Supplementary Information

Charged induced formation of crystalline network polymers

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General

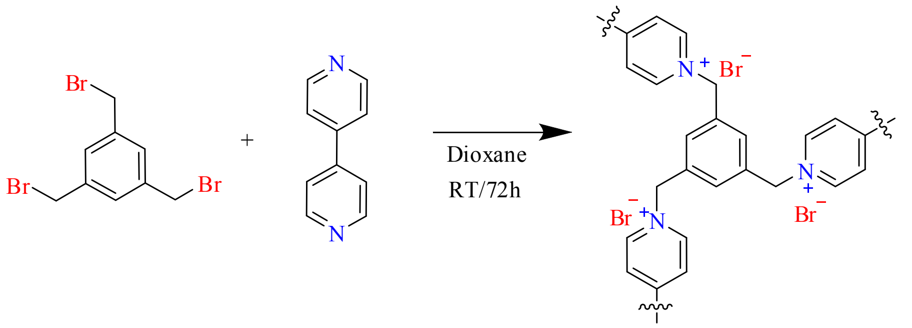
All the chemicals and compounds used were commercially available and used as received without further purification. 1,3,5-tris(bromomethyl)benzene, 4,4′– dipyridyl, 1,2-bis(4-pyridyl)ethane, 4,4'-trimethylenedipyridine, 1,2-bis(4-pyridyl)ethylene, Sodium tetrafluoroborate and Potassium trifluoromethanesulfonate were purchased from Sigma-Aldrich, USA. Ammonium hexafluorophosphate was bought from Acros Organics, USA. 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene was obtained from TCI, Japan. All the solvents purchased from SAMCHUN, South Korea were dried and stored in anhydrous conditions. The elemental analyses (CHN) were performed on Flash 2000 CHNS analyzer, product of Thermo Scientific, USA. FT-IR spectra were recorded as KBr pellet using a Perkin-Elmer FT-IR spectrometer. Solid-state CP/MAS ^{13}C SSNMR spectra were recorded on a Agilent 400MHz, 54mm NMR DD2 spectrometer. Thermogravimetric analysis (TGA) was performed on a NETZSCH-TG 209 F3 instrument by heating the samples to 800^{o}C at 10^{o}C min^{-1} in N_2 and air atmosphere. The graphitic nature of i-COP$_n$ was evaluated from RAMAN spectrum between 1250~1700 cm^{-1},measured by high resolution dispersive RAMAN microscope, ARAMIS by Horiba Jobin Yvon, France. N_2 physiosorption isotherms for i-COPs were obtained with a Micromeritics ASAP 2020 accelerated surface area and porosimetry analyzer at 77 K. Prior to analysis, the samples were degassed at 125 ^{o}C for 5 h under vacuum. The adsorption–desorption isotherms were evaluated to give the pore parameters, including BET and Langmuir surface area, pore size, and pore volume. CO_2 adsorption and desorption isotherms for i-COPs were measured at 273K and 298K by using isochoric system, ASAP 2020, Micrometrics Inc., USA. High power powder X-ray diffraction (PXRD) patterns of the samples were acquired from 2~80^{o} by a Rigaku D/MAX-2500 (18 kW) Micro-area X-ray diffractometer. SEM images for samples, were taken on

Field Emission SEM (Magellan400 by FEI Company, USA), that were prepared by dispersing the material onto a sticky carbon surface attached to a flat-circular aluminium sample holder. Osmium was coated on the samples under pressure of 0.06 mbar for 15 minutes via osmium coater (HPC-1SW, Vacuum Device Inc., Japan) before imaging.

Experimental section

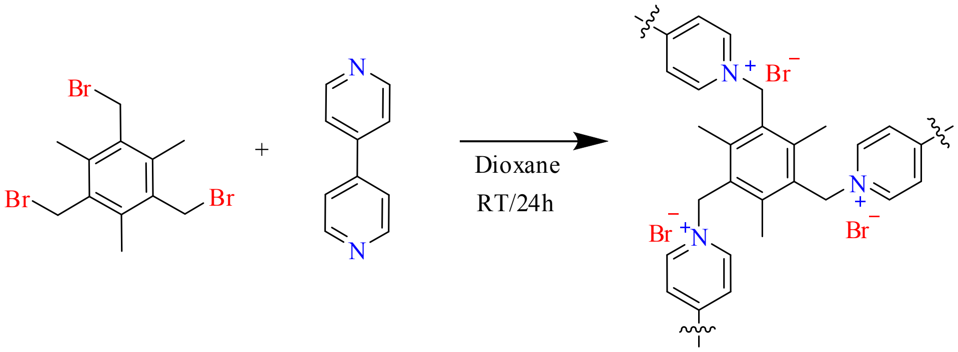
A. Syntheses of i-COP 1~8 using solvent

i-COP 1



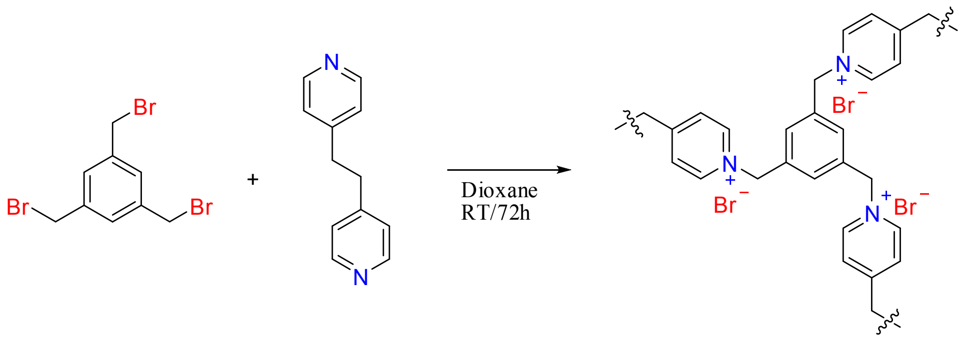
1,3,5-tris(bromomethyl) benzene (0.36g, 1 mmol) dissolved 1,4–dioxane (10 mL) was added dropwise to flask containing 4,4′– dipyridyl (0.24g, 1.5 mmol) dissolved 1,4–dioxane (10 mL) with continuous stirring at ambient temperature. The precipitates were stirred for 72 h before washing with THF. Finally, shining light greenish yellow precipitates were dried at room temperature for 8 h and then at 50°C under vacuum for 12 h to yield i-COP 1 (0.45g) in 75 % yield. Elemental Analysis for CHN (calculated): 44.97 %C (48.76), 3.18 %H (3.58), 5.49 %N (7.11). CP/MAS 13C SSNMR: δ [ppm] =151, 144, 128, 60. FTIR: ν [cm^{-1}]: 3423 (s, pyridinium salt stretch), 3116 (w, alkenyl C–H stretch), 3016 (s,Ar C–H stretch), 2970 (m, Alkyl C–H stretch), 1636 (vs, pyridinium salt ring vibration), 1460 (s, Ar C=C bending), 1160 (s, Ar C–N bending), 829 (vs, Ar C–C bending).

i-COP 2



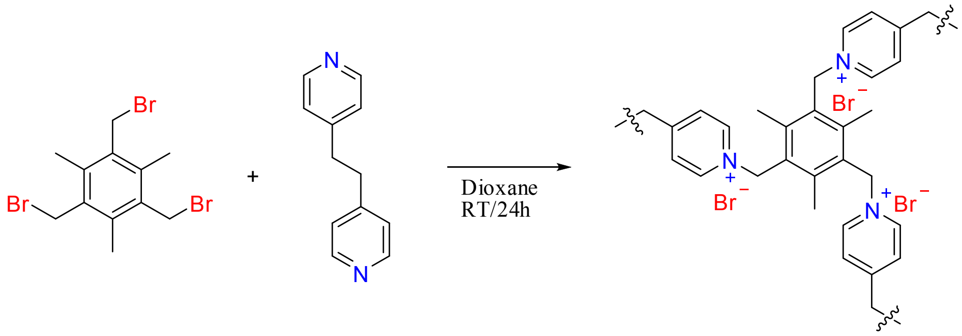
1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (0.4g, 1 mmol) dissolved in 1,4–dioxane (10 mL) was added dropwise to flask containing 4,4′– dipyridyl (0.24g, 1.5 mmol) dissolved in 1,4–dioxane (10 mL) with continuous stirring at ambient temperature. The precipitates were stirred for 24 h before washing with THF. Finally, dark yellow precipitates were dried at room temperature for 8 h and then at 50°C under vacuum for 12 h to yield i-COP 2 (0.52g) in 82 % yield. Elemental Analysis for CHN (calculated): 51.09 %C (51.21), 4.93 %H (4.3), 7.3 %N (6.64). CP/MAS 13C SSNMR: δ [ppm] =151, 144, 128, 60, 16. FTIR: ν [cm^{-1}]: 3415 (s, pyridinium salt stretch), 3108 (w, alkenyl C–H stretch), 3139 (s,Ar C–H stretch), 3029 (w, Alkyl C–H stretch), 1633 (vs, pyridinium salt ring vibration), 1440 (s, Ar C=C bending), 1149 (s, Ar C–N bending), 818 (vs, Ar C–C bending)

i-COP 3



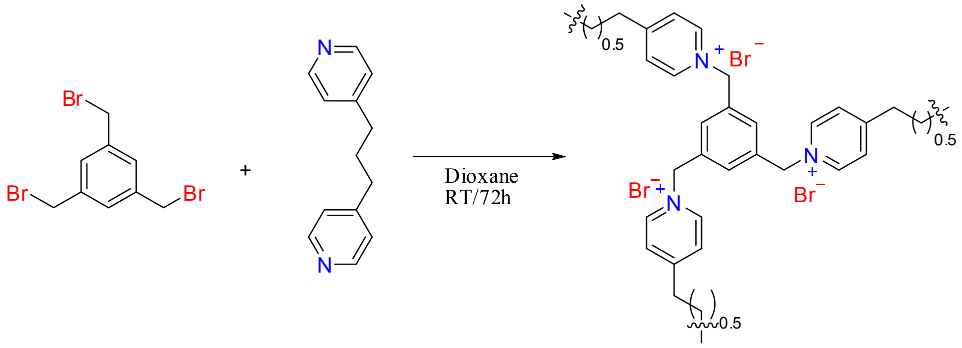
1,3,5-tris(bromomethyl) benzene (0.36g, 1 mmol) dissolved in 1,4–dioxane (10 mL) was added dropwise to flask containing 1,2-Bis(4-pyridyl)ethane (0.32g, 1.75 mmol) dissolved in 1,4–dioxane (10 mL) with continuous stirring at ambient temperature. The precipitates were stirred for 72 h before washing with THF. Finally, fluffy shining light pink precipitates were dried at room temperature for 8 h and then at 50°C under vacuum for 12 h to yield i-COP 3 (0.53g) in 83 % yield. Elemental Analysis for CHN (calculated): 46.36 %C (51.2), 4.18 %H (4.3), 5.75 %N (6.6). CP/MAS 13C SSNMR: δ [ppm] = 151, 144, 128, 60, 29. FTIR: ν [cm^{-1}]: 3406 (s, pyridinium salt stretch), 3116 (w, alkenyl C–H stretch), 3019 (s,Ar C–H stretch), 2946 (m, Alkyl C–H stretch), 1640 (vs, pyridinium salt ring vibration), 1410 (s, Ar C=C bending), 1156 (s, Ar C–N bending), 811 (vs, Ar C–C bending).

