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Poly-Functional Porous-Organic Polymers to access Functionality–CO_2 Sorption Energetics Relationships

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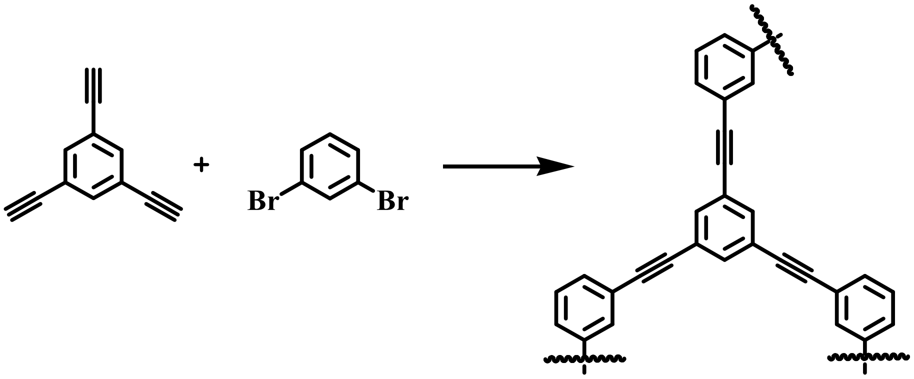
Experimental Procedures

All reagents were used as received without further purification. Solvents, catalysts, and common chemicals were purchased from Sigma-Aldrich or Fisher Scientific-UK. Brominated aromatics were purchased from Combi-Blocks. Triethynylbenzene was purchased from Alfa-Aesar. Nitrogen and CO_2 gases for sorption were purchased from Airliquide (N_2 AlphaGaz2 (99.999%) and CO_2 (99.995%)). Gas sorption analysis was performed on Micromeretics **ASAP2020 and the** variable temperature CO_2 isotherms were recorded in insulated dewar connected to **LAUDA RA-8** circulating chiller. The apparent surface areas were determined from the nitrogen adsorption isotherms collected at 77 K by applying the Brunauer-Emmett-Teller (BET) and Langmuir models. Pore size analyses were performed using a slit NLDFT pore model system by assuming a carbon finite pores surface. The determination of the isosteric heats of adsorption (Qst) for CO_2 was estimated by applying the Clausius-Clapeyron expression using the sorption isotherms measured at variable temperatures. UV-Vis spectra were acquired on ThermoScientific **Evolution 600** UV-Vis spectrophotometer equipped with integrating sphere for solids. CHN elemental analyses were conducted on ThermoScientific **Flash 2000**. Infra-red absorption spectra were recorded on ThermoScientific **Nicolet is-10**. Thermogravimetric analyses were conducted on Thermal Analysis-**Q50**.

For comparative analysis we run the solid state NMR spectra under the sample experimental and instrumental conditions. All NMR experiments were conducted using a 400 MHz SS NMR AVANCE III spectrometer. 13C CP MAS NMR spectra were recorded at a resonance frequency of 100.622 MHz under 12 kHz pining rate using a triple-resonance 4 mm Bruker MAS probe (BrukerBioSpin, Rheinstetten, Germany). The temperature for all experiments was maintained at 298 K. The cross-polarization CP contact time was set to 2 ms employing ramp100 for variable amplitude CP. To achieve a sufficient signal-to-noise ratio in a reasonable amount of time, 12 k transients and 24 k were collected with 7 s recycle delay. Exponential line broadening of 10 Hz applied before Fourier Transformation. Bruker Topspin 3.0 software was used for data collection and for spectral analysis.

Isosteric heats of adsorption. Isosteric heats of adsorption (Qst) were derived from the adsorption data at various temperature using Clausius-Clapeyron equation.

POP_1



In a glass pressure vessel fitted with teflon screw cap (50 mL) charged with a magnetic stirrer a mixture of dry DMF (10 mL) and triethylamine (3 mL) was prepared. The vessel was capped with silicon septum, and the solvent mixture was evacuated and backfilled with nitrogen three times through a needle, then was kept under nitrogen for 10 min. To this mixture and under nitrogen atmosphere was added **1,3-dibromobenzene** (0.54 mmol, 0.127 g), **1,3,5-triethynylbenzene** (0.5 mmol, 0.075 g.), **bis(triphenylphosphine)palladium(II) dichloride** (0.014 mmol, 10 mg), **triphenylphosphine** (0.02 mmol, 0.005 g) and CuI (0.03 mmol, 0.006 g), the flask was then evacuated/backfilled with nitrogen and sealed and the mixture was stirred at 80 °C. After 48h at 80 °C a deep green-brownish precipitate was observed. The reaction was opened to air and the precipitate immediately filtered through a fritted funnel, washed with DMF, DCM, and MeOH. (don't allow to dry) and the solid was kept under MeOH for 4 days for guest exchange prior to gas sorption analysis. Portion of the solid was then transferred while wet to the gas sorption cell and degassed on the gas sorption analyzer by heating (10 ºC/min) to 120ºC under dynamic vacuum for 6 h, BET **S.A = 332 m^2/g**.

The total dry weight of the solid was found to be 0.108 g of deep brown solid (0.484 mmol, 96% yield based on 0.5 mmol of starting triethynylbenzene and product tentative formula $C_{18}H_7$ (Mol. Wt.: 223.25). Elemental Analysis: C, 65.8% (Calc. 96.84%); H, 3.04% (3.16%); N, 0.12% (0%). Note: Discrepancy between calculated and found elemental analysis could be explained in terms of formation of multiple oligomers of the polymer of different chain lengths/connectivity or due to air trapped inside the porous sample under analysis.

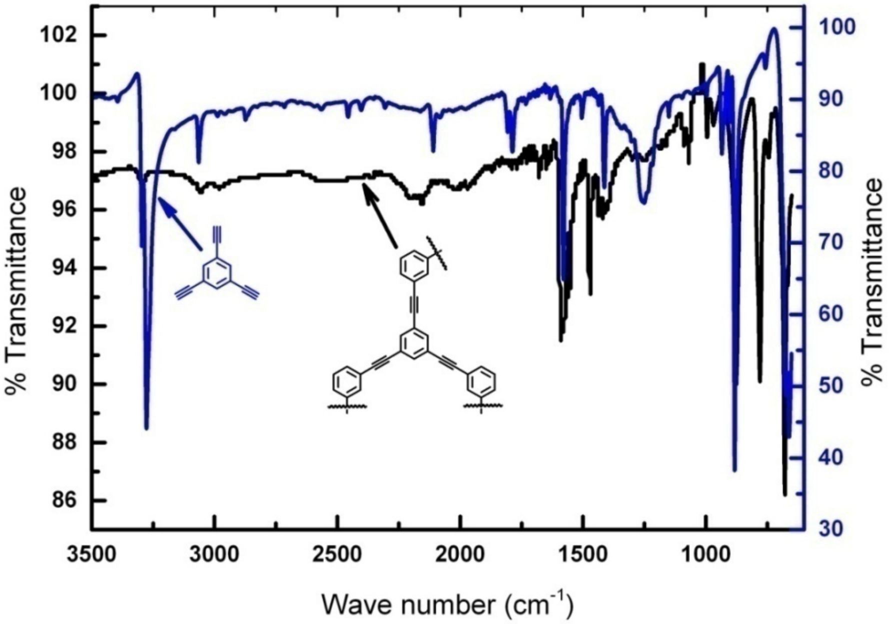


Figure S 1: FT-IR spectra for (1) and starting monomers.

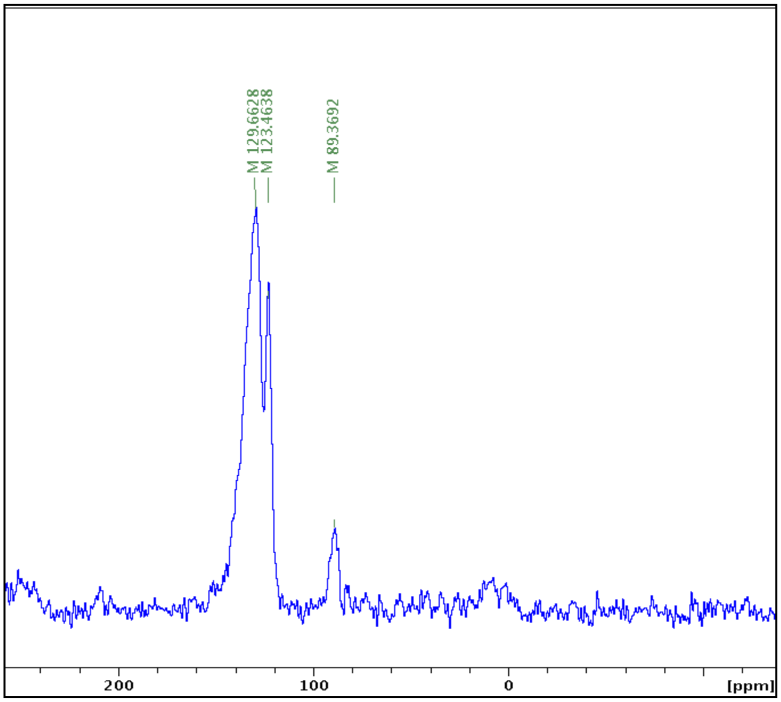


Figure S 2: ^{13}C-CPMAS-NMR spectrum for (1).

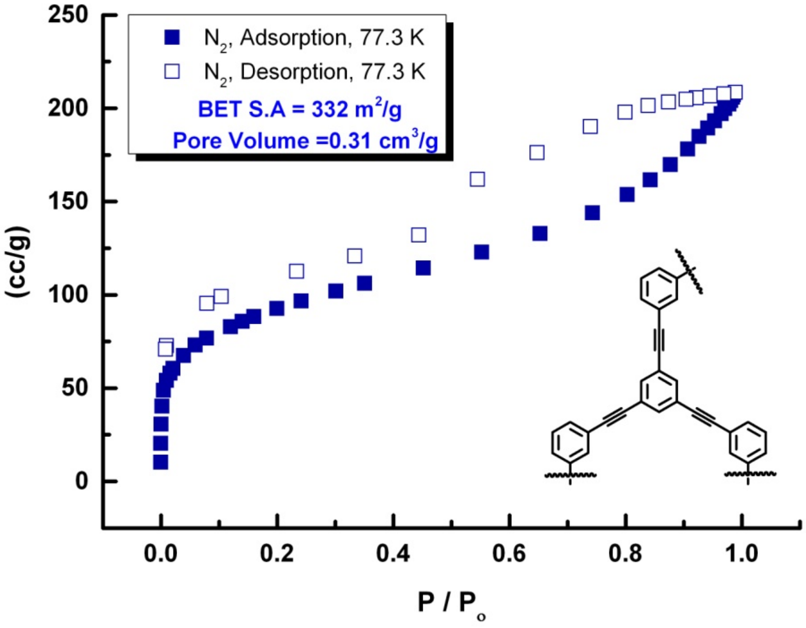


Figure S 3: Nitrogen sorption isotherm for (1)

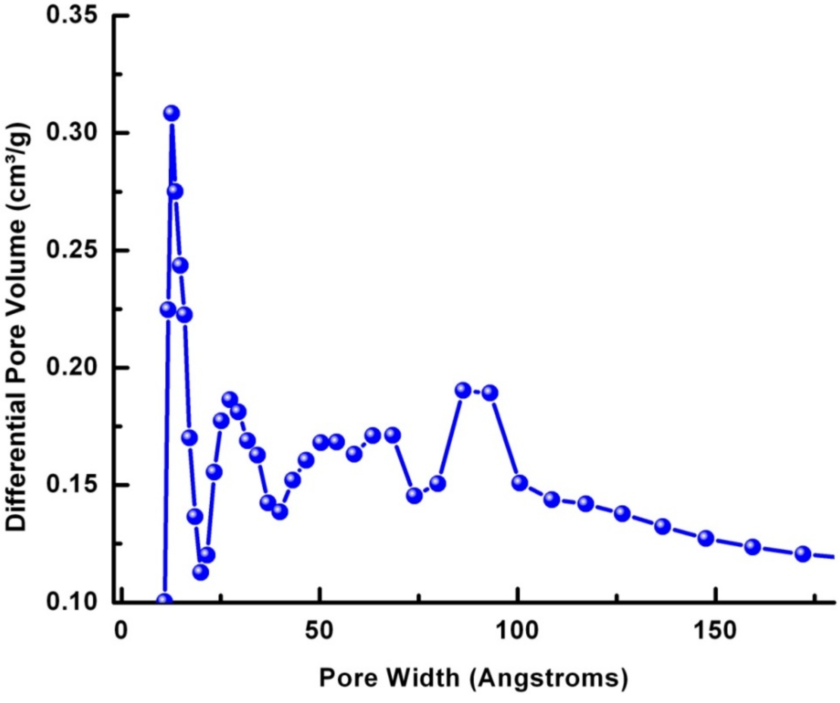


Figure S 4: Pore size distribution for (1)

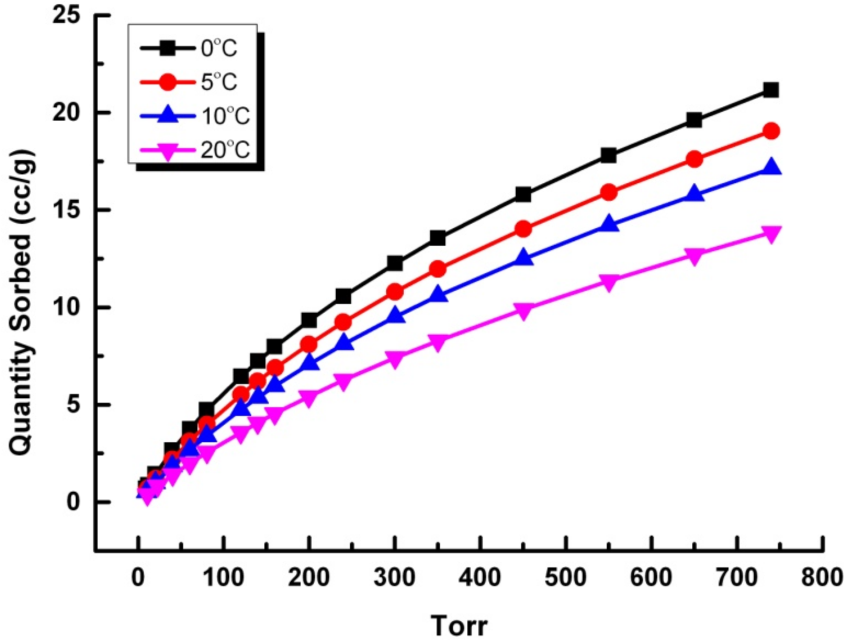
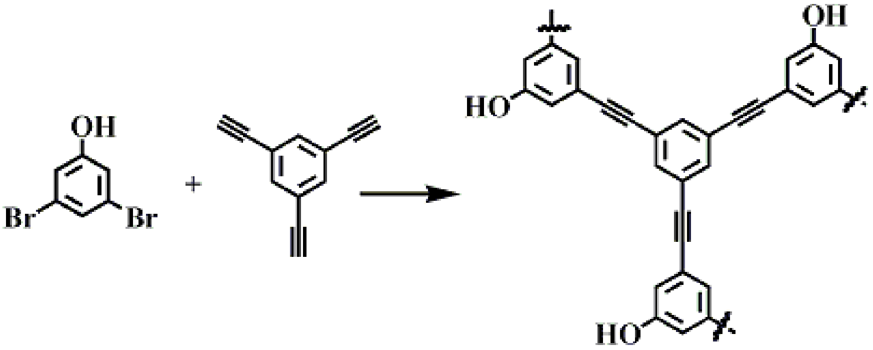


Figure S 5: CO_2 adsorption isotherms for (1)

POP_2:



In a glass pressure vessel fitted with teflon screw cap (50 mL) charged with a magnetic stirrer a mixture of dry DMF (10 mL) and triethylamine (3 mL) was prepared. The vessel was capped with silicon septum, and the solvent mixture was evacuated and backfilled with nitrogen three times through a needle, then was kept under nitrogen for 10 min. To this mixture and under nitrogen atmosphere was added **3,5-dibromophenol** (0.5 mmol, 0.125 g), **1,3,5-triethynylbenzene** (0.5 mmol, 0.075 g.), **bis(triphenylphosphine)palladium(II) dichloride** (0.014 mmol, 10 mg), **triphenylphosphine** (0.02 mmol, 0.005 g) and **CuI** (0.03 mmol, 0.006 g), the flask was then evacuated/backfilled with nitrogen and sealed and the mixture was stirred at 80 °C for 48 h, a deep-brown precipitate was observed. The reaction was opened to air and filtered through a fitted funnel, washed with acetone, water, acetone, then with DCM (don't allow to dry) and the solid was kept under MeOH for one week for guest exchange prior to gas sorption analysis. The MeOH exchanged solid was subsequently degassed by heating (10 ºC/ min) to 120ºC under dynamic vacuum for 4 h at the gas sorption analyzer, BET **S.A = 293 m^2/g**.

The total dry weight of the solid was found to be 0.06 g of deep brown solid (0.25 mmol, 50% yield based on 0.5 mmol of starting triethynylbenzene and product tentative formula $C_{18}H_7O$, Mol. Wt.: 239.25. Elemental Analysis: C, 68.51% (Calc. 90.36%); H, 3.78% (2.95%); N, 0.57% (0%). Note: Discrepancy between calculated and found elemental analysis could be explained in terms of formation of multiple oligomers of the polymer of different chain lengths/connectivity or due to air trapped inside the porous sample under analysis.

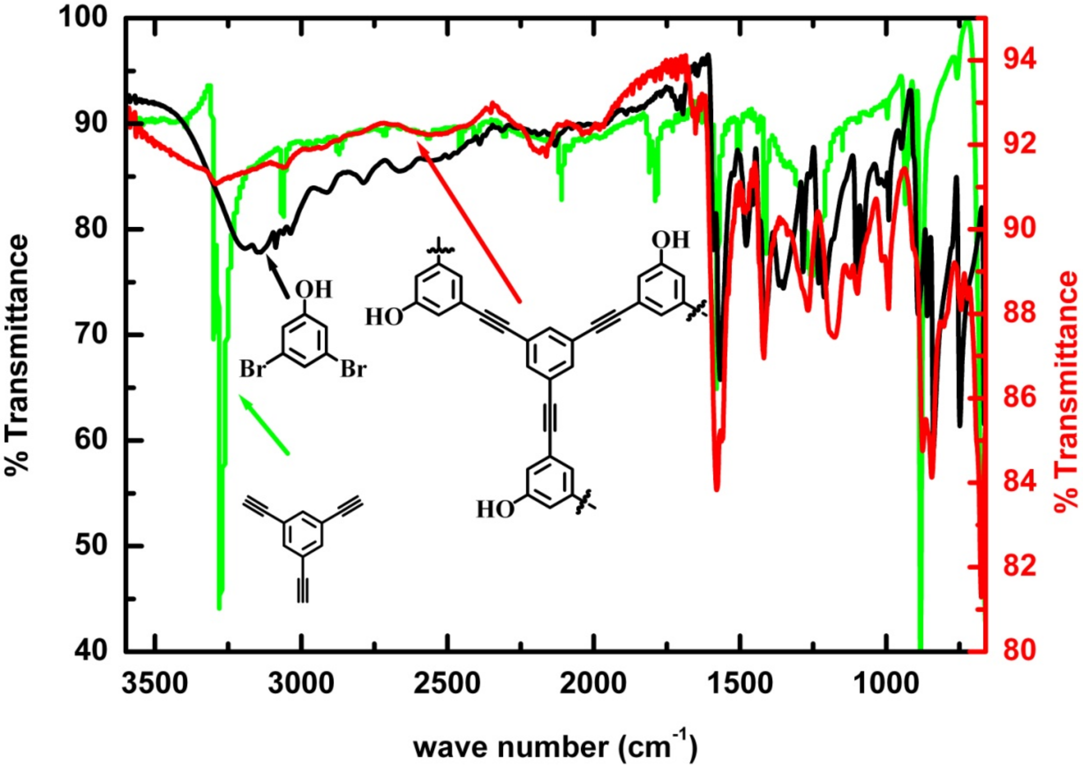


Figure S 6: FT-IR spectra for (2) and starting monomers.

