

Electronic Supporting Information

Targeted Synthesis of A Mesoporous Triptycene-Derived Covalent Organic Framework

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Section S1: Synthetic Procedures for TDCOF-5

General Synthetic Procedures

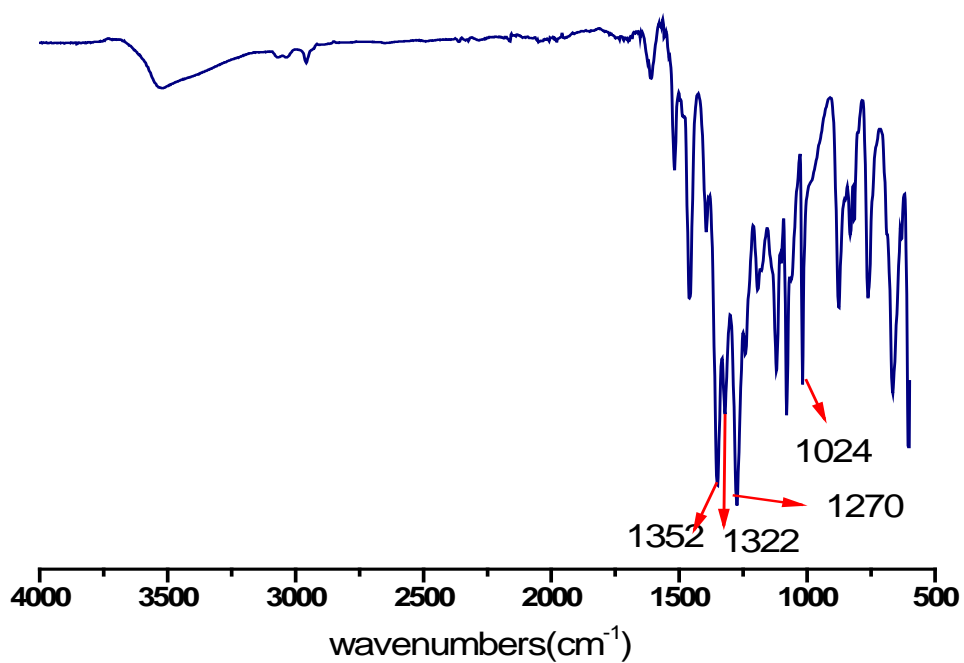
All starting materials, unless noted otherwise, were obtained from Aldrich Chemicals and used without further purification. Dichloromethane was distilled from calcium hydride, and mesitylene was distilled from sodium. All products were handled under a nitrogen atmosphere using glovebox or Schlenk line techniques. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Higher carbon and hydrogen contents may result from residual hydrocarbons in the cavities. 2, 3, 6, 7, 12, 13-hexahydroxytriptycene was prepared according to literature methods.¹

Synthesis of TDCOF-5. A Pyrex tube which has the outer diameter is 12 mm and inner diameter is 10 mm was charged with 2, 3, 6, 7, 12, 13-hexahydroxytriptycene (46 mg, 0.13 mmol) and benzene-1,4-diboronic acid (30 mg, 0.18 mmol) under nitrogen (N₂) flow. 3 mL of a 1:1.5 (v:v) solution of mesitylene:dioxane was added. The tube was flash frozen at 77 K (liquid nitrogen bath) evacuated and flame sealed. The reaction mixture was heated at 120 °C for 5 days with a rate of 0.1 °C per minute and the resulting white precipitate was isolated by filtration over a medium glass frit and washed with anhydrous acetone twice (2x15 mL). The product was immersed in anhydrous acetone (15 mL) for two days and the solvent was changed and freshly replenished five times. The solvent was removed by filtration and dried at 85 °C to give TDCOF-5 as a white powder (37.6 mg, 64%). Anal. Calcd. for (C₂₈H₅₈B₆O₁₂): C, 70.96; H, 2.87. Found: C, 69.39; H, 3.24.

Section S2: FT-IR Spectroscopy for TDCOF-5

FT-IR spectra were obtained as KBr pellets using a Nicolet Nexus 670 FT-IR spectrometer. The formation of the BC_2O_2 ring is supported by the following IR-bands (cm^{-1}): B-O (1352), B-C (1270), C-O (1024). FT-IR results are in line with previous reported COFs ².

Figure S1: FT-IR spectrum for TDCOF-5



Section S3: *Solid-State ^{11}B and ^{13}C Multiple Quantum Magic Angle Spinning (MQMAS)*

Nuclear Magnetic Resonance for TDCOF-5

Solid-state nuclear magnetic resonance (NMR) spectra were recorded at ambient temperature on a Bruker DSX-300 spectrometer using a Bruker magic angle spinning (MAS) probe with 4 mm (O.D.) 80 μL volume zirconia rotors with Kel-F drive caps. TDCOF-5 was packed in a nitrogen environment. Cross-polarization with MAS (CPMAS) was used to acquire ^{13}C data at 75.47 MHz. The ^1H and ^{13}C ninety-degree pulse widths were both 4 μs , and the CP contact time was 1.5 ms. High power two-pulse phase modulation (TPPM) ^1H decoupling was applied during data acquisition. The decoupling frequency corresponded to 72 kHz. The MAS sample spinning rate was 10 kHz. Recycle delays between scans varied between 10 and 30 s, depending upon the compound as determined by observing no apparent loss in ^{13}C signal intensity from one scan to the next. The ^{13}C chemical shifts are given relative to tetramethylsilane as zero ppm, calibrated using the methane carbon signal of adamantane assigned to 29.46 ppm as a secondary reference. Multiple quantum MAS (MQMAS) spectroscopy was used to acquire ^{11}B data at 96.29 MHz. The ^{11}B solution-state ninety-degree pulse width was 2 μs . TPPM ^1H decoupling was applied during data acquisition. The decoupling frequency corresponded to 72 kHz. The MAS spinning rate was 14.9 kHz. A recycle delay of 3 s was used. The ^{11}B chemical shifts are given relative to BF_3 etherate as zero ppm, calibrated using aqueous boric acid at pH = 4.4 assigned to -19.6 ppm as a secondary reference.

Figure S2: Solid-state ^{11}B multiple quantum MAS (MQMAS) NMR spectrum of TDCOF-5; asterisks denote spinning-side bands.