i-COP 4



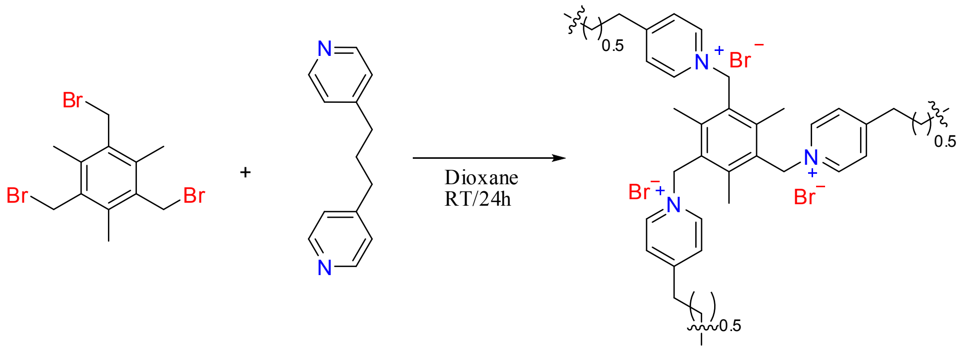
1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (0.4g, 1 mmol) dissolved in 1,4–dioxane (10 mL) was added dropwise to flask containing 1,2-Bis(4-pyridyl)ethane (0.32g, 1.75 mmol) dissolved in 1,4–dioxane (10 mL) with continuous stirring at ambient temperature. The precipitates were stirred for 24 h before washing with THF. Finally, light yellow precipitates were dried at room temperature for 8 h and then at 50°C under vacuum for 12 h to yield i-COP 4 (0.58g) in 86 % yield. Elemental Analysis for CHN (calculated): 49.82 %C (53.4), 6.14 %H (5), 6.11 %N (6.2). CP/MAS 13C SSNMR: δ [ppm] = 151, 144, 128, 60, 29, 16. FTIR: ν [cm^{-1}]: 3400 (s, pyridinium salt stretch), 3116 (w, alkenyl C–H stretch), 3039 (s,Ar C–H stretch), 3000 (m, Alkyl C–H stretch), 1640 (vs, pyridinium salt ring vibration), 1464 (s, Ar C=C bending), 1141 (s, Ar C–N bending), 842 (vs, Ar C–C bending).

i-COP 5



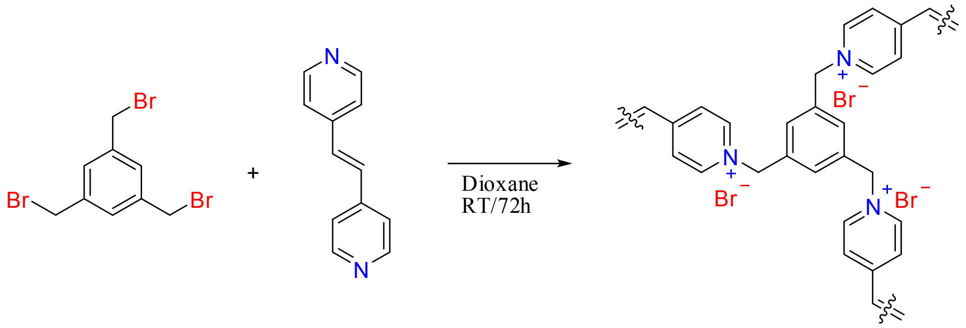
1,3,5-tris(bromomethyl) benzene (0.36g, 1 mmol) dissolved in 1,4–dioxane (10 mL) was added dropwise to flask containing 4,4'-Trimethylenedipyridine (0.32g, 1.6 mmol) dissolved in 1,4–dioxane (10 mL) with continuous stirring at ambient temperature. The precipitates were stirred for 72 h before washing with THF. Finally, slightly fluffy shining mint green precipitates were dried at room temperature for 8 h and then at 50°C under vacuum for 12 h to yield i-COP 5 (0.47g) in 71 % yield. Elemental Analysis for CHN (calculated): 48 %C (52.32), 3.44 %H (4.6), 5.24 %N (6.4). CP/MAS 13C SSNMR: δ [ppm] = 151, 144, 128, 60, 29. FTIR: ν [cm^{-1}]: 3423 (s, pyridinium salt stretch), 3116 (w, alkenyl C–H stretch), 3023 (s,Ar C–H stretch), 2947 (m, Alkyl C–H stretch), 1640 (vs, pyridinium salt ring vibration), 1464 (s, Ar C=C bending), 1156 (s, Ar C–N bending), 844 (vs, Ar C–C bending).

i-COP 6



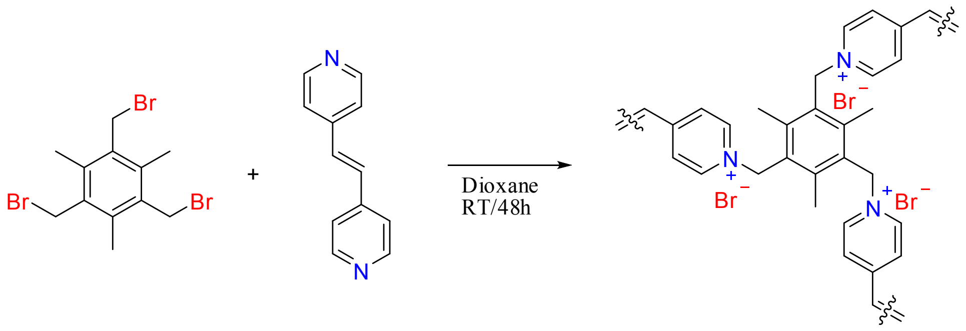
1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene (0.4 g, 1 mmol) dissolved in 1,4–dioxane (10 mL) was added dropwise to flask containing 4,4'-Trimethylenedipyridine (0.3g, 1.5 mmol) dissolved in 1,4–dioxane (10 mL) with continuous stirring at ambient temperature. The precipitates were stirred for 24 h before washing with THF. Finally, off white precipitates were dried at room temperature for 8 h and then at 50°C under vacuum for 12 h to yield i-COP 6 (0.65g) in 93 % yield. Elemental Analysis for CHN (calculated): 53 %C (54.3), 5.04 %H (5.2), 5.5 %N (6). CP/MAS 13C SSNMR: δ [ppm] = 151, 144, 128, 60, 29, 16. FTIR: ν [cm^{-1}]: 3407 (s, pyridinium salt stretch), 3116 (w, alkenyl C–H stretch), 3039 (s,Ar C–H stretch), 2985 (m, Alkyl C–H stretch), 1640 (vs, pyridinium salt ring vibration), 1464 (s, Ar C=C bending), 1140 (s, Ar C–N bending), 834 (vs, Ar C–C bending).

i-COP 7



1,3,5-tris(bromomethyl) benzene (0.36g, 1 mmol) dissolved in 1,4–dioxane (10 mL) was added dropwise to flask containing 1,2-Di(4-pyridyl)ethylene (0.29g, 1.6 mmol) dissolved in 1,4–dioxane (10 mL) with continuous stirring at ambient temperature. The precipitates were stirred for 72 h before washing with THF. Finally, light cream precipitates were dried at room temperature for 8 h and then at 50°C under vacuum for 12 h to yield i-COP 7 (0.46g) in 72% yield. Elemental Analysis for CHN (calculated): 47.68 %C (51.5), 3.78 %H (3.8), 5.69 %N (6.7). FTIR: ν [$\mathrm{cm^{-1}}$]: 3413 (s, pyridinium salt stretch), 3111 (w, alkenyl C–H stretch), 3020 (s,Ar C–H stretch), 2973 (m, Alkyl C–H stretch), 1629 (vs, pyridinium salt ring vibration), 1463 (s, Ar C=C bending), 1154 (s, Ar C–N bending), 834 (m, Ar C–C bending).

i-COP 8



1,3,5-tris(bromomethyl)-2,4,6-trimethyl benzene (0.4g, 1 mmol) dissolved in 1,4–dioxane (10 mL) was added dropwise to flask containing 1,2-Di(4-pyridyl)ethylene (0.3g, 1.6 mmol) dissolved in 1,4–dioxane (10 mL) with continuous stirring at ambient temperature. The precipitates were stirred for 48 h before washing with THF. Finally, dark yellow precipitates were dried at room temperature for 8 h and then at 50°C under vacuum for 12 h to yield i-COP 8 (0.56g) in 83% yield. Elemental Analysis for CHN (calculated): 51.08 %C (53.6), 5.40 %H (4.5), 5.85 %N (6.2). FTIR: ν [cm^{-1}]: 3403 (s, pyridinium salt stretch), 3110 (w, alkenyl C–H stretch), 3036 (m,Ar C–H stretch), 3002 (w, Alkyl C–H stretch), 1630 (vs, pyridinium salt ring vibration), 1461 (s, Ar C=C bending), 1144 (s, Ar C–N bending), 849 (m, Ar C–C bending).

B. Solid state synthesis of i-COP 1~8

Finely grinded core was mixed with grounded linker in mortar to yield i-COPs in 20~40 minutes with the assistance of few drops of solvent. On completion of reaction the colour of solid products resembled to the i-COPs produced in solvent. The solid was washed with THF, filtered and dried at room temperature for 8 h and then at 50°C under vacuum for 12 h. To compare with i-COPs synthesized using solvent, i-COPs prepared in solid state synthesis were characterized by the FTIR spectroscopy, TGA and PXRD. Please refer to figure S2 for PXRD, figure S11 and S12 for FTIR spectrum and TGA, respectively.

Supplementary Figures

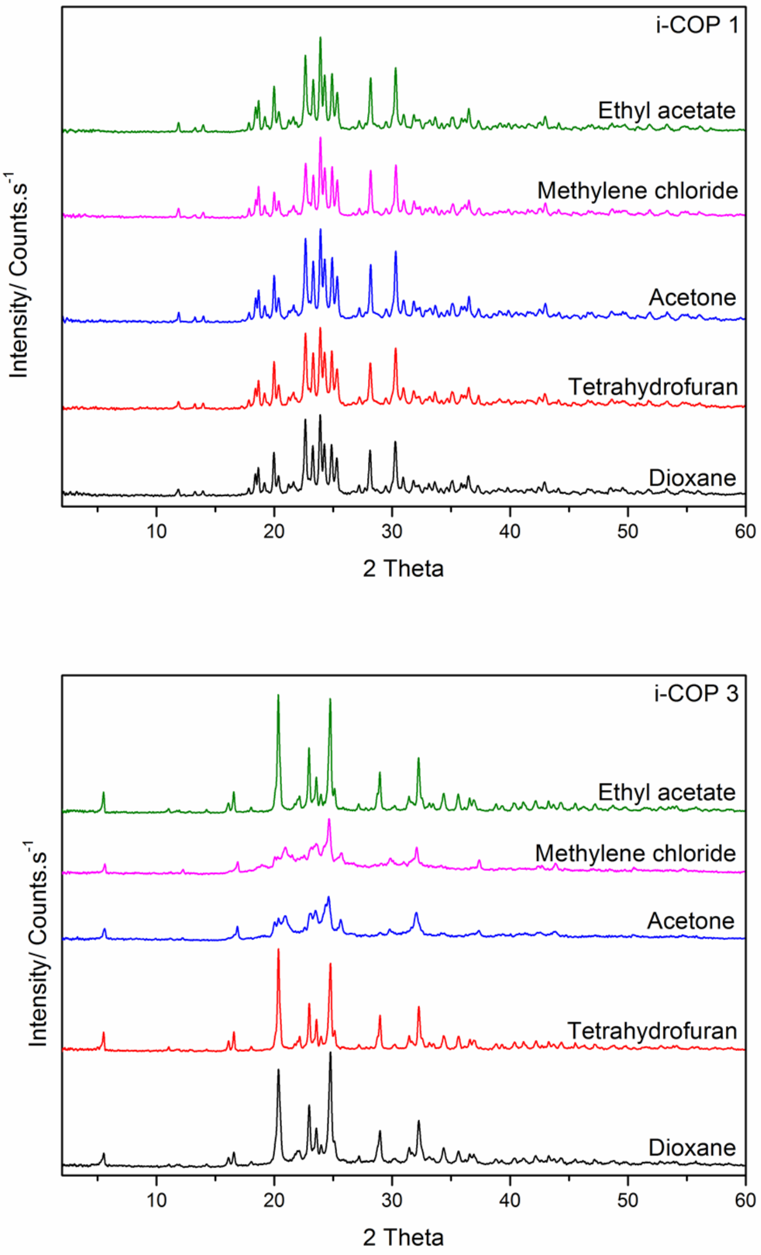


Figure S1-a: XRD for i-COP 1 and i-COP 3 that are synthesized in various solvents at room temperature