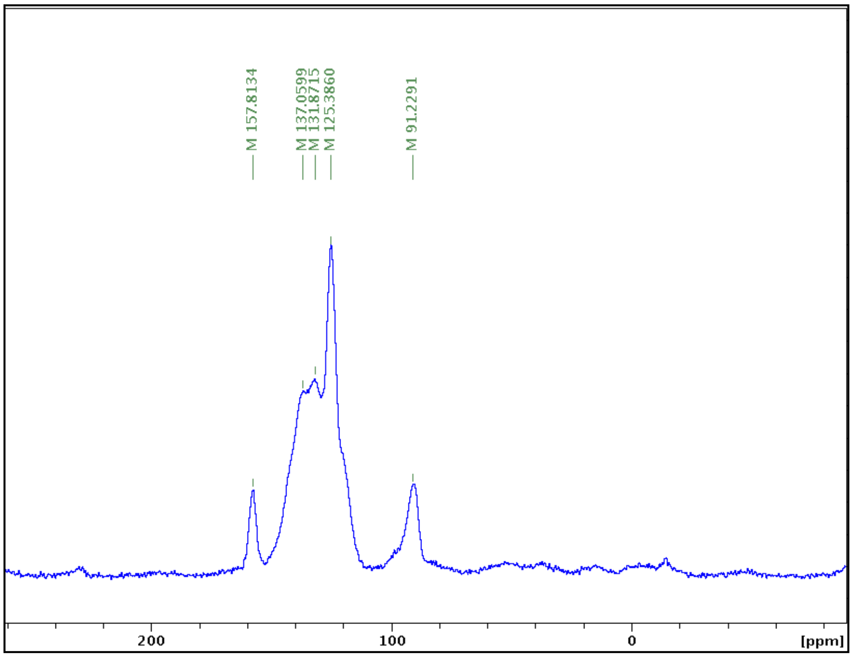


Figure S 7: ^{13}C-CPMAS-NMR spectrum for (2).

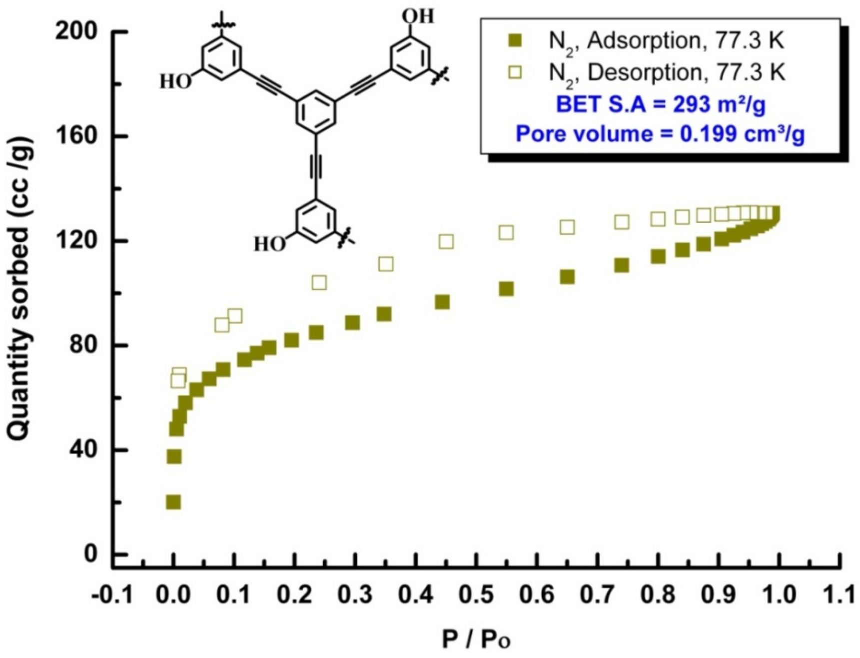


Figure S 8: Nitrogen sorption isotherm for (2)

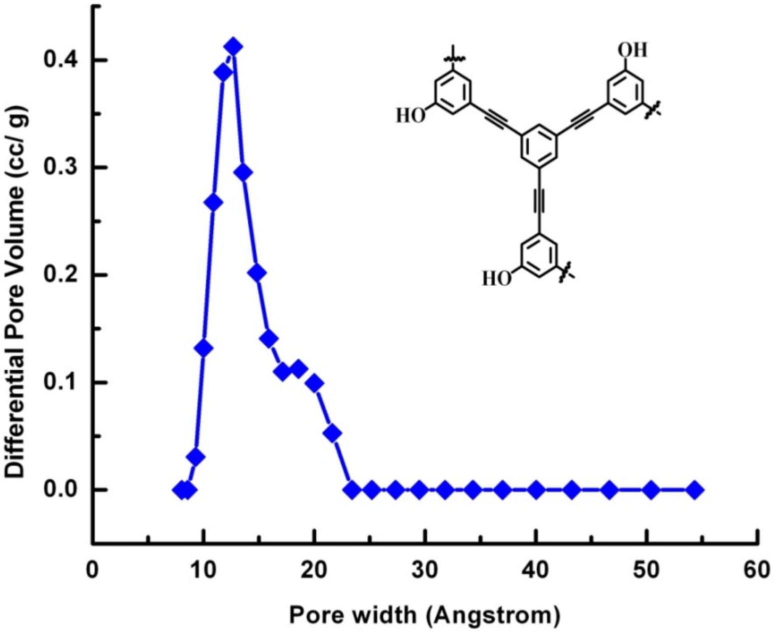


Figure S 9: Pore size distribution for (2)

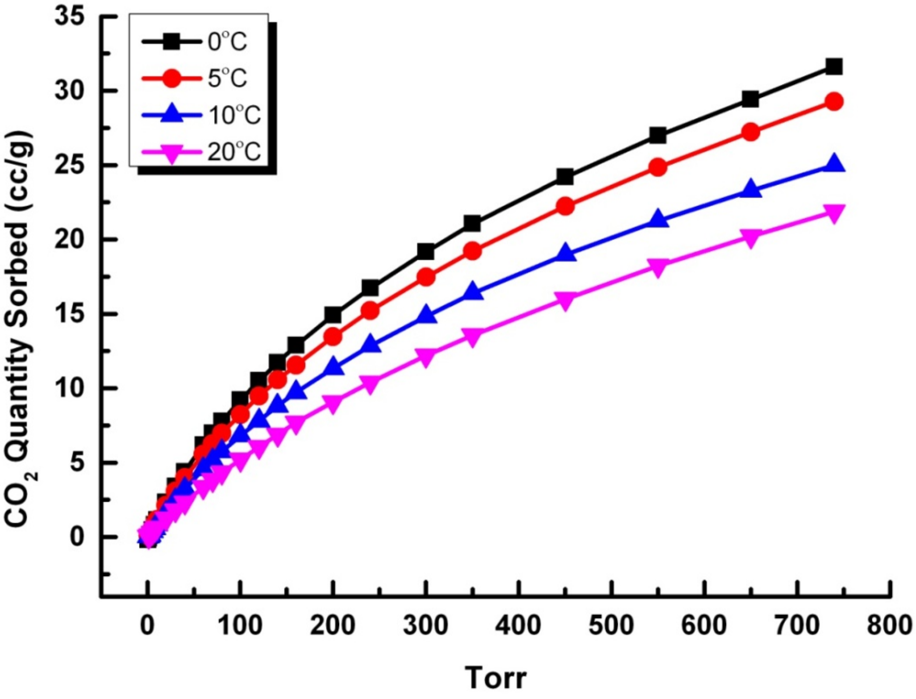
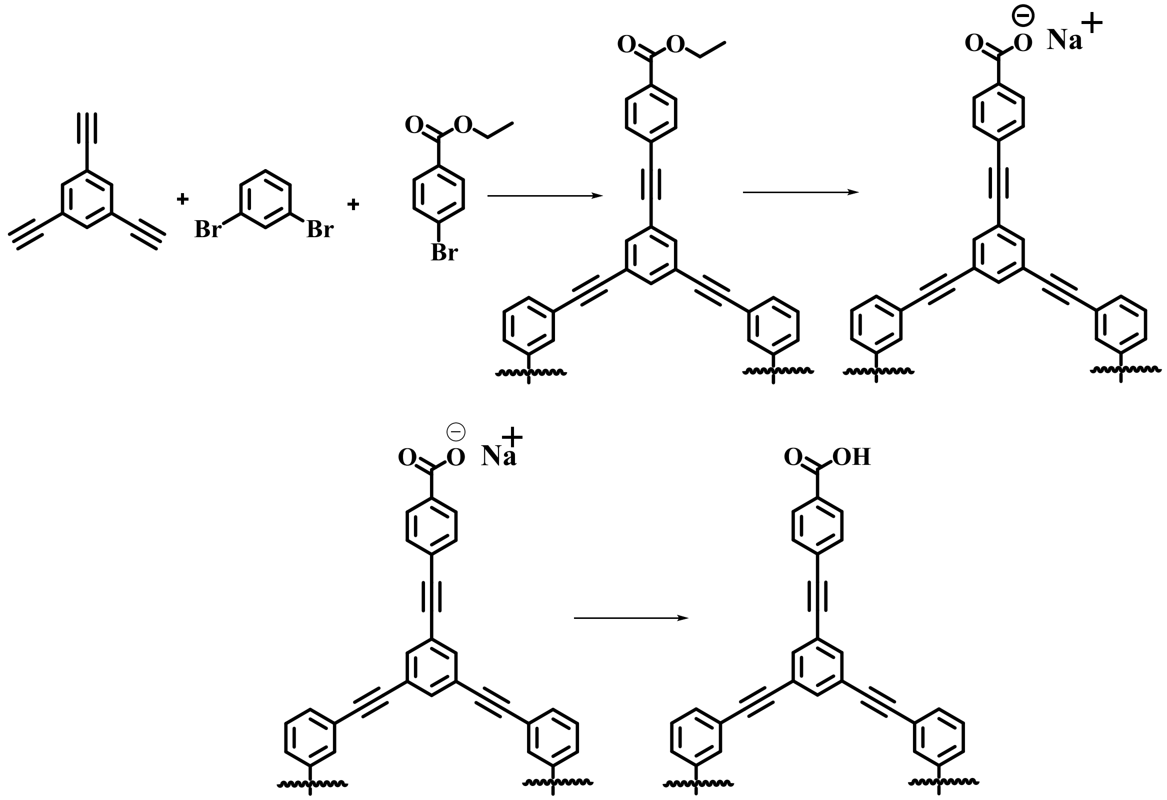


Figure S 10: CO$_2$ adsorption isotherms for (2)

POP_3:



In a glass pressure vessel fitted with teflon screw cap (100 mL) charged with a magnetic stirrer a mixture of dry DMF (20 mL), triethylamine (5 mL), **1,3-Dibromobenzene** (0.62 mmol, 0.146 g), and **ethyl-4-bromobenzoate** (0.63 mmol, 0.144 g) was prepared. The vessel was capped with silicon septum and immersed in liquid nitrogen bath and the mixture was subjected to three freeze-pump-thaw cycles and backfilled with nitrogen. To this mixture and under nitrogen atmosphere was added **1,3,5-triethynylbenzene** (1 mmol, 0.15 g.), **bis(triphenylphosphine) palladium(II) dichloride** (0.028 mmol, 20 mg), **triphenylphosphine** (0.04 mmol, 0.011 g) and **CuI** (0.057 mmol, 11 mg), the flask was then evacuated/backfilled with nitrogen and sealed and the mixture was stirred at 80 °C for 48 h, a dark brown solution with no precipitate was observed. The vessel was opened under nitrogen and extra **1,3,5-triethynylbenzene** (0.2 mmol, 0.03 g.) was added and the vessel sealed again and placed in oil bath at 80 °C for 24 h, a deep brown precipitate formed. The reaction was opened to air and filtered through a fritted funnel, washed with DMF/ Acetone/ MeOH/ DCM then kept under MeOH. Elemental Analysis: C, 77.91% (Calc. 88.37); H, 4.39% (4.495%); N, 0.867% (0%). Note: Discrepancy between calculated and found elemental analysis could be explained in terms of formation of multiple oligomers of the polymer of different chain lengths/connectivity or due to air trapped inside the porous sample under analysis.

To hydrolyze the ester, approximately half of the pristine solid was suspended in a round bottom flask in 20 mL H_2O and NaOH (4 mmol, 0.16 g) was added, the mixture was kept stirred at 80 °C for 24h, filtered, washed with deionized water and kept in water for 24h before soaking in MeOH for solvent exchange. The FT-IR spectra confirmed the progress of the hydrolysis step as evident from decreased absorbance for the ester carbonyl at $\nu_{C=O}$ = 1716 cm^{-1} among other changes (figure S9). The solid-state NMR spectrum of the solid indicated presence of the carbonyl carbon (δ = 164.9 ppm) with residual ester groups as evident from the low intensity for the peaks (δ ~13, 60 ppm for the ethyl group). Moreover, conversion into the free acid form can be readily accomplished by soaking the sodium salt of the polymer into 1M HCl at 80°C for 4 hours, see IR spectra below. After soaking into the acid solution, the solid was filtered, washed with deionized water, then MeOH, prior to degassing on the gas sorption analyzer by heating (10 ºC/min) to 120ºC under dynamic vacuum for 4 h, BET **S.A = 532 m^2/g**.

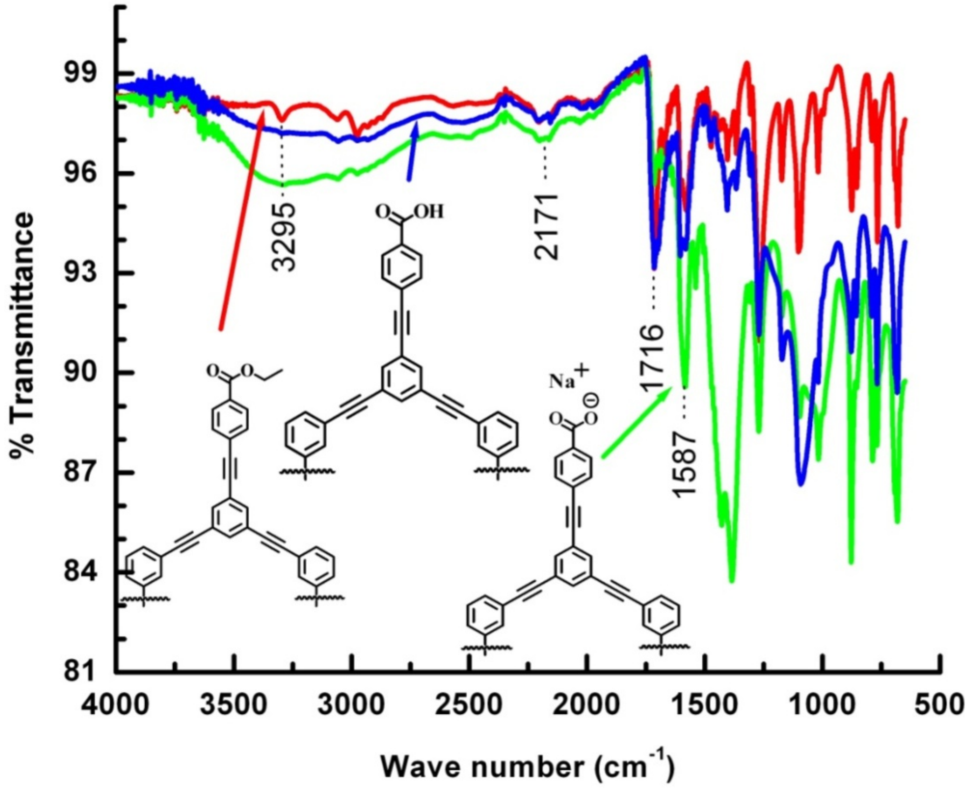


Figure S 11: FT-IR spectra for (3), the conjugate base, and starting ester.

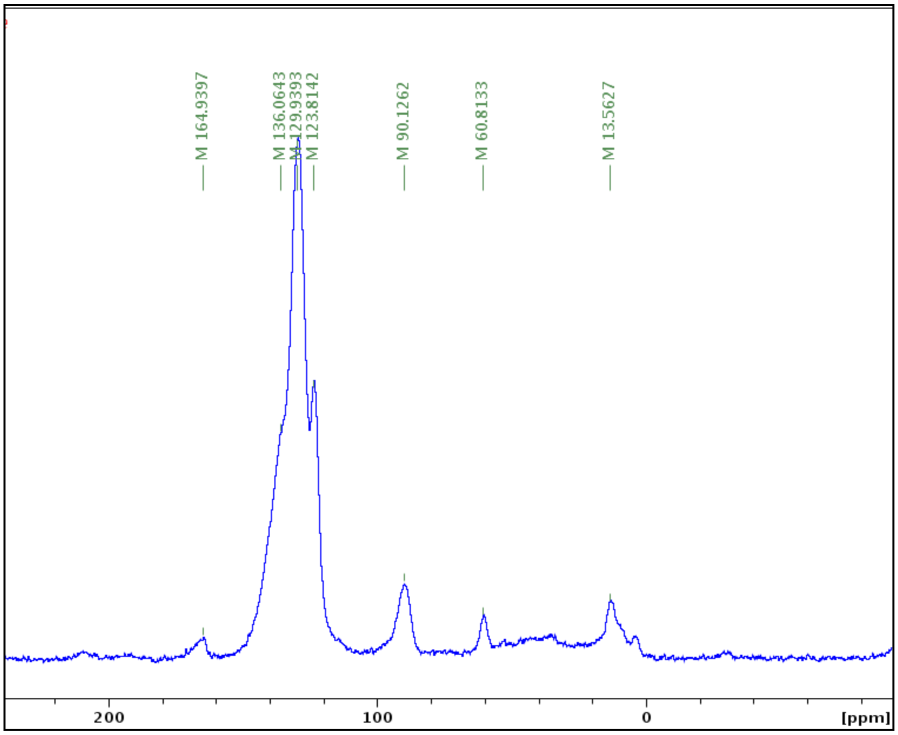


Figure S 12: ^{13}C-CPMAS-NMR spectrum for (3).

