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Supplementary Information

An Azine-Linked Hexaphenylbenzene Based Covalent Organic Framework

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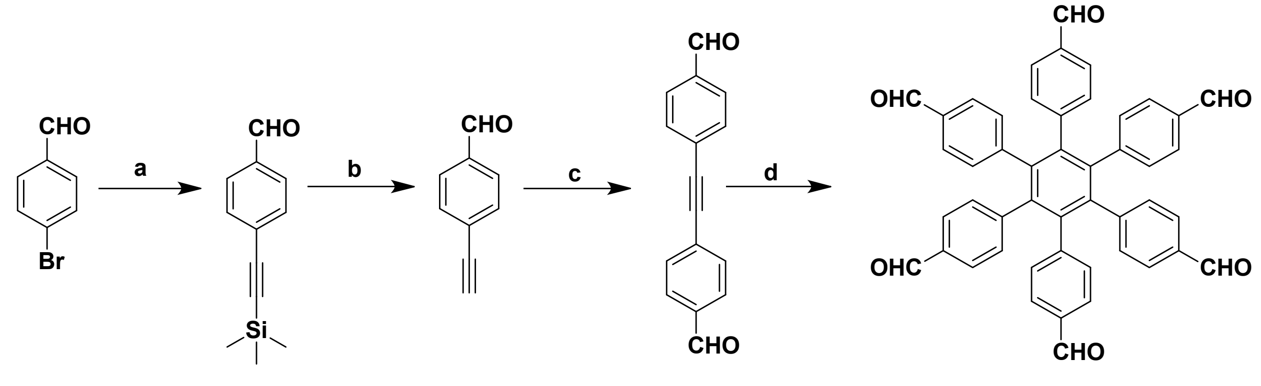
Table of Contents

1. General Methods

All reagents were purchased from commercial suppliers (Sigma-Aldrich and Fisher Scientific) and used as received. Compounds up to 1[1-3] (Scheme 1) were synthesized as previously reported. FT-IR spectra were taken on a Nicolet 360 FT-IR spectrophotometer with a SmartOrbit diamond attenuated total reflectance (ATR) cell. The thermogravimetric analyses were performed using a TA Instruments SDT Q600 Analyzer under nitrogen atmosphere with a heating rate of 10 °C min^{-1} from 30–1000 °C. Low-pressure gas adsorption experiments (up to 760 torr) were carried out on a Micromeritics ASAP 2020 surface area analyzer. Ultrahigh-purity-grade N_2, H_2, CO_2 and CH_4 gases (obtained from Airgas Corporation) were used in all adsorption measurements. N_2 (77 K) and H_2 (77 K) isotherms were measured using a liquid nitrogen bath. CO_2 and CH_4 isotherms were measured using either a water ice bath (273 K) or in room temperature water bath (298 K) whose temperature was measured prior to use for accuracy. The pore volume of each material was estimated from the Dubinin-Raduskevich (DR) model with the assumption that the adsorbate is in the liquid state and that the adsorption involves a pore-filling process. Pore size distributions were determined using a non-local density functional theory (NLDFT) carbon slit-pore model in the Micromeritics Software Package. Enthalpy of adsorption values were calculated using Van't Hoff plots from CO_2 and CH_4 isotherms at 273 and 298 K. Powder X-ray diffraction of HEX-COF 1 was carried out on a Bruker D8 Advance diffractometer with a sealed tube radiation source (Cu Kα, $\lambda = 1.54184$ Å), a low background sample holder, and Lynxeye XE detector. Raw diffraction data was processed using the MDI Jade software package (Kα background correction and peak smoothing using the Savitzky-Golay method). MALDI-ToF measurements were carried out on a Shimadzu Biotech Axima Confidence instrument. All spectra were obtained using tetracyanoquinodimethane (TCNQ) as a matrix. The general procedure for sample preparation was as follows: To a mortar was added TCNQ (10 mg) and the compound of interest (1 mg). This mixture was ground together to form a uniform solid. An aliquot (1 mg) of this solid was then transferred to a separate vial and chloroform (1 mL) was added. The resulting suspension was then spotted onto the MALDI plate and analyzed. ^1H and ^{13}C NMR spectra were carried out on a Bruker 400 or 500 MHz Advance Spectrometer. Microwave reactions were carried out in a CEM Discover reactor. Elemental analyses were performed by Micro-Analysis, Inc. 2038 Telegraph Rd, Wilmington, Delaware 19808.