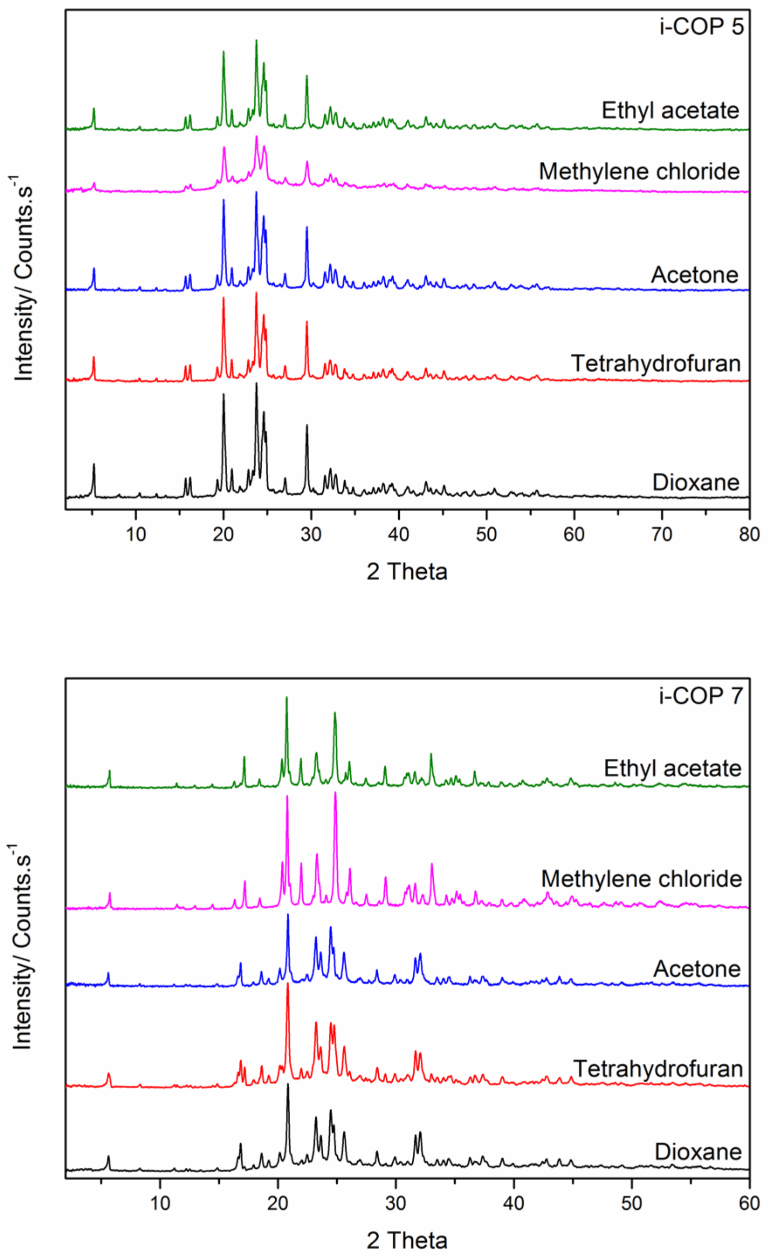


Figure S1-b: XRD for i-COP 5 and i-COP 7 that are synthesized in various solvents at room temperature

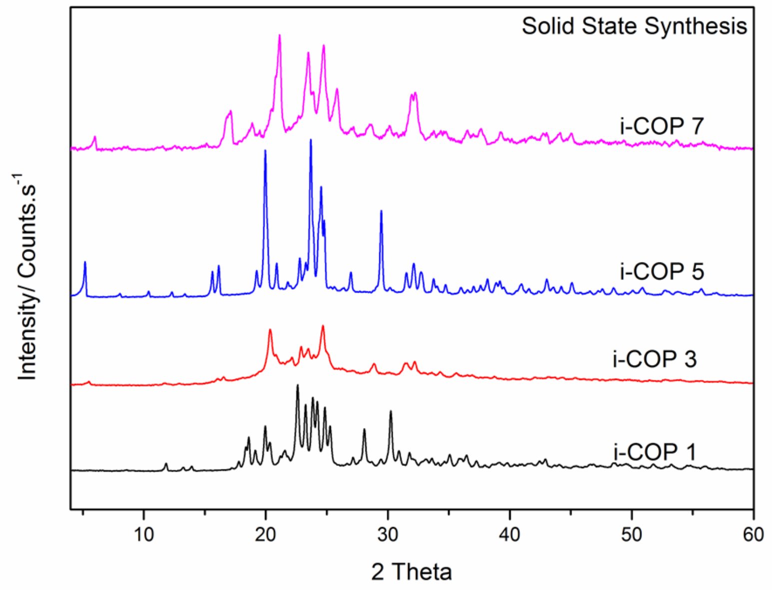


Figure S2: XRD for i-COP$_n$ (n= 1,3,5,7) that are synthesized in solid state

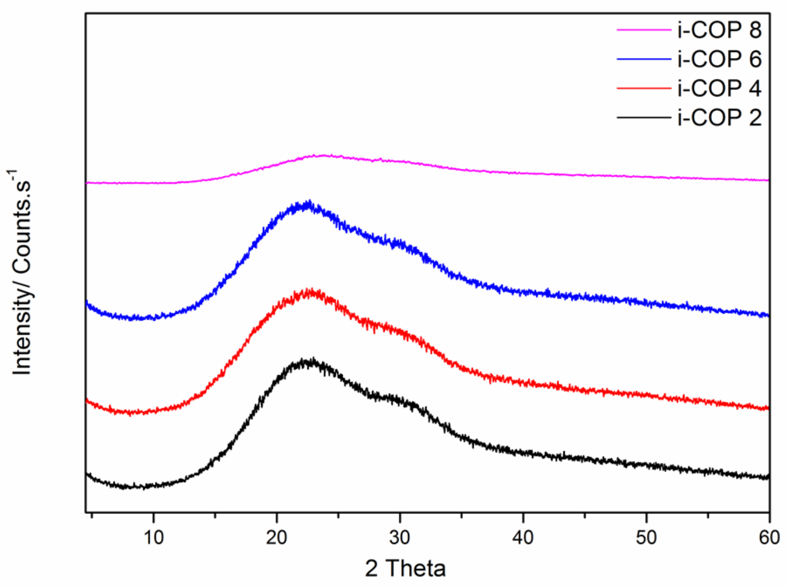
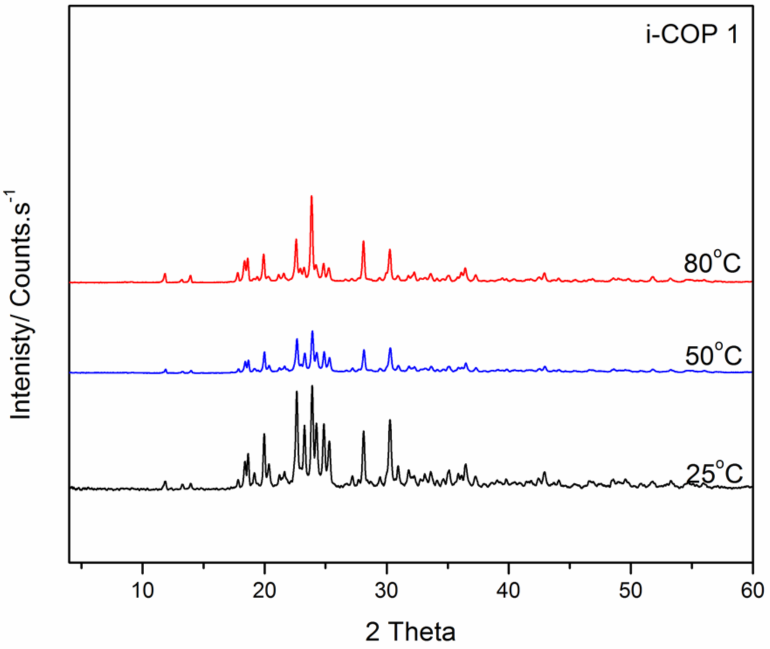


Figure S3: XRD for i-COP$_m$ (m= 2,4,6 and 8) that are synthesized at room temperature using dioxane



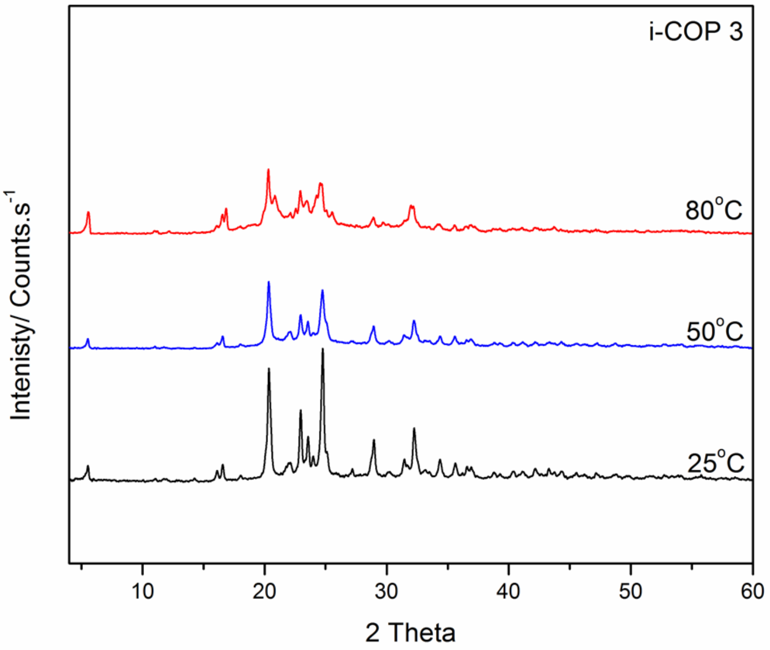
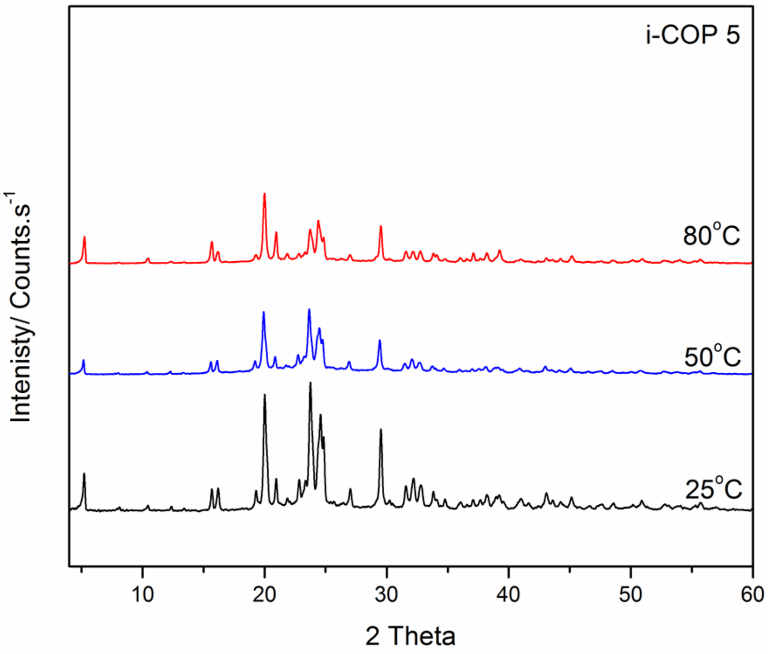