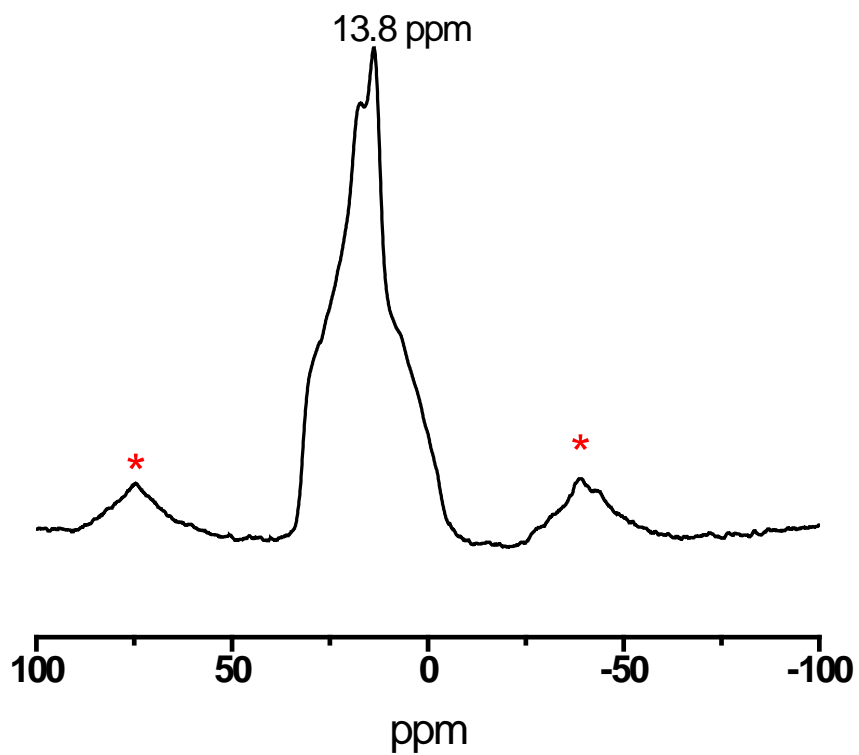
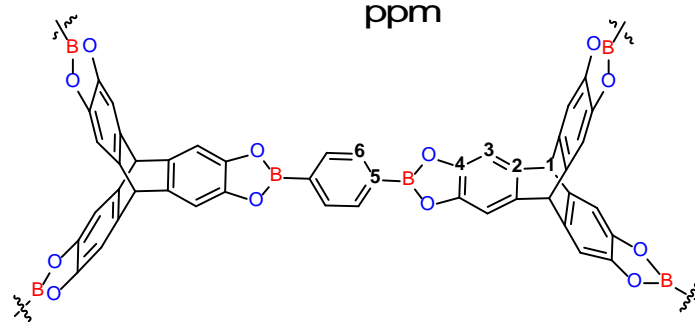
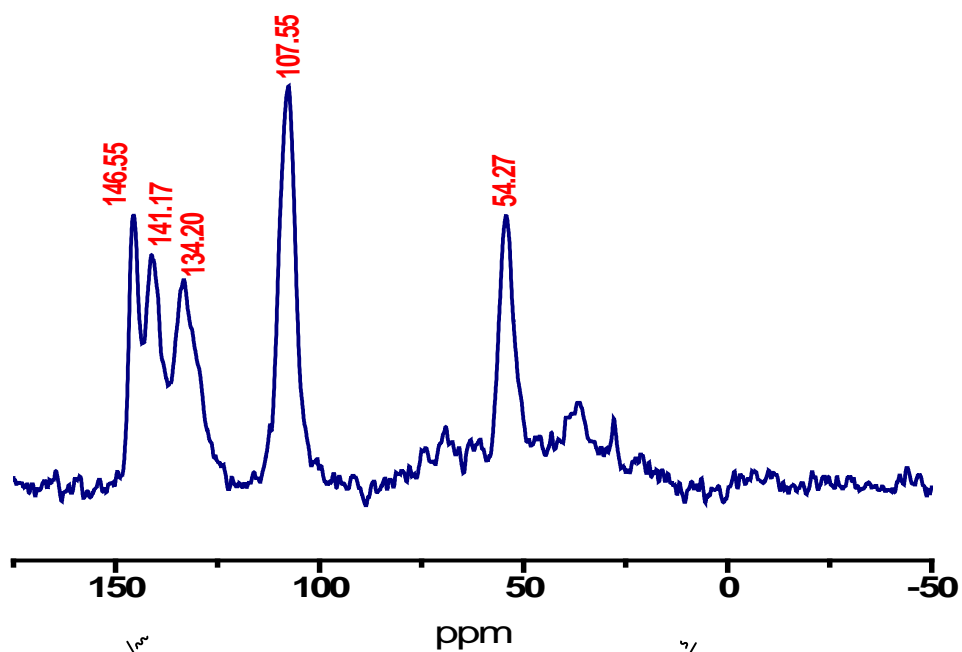


Figure S3: Solid-State ^{13}C CP-MAS NMR spectrum for TDCOF-5.

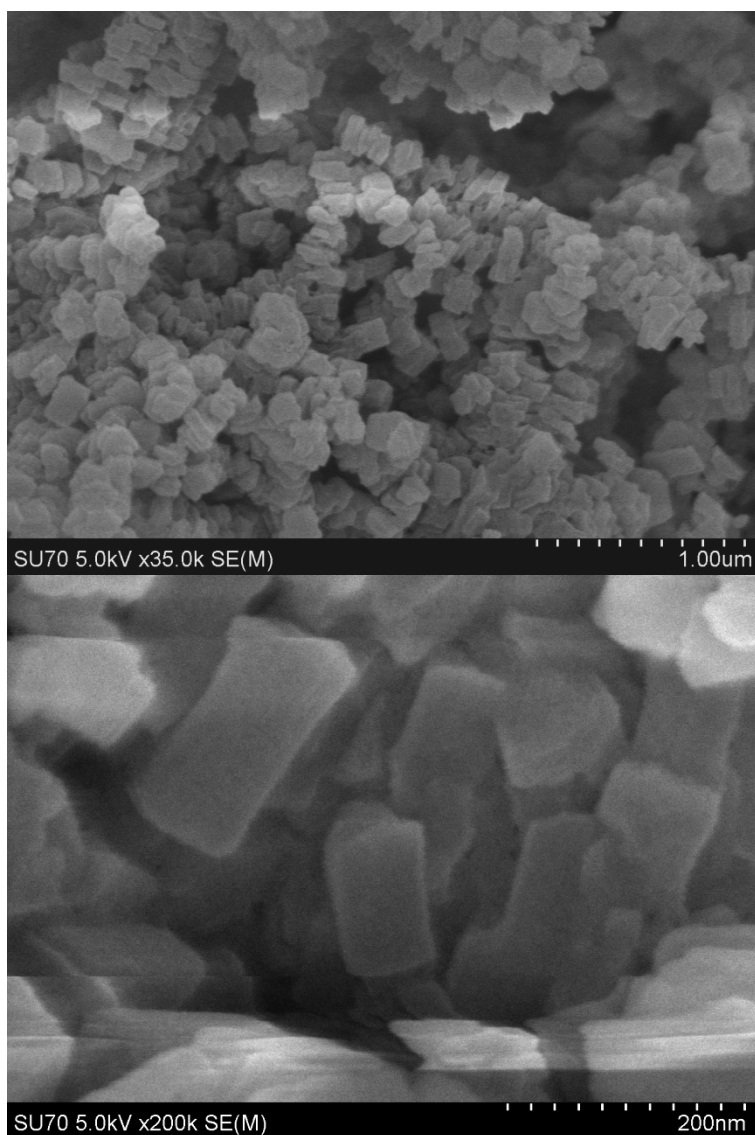


| Carbon | Chemical Shift (ppm) |
|--------|----------------------|
| 1 | 54.27 |
| 2 | 141.17 |
| 3 | 107.55 |
| 4 | 146.55 |
| 5 | 134.20 |
| 6 | 134.20 |