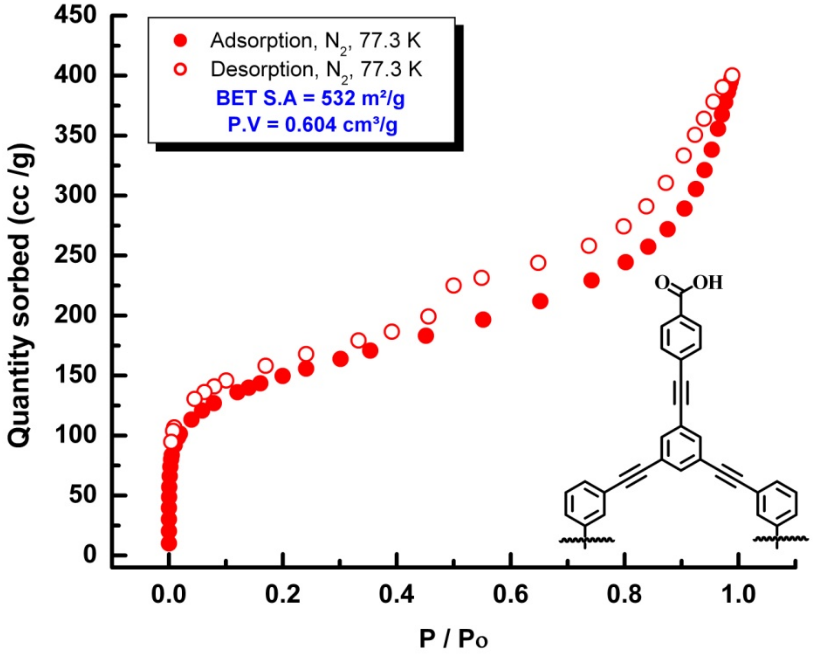


Figure S 13: Nitrogen sorption isotherm for (3)

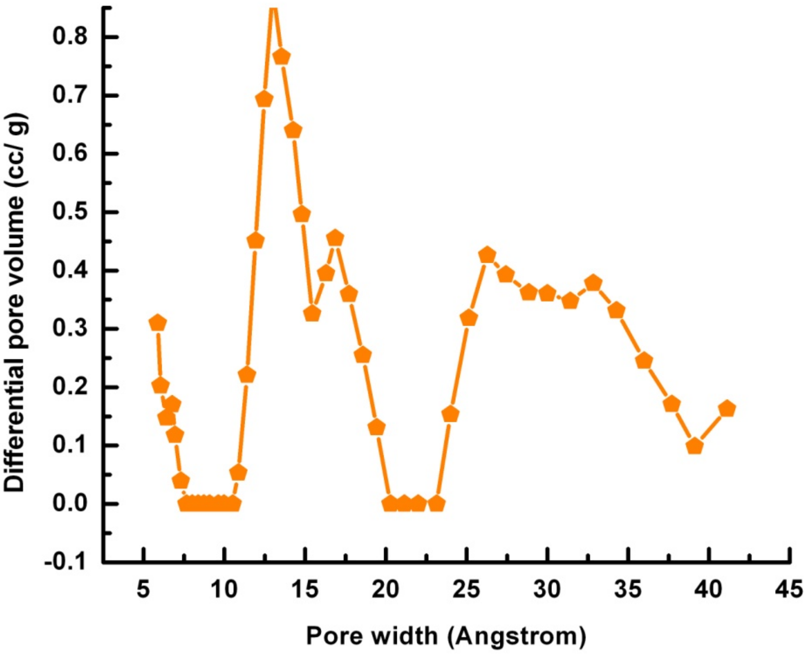


Figure S 14: Pore size distribution for (3)

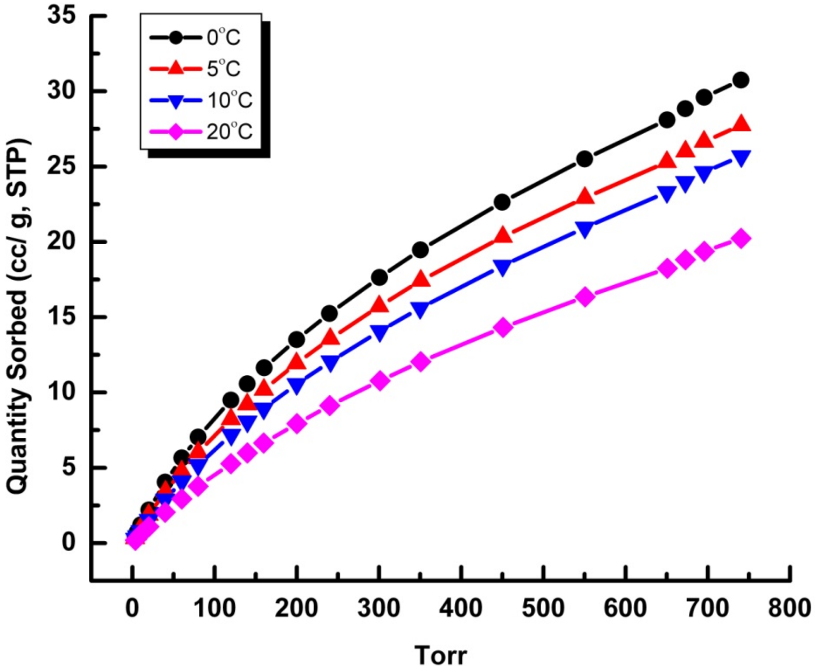


Figure S 15: CO_2 adsorption isotherms for (3)

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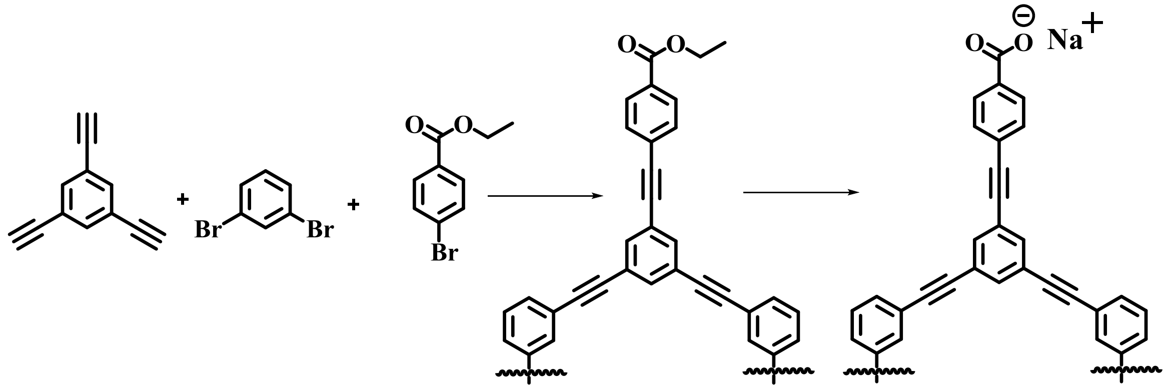


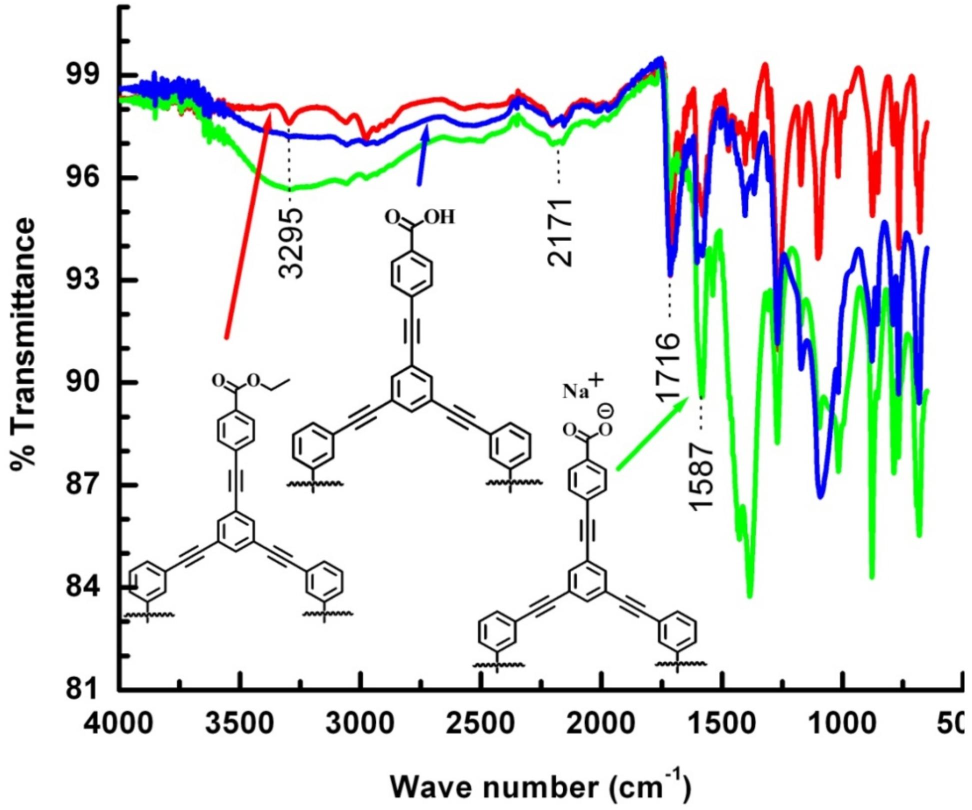


Figure S 16: FT-IR spectra for (4) and starting free acid polymer.

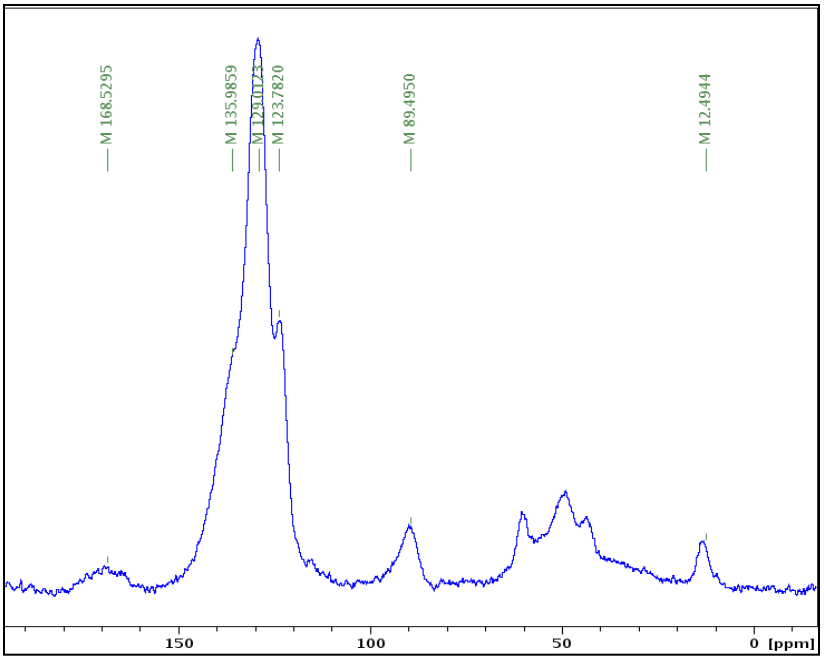


Figure S 17: ^{13}C-CPMAS-NMR spectrum for (4).

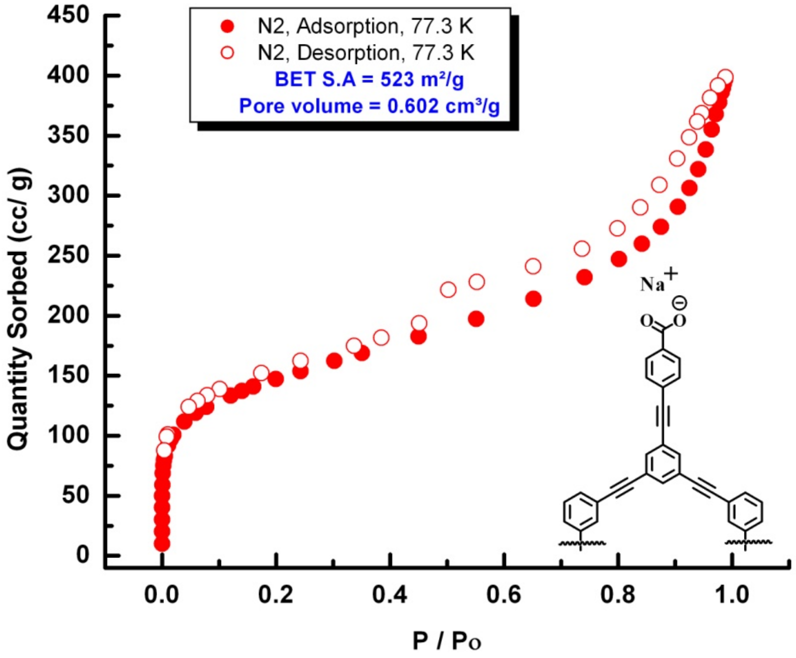


Figure S 18: Nitrogen sorption isotherm for (4)

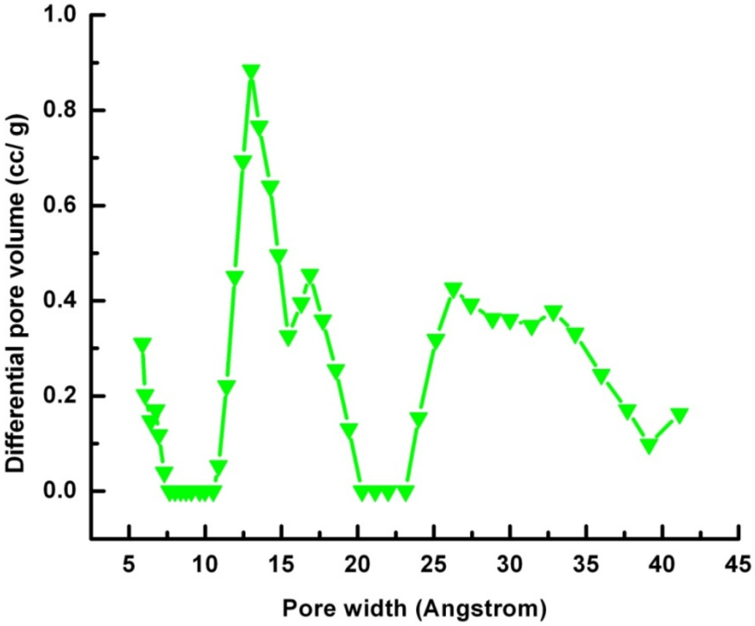


Figure S 19: Pore size distribution for (4)

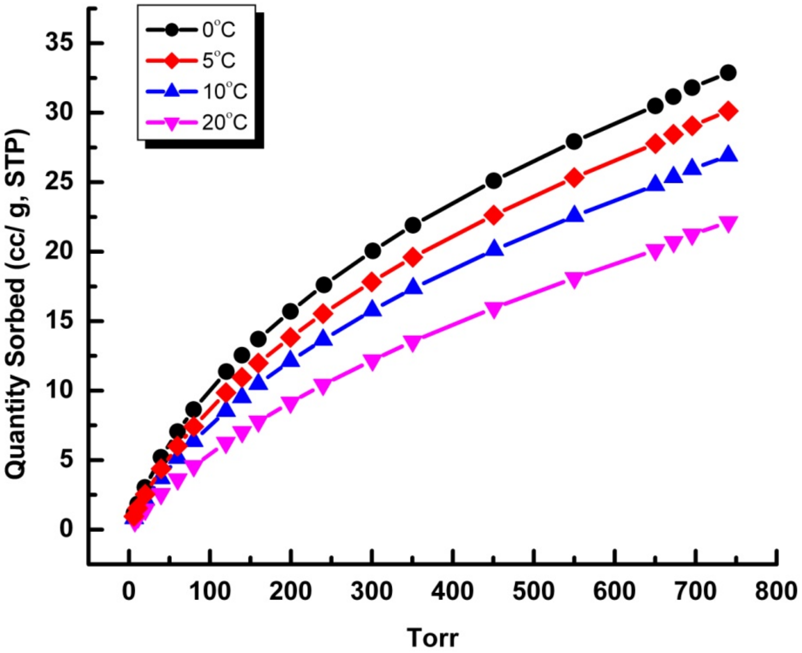
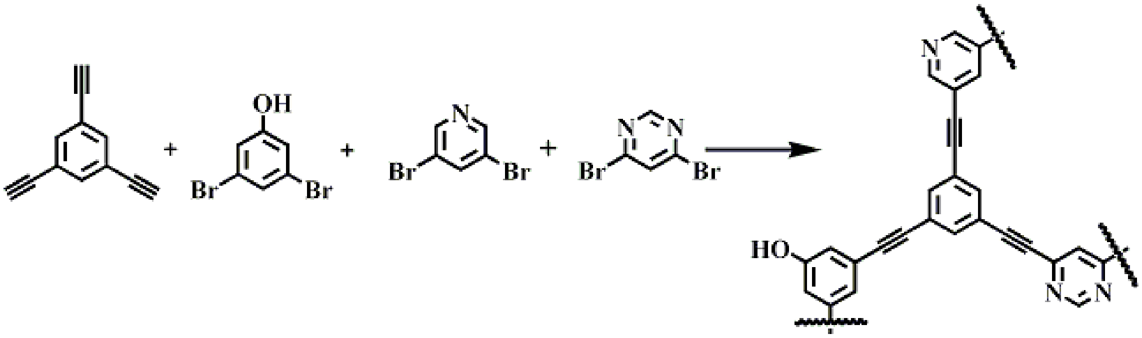


Figure S 20: CO_2 adsorption isotherms for (4)

POP_5



In a glass pressure vessel fitted with teflon screw cap (50 mL) charged with a magnetic stirrer a mixture of dry DMF (10 mL) and triethylamine (3 mL) was prepared. The vessel was capped with silicon septum, and the solvent mixture was evacuated and backfilled with nitrogen three times through a needle, then was kept under nitrogen for 10 min. To this mixture and under nitrogen atmosphere was added **3,5-Dibromophenol** (0.25 mmol, 0.062 g), **3,5-dibromopyridine** (0.25 mmol, 0.059 g), **4,6-dibromopyrimidine** (0.25 mmol, 0.059 g), **1,3,5-triethynylbenzene** (0.75 mmol, 0.120 g.), **bis(triphenylphosphine)palladium(II) dichloride** (0.028 mmol, 20 mg), **triphenylphosphine** (0.04 mmol, 0.011 g) and CuI (0.057 mmol, 11 mg), the flask was then evacuated/backfilled with nitrogen and sealed and the mixture was stirred at 80 °C for 30 h, a dark brown precipitate was observed. The reaction was opened to air and filtered through a fritted funnel, washed with DCM (Note: the solid floats in DCM indicating lower density than that of DCM) then with MeOH (don't allow to dry). The solid was then filtered and washed with MeOH and kept under MeOH for 4 days, refreshed every 24h. Portion of the solid was then degassed briefly under reduced pressure before submission for gas sorption analysis. The solid was degassed on the gas sorption analyzer by heating (10 ºC/min) to 120ºC under dynamic vacuum for 4 h at the gas sorption analyzer, BET **S.A = 686 m^2/g**. The total dry weight of the solid was found to be 0.116 g of brown solid (0.49 mmol, 66% yield based on starting triethynylbenzene and a tentative average formula ($C_{17}H_6N$/ $C_{16}H_5N_2$/ $C_{19}H_7O$, Average Mol. Wt.: 233.57). Elemental Analysis: C, 70.86% (Calc.82.22~91.06%); H, 3.74% (2.24~2.7%); N, 3.37% (0~12.44%). Note: Discrepancy between calculated and found elemental analysis could be explained in terms of formation of multiple oligomers of the polymer of different chain lengths/connectivity or due to air trapped inside the porous sample under analysis.