2. Synthetic Procedures



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HEX

Scheme 1: Synthesis of **HEX**.

Reagents and conditions: (a) Trimethylsilylacetylene (1.5 equiv of 4-bromobenzaldehyde), $PdCl_2(PPh_3)_2$ (0.05 equiv of 4-bromobenzaldehyde), CuI (0.1 equiv of 4-bromobenzaldehyde), triethylamine, N_2, 80 °C, 12 h; (b) Sat. K_2CO_3 in methanol, CH_2Cl_2, rt, 3 h; (c) 4-bromobenzylbromide (1.0 equiv of 4-ethynylbenzaldehyde), $PdCl_2(PPh_3)_2$ (0.05 equiv of 4-ethynylbenzaldehyde), CuI (0.1 equiv. of 4-ethynylbenzaldehyde), triethylamine, N_2, 80 °C, 12 h; (d) $Co_2(CO)_8$ (5 mol % of 4,4'-(ethyne-1,2-diyl)dibenzaldehyde), dioxane, N_2, 160 °C, microwave 300 W, 1 h.

HEX: To a microwave tube containing **1** (0.500 g, 2.13 mmol) in dioxane (2 mL) was purged with nitrogen for 15 min before $Co_2(CO)_8$ (36.5 mg, 0.107 mmol) was added. The reaction was heated at 160 °C at 300 W for 1 h in the microwave reactor. After that time hexane was added in to the tube and the resultant brown precipitate was collected by filtration and washed with hexane until the filtrate was colorless. The collected solid was dissolved in CH_2Cl_2 and filtered through a silica gel plug. Finally, the resultant solution was evaporated to dryness to obtain a brown solid (0.275 g, 55% yield). ^{1}H NMR (400 MHz, DMSO, δ): 7.20 (d, *J* = 8 Hz, 12H, Ar), 7.46 (d, *J* = 8 Hz, 12H, Ar), 9.73 (s, 6H, ArCHO). ^{13}C NMR (400 MHz, DMSO, δ): 128.63, 132.04, 134.31, 139.63, 145.46, 193.15. MALDI-ToF-MS (*m/z*) Calculated for $[C_{48}H_{30}O_6]^+$: 702.2. Found: 702.0

HEX-COF 1: A 4 mL ampoule was charged with **HEX** (25.0 mg, 0.0356 mmol), N_2H_4 (3.34 μL, 0.1067 mmol), mesitylene (0.67 mL) and dioxane (0.33 mL). The mixture was sonicated for 10 min and 6M AcOH (0.1 mL) was added. The ampoule was sealed under vacuum after freezing the contents in it with liquid nitrogen. Once it reached RT the ampoule was heated at 120 °C for 3 d. After that time the mixture was cooled to RT, the obtained light yellow precipitate was soaked in tetrahydrofuran for 2 h and then washed with tetrahydrofuran (20 ml x 3). The remaining yellow solid was dried under vacuum to afford 18.4 mg (75% yield) of HEX-COF 1. Elemental analysis (%) Calcd: C, 83.46; H, 4.38; N, 12.17; Found: C, 75.96; H, 4.35; N, 8.40. The elemental analyses are often reported to be different from the expected values as a result of incomplete combustion, as has also been found in other reports of carbon-rich porous materials[4-6] including our previous work.[7,8]