Section S4: Scanning Electron Microscopy (SEM) Imaging of TDCOF-5

A sample TDCOF-5 was prepared by dispersing the material onto a sticky carbon surface attached to a flat aluminum sample holder. The sample was then gold coated using an EMS (Electron Microscopy Sciences) 550x Sputter Coater at 1×10^{-1} mbar of pressure in a nitrogen atmosphere for 90 seconds while maintaining 20 mA of current.

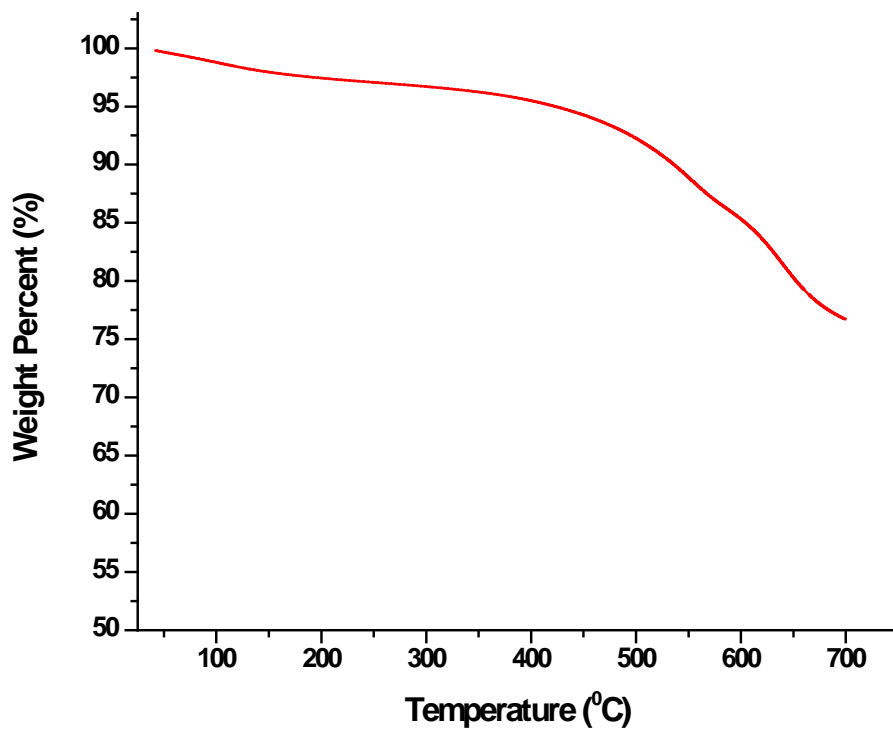
Figure S4: SEM images of as-prepared TDCOF-5



Section S5: Thermogravimetric Analysis (TGA) for TDCOF-5

Thermogravimetric analysis was obtained using a TA Instruments TGA Q5000 analyzer with 50 μL platinum pans to assess the thermal stability of the polymer. Experiments were run at a ramp rate of 5 $^{\circ}\text{C}/\text{minute}$ under argon atmosphere.

Figure S5: TGA for an activated sample of TDCOF-5



Section S6: Porosity and Low Pressure (0 – 1.0 bar) Gas Adsorption Measurements

Activation of TDCOF-5 for gas adsorption measurements: A sample TDCOF-5 (~75 mg) was loaded into an autosorb cell inside a glovebox filled with nitrogen and then heated to 85 °C under dynamic vacuum (1.0×10^{-5} torr) for 10 h. All adsorption measurements were performed on an Autosorb-1 C (Quantachrome) volumetric analyzer. The Argon sorption experiment was ran at 87 K. Pore Size Distribution (PSD) was calculated using Non-Local Density Functional Theory (NLDFT) on the adsorption branch with a cylindrical pore model. Hydrogen sorption experiments were collected at 77 K and 87 K. Using the data taken at 77 K and 87 K, the hydrogen isosteric heat of adsorption was calculated according to literature methods³ by solving the virial-type expression:

$$\ln P = \ln N + (1/T) \sum_{i=0}^m a_i N^i + \sum_{i=0}^n b_i N^i$$

where P is pressure in torr, T is temperature in Kelvin, and N is the mmol of H₂ adsorbed per gram of sample. The values for m and n were varied such that $m \geq n$ and resulted in the best fit as determined by the sum of the squares of the errors. The values for a_0, a_1, \dots, a_m were used in the calculation for the isosteric heat of adsorption,

$$Q_{\text{st}} = -R \sum_{i=0}^m a_i N^i$$

The calculated values were plotted against surface coverage, and the isosteric heat of adsorption values at zero-coverage were highlighted in the text.

Figure S6: Argon isotherm for TDCOF-5 measured at 87 K. The filled circles are adsorption points and the empty circles are desorption points.