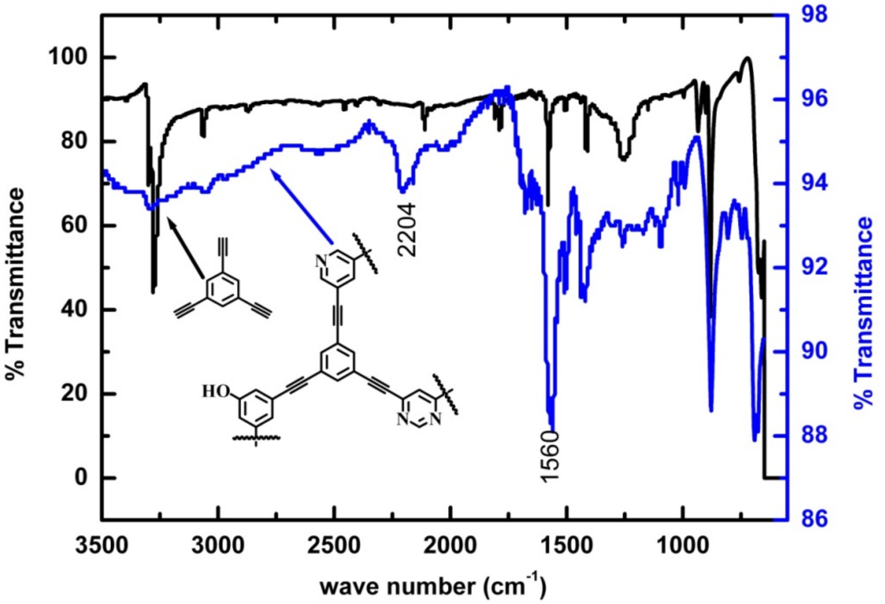


Figure S 21: FT-IR spectra for (5) and triethynylbenzene starting monomer.

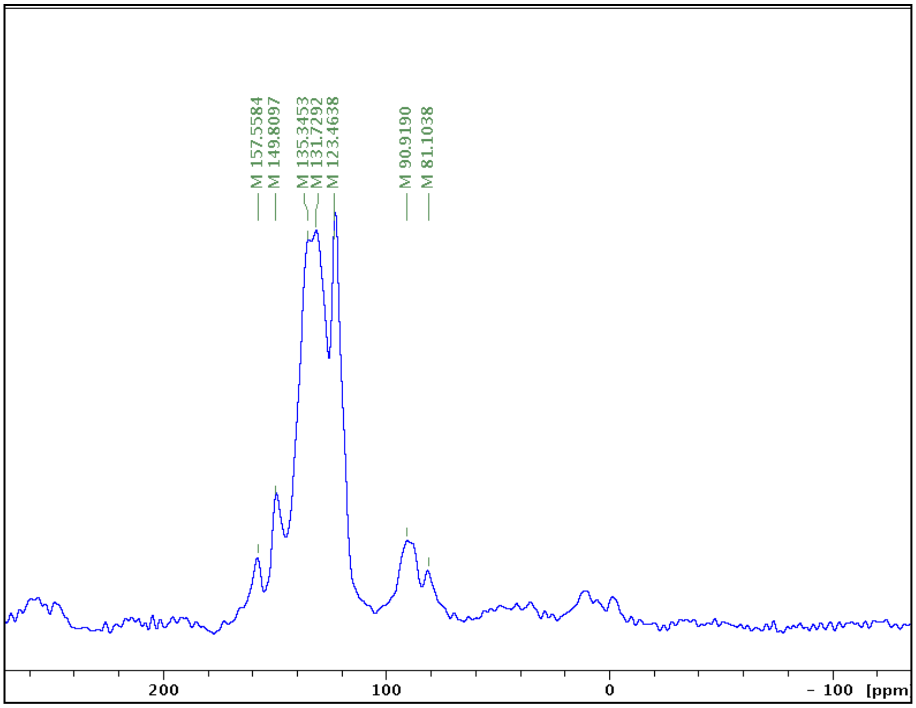


Figure S 22: ^{13}C-CPMAS-NMR spectrum for (5).

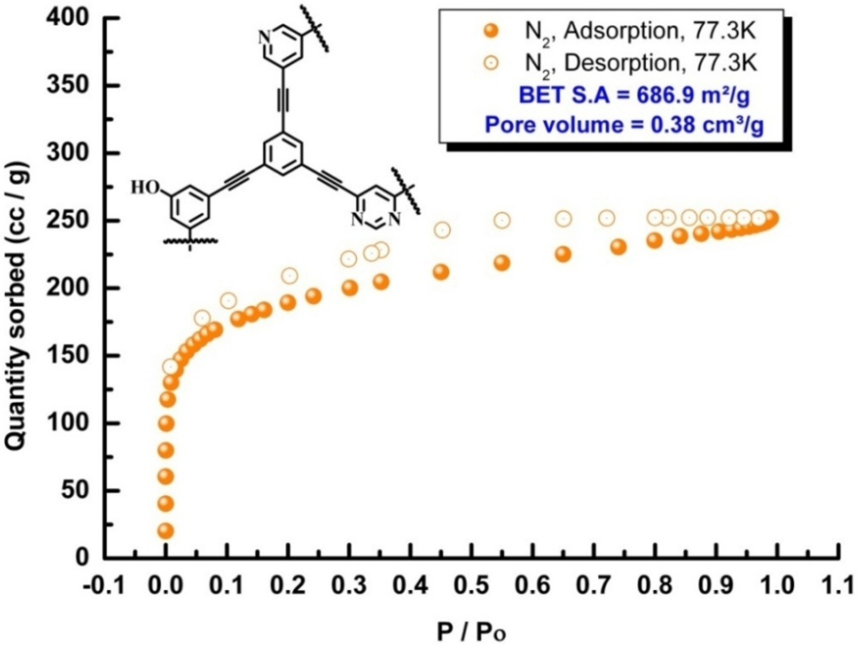


Figure S 23: Nitrogen sorption isotherm for (5)

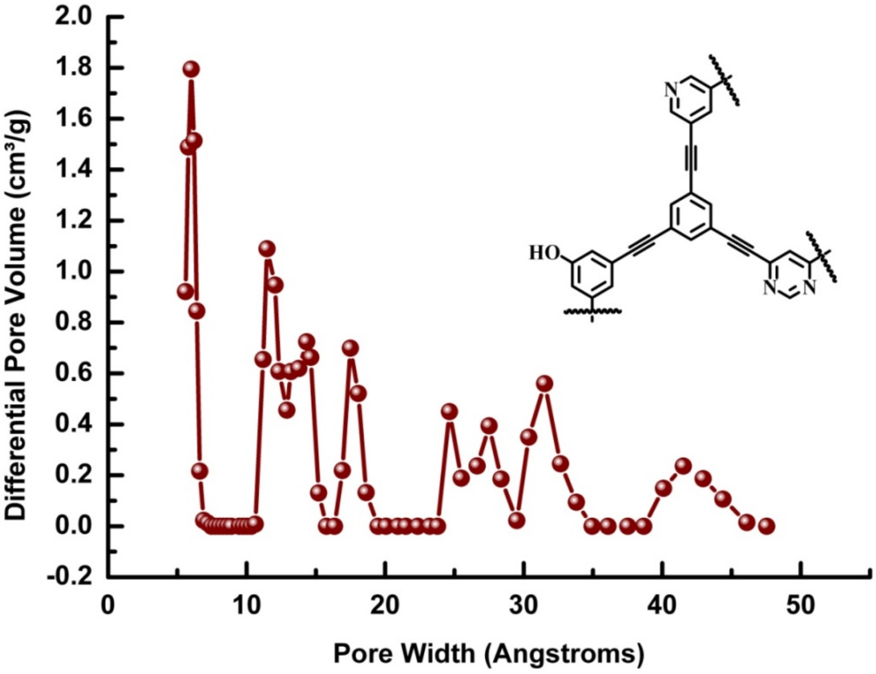


Figure S 24: Pore size distribution for (5)

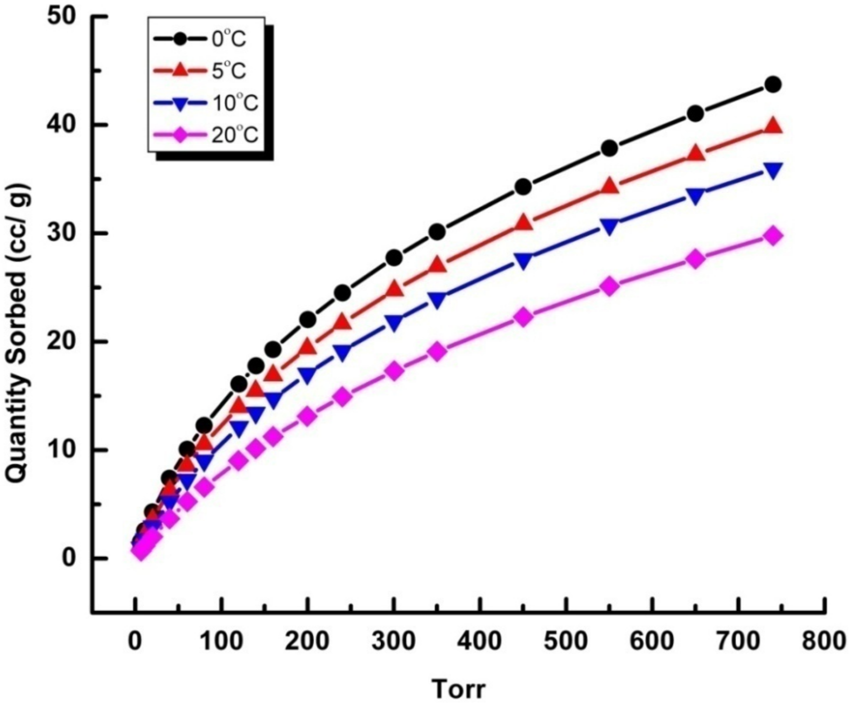
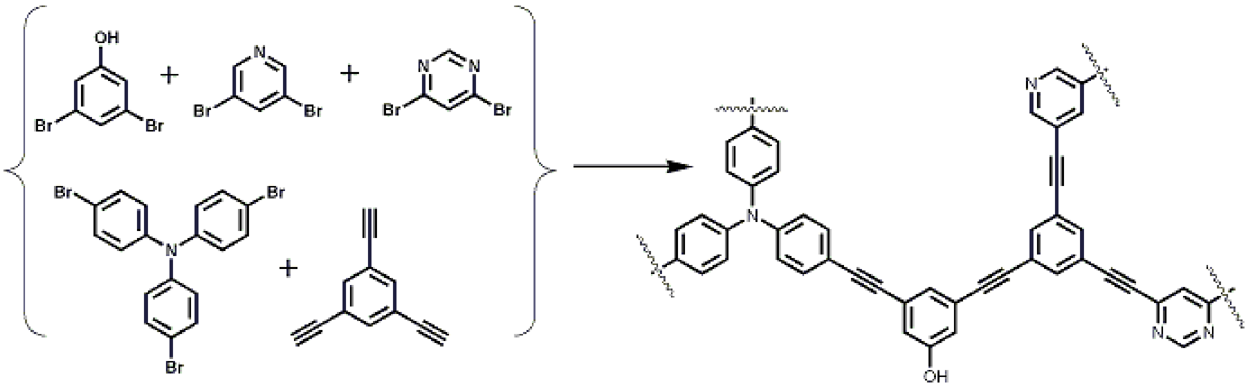


Figure S 25: CO_2 adsorption isotherms for (5)

POP_6:



In a glass pressure vessel fitted with teflon screw cap (50 mL) charged with a magnetic stirrer a mixture of dry DMF (10 mL) and triethylamine (3 mL) was prepared. The vessel was capped with silicon septum, and the solvent mixture was evacuated and backfilled with nitrogen three times through a needle, then was kept under nitrogen for 10 min. To this mixture and under nitrogen atmosphere was added **3,5-Dibromophenol** (0.2 mmol, 0.050 g), **3,5-dibromopyridine** (0.2 mmol, 0.047 g), **4,6-dibromopyrimidine** (0.2 mmol, 0.047 g), **tris-(4-bromophenyl)-amine** (0.1 mmol, 0.048g), **1,3,5-triethynylbenzene** (0.75 mmol, 0.112 g.), **bis(triphenylphosphine)palladium(II) dichloride** (0.028 mmol, 20 mg), **triphenylphosphine** (0.04 mmol, 0.011 g) and **CuI** (0.057 mmol, 11 mg), the flask was then evacuated/backfilled with nitrogen and sealed and the mixture was stirred at 80 °C for 12 h, a dark brown precipitate was observed. The reaction was opened to air and filtered through a fritted funnel, washed with DCM then with MeOH. The solid was then kept under MeOH in a sealed scintillation vial at 80ºC under autogenous pressure for 24h, filtered and submitted for gas sorption analysis

The sample was degassed by applying dynamic vacuum and heated gradually to 120ºC , held at this temperature for 4h prior to gas sorption measurements. The BET **S.A = 830 m^2/g**.

The total dry weight of the solid was found to be 0.098 g of brown solid (53% yield based on sum of masses of starting materials excluding bromine atoms) tentative formula ($C_{58}H_{30}N_4O$ Mol. Wt.: 798.88). Elemental Analysis: C, 68.88 % (calc. 87.20 %); H, 4.35 % (3.79 %); N, 4.08% (7.01%). Note: Discrepancy between calculated and found elemental analysis could be explained in terms of formation of multiple oligomers of the polymer of different chain lengths/connectivity or due to air trapped inside the porous sample under analysis.

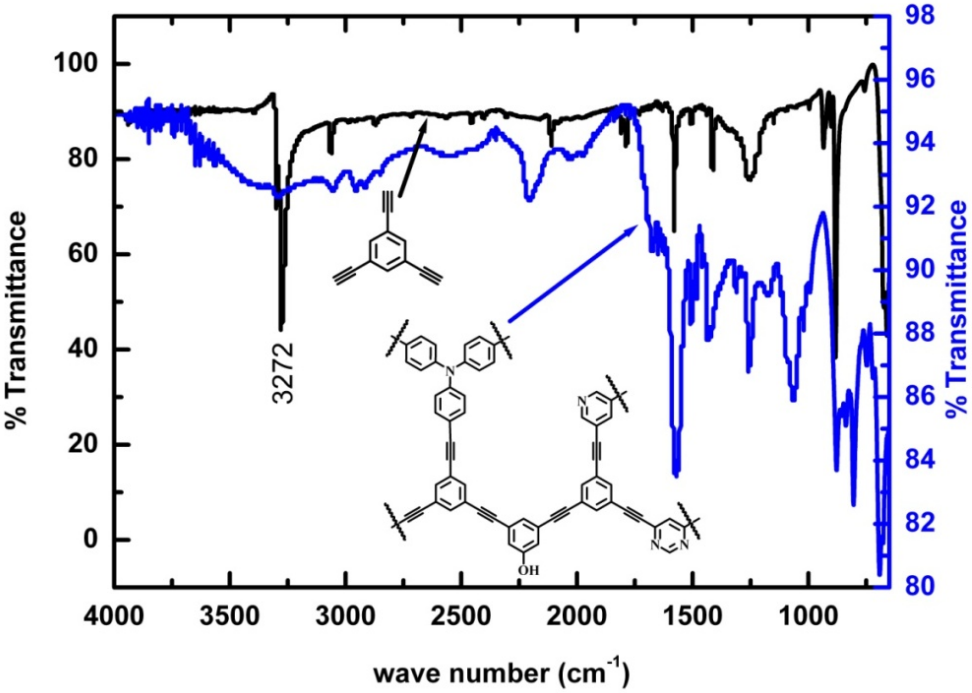


Figure S 26: FT-IR spectra for (6) and triethynylbenzene starting monomer.

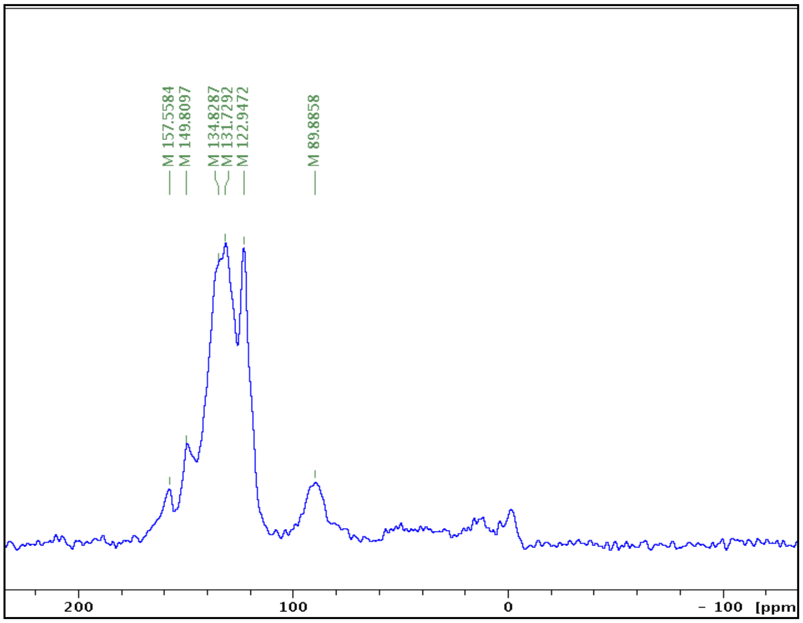


Figure S 27: ^{13}C-CPMAS-NMR spectrum for (6).