3. NMR Characterization

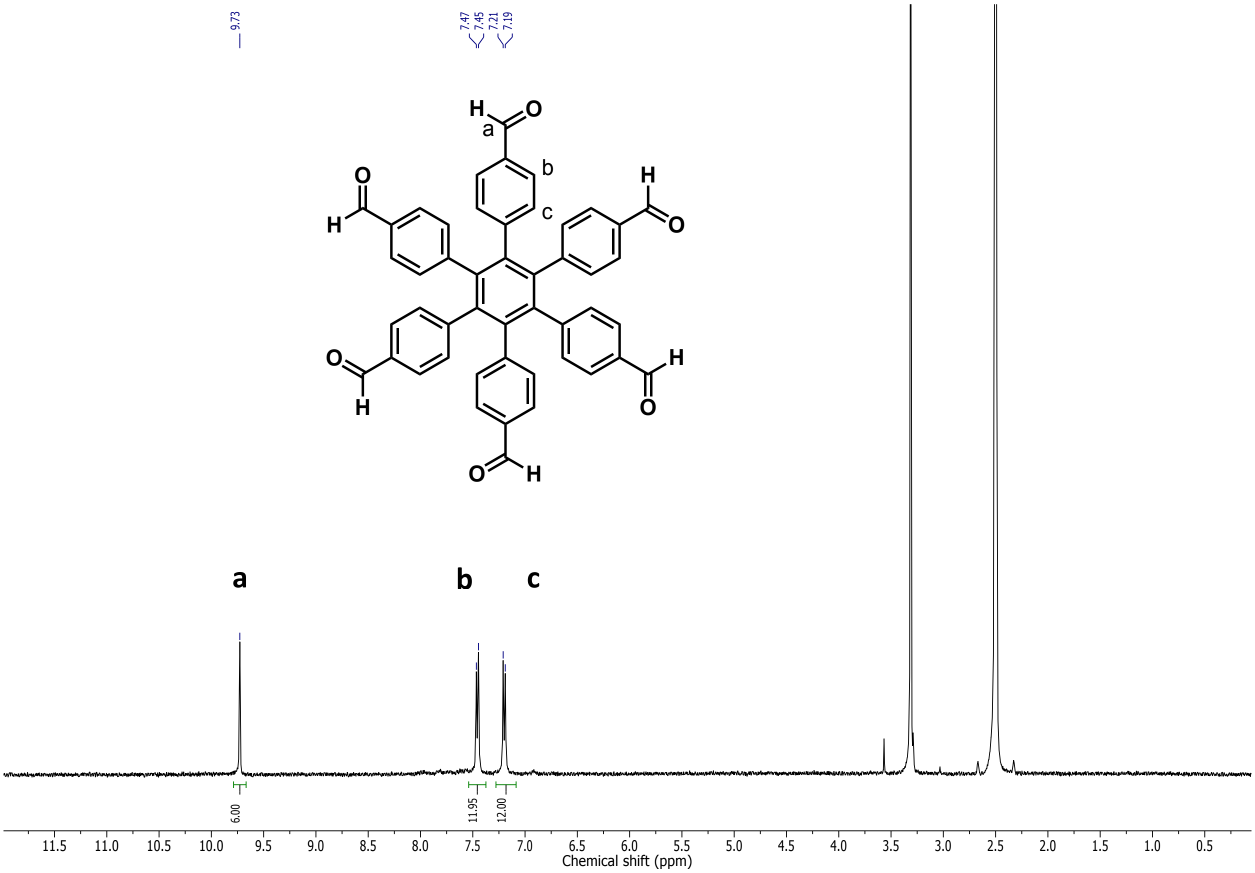


Figure 1: ^{1}H NMR (400 MHz) of HEX in DMSO-d_6

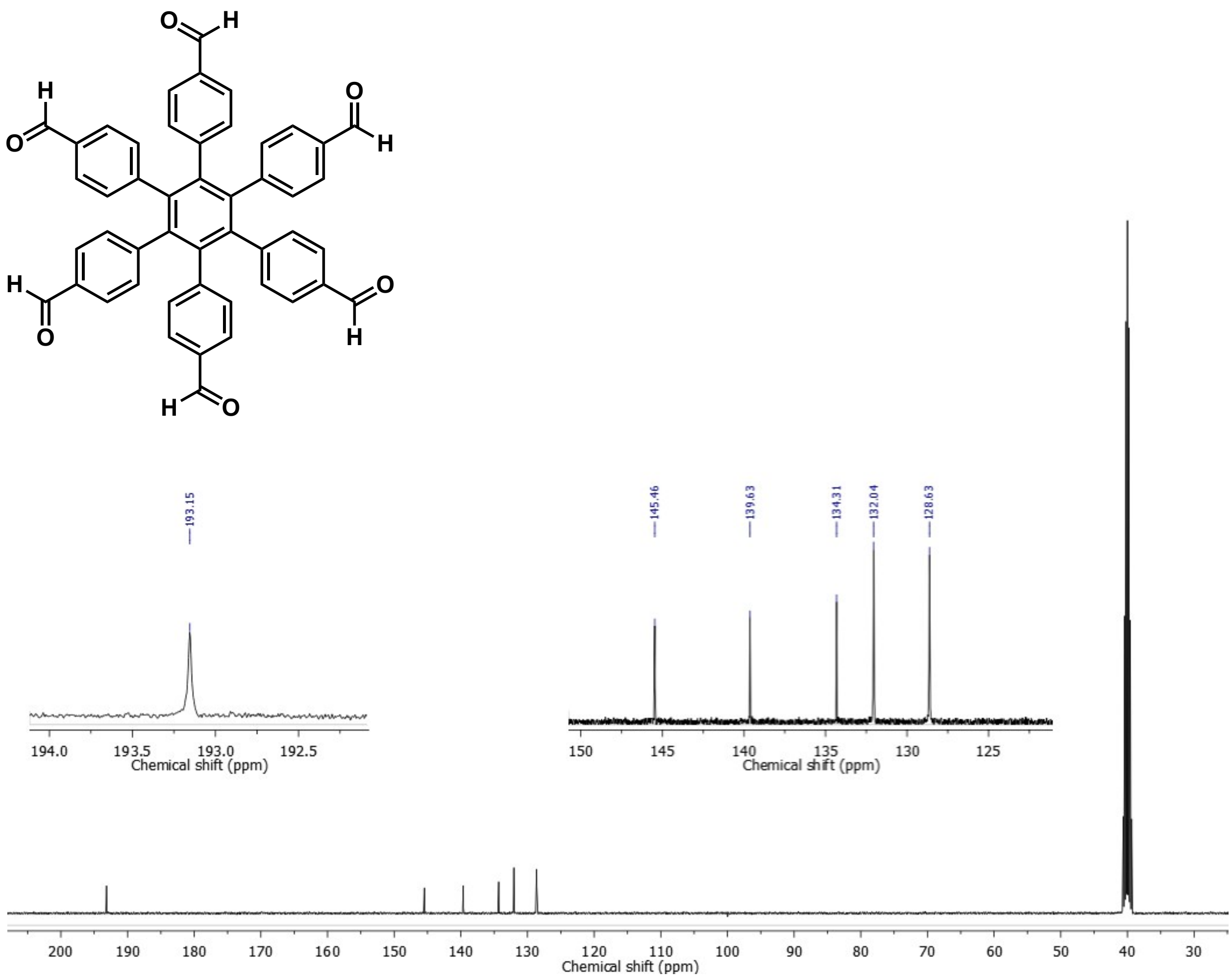