Figure S4-a. Powder X-ray diffraction patterns for crystalline ionic covalent organic polymers (i-COP 1 and 3); spectrum in black, blue and red represents diffraction pattern for i-COP 1and 3 synthesized at 25, 50 and 80°C, respectively


i-COP 5
80°C
50°C
25°C
Intenisty/ Counts.s-1
10
20
30
40
50
60
2 Theta

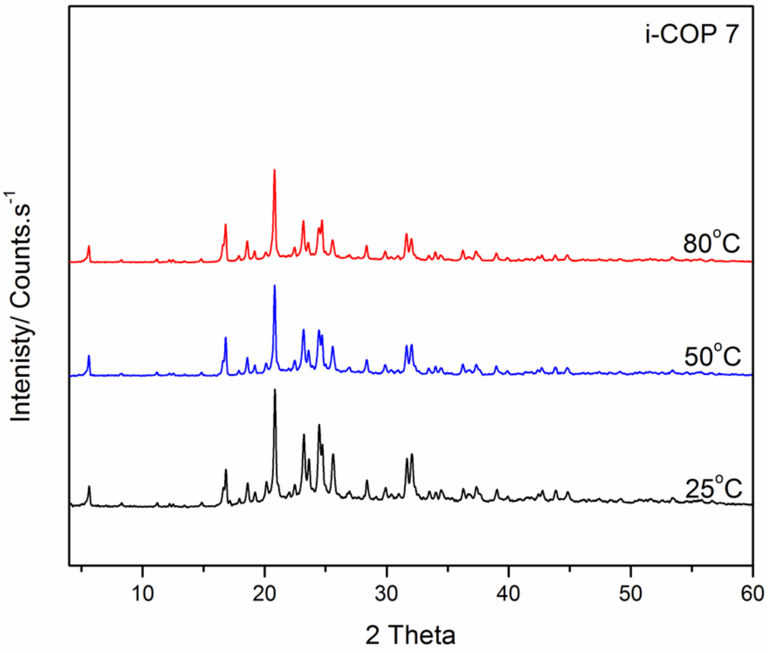

i-COP 7
80°C
50°C
25°C
Intenisty/ Counts.s-1
10
20
30
40
50
60
2 Theta

Figure S4-b. Powder X-ray diffraction patterns for crystalline ionic covalent organic polymers (i-COP 5 and 7); spectrum in black, blue and red represents diffraction pattern for i-COP 5 and 7 synthesized at 25, 50 and 80°C, respectively

