed under nitrogen in a 20 mL glass microwave tube and heated by microwave irradiation at 100 °C with stirring for 60 min using a CEM Explorer microwave synthesizer. The resulting powder was filtered and washed with mesitylene and acetone. Then the powder was collected and washed by employing THF as solvent using standard soxhlet method to remove any impurities adsorded in the porous structure. After dried under vacuum at 100 °C for 24 hours, the TpPa-COF (MW) was obtained as a red powder in 83% yield based on the starting materials. Anal. Calcld. For $C_{80}O_{12}N_{13}H_{48}$: C, 69.5; H, 3.47; N, 13.87; found: C, 67.7; H, 3.65; N, 13.51.

Section 2. Supporting Figures

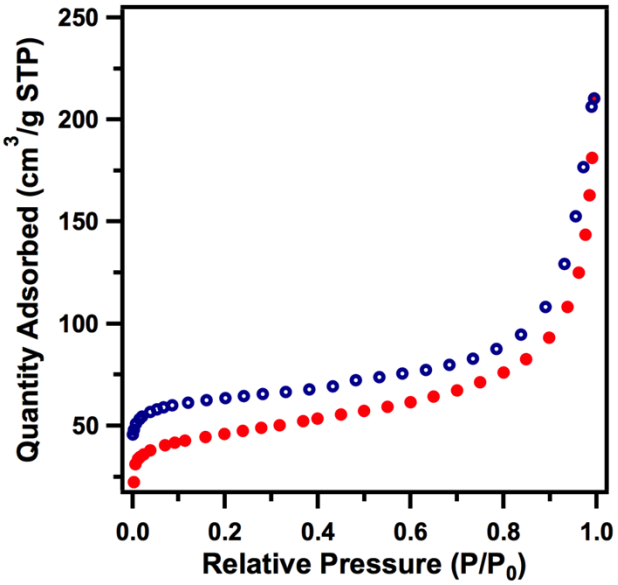


Figure S1: N_2 adsorption measurements for TpPa-COF (CE).

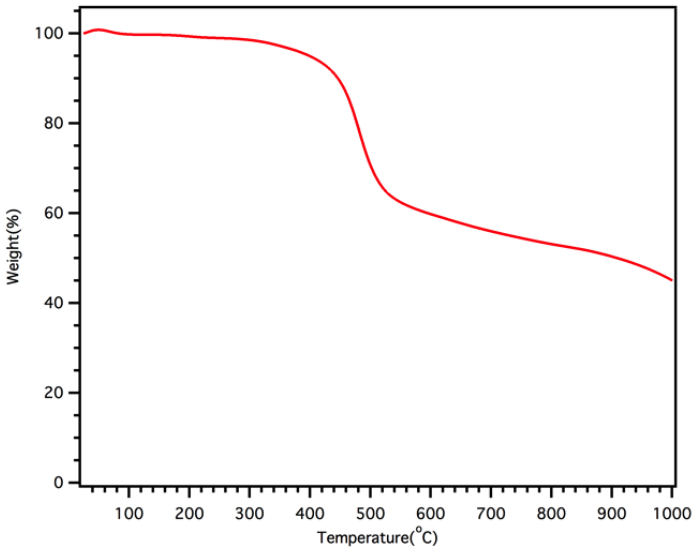


Figure S2: TGA of the TpPa-COF (MW).