Figure 2: ^{13}C NMR (400 MHz) of HEX in DMSO-d_6

4. Thermogravimetric analysis

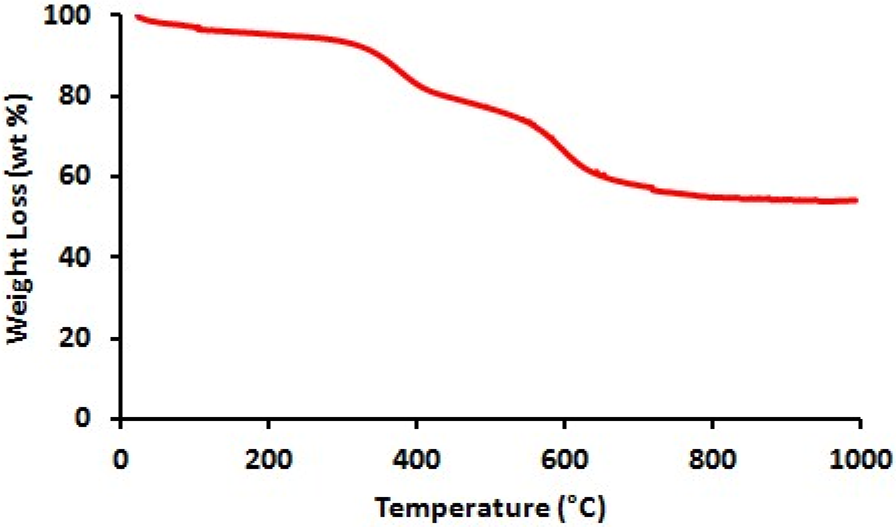


Figure 3: TGA of HEX-COF 1 