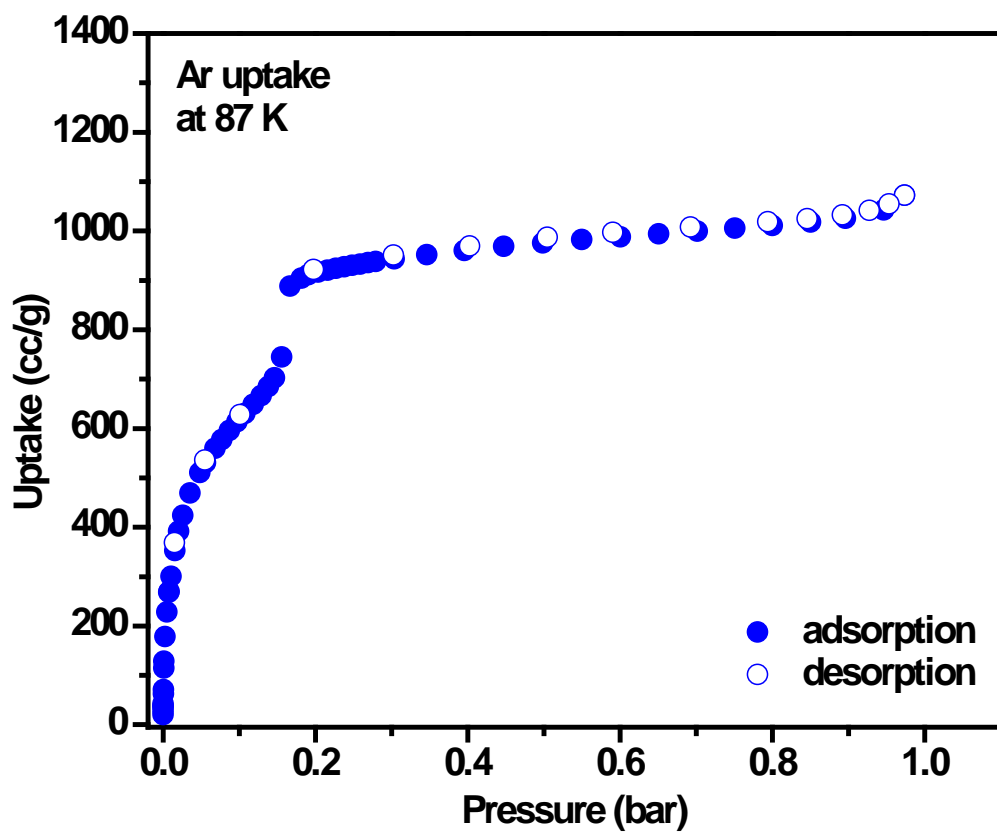


Figure S7: Pore Size Distribution (PSD) for TDCOF-5 from NLDFT.

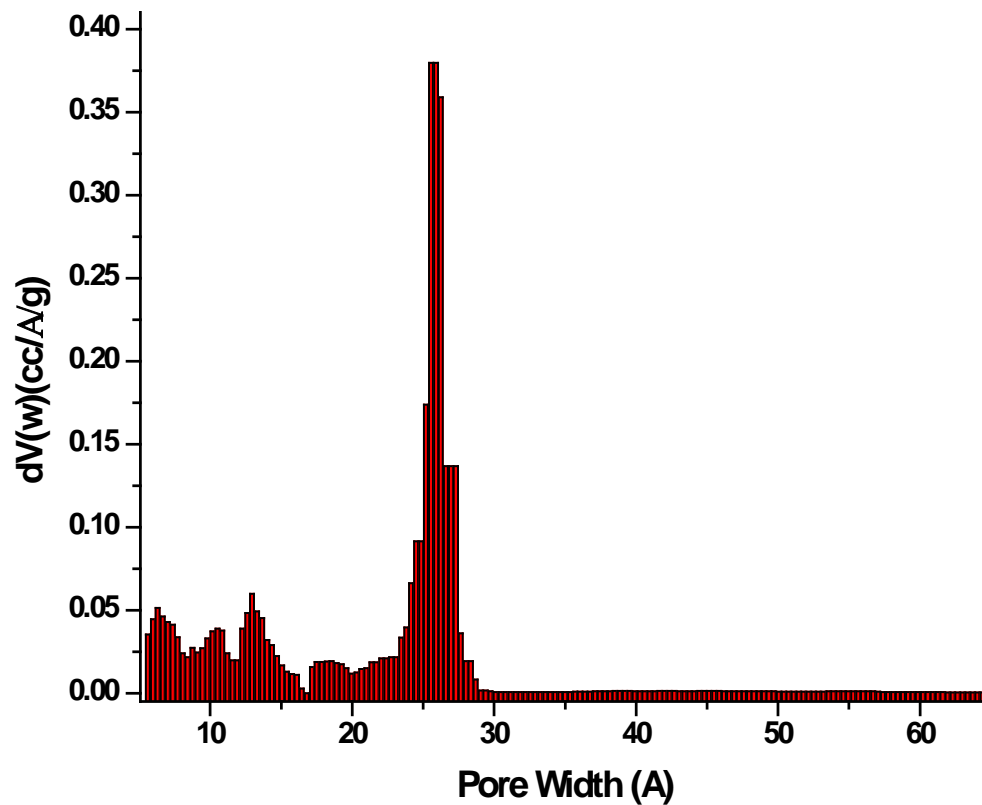


Figure S8: NLDFT calculated isotherm for TDCOF-5 overlaid with the experimental argon isotherm. A fitting error less than 1% indicates validity of the model.

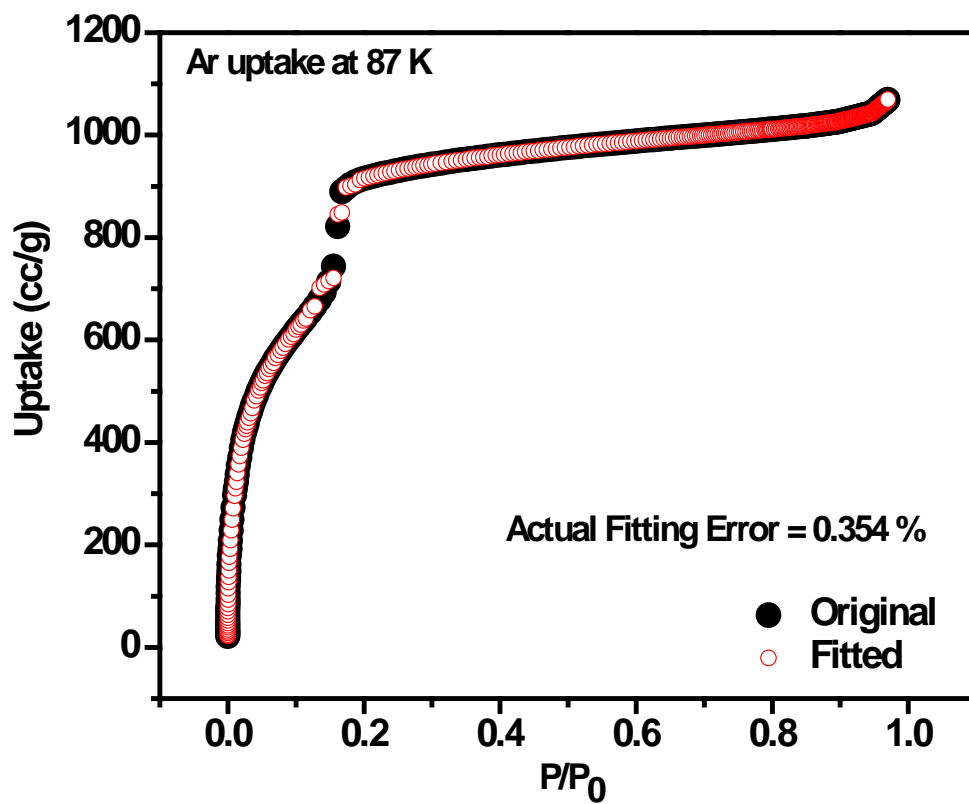


Figure S9: Langmuir plot for TDCOF-5 calculated from the argon adsorption in the range of $P/P_o = 0.17$ - 0.30 .