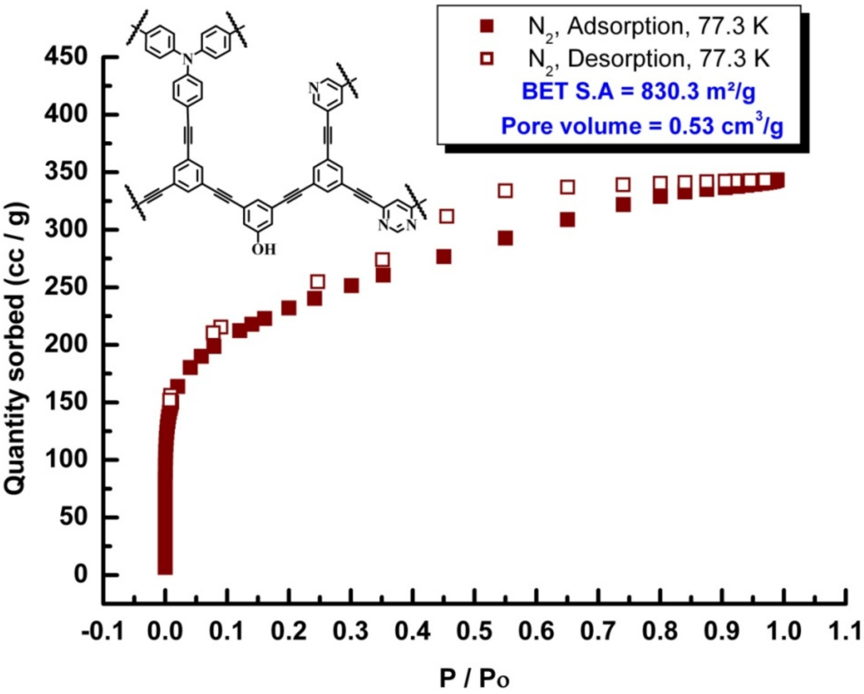


Figure S 28: Nitrogen sorption isotherm for (6)

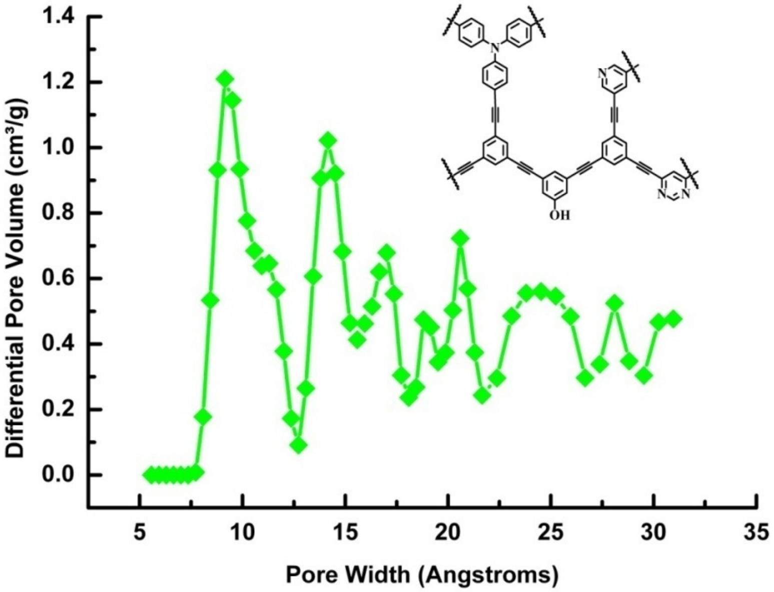


Figure S 29: Pore size distribution for (6)

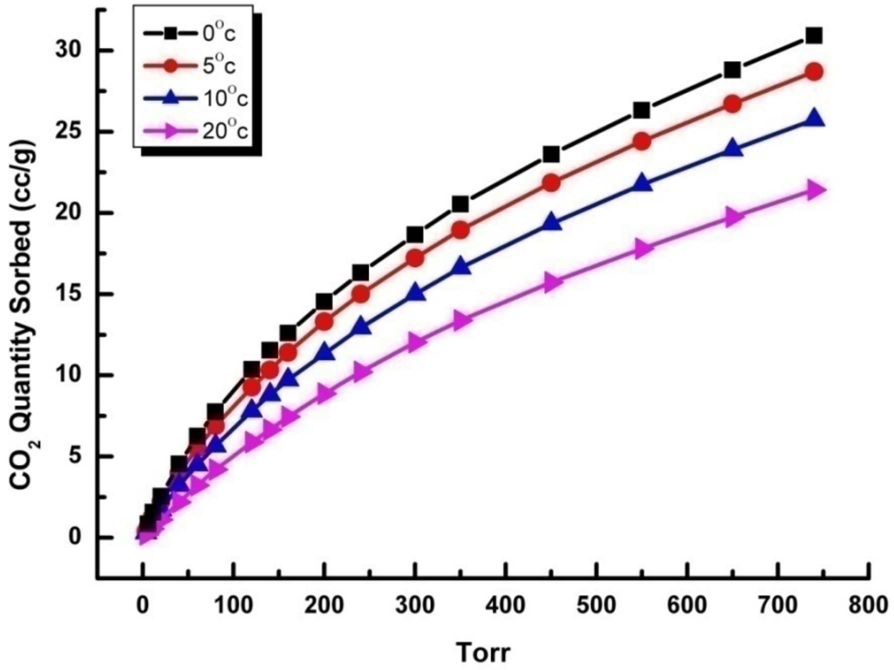
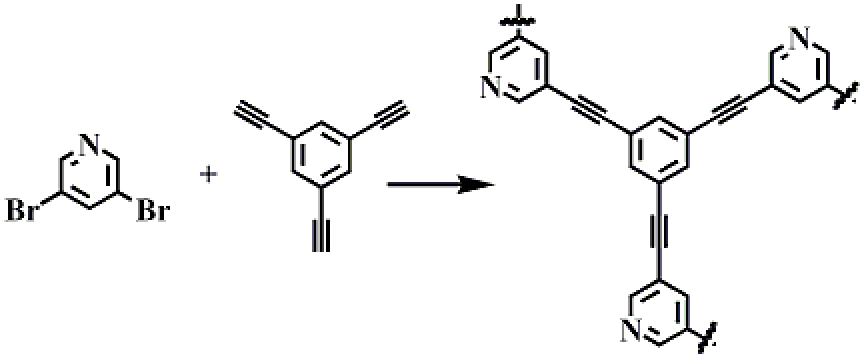


Figure S 30: CO_2 adsorption isotherms for (6)

POP_7:



In a glass pressure vessel fitted with teflon screw cap (50 mL) charged with a magnetic stirrer a mixture of dry DMF (10 mL) and triethylamine (3 mL) was prepared. The vessel was capped with silicon septum, and the solvent mixture was evacuated and backfilled with nitrogen three times through a needle, then was kept under nitrogen for 10 min. To this mixture and under nitrogen atmosphere was added **3,5-dibromopyridine** (0.75 mmol, 0.177 g), **1,3,5-triethynylbenzene** (0.5 mmol, 0.075 g.), **bis(triphenylphosphine)palladium(II) dichloride** (0.014 mmol, 10 mg), **triphenylphosphine** (0.02 mmol, 0.005 g) and **CuI** (0.03 mmol, 0.006 g), the flask was then evacuated/backfilled with nitrogen and sealed and the mixture was stirred at 80 °C for 24 h, a buff precipitate was observed. The reaction was opened to air and filtered through a fritted funnel, washed with acetone, water, acetone, then with DCM (don't allow to dry) and the solid was kept under DCM for one week for guest exchange prior to gas sorption analysis. Portion of the solid was then transferred while wet to the gas sorption cell, the cell then was immersed in liquid nitrogen briefly, removed from the LN_2 bath and the sample lyophilized by applying unrestricted vacuum on the sorption analyzer. After the sample reached room temperature, the solid was further degassed on the gas sorption analyzer by heating (10 ºC/min) to 120ºC under dynamic vacuum for 4 h, BET **S.A = 356 m^2/g**. Applying regular degassing procedure without prior lyophilization resulted in greatly reduced S.A.

The total dry weight of the solid was found to be 0.105 g of buff solid (0.47 mmol, 93% yield based on 0.5 mmol of starting triethynylbenzene and product tentative formula ($C_{17}H_6N$ Mol. Wt.: 224.24). Elemental Analysis: C, 74.71% (Calc. 91.06%); H, 3.38% (2.70%); N, 5.11% (6.25%). Note: Discrepancy between calculated and found elemental analysis could be explained in terms of formation of multiple oligomers of the polymer of different chain lengths/connectivity or due to air trapped inside the porous sample under analysis.

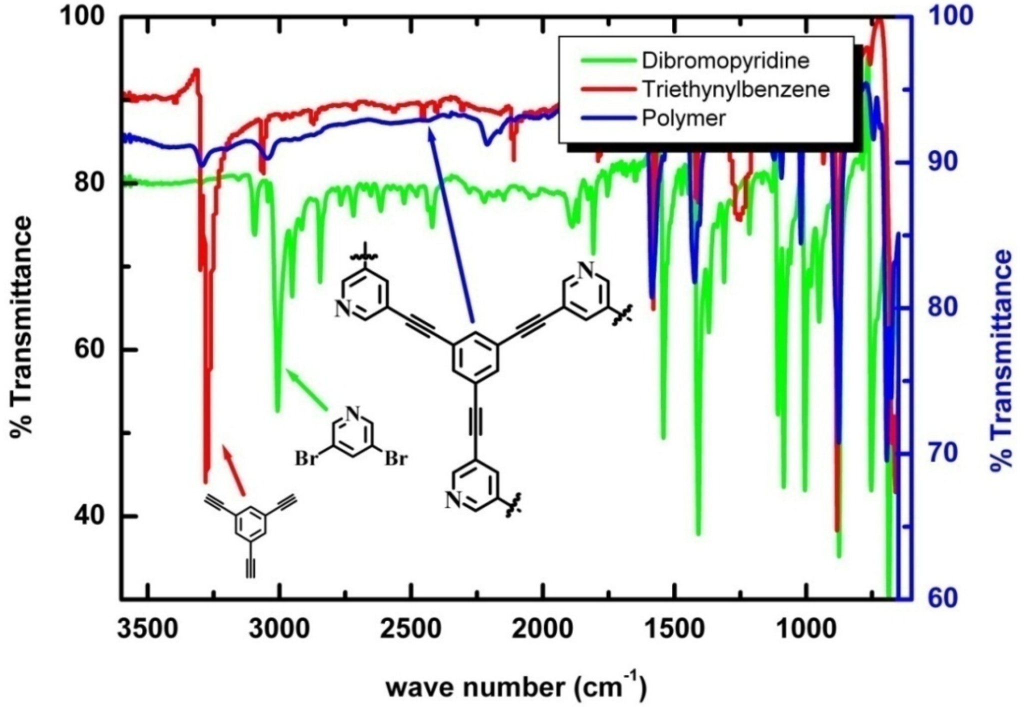


Figure S 31: FT-IR spectra for (7) and starting monomers.

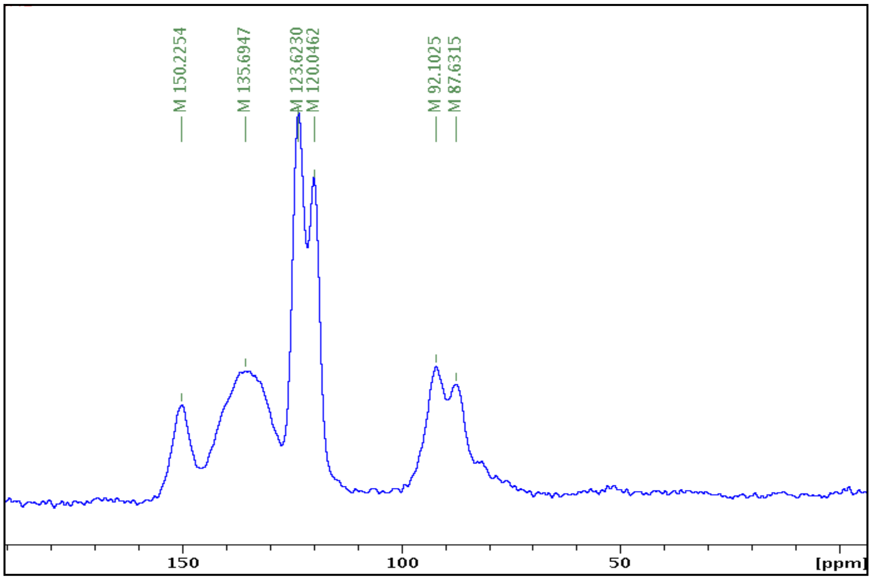


Figure S 32: ^{13}C-CPMAS-NMR spectrum for (7).

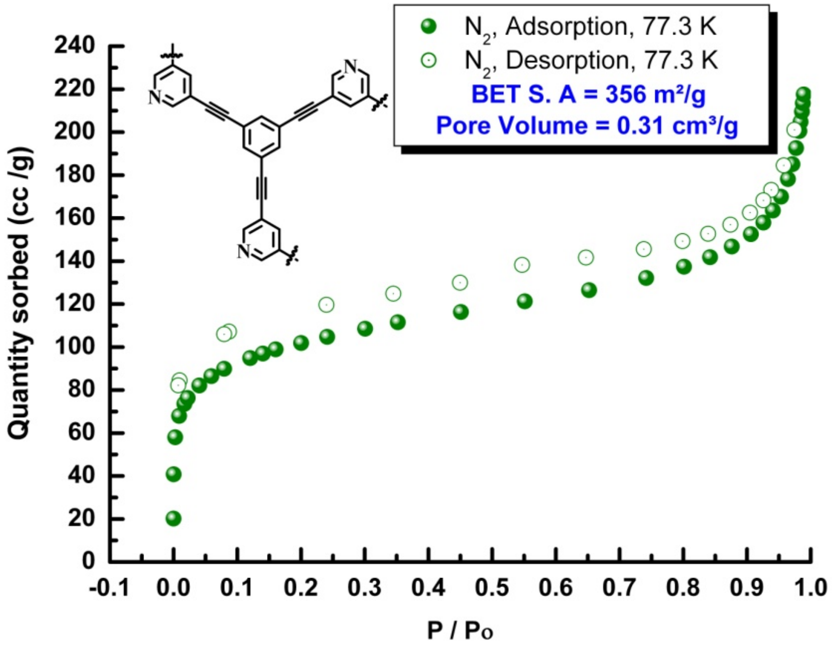


Figure S 33: Nitrogen sorption isotherm for (7)

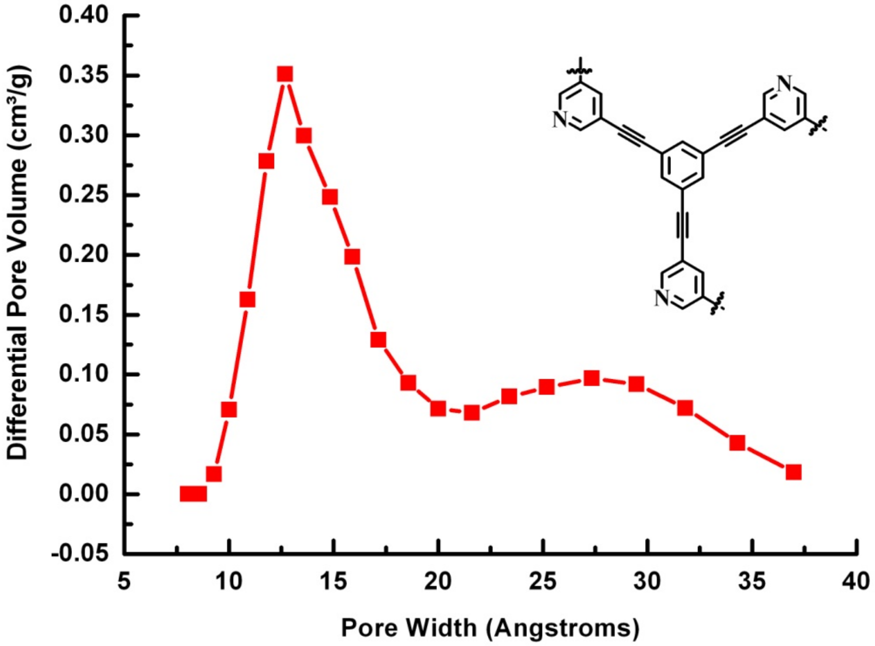


Figure S 34: Pore size distribution for (7)

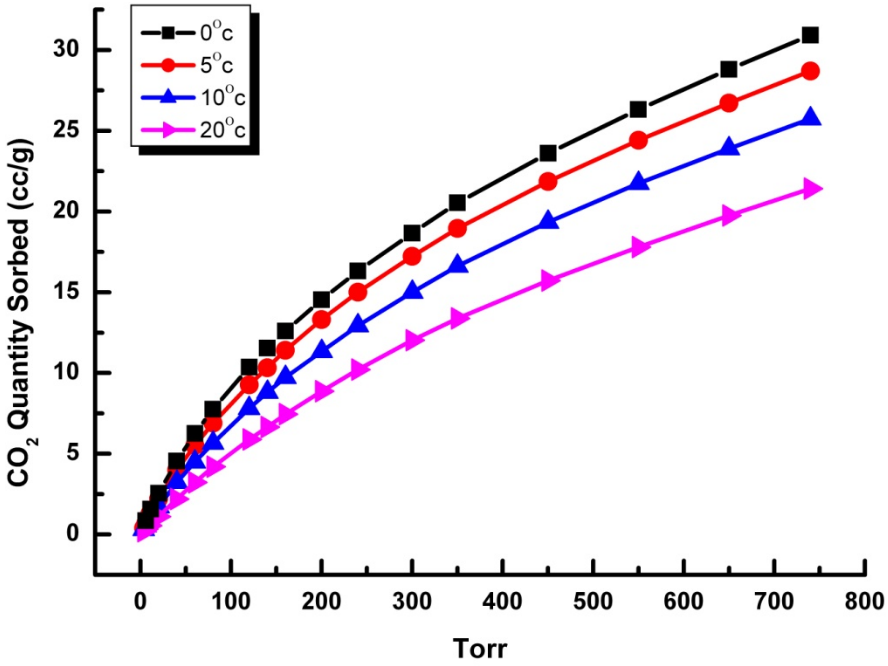
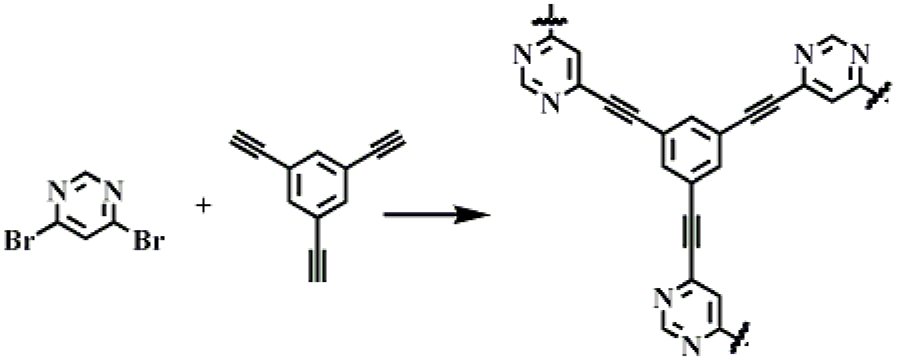


Figure S 35: CO_2 adsorption isotherms for (7)

POP_8:



In a glass pressure vessel fitted with teflon screw cap (50 mL) charged with a magnetic stirrer a mixture of dry DMF (10 mL) and triethylamine (3 mL) was prepared. The vessel was capped with silicon septum, and the solvent mixture was evacuated and backfilled with nitrogen three times through a needle, then was kept under nitrogen for 10 min. To this mixture and under nitrogen atmosphere was added **3,5-dibromopyrimidine** (0.5 mmol, 0.177 g), **1,3,5-triethynylbenzene** (0.5 mmol, 0.075 g.), **bis(triphenylphosphine)palladium(II) dichloride** (0.014 mmol, 10 mg), **triphenylphosphine** (0.02 mmol, 0.005 g) and CuI (0.03 mmol, 0.006 g), the flask was then evacuated/backfilled with nitrogen and sealed and the mixture was stirred at 80 °C. After 30 minutes at 80 °C a buff colored precipitate was observed. The reaction was continued for further 2 h, opened to air and the precipitate immediately filtered through a fritted funnel, washed with DMF, DCM, and MeOH. (don't allow to dry) and the solid was kept under MeOH for 4 days for guest exchange prior to gas sorption analysis. Portion of the solid was then transferred while wet to the gas sorption cell, the cell then was immersed in liquid nitrogen briefly, removed from the LN_2 bath and the sample lyophilized by applying unrestricted vacuum on the sorption analyzer. After the sample reached room temperature, the solid was further degassed on the gas sorption analyzer by heating (10 ºC/min) to 120ºC under dynamic vacuum for 4 h, BET **S.A = 215 m^2/g**.