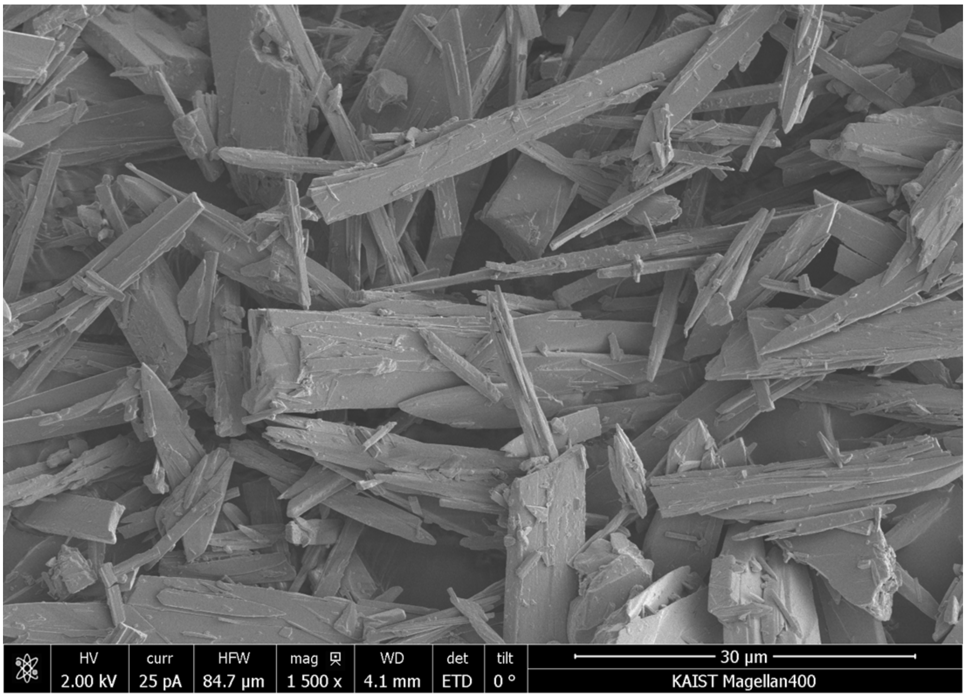


Figure S5-a: Crystalline i-COP-1 raw SEM micrograph

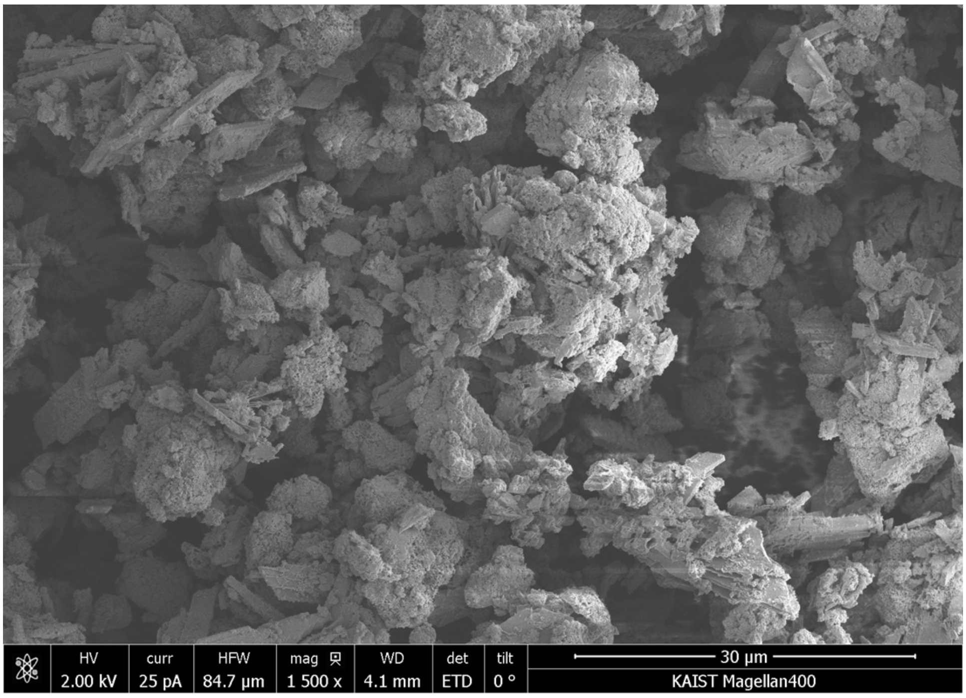


Figure S5-b: Amorphous i-COP-2 raw SEM micrograph

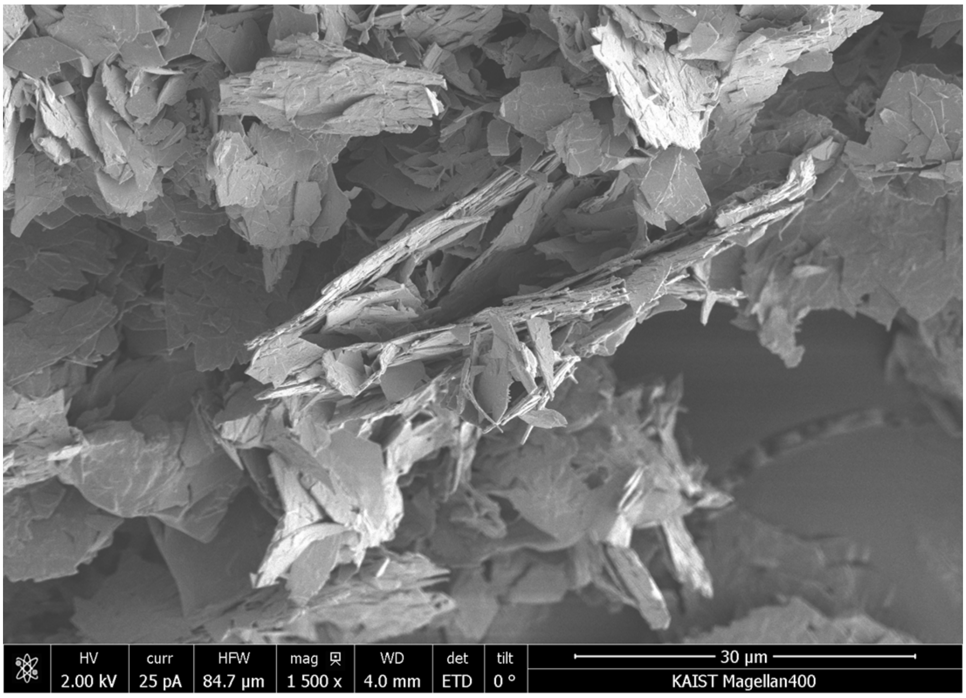


Figure S5-c: Crystalline i-COP-3 raw SEM micrograph

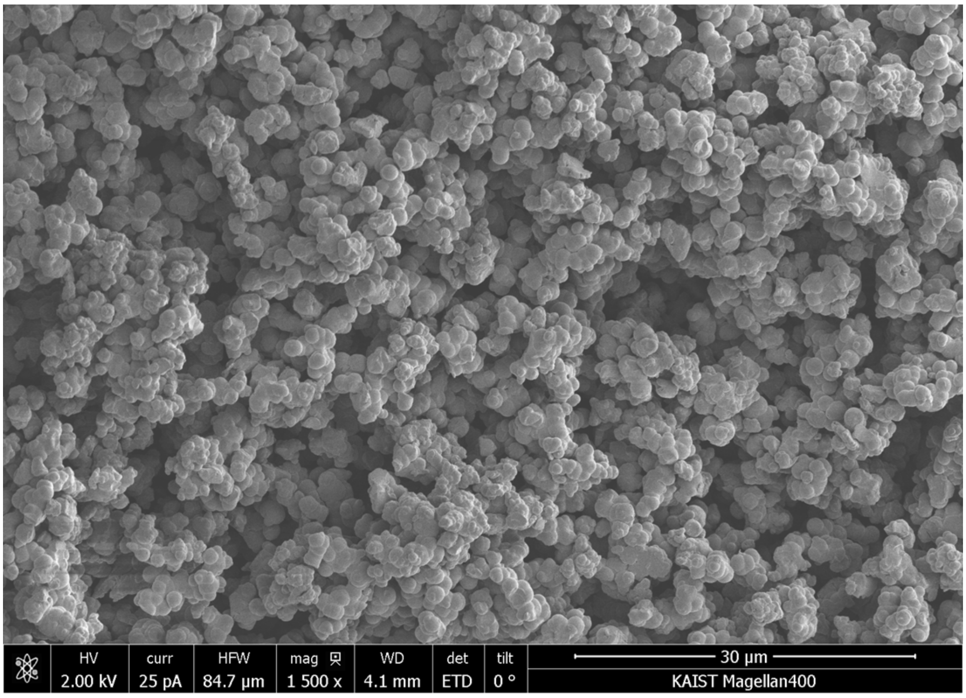


Figure S5-d: Amorphous i-COP-4 raw SEM micrograph

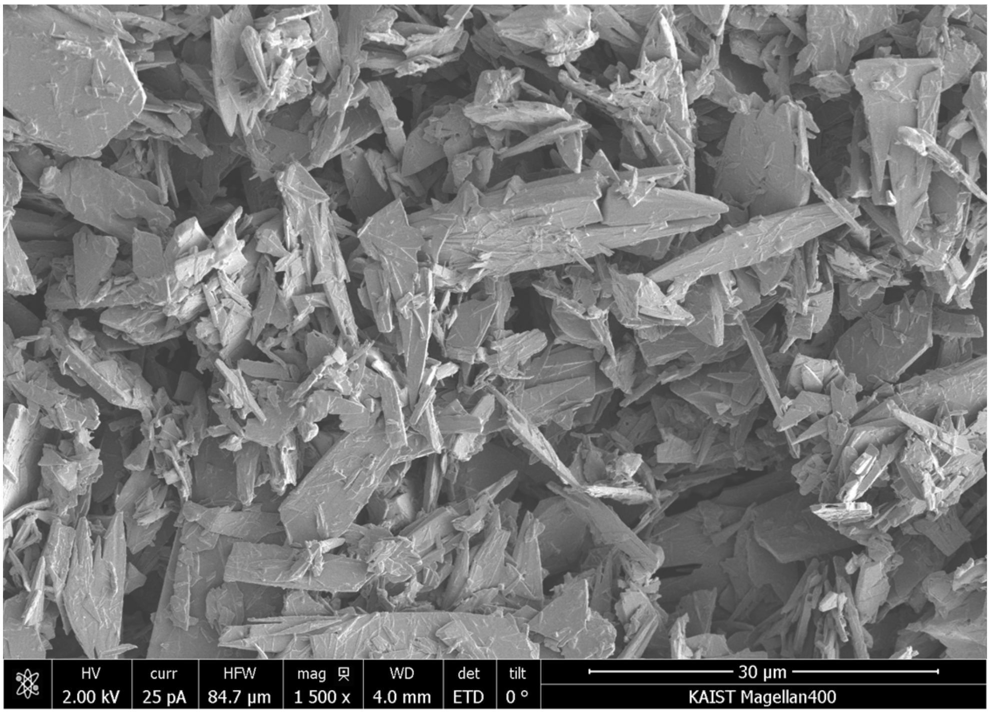


Figure S5-e: Crystalline i-COP-5 raw SEM micrograph

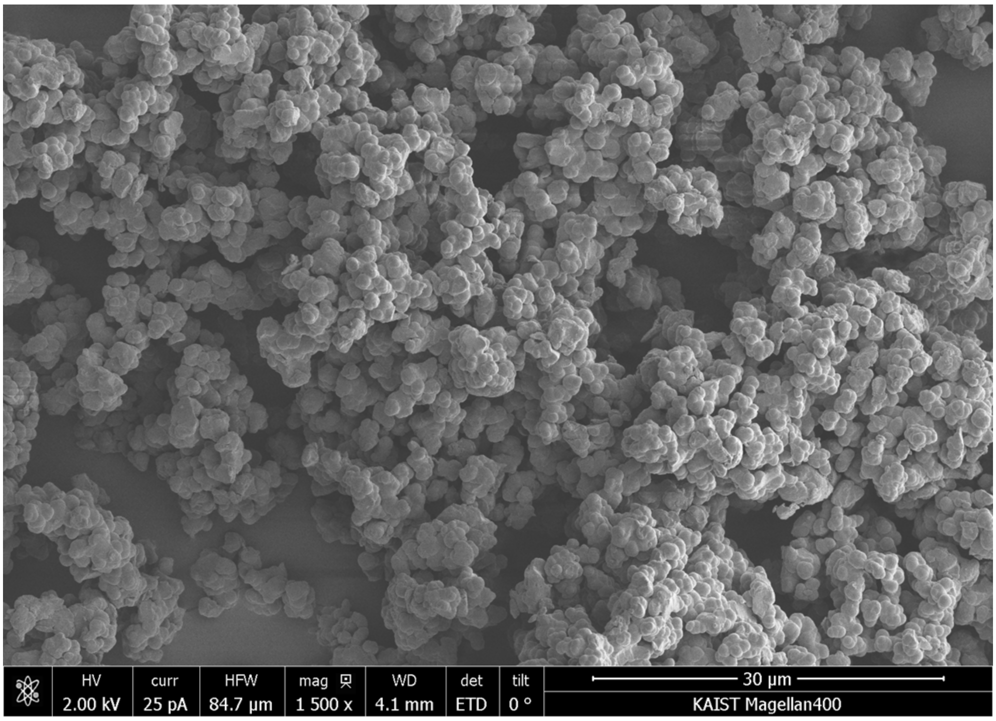


Figure S5-f: Amorphous i-COP-6 raw SEM micrograph

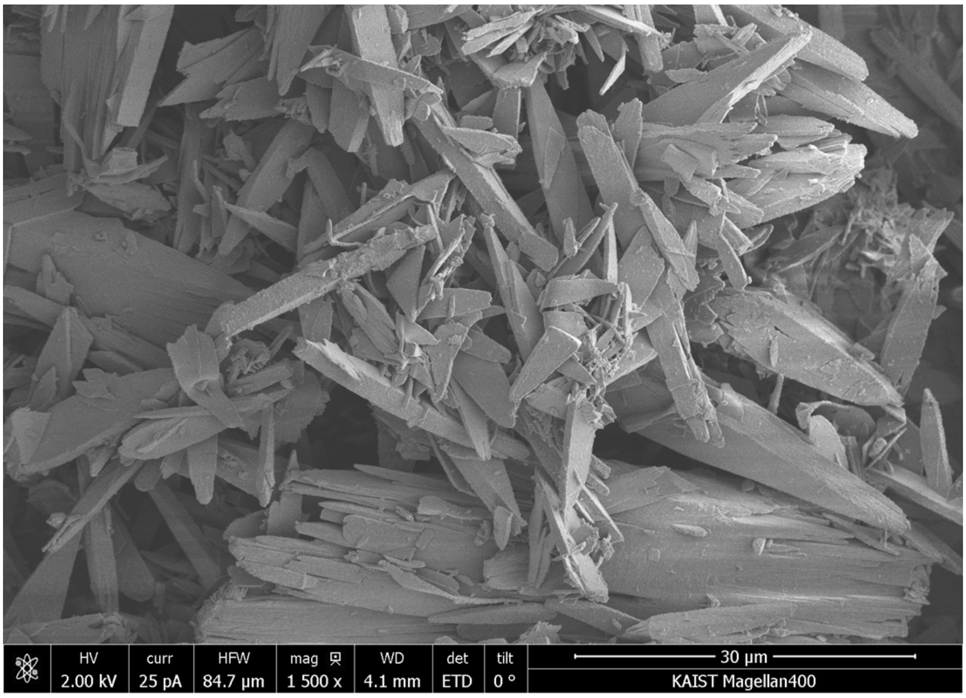


Figure S5-g: Crystalline i-COP-7 raw SEM micrograph

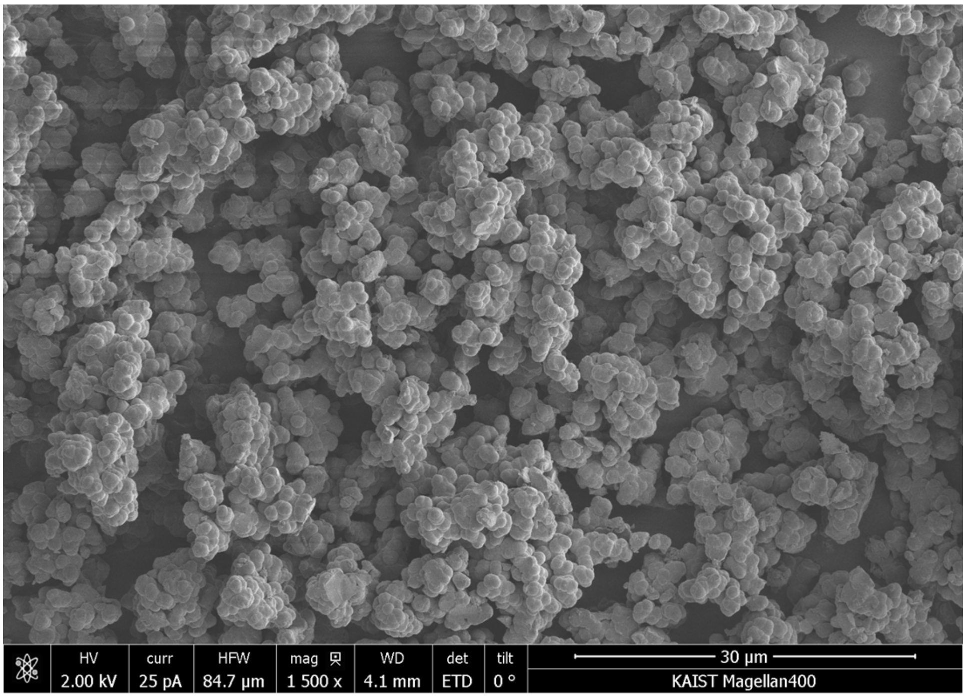


Figure S5-h: Amorphous i-COP-8 raw SEM micrograph

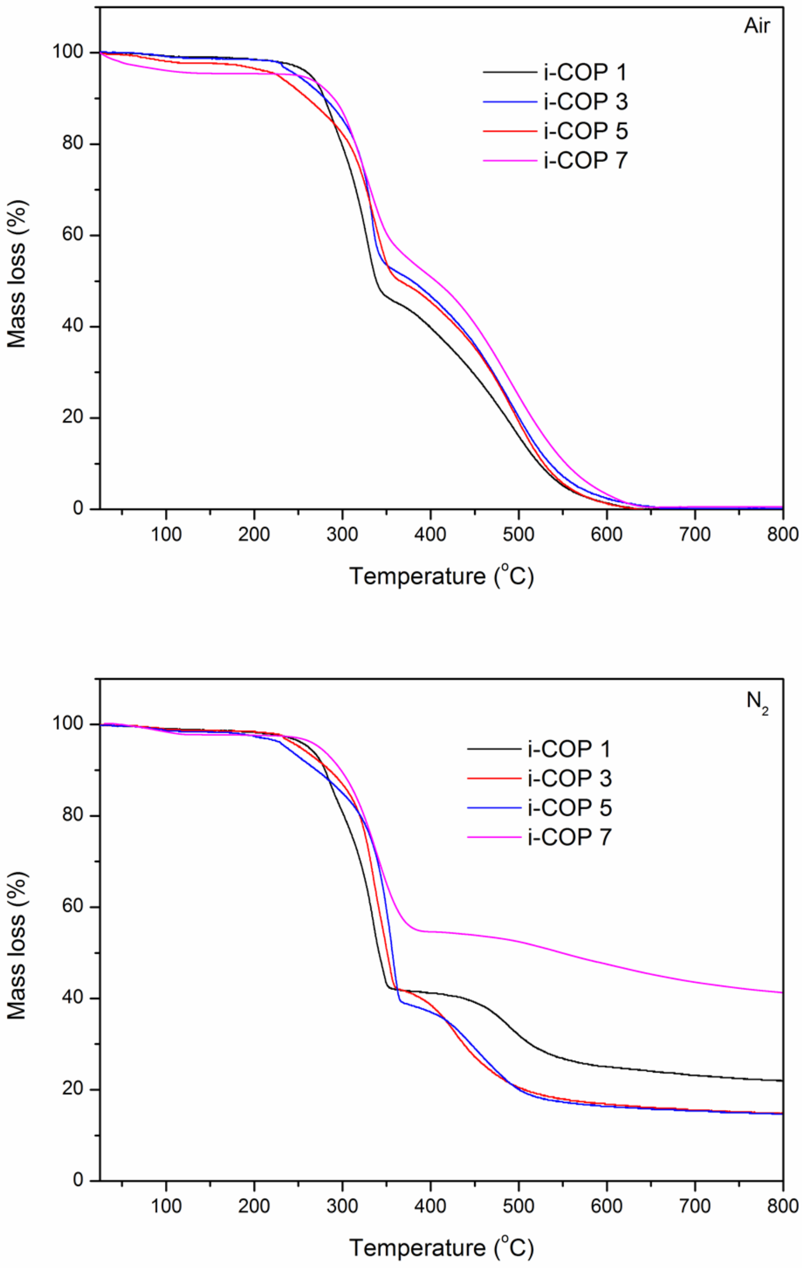


Figure S6-a: Thermogravimetric analysis for i-COP$_n$ under air and N_2 environment