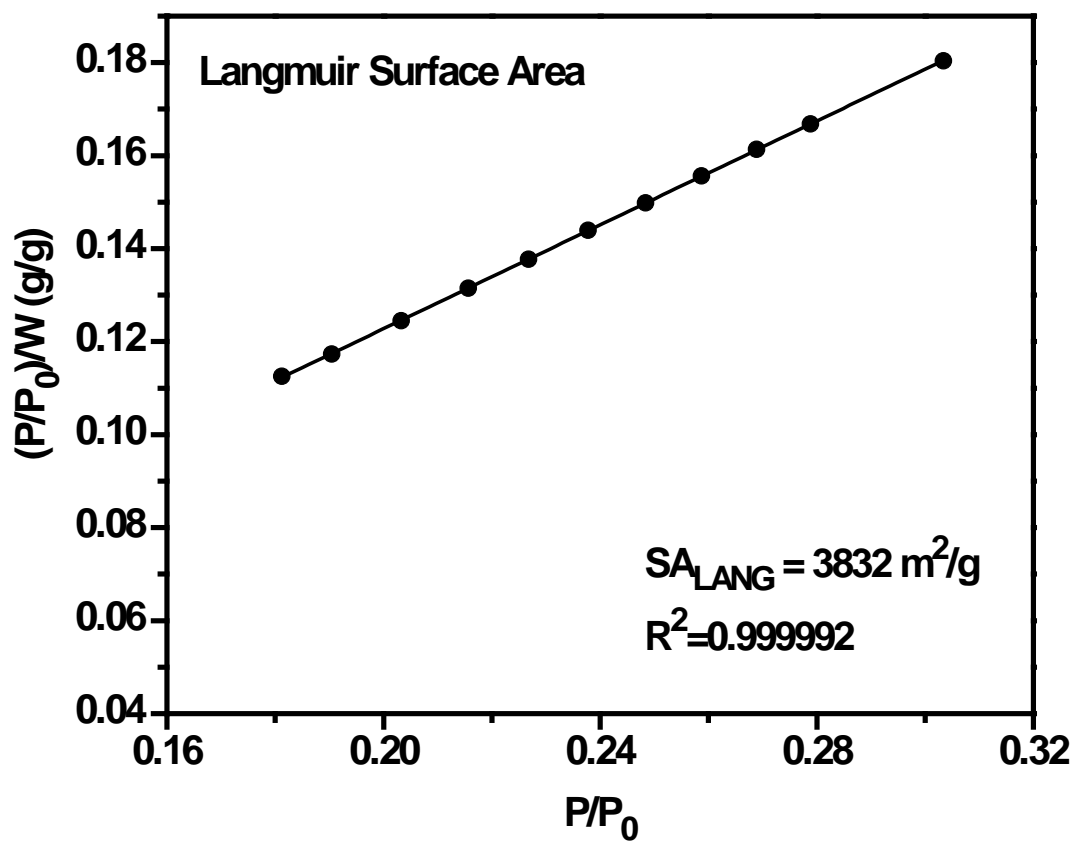


Figure S10: Multipoint BET plot for TDCOF-5 calculated from the argon adsorption in the range of $P/P_o = 0.02-0.15$.

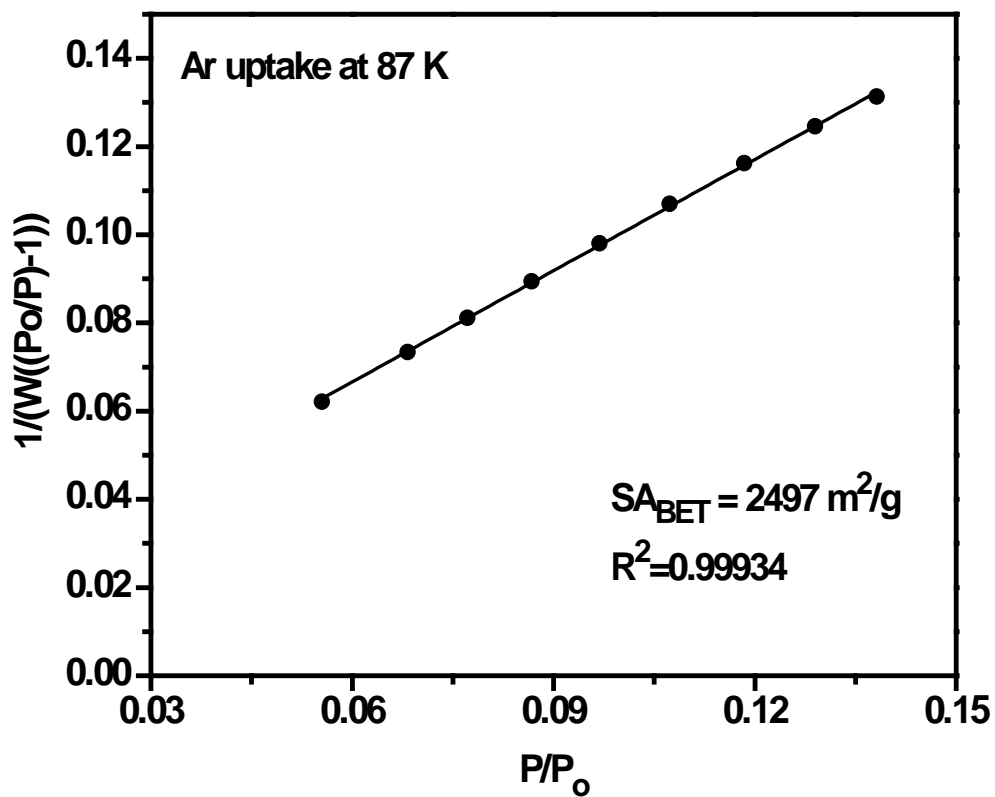


Figure S11: Hydrogen isotherm for TDCOF-5 measured at 77K and 87K.

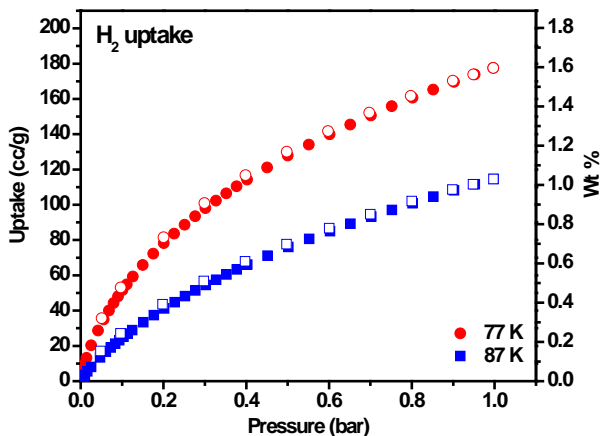


Figure S12: Hydrogen isosteric heat of adsorption (Q_{st}) for TDCOF-5.