under a nitrogen atmosphere.

5. FT-IR Characterization

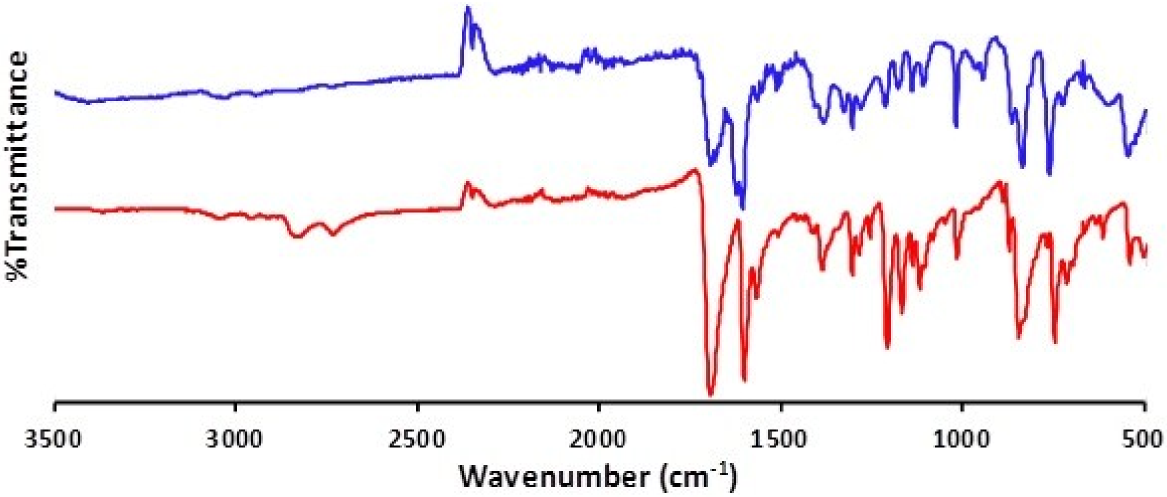


Figure 3: FT-IR spectra of HEX-COF 1 (Blue) and HEX (Red)