The total dry weight of the solid was found to be 0.114 g of yellow solid (0.5 mmol, quantitative yield based on 0.5 mmol of starting triethynylbenzene and product tentative formula ($C_{16}H_5N_2$, Mol. Wt.: 225.22). Elemental Analysis : C, 70.52% (Calc. 85.32%); H, 3.11% (2.24%); N, 11.64% (12.44%). Note: Discrepancy between calculated and found elemental analysis could be explained in terms of formation of multiple oligomers of the polymer of different chain lengths/connectivity.

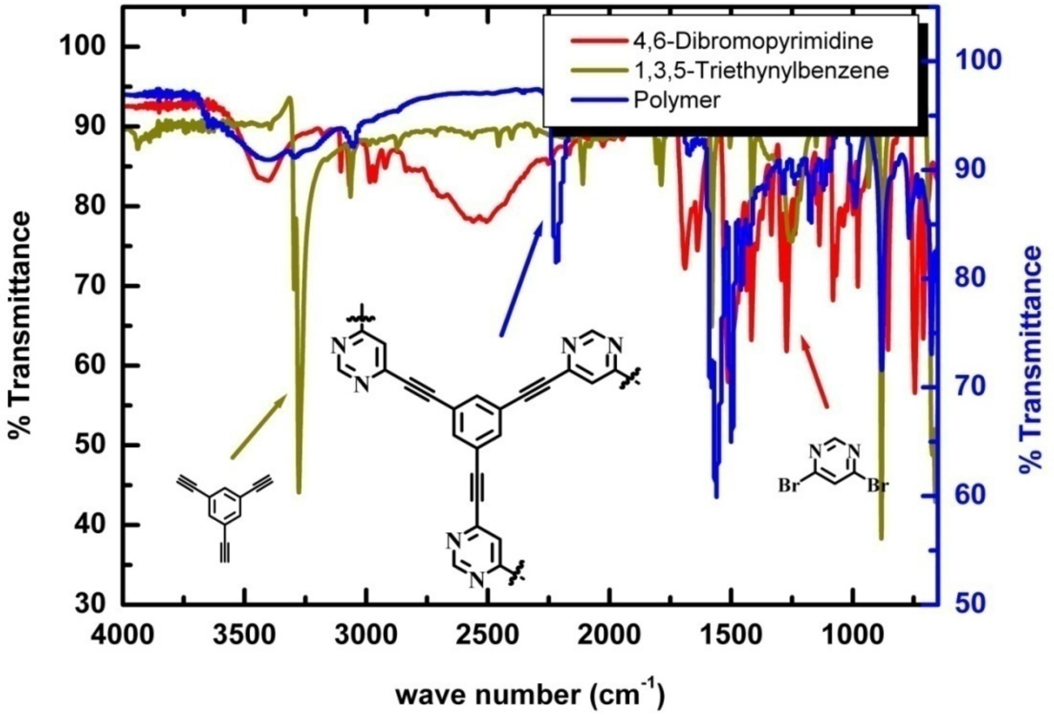


Figure S 36: FT-IR spectra for (8) and starting monomers.

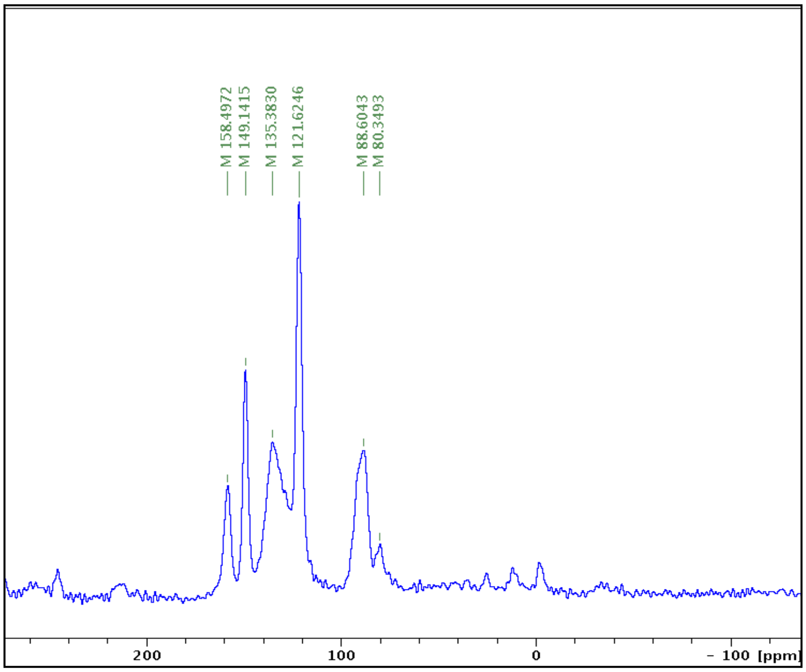


Figure S 37: ^{13}C-CPMAS-NMR spectrum for (8).

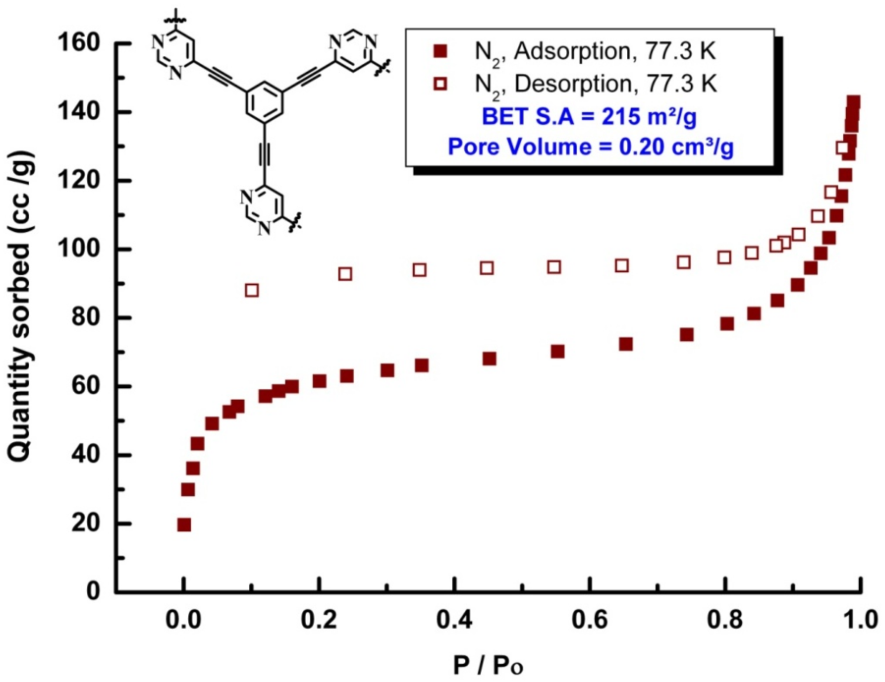


Figure S 38: Nitrogen sorption isotherm for (8)

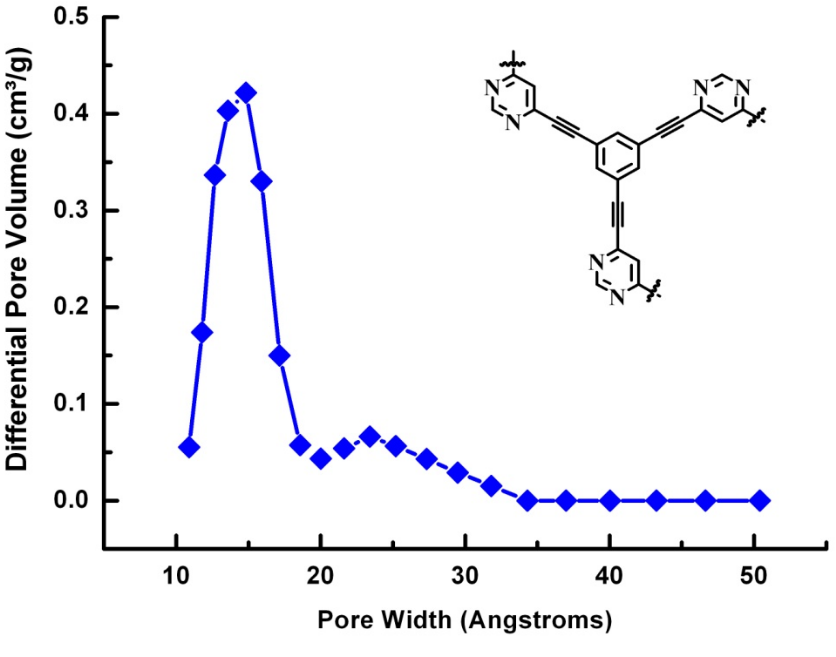


Figure S 39: Pore size distribution for (8)

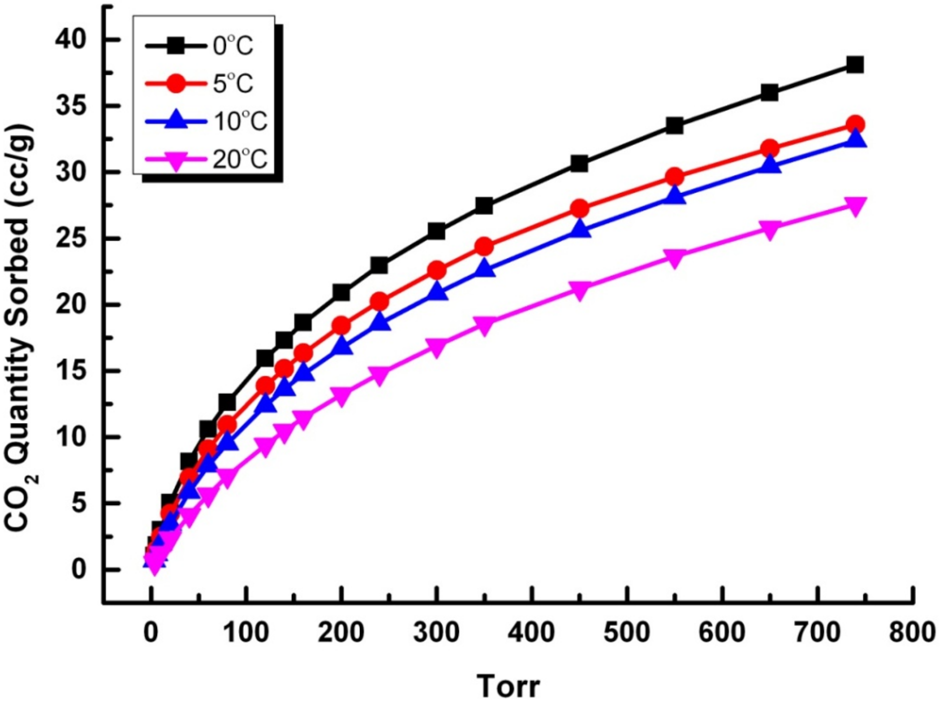
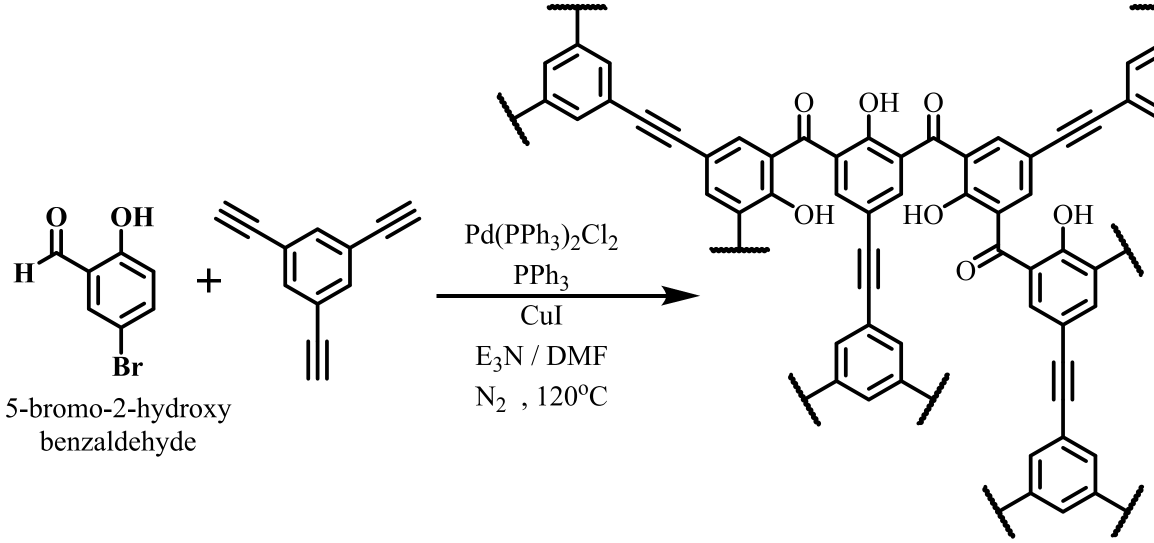


Figure S 40: CO$_2$ adsorption isotherms for (8)

POP-9:



In a glass pressure vessel fitted with teflon screw cap (150 mL) charged with a magnetic stirrer a mixture of dry THF (10 mL) and triethylamine (3 mL) was prepared. The vessel was capped with silicon septum, and the solvent mixture was evacuated and backfilled with nitrogen three times through a needle, then was kept under nitrogen for 10 min. To this mixture and under nitrogen atmosphere was added **5-bromo-2-hydroxybenzaldehyde** (1 mmol, 0.201 g), **1,3,5-triethynylbenzene** (0.3 mmol, 0.045 g.), **bis(triphenylphosphine)palladium(II) dichloride** (0.028 mmol, 20 mg), **triphenylphosphine** (0.04 mmol, 0.01 g) and CuI (0.052 mmol, 0.01 g), the flask was then evacuated/backfilled with nitrogen and sealed and the mixture was stirred at 120 °C. After 24h at 120 °C a buff colored precipitate was observed. The reaction was allowed to cool to room temperature, opened to air and the precipitate immediately filtered through a fritted funnel, washed with DMF, DCM, and MeOH. (don't allow to dry) and the solid was kept under MeOH for 7 days for guest exchange prior to gas sorption analysis. Portion of the solid was then dried at a heating oven at 85C, transferred to the gas sorption cell, the cell then was degassed on the gas sorption analyzer by heating (10 ºC/min) to 120ºC under dynamic vacuum for 4 h, BET **S.A = 316 m²/g**. The total dry weight of the solid was found to be 0.078 g of yellow solid (0.15 mmol, 50% yield based on 0.3 mmol of starting triethynylbenzene and product tentative formula ($C_{33}H_{12}O_6$, Mol. Wt.: 504.45). Elemental Analysis : C, 77.8% (Calc. 78.57%); H, 3.93% (2.40%).

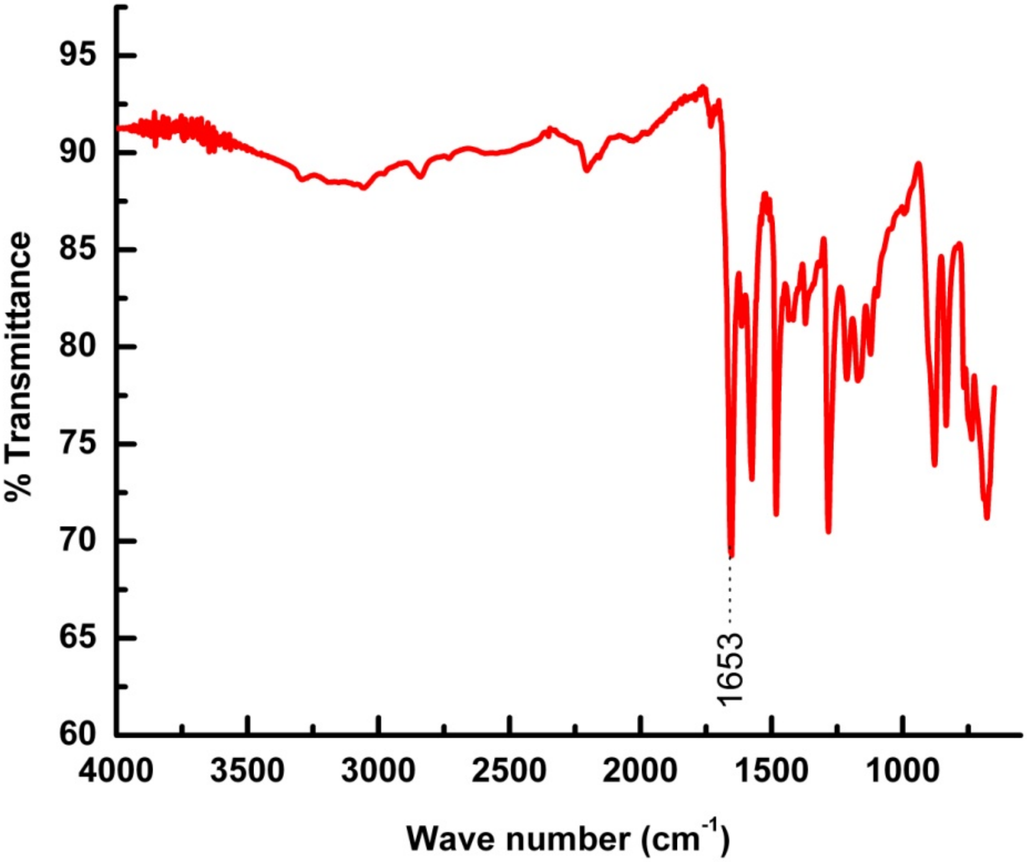


Figure S 41: FT-IR spectra for (9).