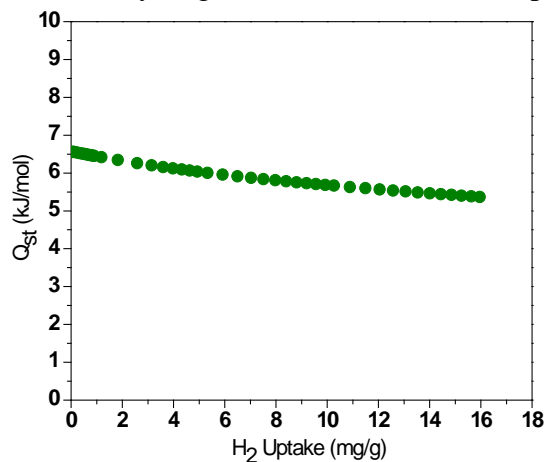


Figure S13: Virial analysis of H₂ adsorption data for TDCOF-5.

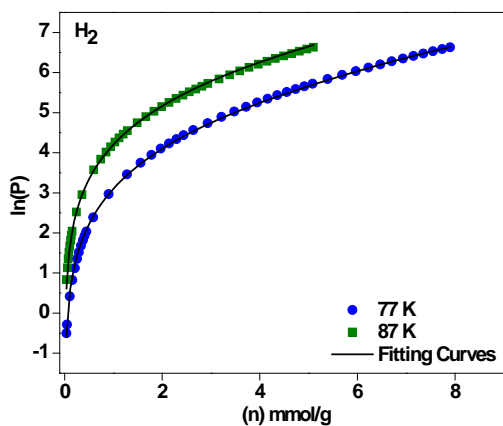


Figure S14: Carbon dioxide isotherm for TDCOF-5 measured at 273K and 298K.

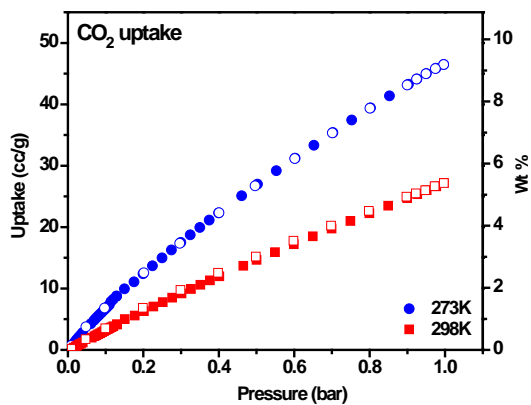


Figure S15: Carbon dioxide isosteric heat of adsorption (Q_{st}) for TDCOF-5.

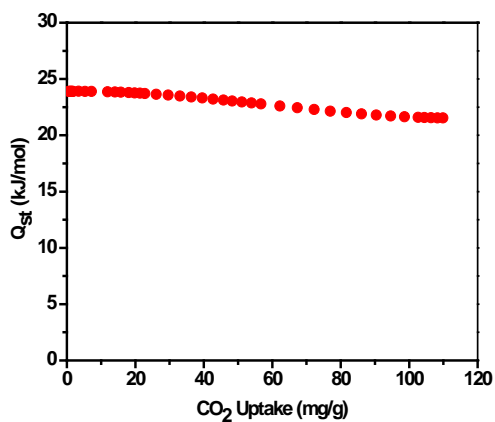


Figure S16: Virial analysis of CO₂ adsorption data for TDCOF-5.

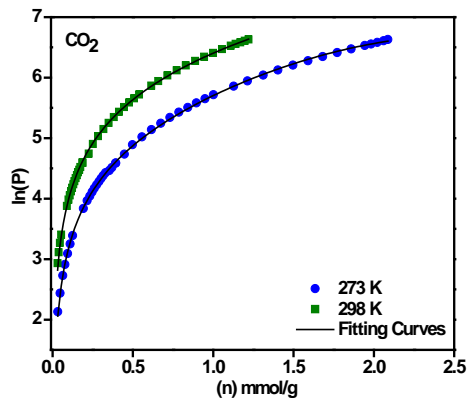


Figure S17: Methane isotherm for TDCOF-5 measured at 273K and 298K.

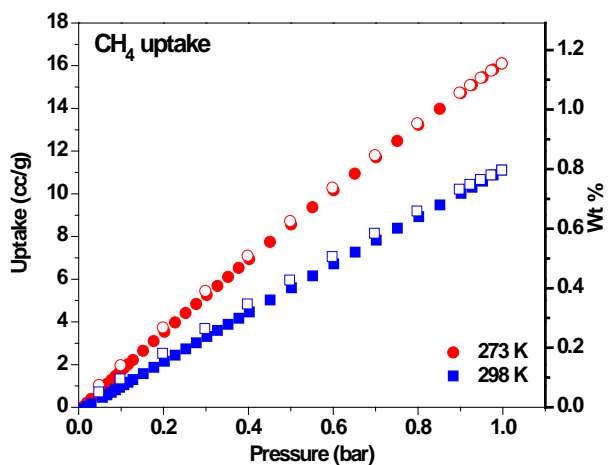


Figure S18: Methane isosteric heat of adsorption (Q_{st}) for TDCOF-5.

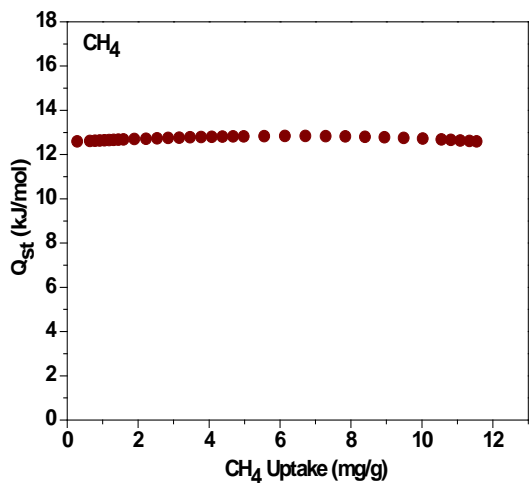
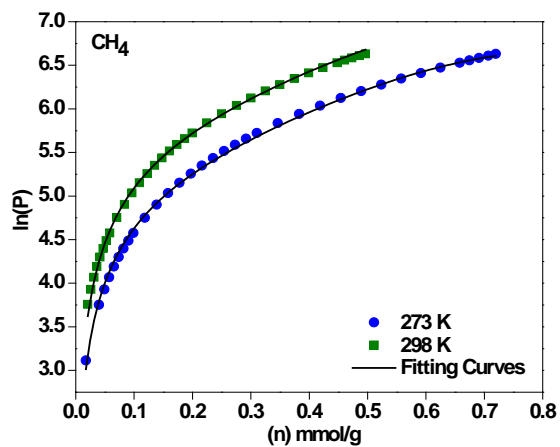


Figure S19: Virial analysis of CH₄ adsorption data for TDCOF-5.



