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Cationic Microporous Polymer Networks by Polymerisation of Weakly Coordinating Cations with CO_2-storage Ability

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General:

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Inert reactions were carried out using standard schlenk technique or in an MBraun glovebox type MB 120 BG. Nitrogen physisorption isotherms were measured at 77 K up to 1 bar using an Autosorb-1 MP from Quantachrome. Pore size distributions were calculated using the Autosorb software and a pore model for carbon with slit pores. ^{1}H-NMR, ^{31}P-NMR and ^{13}C-NMR were recorded on a Bruker DRX 200 spectrometer in the given solvent. Data are reported in the following order: chemical shift (δ) in ppm; number of protons; multiplicities are indicated br (broadened singlet), s (singlet), d (doublet), t (triplet), m (multiplet); coupling constants (J) are in Hertz (Hz). Solid state CP/MAS NMR spectras was recorded with a Bruker AVANCE II 400 spectrometer and 4 mm double resonance MAS (Magic angle spinning) probes. IR measurements were performed on a Varian IR spectrometer equipped with the attenuated total reflectance (ATR) cell and are reported in terms of frequency of absorption (cm^{-1}); intensities are indicated vs (very strong), s (strong), m (medium), w (weak). CO_2-sorption studies were performed on a Micromeritics Gemini III 2375 at 195 and 273 K. The EDX-spectra was recorded with a Philips XL 20, equipped with EDX-Detector.

Experimental section:

Materials.

PCl_3 and $Ni(COD)_2$ were obtained from Acros and were used as received. All other chemicals and solvents were obtained from Sigma-Aldrich and used as received. Anhydrous grade solvents were used throughout (Sigma-Aldrich and Acros). All chemicals used had a purity of 97% or greater. Tetrakis(4-bromophenyl) methane was synthesised according to previously reported literature.[1]

Synthesis of tris(4-bromophenyl)phosphine:

1,4-Dibromobenzene (3.51 g, 15 mmol) was dissolved in THF (30 mL) in a pre-dried schlenk flask. A solution of *n*-buthyllithium (2.5 M solution in hexane, 6.60 mL, 16.5 mmol) was added dropwise over 30 min while stirring. The resulting colourless suspension was stirred for 90 min at -78 °C. Phosphorous trichloride (0.48 mL, 5.50 mmol) was added drop wise to the stirred suspension over 45 minutes at -78 °C upon which the suspension turned increasingly red and clear. Towards the end of the addition, the solution turned quickly yellow. The mixture was then slowly warmed to room temperature over two hours. A saturated solution of sodium chloride (20 mL) was added, the organic layer separated and the aqueous layer extracted with diethyl ether (3 x 100 mL). The combined organic layers were dried over sodium sulfate and the solvent was removed *in vacuo*. The raw product was purified *via* column chromatography from *n*-hexane. After removal of the solvent the oily residue was dissolved in chloroform and the solvent removed *in vacuo* twice. The product was obtained as a colourless solid (1.472 g, 60 % yield).

^{1}H-NMR (200 MHz, $CDCl_3$): δ [ppm] = 7.46 (*d*, ^3J (H,H) = 7.7 Hz, 6H, Ar), 7.12 (*dd*, ^3J (H,H) = 8.3, ^2J (H,P) = 7.2 Hz, 6H, Ar).

^{31}P{^{1}H}-NMR (80 MHz, $CDCl_3$): δ [ppm] = -8.42 (s).

^{13}C{^{1}H,^{13}C}-NMR (50 MHz, $CDCl_3$): δ [ppm] = 135.3 (d, ^1J(C,P) = 12.4 Hz, *C*-P), 134.9 (d, ^2J(C,P) = 20.4 Hz, *C*-C-P), 132.0 (d, ^3J(C,P) = 7.1 Hz, *C*-C-Br), 124.0 (s, *C*-Br).

Synthesis of tetrakis(4-bromophenyl)phosphonium bromide:

Tris(4-bromophenyl)phosphine (100 mg, 200 µmol) was dissolved in o-xylene (0.4 mL) in a glove-box. 1,4-dibromobenzene (47 mg, 200 µmol) and $Pd(OAc)_2$ (84.5 mg, 20 µmol, 10 mol%) were added to the mixture. The reaction mixture was stirred under a N_2-atmosphere at 160 °C for 24 h. It was then cooled to room temperature and diethylether was added. After 5 min of stirring the participate was filtered off and washed with diethylether. The product was obtained as a yellow solid (60 mg, 81.6 µmol, 41% yield).

^{1}H-NMR (200 MHz, DMSO): δ [ppm] = 8.08 - 7.94 (*m*, 8H, Ar), 7.75 - 7.66 (*m*, 8H, Ar).

^{31}P{^{1}H}-NMR (80 MHz, DMSO): δ [ppm] = 23.5 (s).

^{31}P{^{1}H}-ss-NMR: δ [ppm] = 22.3 (s).