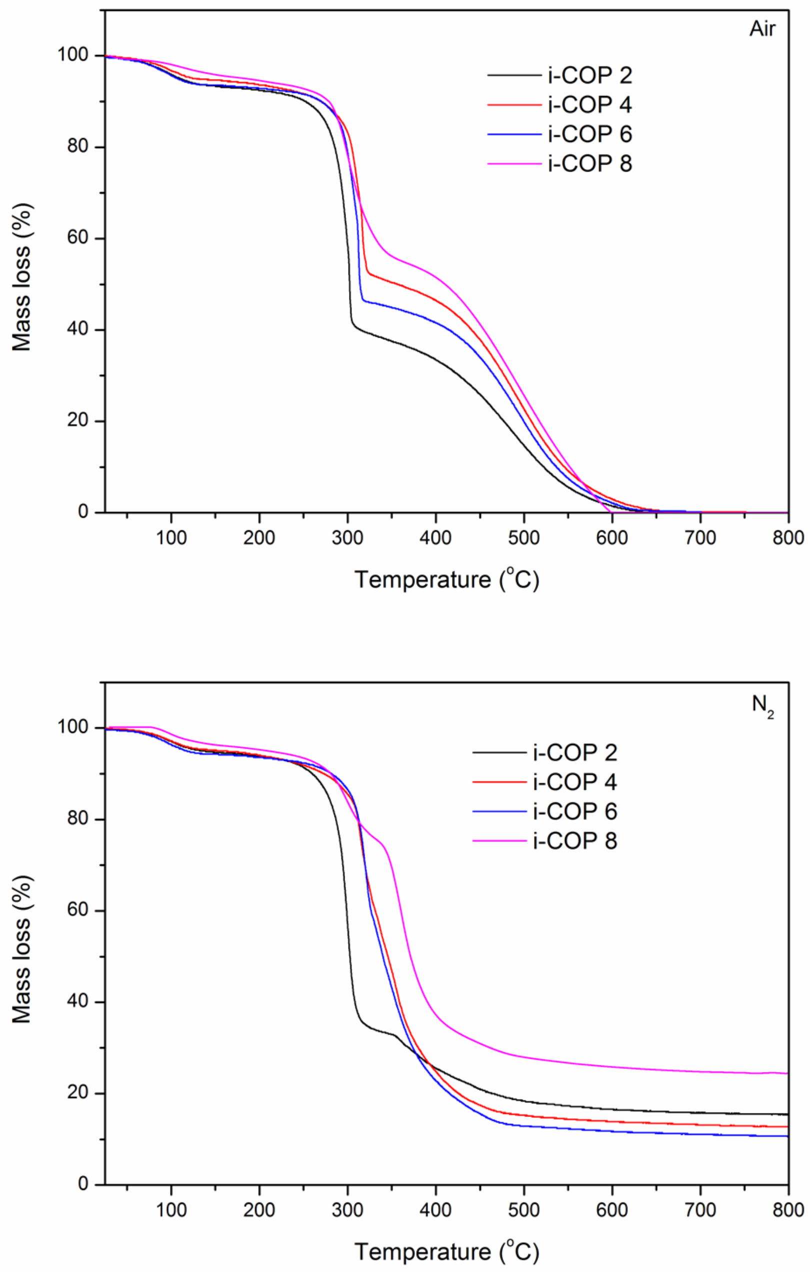
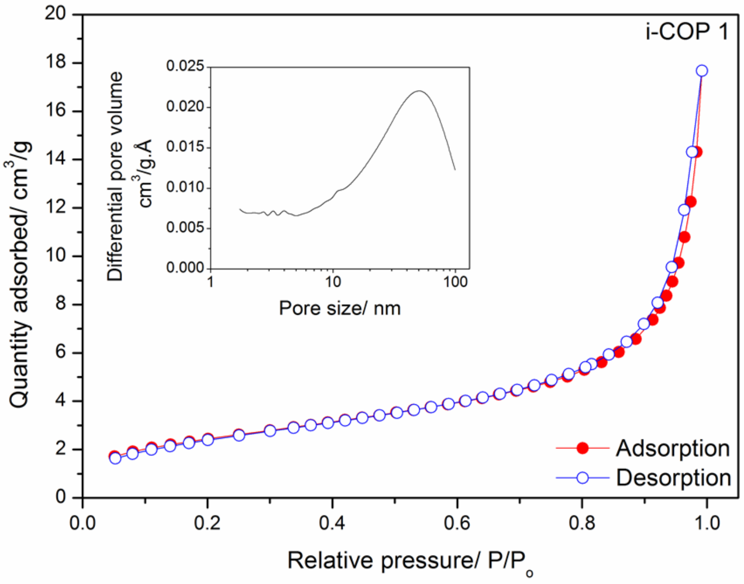


Figure S6-b: Thermogravimetric analysis for i-COP$_m$ under air and N_2 environment



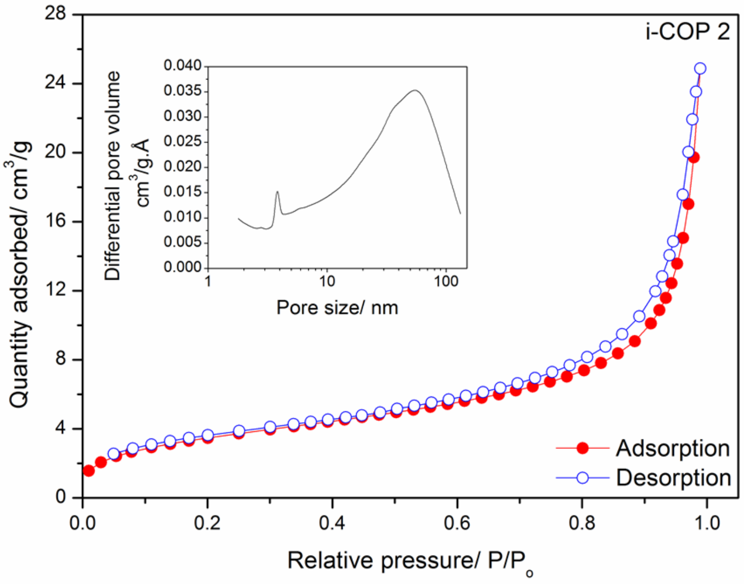


Figure S7-a: Nitrogen Physisorption Isotherms

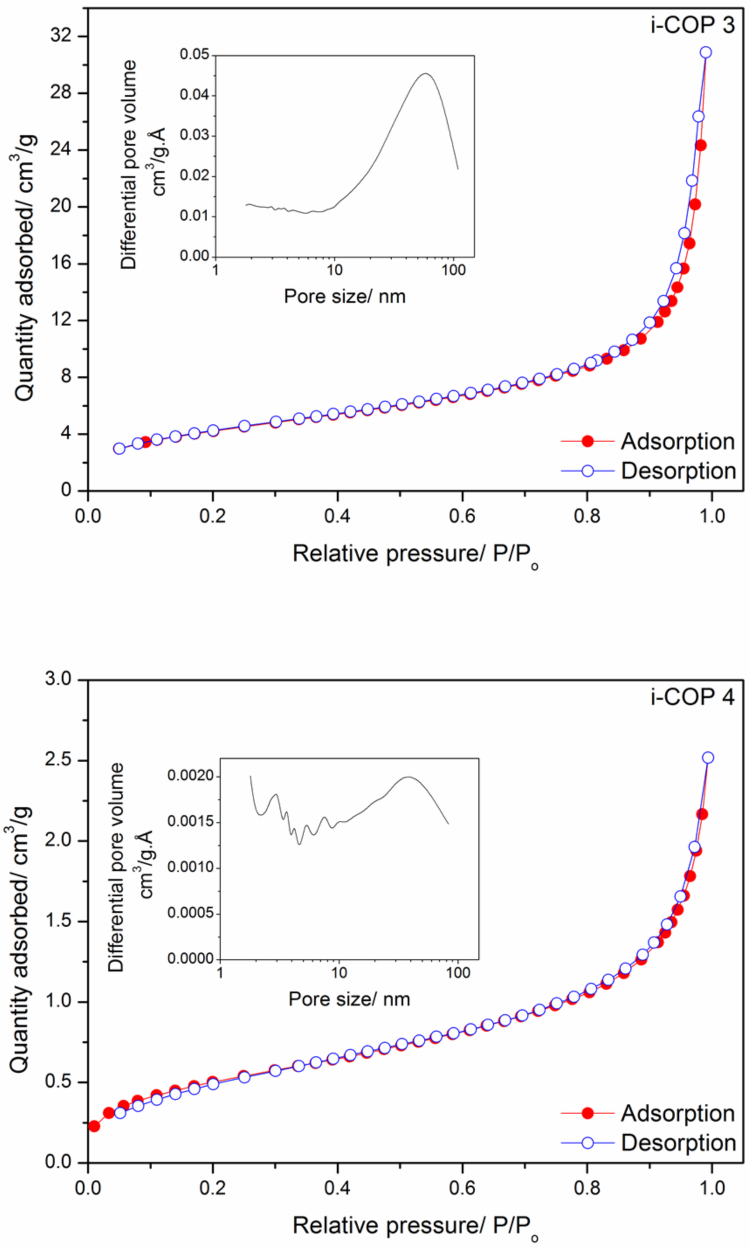
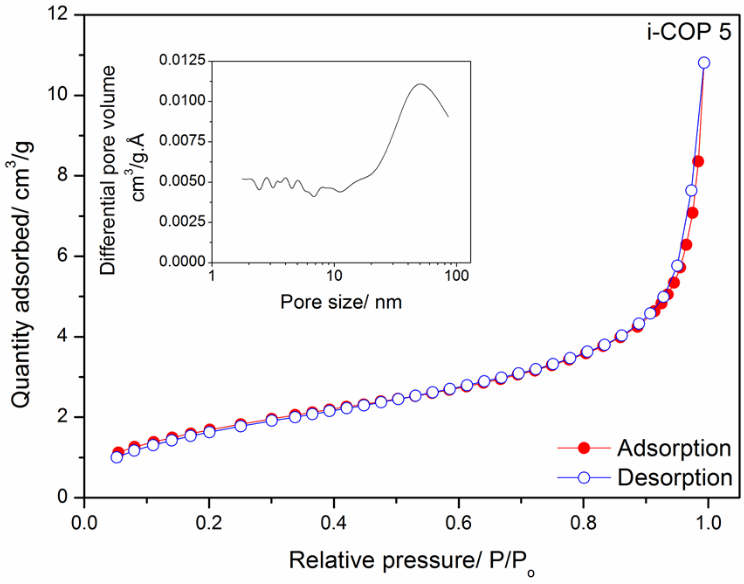