Section S7: TDCOF-5 Structural Models and Atomic Coordinates

TDCOF-5 models were constructed using *Materials Studio Visualizer*⁴ utilizing the Forcite module. The eclipsed conformation for polymer was modeled using boron nitride space group (*P6/mmm*) and staggered conformation was modeled using with a graphite topology of space group (*P6₃/mmc*). Vertex positions were obtained from the Reticular Chemistry Structure Resource⁵. The vertices were replaced by a triptycene with the BO₂C₂ ring pointing along the extension. The midpoint of each extension was replaced by benzene for *TDCOF-5*.

The positions of atoms in the unit cell were obtained from the above models by using *CrystalMaker* for *Windows Version 1.4.5* and are shown as fractional atomic coordinates in Tables S1-S2.

Table S1: Fractional atomic coordinates for the eclipsed conformation of TDCOF-5 calculated from *Materials Studio* modeling.

| | | | |
|--|---------|---------|----------|
| Eclipsed model | | | |
| <i>P6/mmm</i> | | | |
| a = b = 31.3283 Å; c = 7.51830 Å | | | |
| $\alpha = \beta = 90^\circ$; $\gamma = 120^\circ$ | | | |
| Hexagonal | | | |
| | X | Y | Z |
| B | 0.55701 | 0.44299 | 1.00000 |
| C1 | 0.28159 | 0.64080 | 0.10278 |
| C3 | 0.19057 | 0.59528 | -0.09697 |
| C4 | 0.33333 | 0.66666 | 0.18683 |
| C5 | 0.48599 | 0.51401 | 1.17676 |
| C6 | 0.52779 | 0.47221 | 1.00000 |
| H1 | 0.23176 | 0.61588 | -0.34269 |
| H2 | 0.33330 | 0.66666 | -0.33441 |
| H3 | 0.47588 | 0.52412 | 1.30519 |
| O5 | 0.14311 | 0.57156 | -0.16455 |

Table S2: Fractional atomic coordinates for the staggered conformation of TDCOF-5 calculated from *Materials Studio* modeling.

| | | | |
|--|---------|---------|---------|
| Staggered model | | | |
| <i>P6₃/mmc</i> | | | |
| a = b = 30.5978 Å; c = 14.1705 Å | | | |
| $\alpha = \beta = 90^\circ$; $\gamma = 120^\circ$ | | | |
| Hexagonal | | | |
| | X | Y | Z |
| B1 | 0.22270 | 0.44540 | 0.25000 |
| B2 | 0.88939 | 0.77879 | 0.75000 |
| C1 | 0.30706 | 0.61412 | 0.30043 |
| C2 | 0.30692 | 0.15346 | 0.83552 |
| C3 | 0.38637 | 0.19318 | 0.75000 |
| C4 | 0.28024 | 0.14012 | 0.75000 |
| C5 | 0.97373 | 0.94745 | 0.80041 |
| C6 | 0.33333 | 0.66666 | 0.34456 |
| C7 | 0.43139 | 0.71570 | 0.14921 |
| C8 | 0.47625 | 0.73813 | 0.20115 |
| C9 | 0.00000 | 0.00000 | 0.84436 |
| C10 | 0.09803 | 0.04901 | 0.64916 |
| C11 | 0.14288 | 0.07144 | 0.70114 |
| C12 | 0.35969 | 0.17984 | 0.83551 |
| H1 | 0.33333 | 0.66666 | 0.42300 |
| H2 | 0.43190 | 0.71595 | 0.07285 |
| H3 | 0.00000 | 0.00000 | 0.92231 |
| H4 | 0.09851 | 0.04926 | 0.57278 |
| H5 | 0.37950 | 0.18975 | 0.90240 |
| H6 | 0.28710 | 0.14355 | 0.90240 |
| O1 | 0.23778 | 0.47556 | 0.16330 |
| O2 | 0.90447 | 0.80893 | 0.66330 |

Section S8: Powder X-ray Diffraction Analysis of TDCOF-5

Powder X-ray diffraction data of TDCOF-5 were collected on a Panalytical X'pert Pro Multipurpose Diffractometer (MPD). Samples were mounted on a zero background sample holder measured in transmission mode using Cu K α radiation with a 2θ range of 1.5-35°. The powder XRD data was subjected to refinement by the Rietveld method utilizing the GSAS and EXP-GUI software packages with a general least squares fit. Refinement produced a PXRD curve with lattice parameters of $a = b = 29.9608 \text{ \AA}$ and $c = 7.5266 \text{ \AA}$. The wRp and Rp values converged to 0.028 and 0.0204 respectively. The positions of atoms in the unit cell were determined using EXP-GUI and are shown as fractional atomic coordinates in Tables S1-S3.

Figure S20: PXRD pattern of TDCOF-5 with the experimental pattern in black, the Reitveld refined profile in red, the difference plot in blue and the eclipsed crystal model is green.