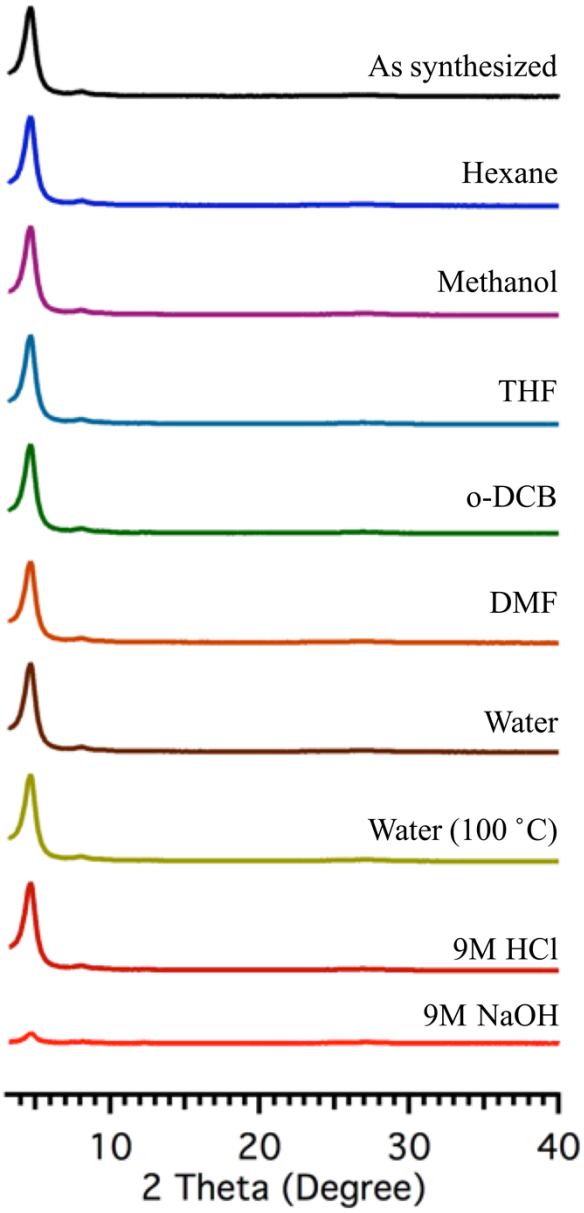


Figure S3: PXRD of TpPa-COF (MW) after chemical stability test. (From top to bottom: 1) As synthesized; 2) In hexane for 7 days at R.T.; 3) In methanol for 7 days at R.T.; 4) In THF for 7 days at R.T.; 5) In o-DCB for 7 days at R.T.; 6) In DMF for 7 days at R.T.; 7) In water for 7 days at R.T.; 8) In water for 7 days at 100 ˚C; 9) In 9M HCl for 7 days at R.T.; 10) In 9M NaOH for 3 days at R.T.

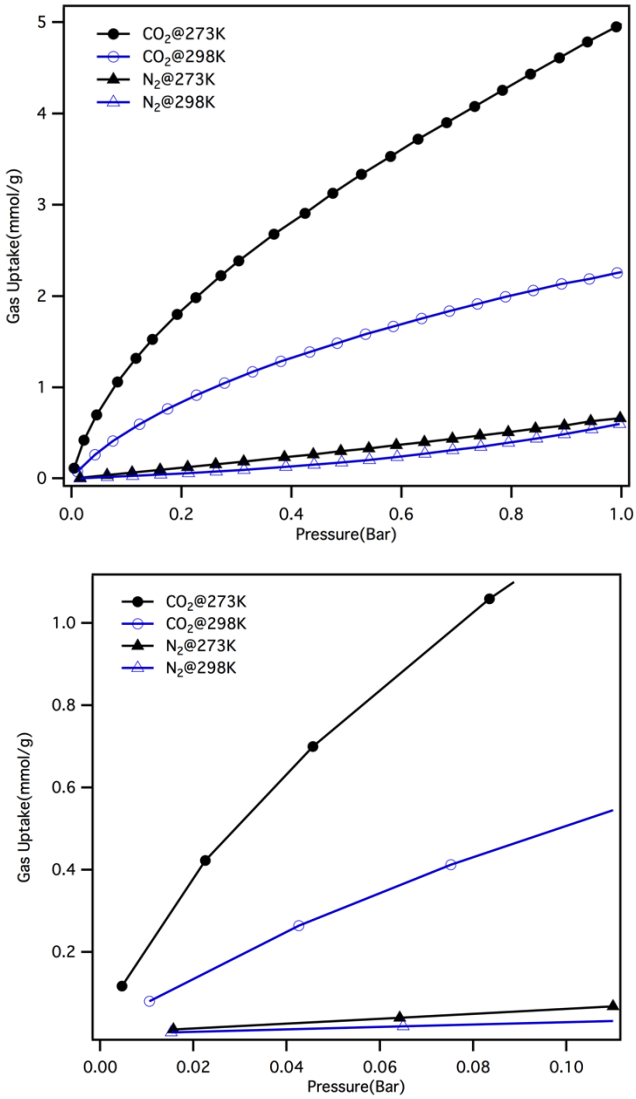


Figure S4: Gas adsorption measurements for TpPa-COF (MW): CO_2 and N_2

Section 3. Supporting References

(1) Chong, J. H.; Sauer, M.; Patrick, B. O.; MacLachlan, M. J. Highly stable keto-enamine salicylideneanilines. *Organic letters,* **2003**, *5*, 3823–3826.