Figure S7-b: Nitrogen Physiosorption Isotherms



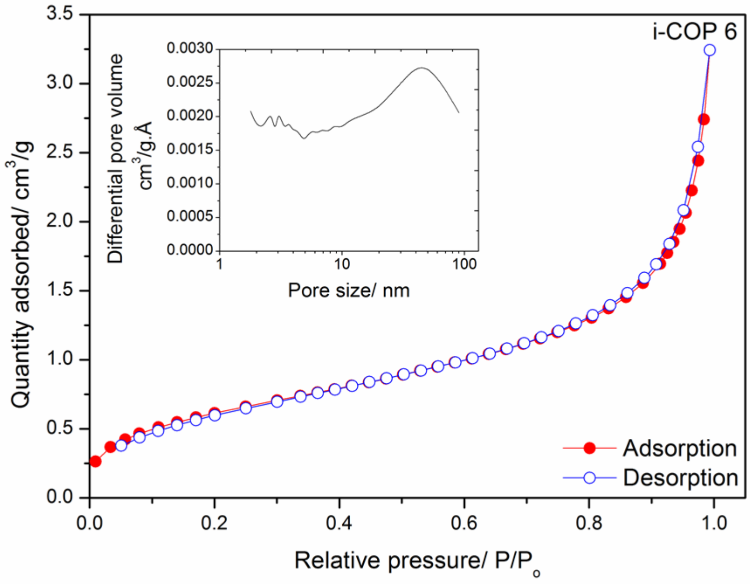


Figure S7-c: Nitrogen Physiosorption Isotherms

Note: i-COP 7 and 8 acquired very low surface area

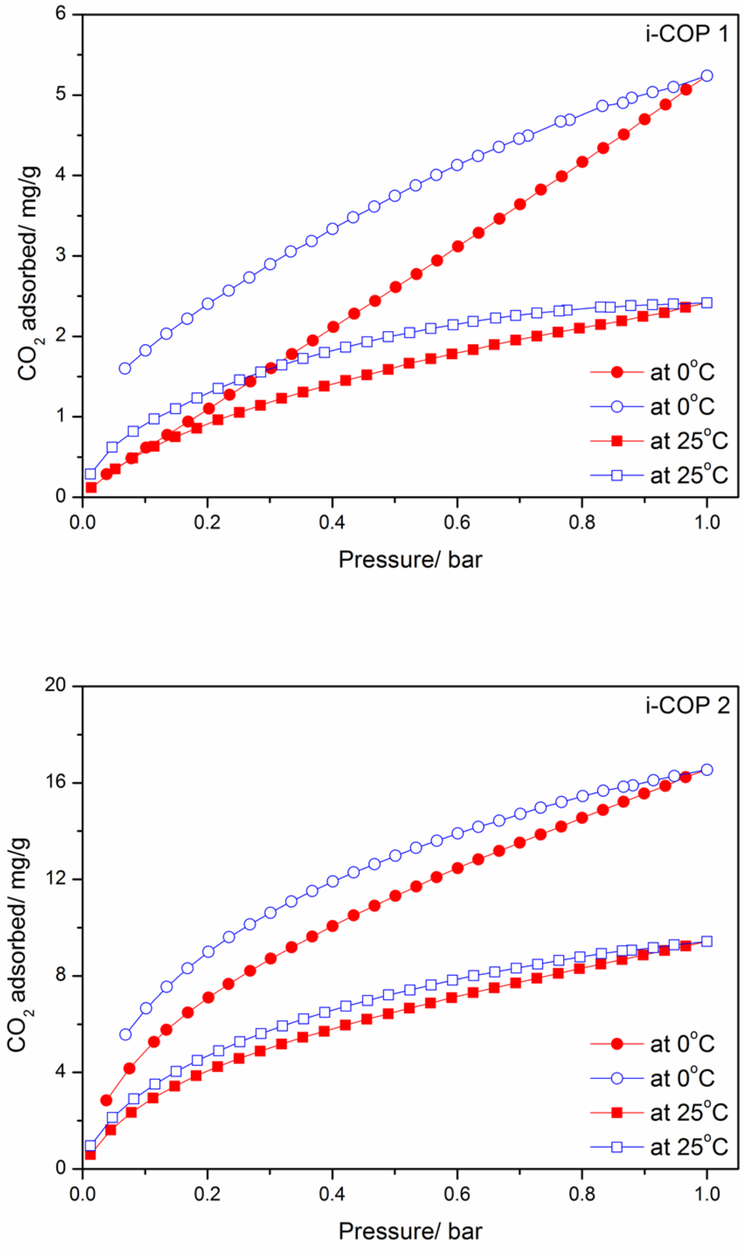
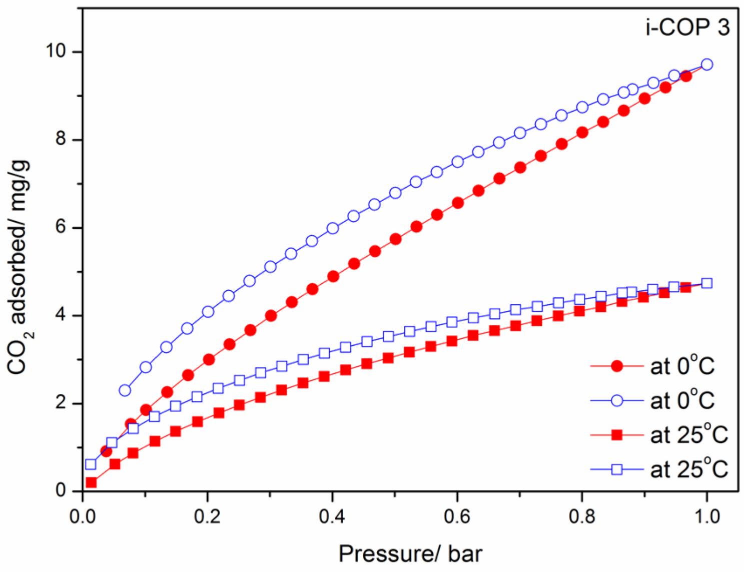


Figure S8-a: Carbon dioxide adsorption capacity



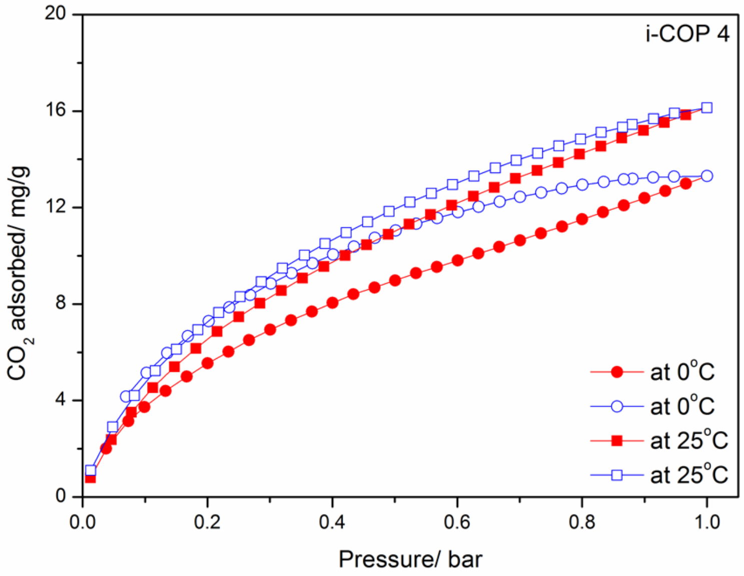
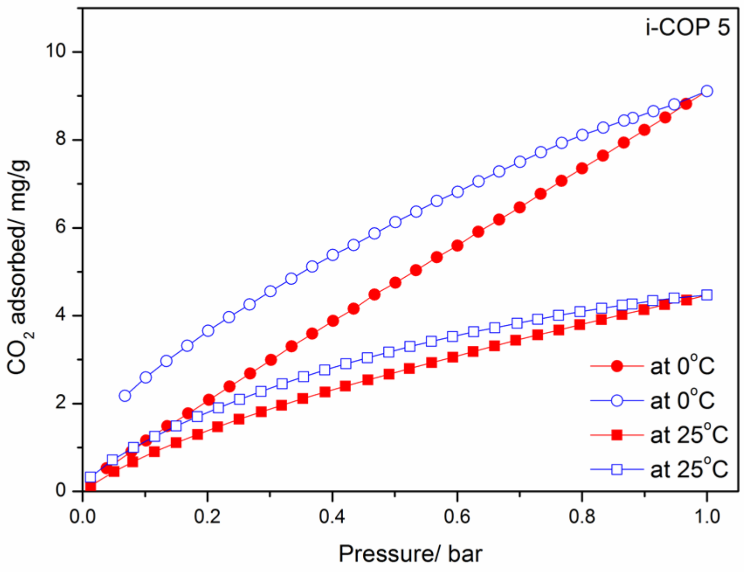


Figure S8-b: Carbon dioxide adsorption capacity



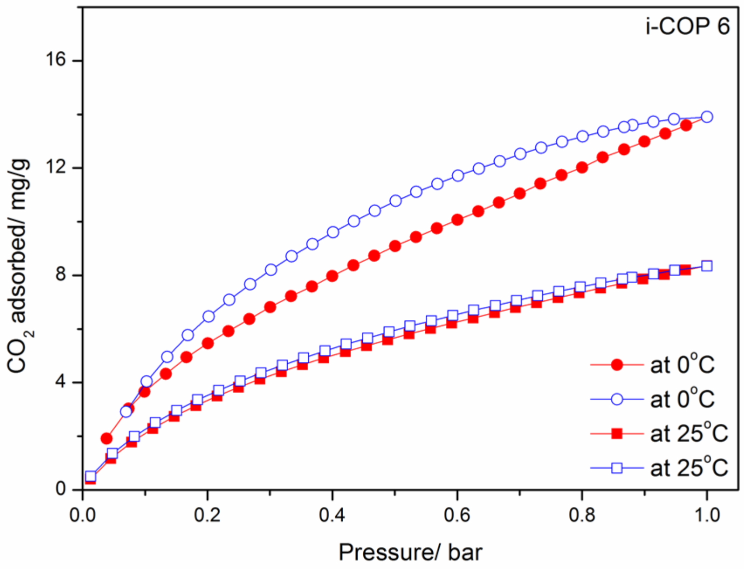
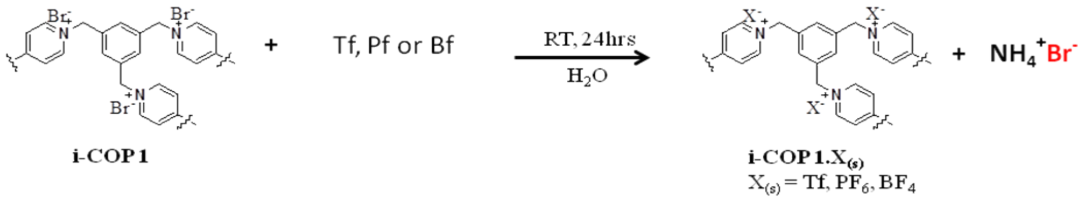


Figure S8-c: Carbon dioxide adsorption capacity

Procedure

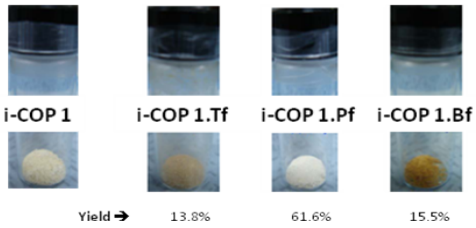
i-COP 1 (100mg/40ml H_2O) $\xrightarrow{\text{Tf/Pf/Bf}}$ **Mixed** (H_2O/RT/24hrs) → **Centrifuged** (15,000rpm/30min) → **Washed** (acetone/ethanol) → **i-COP 1.X$_{(s)}$** (dried at 60°C under vacuum)



i-COP 1 **i-COP 1.X$_{(s)}$**

$X_{(s)}$ = Tf, PF_6, BF_4

$CF_3SO_3^-K^+$ (Tf), $NH_4^+PF_6^-$ (Pf), $Na^+BF_4^-$ (Bf)