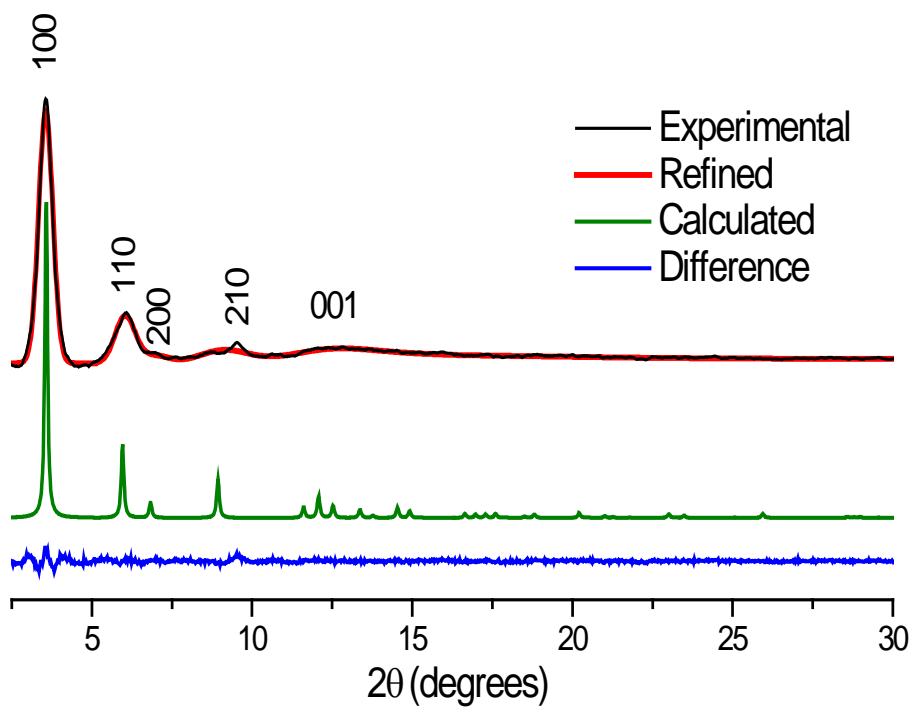
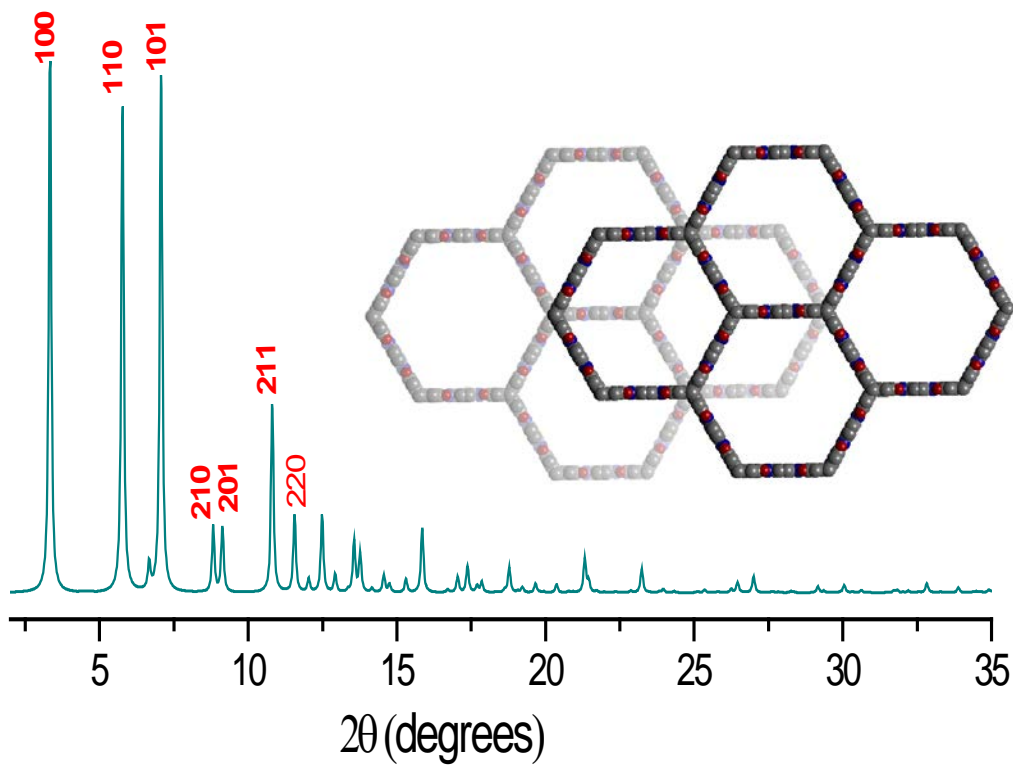
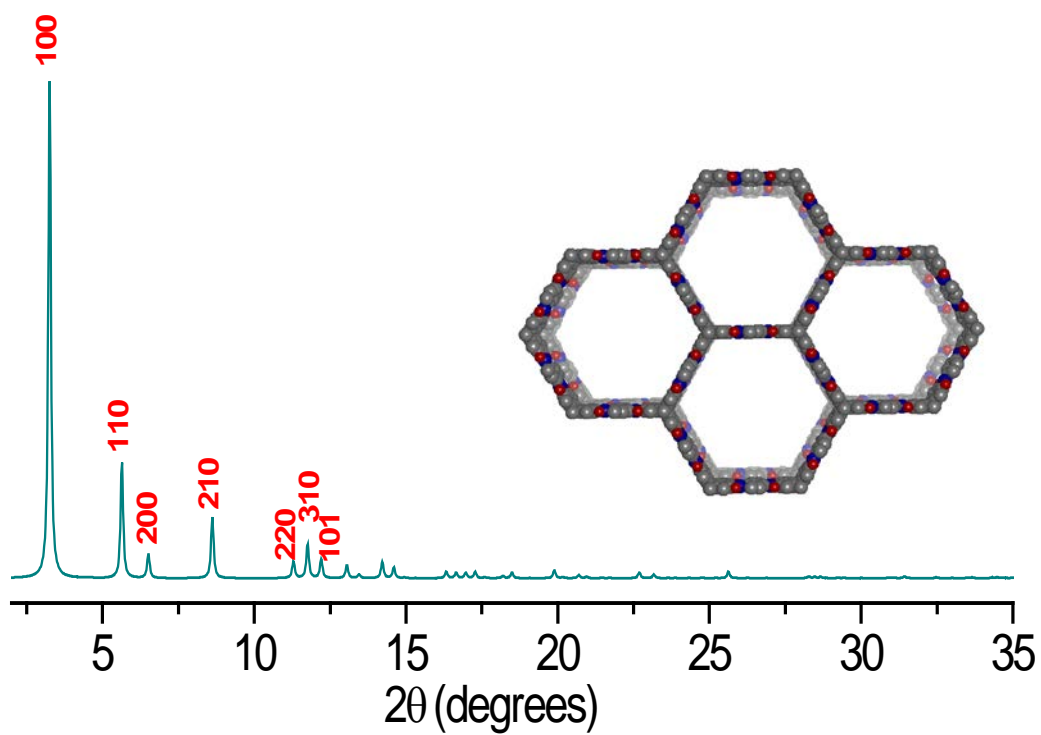


Table S3: Fractional atomic coordinates for the refined unit cell parameters for TDCOF-5
calculated from GSAS and EXP-GUI software packages.

| | | | |
|--|--------|--------|---------|
| Refined | | | |
| <i>Hexagonal</i> | | | |
| a = b = 30.5978 Å ; c = 14.1705 Å | | | |
| $\alpha = \beta = 90^\circ ; \gamma = 120^\circ$ | | | |
| | X | Y | Z |
| B1 | 0.557 | 0.443 | 1 |
| C1 | 0.2816 | 0.6408 | 0.1028 |
| C2 | 0.2333 | 0.6167 | -0.1992 |
| C3 | 0.1906 | 0.5953 | -0.097 |
| C4 | 0.3333 | 0.6667 | 0.1868 |
| C5 | 0.486 | 0.514 | 1.1768 |
| C6 | 0.5278 | 0.4722 | 1 |
| H1 | 0.2318 | 0.6159 | 0.3427 |
| H2 | 0.3333 | 0.6667 | -0.3344 |
| H3 | 0.4759 | 0.5241 | 1.3052 |
| O1 | 0.1431 | 0.5716 | -0.1646 |

Figure S21: Calculated PXRD patterns for eclipsed (top) and staggered (bottom) models of TDCOF-5.



References

1. B. S. Ghanem, M. Hashem, K. D. M; Harris, K. J. Msayib, M. Xu, P. M. Budd, N. Chaukura, D. Book, S. Tedds, A. Walton and N. B. McKeown, *Macromolecules*, 2010, **43**, 5287.
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4. Accelrys, Inc. Materials Studio 4.3 V; Accelrys, Inc: San Diego, CA, 2003.
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