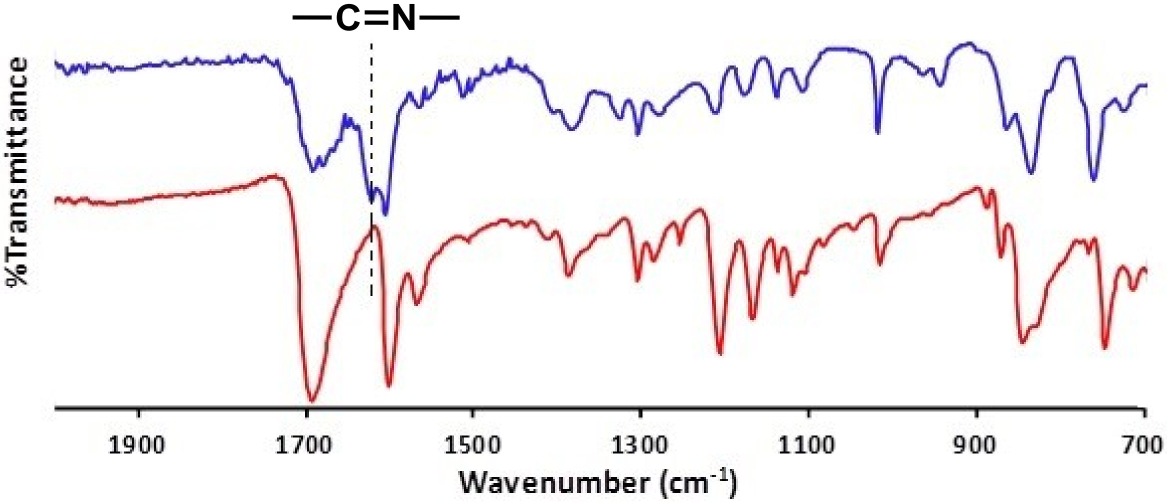
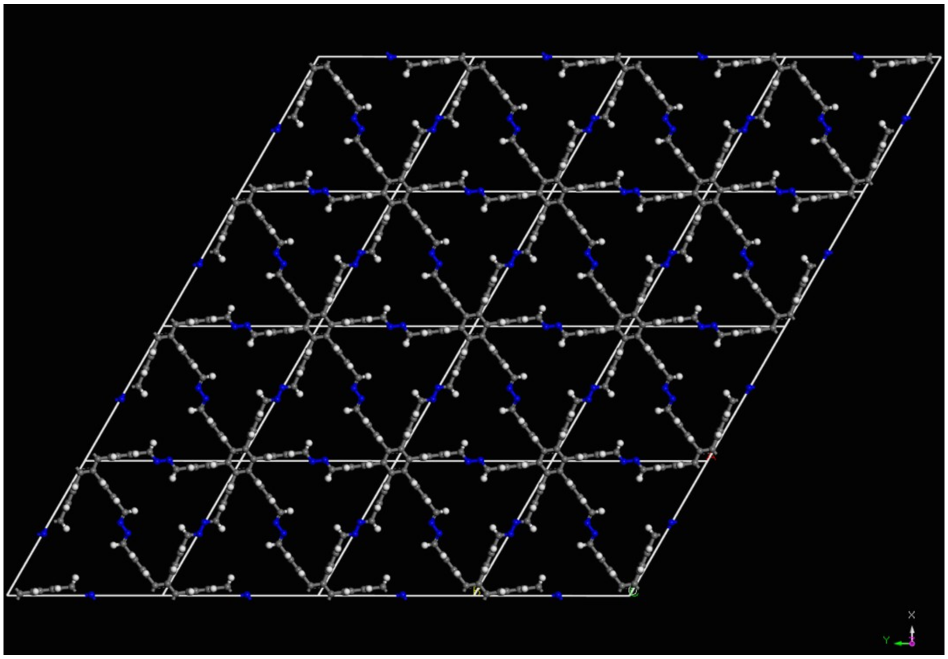