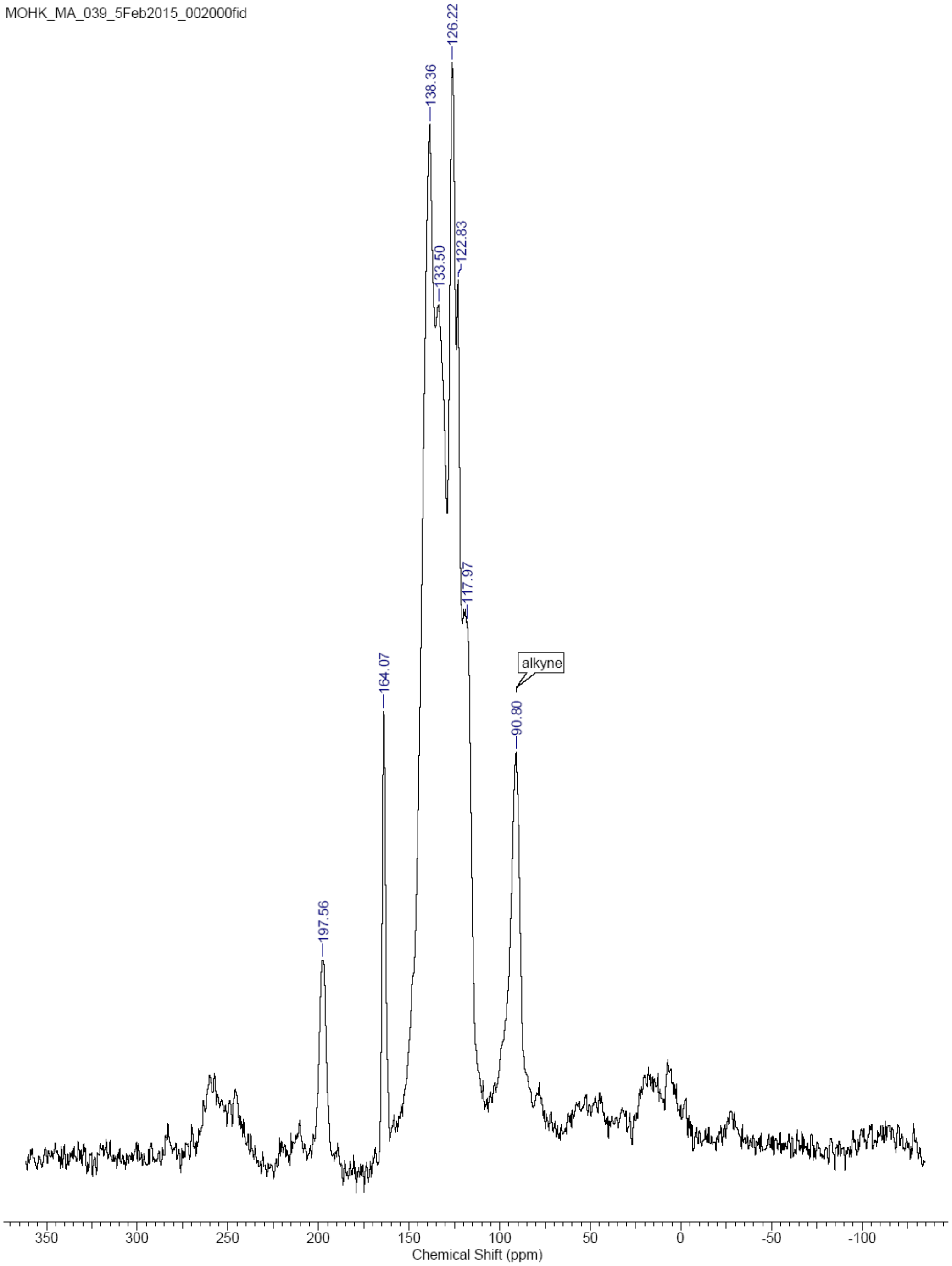


Figure S 42: ^{13}C-CPMAS-NMR spectrum for (9).

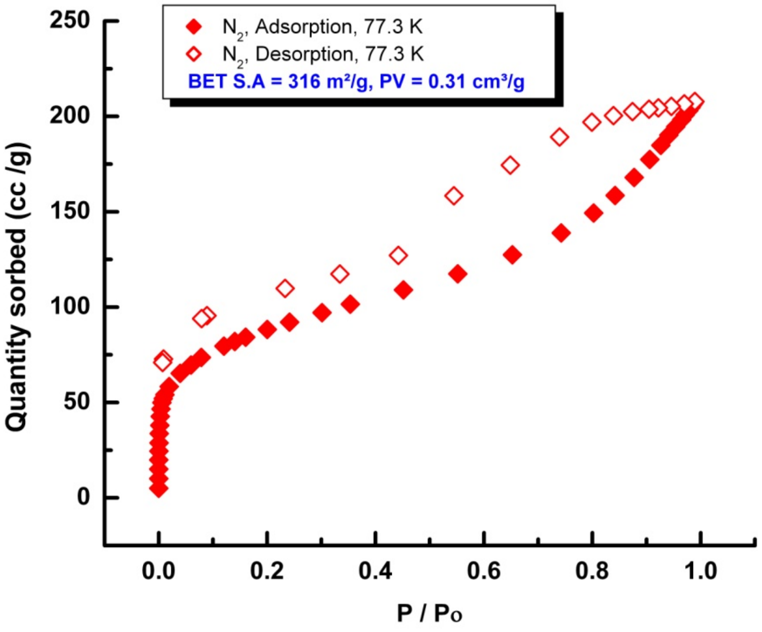


Figure S 43: Nitrogen sorption isotherm for (9)

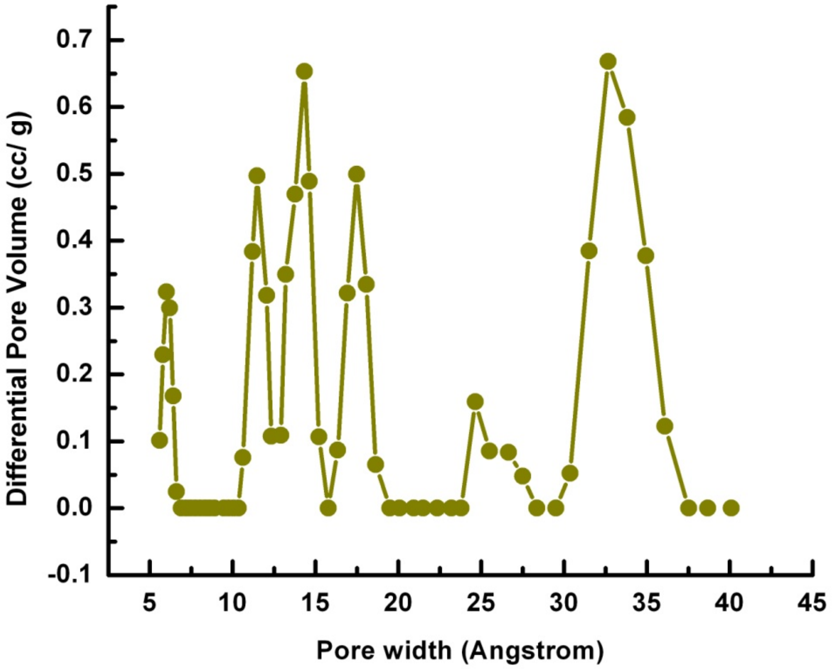


Figure S 44: Pore size distribution for (9)

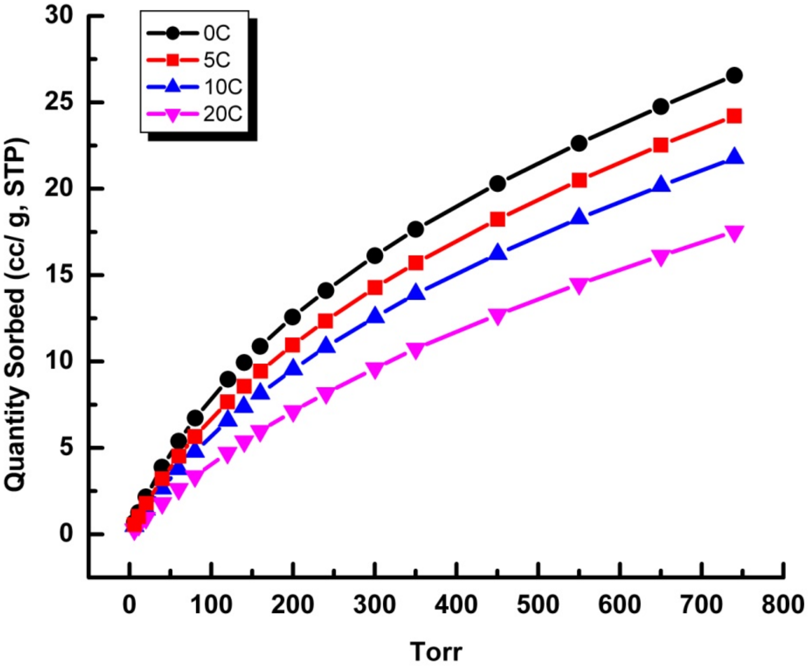


Figure S 45: CO_2 adsorption isotherms for (9)

POP-10:

Part of the formed ppt of POP-9 was filtered through a sintered glass funnel and transferred to a vial to which 1M KOH (10 ml) was added. The vial was capped and left in the oven at 85 ^{0}C for 4h, then left overnight at room temperature. The ppt was then filtered through a sintered glass funnel, washed with MeOH, then left to exchange in MeOH overnight. Elemental Analysis : C, 71.63% (Calc. 72.25%); H, 4.09% (3.12%) based on a tentative formula ($C_{33}H_{17}O_6K$, Mol. Wt.: 548.58), note that accurate formula can't be readily predicted due to uncertainty in the number of K-coordinated water molecules or the coordination number of K ions inside the polymer.

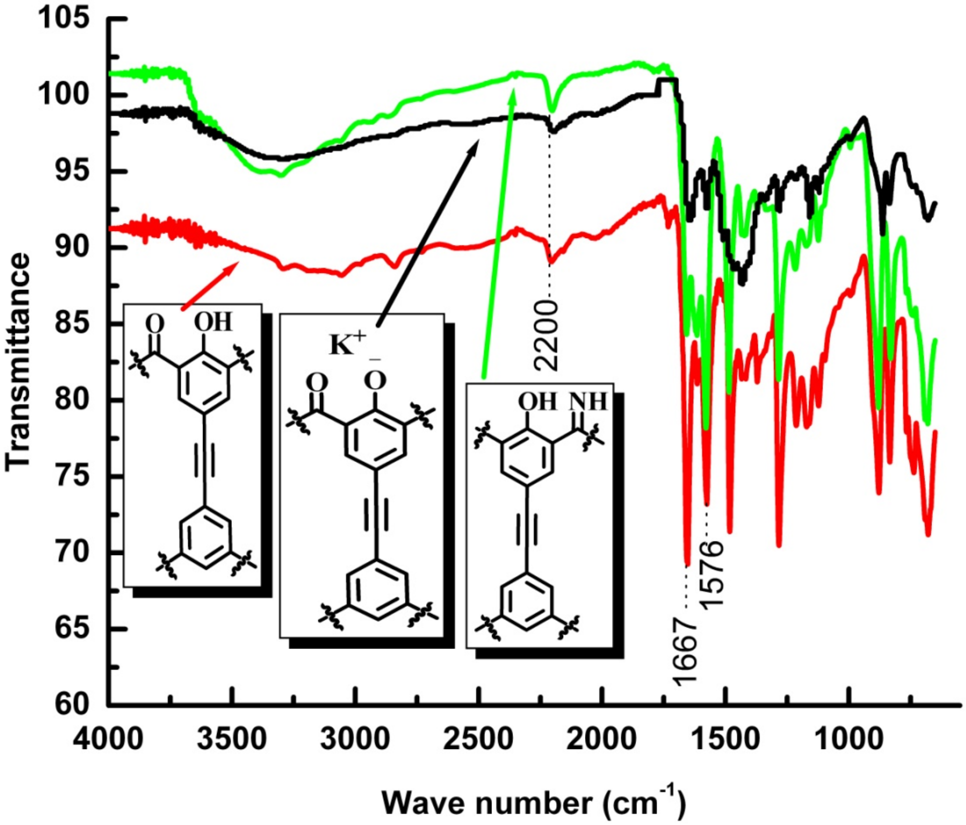


Figure S 46: FT-IR spectra for (10) and comparison to those for 9 and 11.

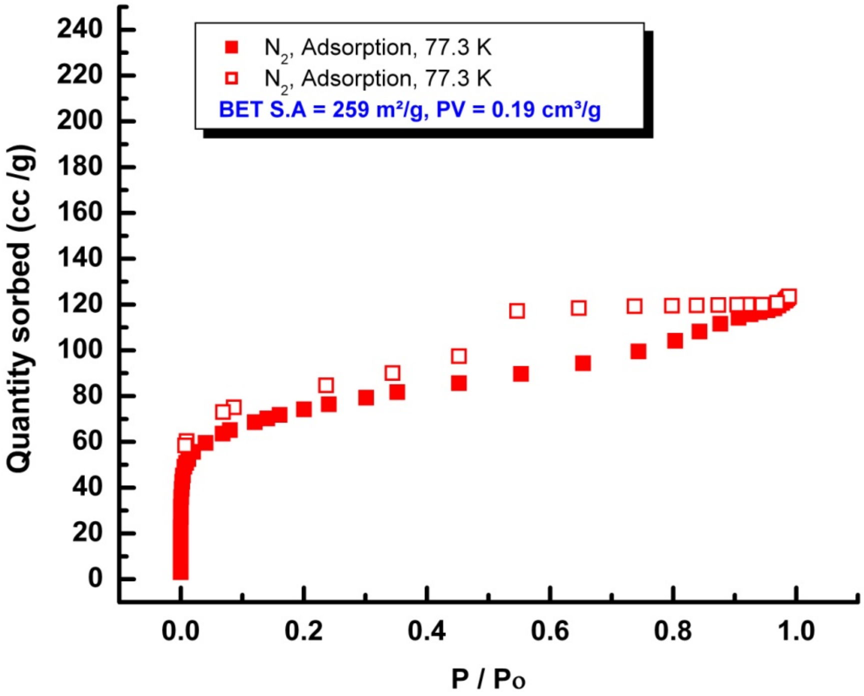


Figure S 47: Nitrogen sorption isotherm for (10)

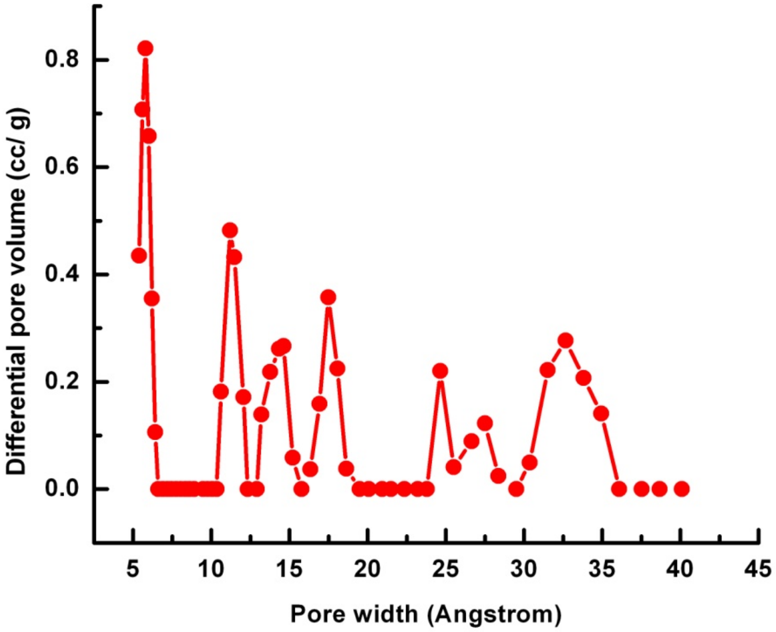


Figure S 48: Pore size distribution for (10)

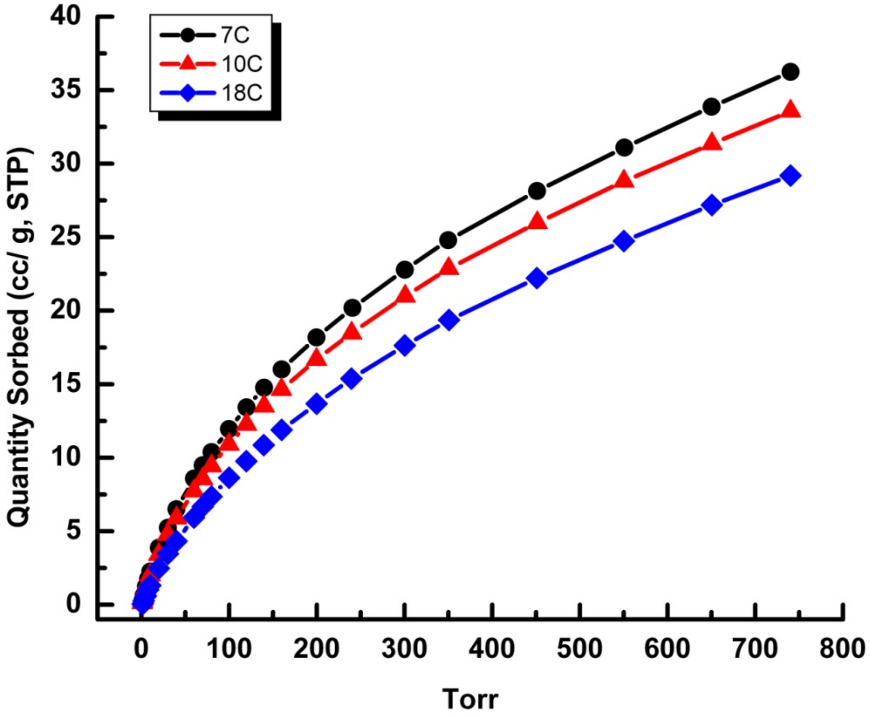


Figure S 49: CO_2 adsorption isotherms for (10)

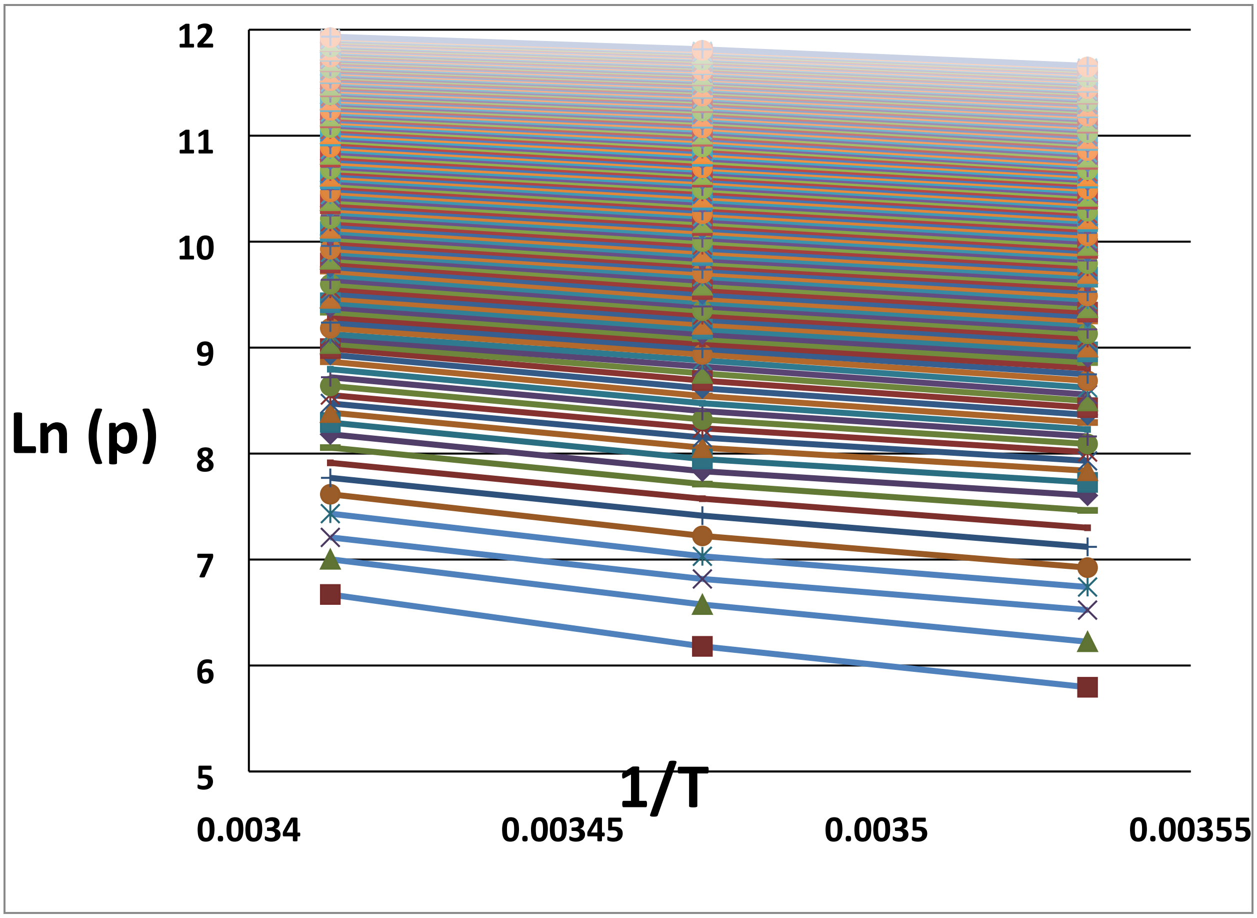


Figure S 50: Isosters plot for CO_2 adsorption isotherms for (10)

POP-11:

Part of the formed ppt of POP-9 was filtered through a sintered glass funnel and transferred to a pressure vessel fitted with Teflon screw cap (150 mL). To the solid was added methanolic ammonia solution (2 M, 20 mL) and the vessel sealed and the suspension heated at 60C for 24h. The vessel was then allowed to cool to room temperature, opened to air, and the solid was filtered and dried in a drying oven at 80C prior to loading into the gas sorption measurement cell. Elemental analysis based on tentative formula ($C_{33}H_{15}O_3N_3$, Mol. Wt.: 501.49): C, 77.97% (Calc. 79.03%); H, 4.06% (3.01%); N, 2.84 (8.37%).