FTIR

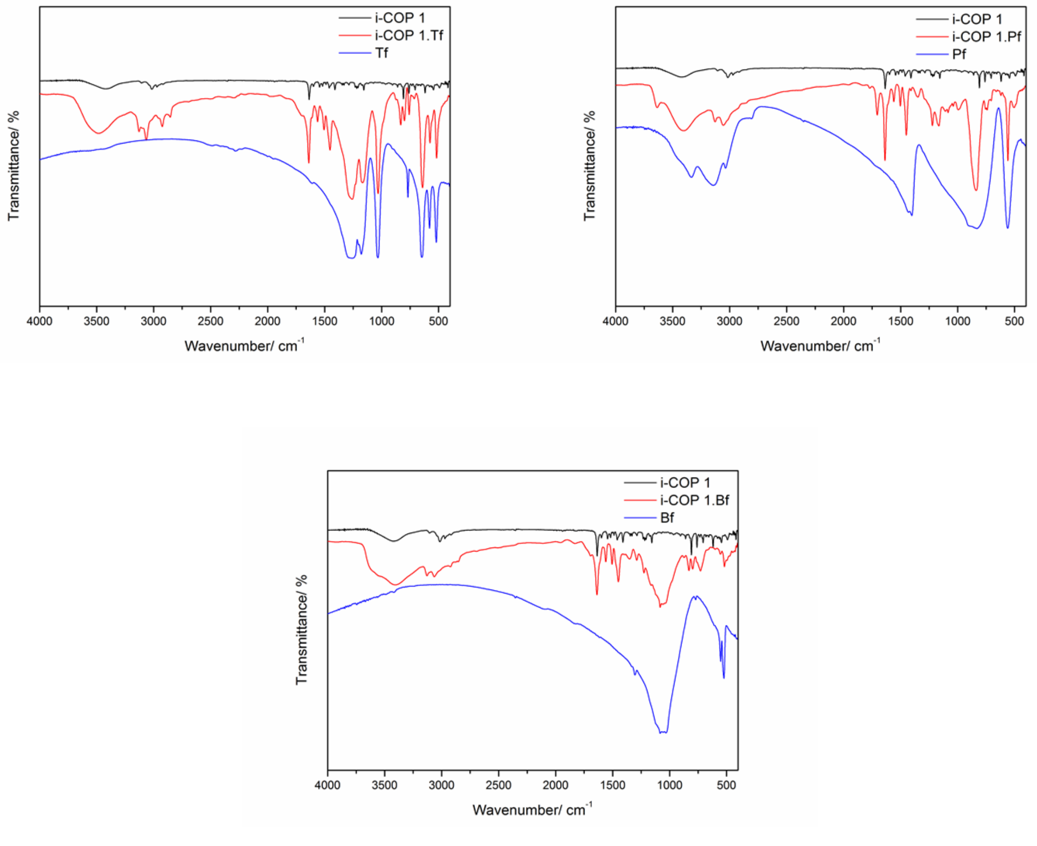


Figure S9: Ion exchange

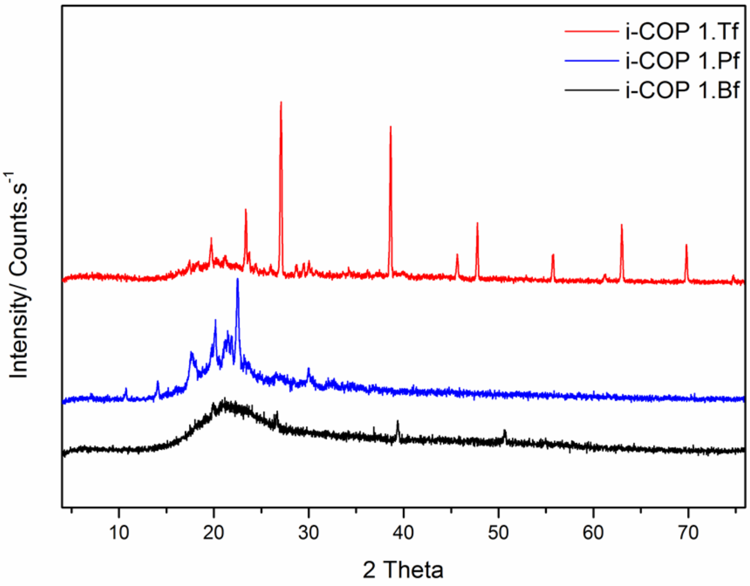
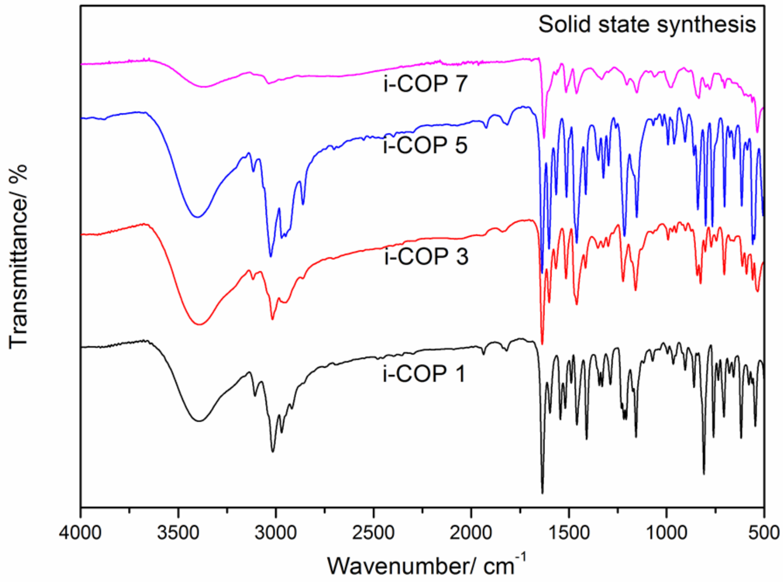


Figure S10: XRD spectrum after ion exchange



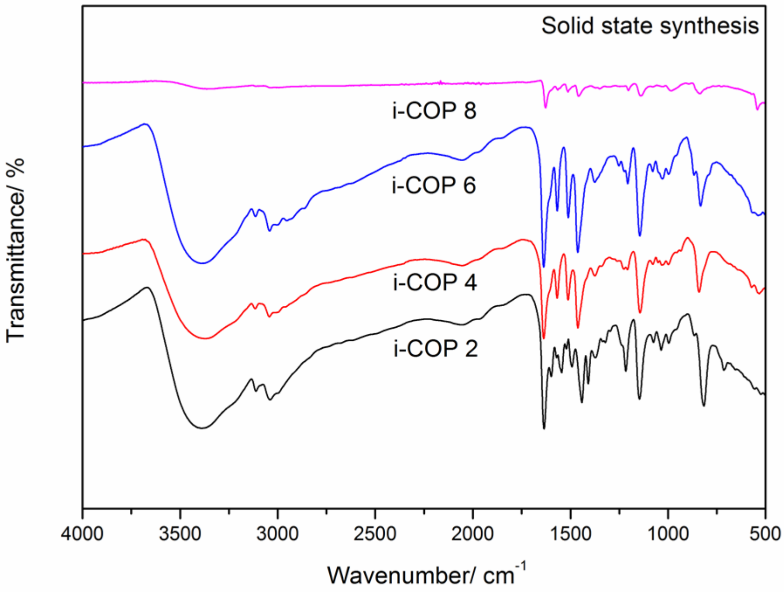
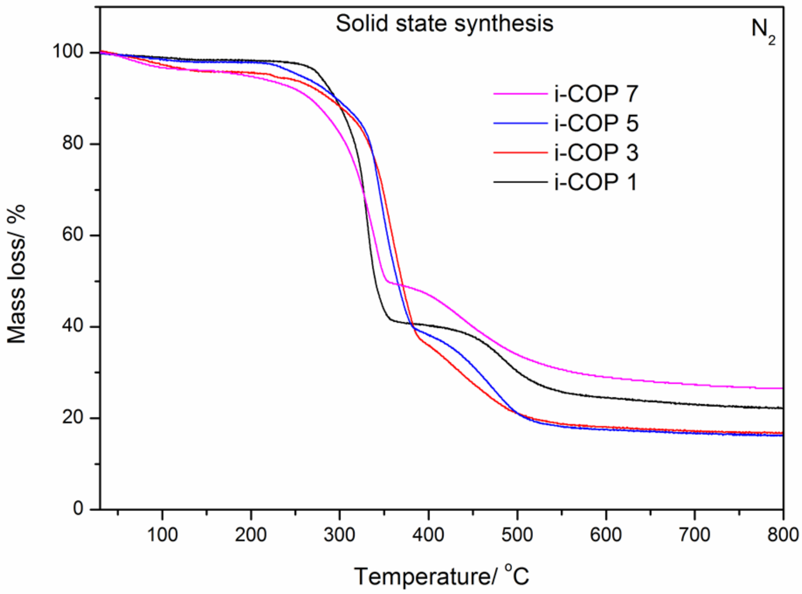


Figure S11: FTIR spectrum for i-COPs, synthesized in solid state



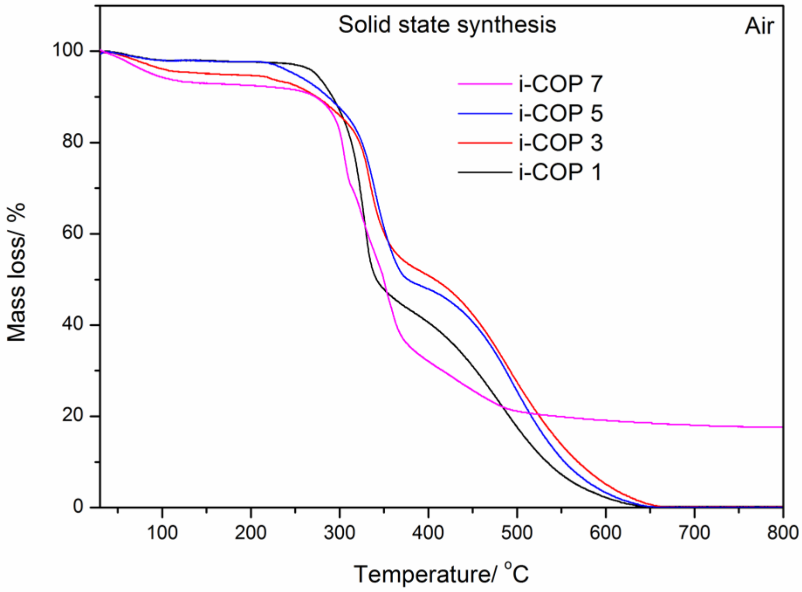


Figure S12-a: TGA for i-COPs, synthesized in solid state

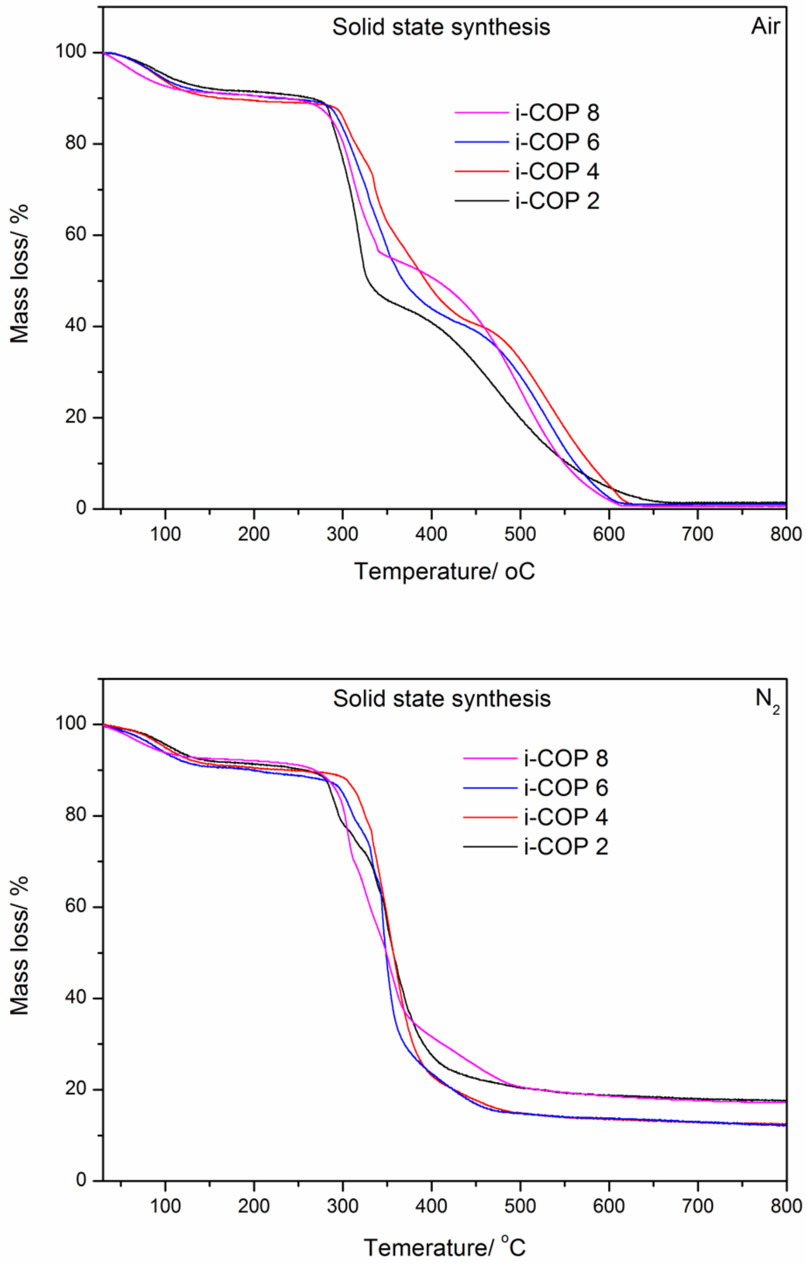


Figure S12-b: TGA for i-COPs, synthesized in solid state

Supplementary Tables

Table S1: Ratio of intensity for D to G peaks calculated from RAMAN spectrum

i-COP$_n$	**I_D (counts.s^{-1})**	**I_G (counts.s^{-1})**	**I_D/I_G**
i-COP 1	299	73	4.1
i-COP 3	28	17	1.6
i-COP 5	91	61	1.5
i-COP 7	20	327	0.06

Table S2: Surface area and pore dimensions

i-COPs / Surface and pore dimensions	i-COP$_n$				i-COP$_m$			
	1	**3**	**5**	**7**	**2**	**4**	**6**	**8**
BET, m^2.g^{-1}	9.01	15.50	6.39	-	12.93	1.88	2.31	-
Langmuir, m^2.g^{-1}	13.66	23.42	10.06	-	18.10	2.88	3.56	-
Pore size, nm	12.14	12.33	10.47	-	11.90	8.30	8.68	-
Pore volume, cm^3.g^{-1}	0.027	0.048	0.017	-	0.036	0.004	0.005	-