^{13}C{^{1}H,^{13}C}-NMR (50 MHz, DMSO): δ [ppm] = 137.0 (d, ^{1}J(C,P) = 11.6 Hz, *C*-P), 134.1 (d, ^{2}J(C,P) = 13.7 Hz, *C*-C-P), 132.7 (s, *C*-C-Br), 99.9 (s, *C*-Br).

IR (ATR) ũ [cm^{-1}] = 2226, 2171, 2144, 2105, 2054, 2005, 1984, 1963, 1933, 1903, 1897, 1562, 1469, 1381, 1189, 1107, 1065, 1002, 812, 742, 558.

Synthesis of CPN-1-Br:

$Ni(COD)_2$ (314 mg, 1.14 mmol, 8.14 eq.) and 2,2 '-bipyridine (178 mg, 1.14 mmol, 8.14 eq.) were weighed in a glove box and dissolved in anhydrous DMF (10 mL). 1,5-cyclooctadiene (139 mL, 1.14 mmol, 8.14 eq.) was then added and the reaction mixture was stirred at 80 °C for 1 h. A solution of tetrakis(4-bromophenyl) phosphonium bromide (100 mg, 136 µmol, 1.0 eq.) and tetrakis(4-bromophenyl)methane (95 mg, 154 µmol, 1.1 eq.) in anhydrous DMF (6 mL) was added to the reaction mixture and stirred overnight at 80 ° C. The reaction was quenched using 10 mL of conc. HCl and the precipitate was filtered off and soxhlet extracted with methanol over a day. The product was obtained as a white powder (102 mg, 97% yield).

^{31}P{^{1}H}-ssNMR: δ [ppm] = 23.9 (br).

^{13}C{^{1}H,^{13}C}-ssNMR: δ [ppm] = 143.4, 137.5, 129.3, 125.3, 62.9.

IR (ATR) ũ [cm^{-1}] **=** 3024, 2931, 2244, 1855, 1599, 1484, 1186, 1113, 999, 917, 806, 697.

Synthesis of CPN-1-Cl:

Ion exchange was carried out by slurrying 100 mg CPN-1-Br overnight in a mixture of brine (50 mL) and MeOH (50 mL) and then filtered off. This procedure was repeated two more times. After the third repetition the material was washed by soxhlet extraction with methanol and dried overnight at 50° C in a vacuum oven. A yellowish fluffy powder was obtained.

Synthesis of CPN-2-Br:

In a glovebox under inert atmosphere a schlenk tube was charged tetrakis(4-bromophenyl)phosphonium bromide (200 mg, 0.27 mmol), $Pd(PPh_3)_4$ (14.0 mg, 12 µmol, 4.5 mol%) and CuI (4.4 mg, 23 µmol, 8.5 mol%) and dissolved in anhydrous DMF (4 mL) and triethylamine (4 mL). The reaction mixture was stirred for 5 min and 1,3,5-triethynylbenzene (52,4 mg, 0,35 mmol) was added then stirred at 90 °C for 72 h.

The precipitated material was separated from the solution and washed several times with H_2O, methanol and dichloromethane. The product was washed by soxhlet extraction with dichloromethane and dried under high vacuum for 1 h. The product was obtained after a soxhlet extraction with MeOH over three days as a dark brownish powder (160 mg, 99 %).

$^{31}P\{^1H\}$-ssNMR: δ [ppm] = 25.4 (br).

$^{13}C\{^1H,^{13}C\}$-ssNMR: δ [ppm] = 129.7, 126.6, 122.0, 89.1.

IR (ATR) ũ [cm^{-1}] = 2241, 2213, 2165, 2108, 2048, 2021, 1978, 1963, 1927, 1680, 1592, 1484, 1436, 1391, 1186, 1110, 1011, 872, 824, 745, 724, 688.