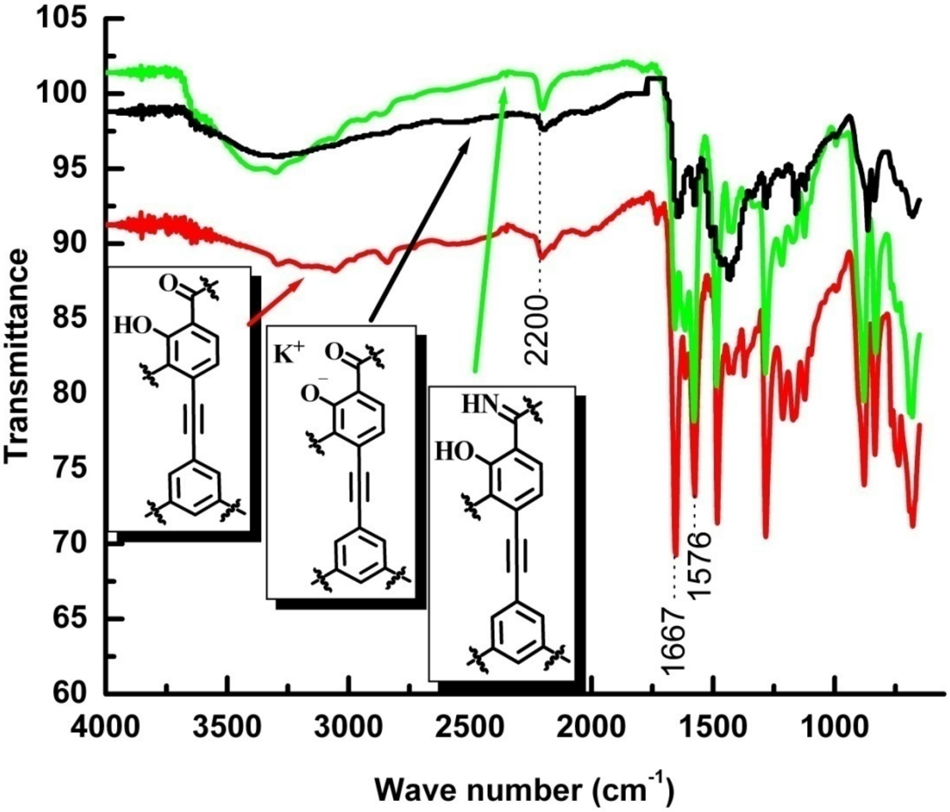


Figure S 51: FT-IR spectra for (11) in comparison to the spectrum of (9) showing changes to the bands 1567~1667 cm^{-1} and 3000~3700 cm^{-1}.

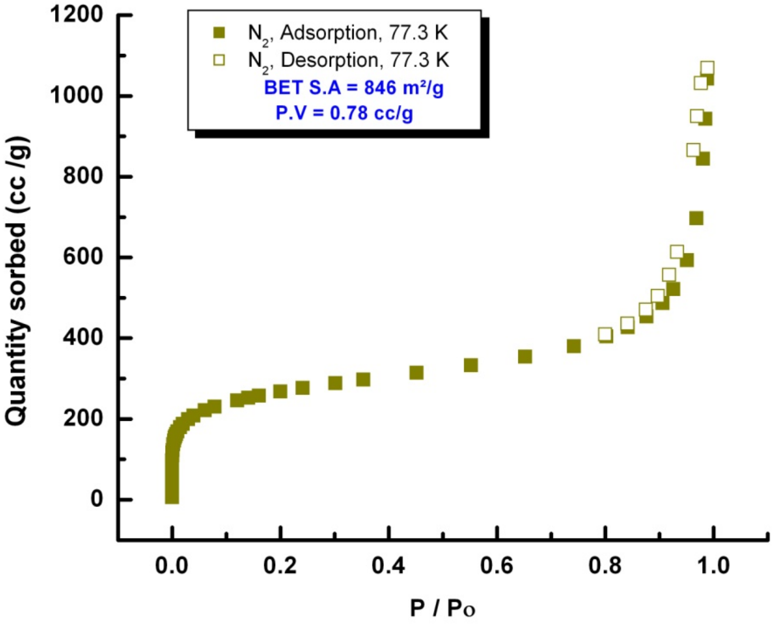


Figure S 52: Nitrogen sorption isotherm for (11)

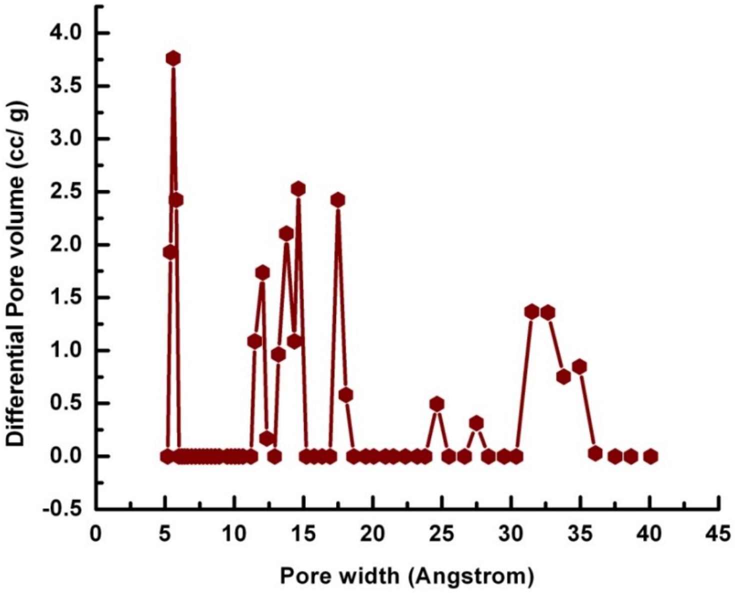


Figure S 53: Pore size distribution for (11)

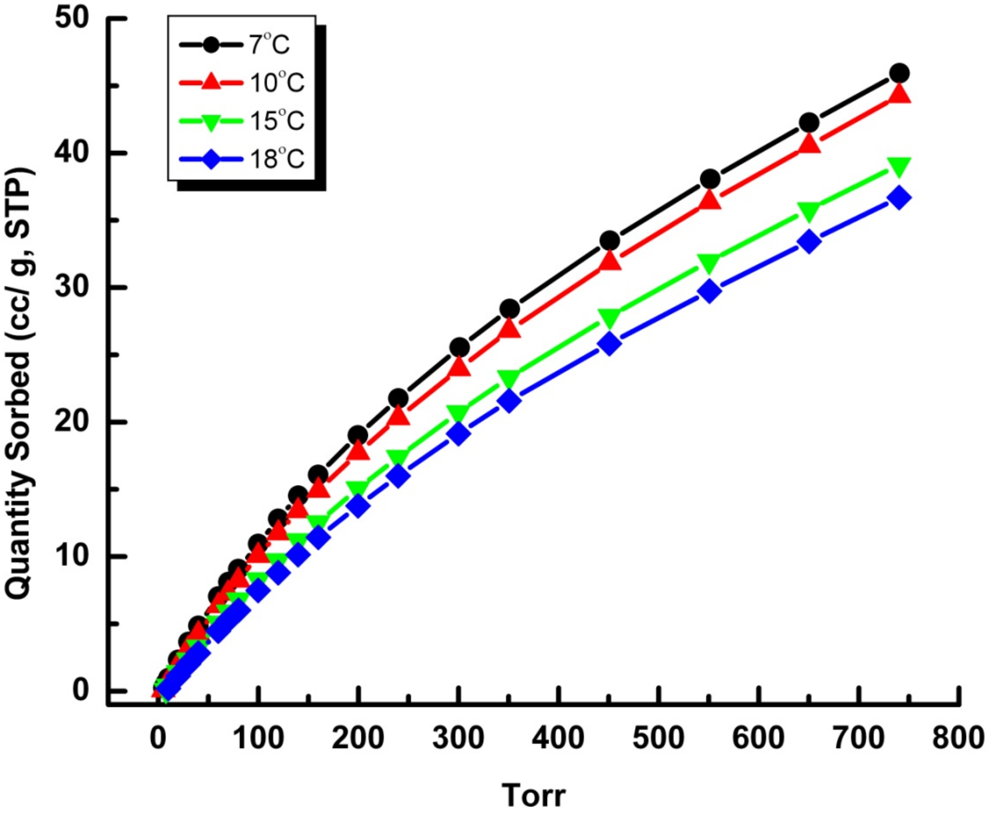


Figure S 54: CO$_2$ adsorption isotherms for (11)

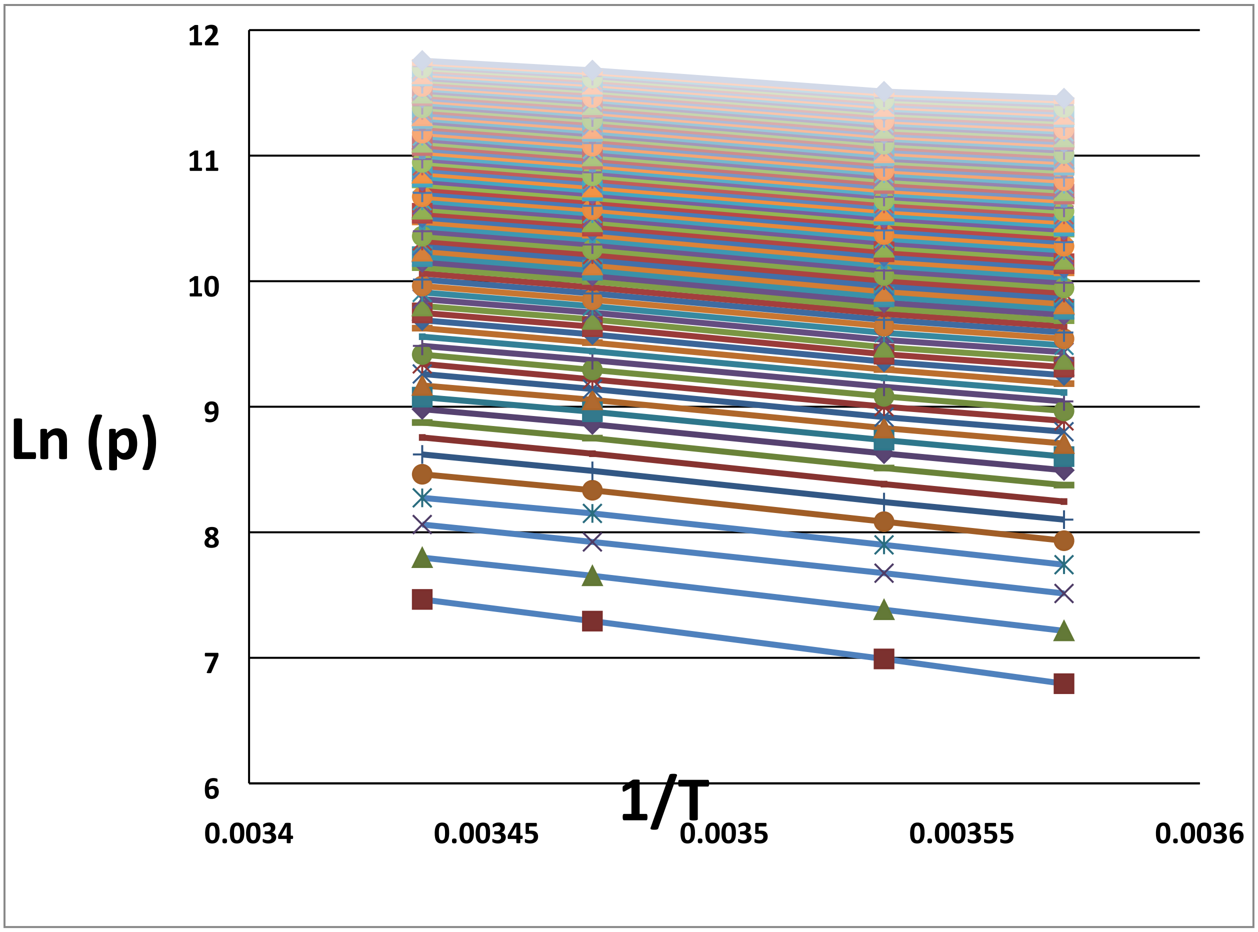


Figure S 55: Isosters plot for CO_2 adsorption isotherms for (11)

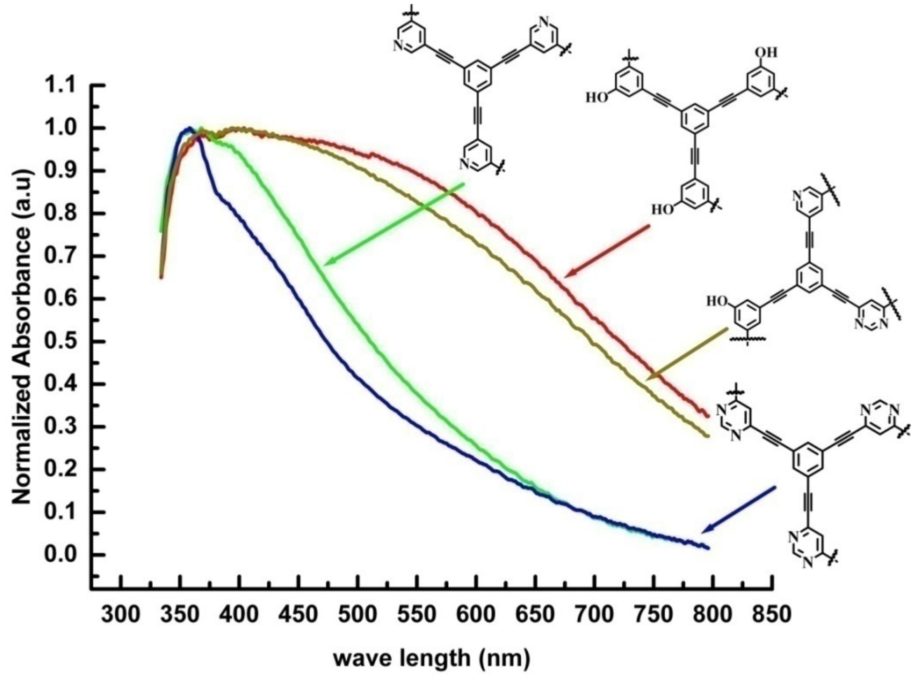


Figure S 55: UV-Vis diffuse reflectance spectra for selected POPs.

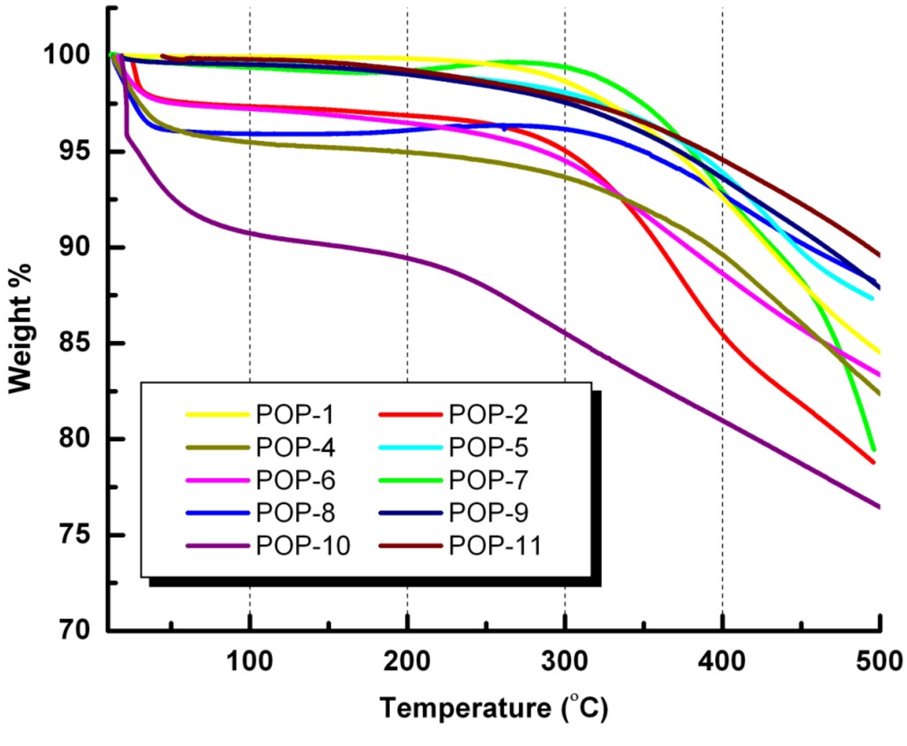


Figure S 56. TGA for POPs.