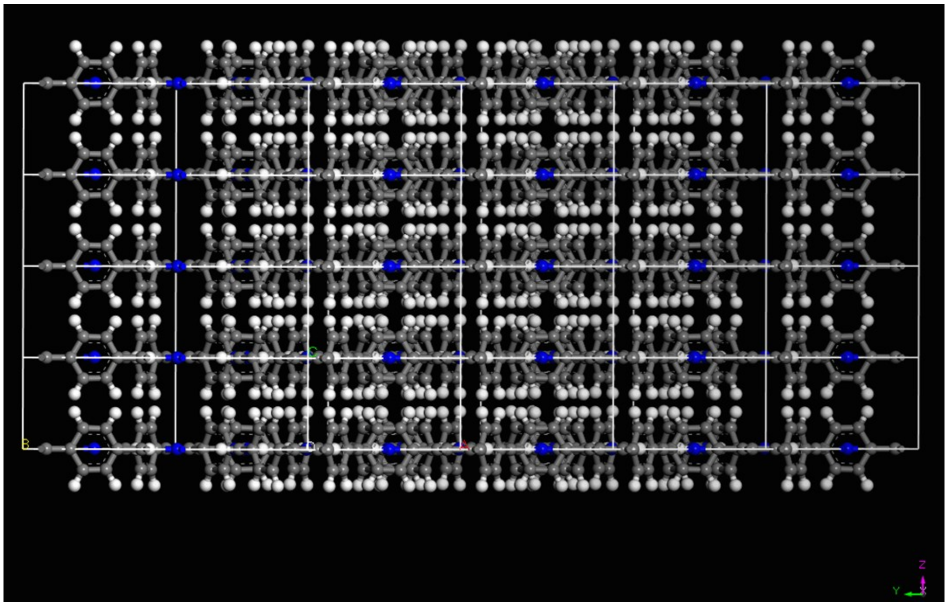
Figure 4: Zoomed in image of FT-IR spectra of HEX-COF 1 (Blue) and HEX (Red).

FT-IR spectroscopy of the HEX-COF 1 exhibited a stretching vibration band at 1622 cm^{-1} which can be assigned to C=N bond based on previously reported azine COFs.[9]

6. Molecular Modeling and X-Ray Diffraction Pattern Simulation

Molecular modeling studies were carried out in Accelrys Materials Studio 7.0. HEX-COF 1 was modeled in the *P*6/*m* space group and minimized using the universal force field (UFF) in the Forcite module. PXRD patterns were simulated from the model using the Reflex module. Shown below are expanded views of HEX-COF 1 with the lattice boundaries.

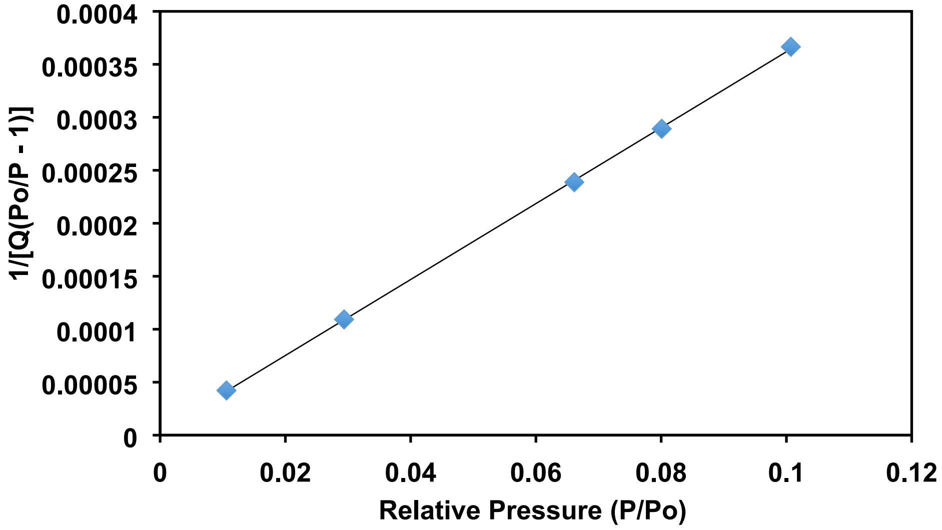




7. Porosity parameters

	BET (m^2/g)	Langmuir (m^2/g)	t-plot micropore area (m^2/g)	Horvath - Kawazoe pore volume (cm^3/g)
HEX-COF 1	1214	1314	863	0.62

BET Plot for HEX-COF 1



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