Reference

L. M. Wilson and A. C. Griffin, *J. Mater. Chem.*, **1993**, *3*, 991-994.

S3 Analysis results

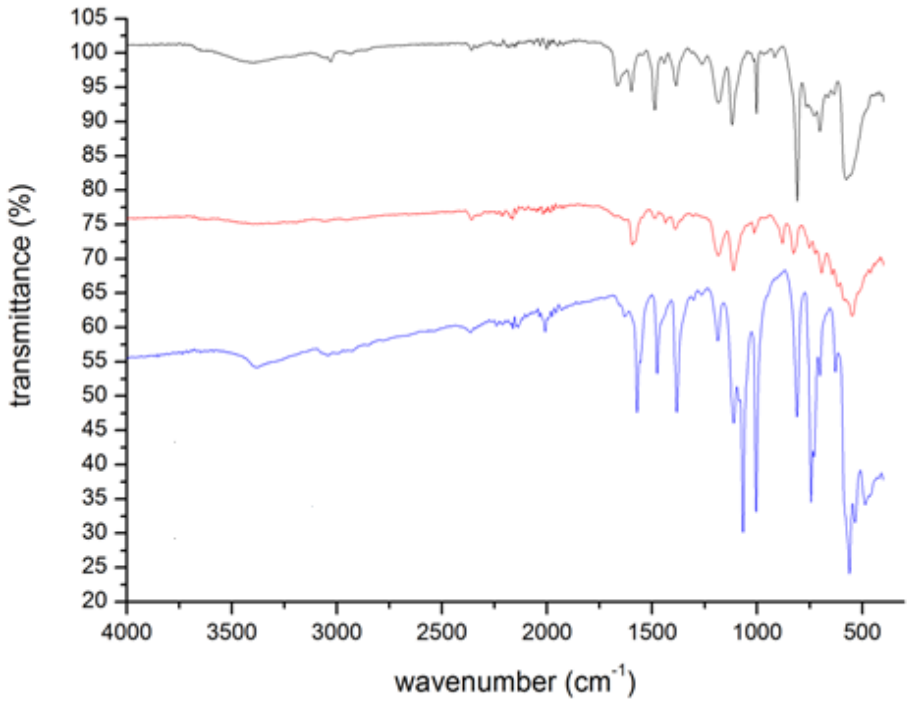

Figure S1: Infrared Spectrum of the monomer (blue) and the corresponding networks CPN-1-Br (black) and CPN-2-Br (red).

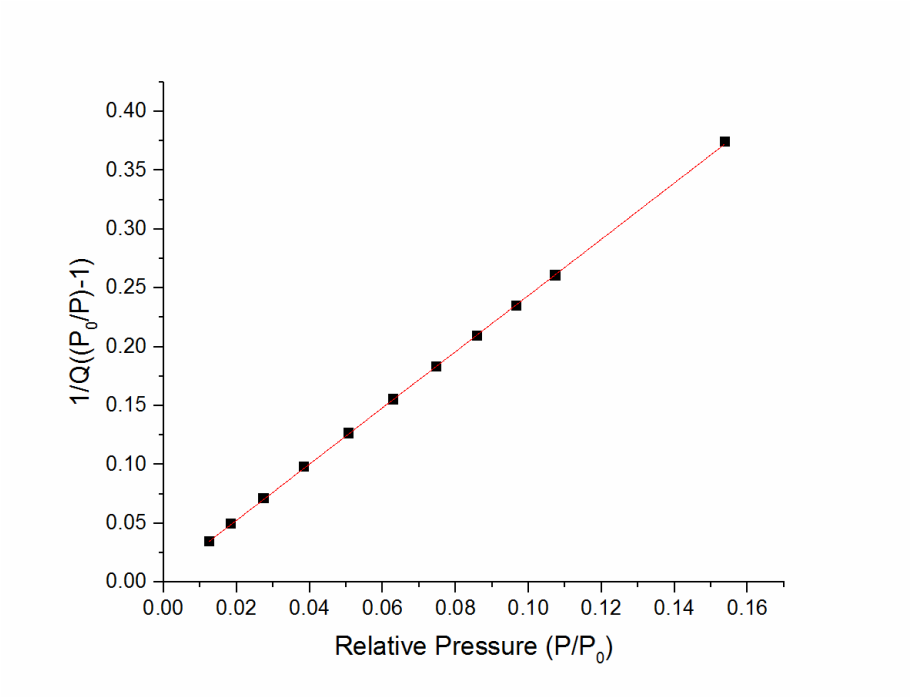

Figure S2: BET plot for CPN-1-Br.

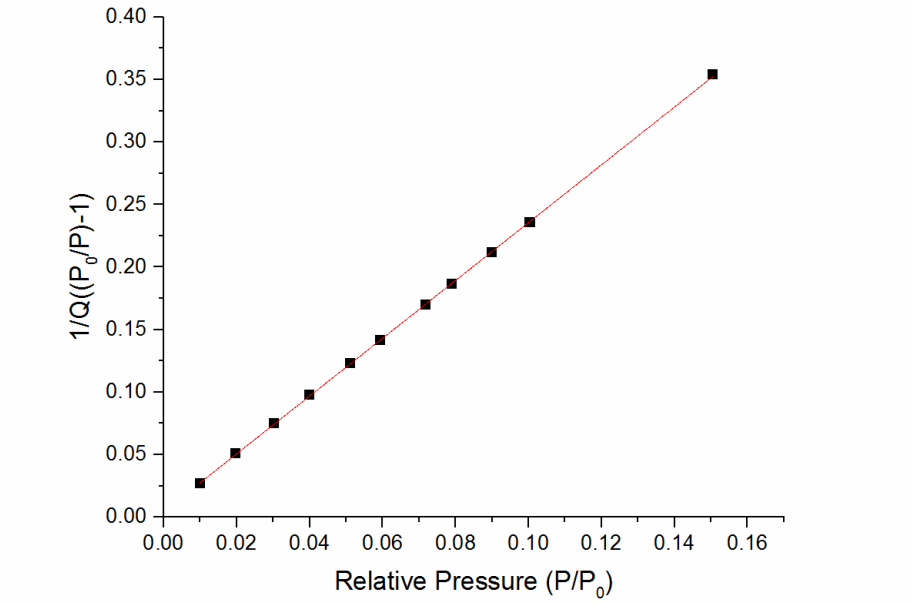

Figure S3: BET plot for CPN-1-Cl.

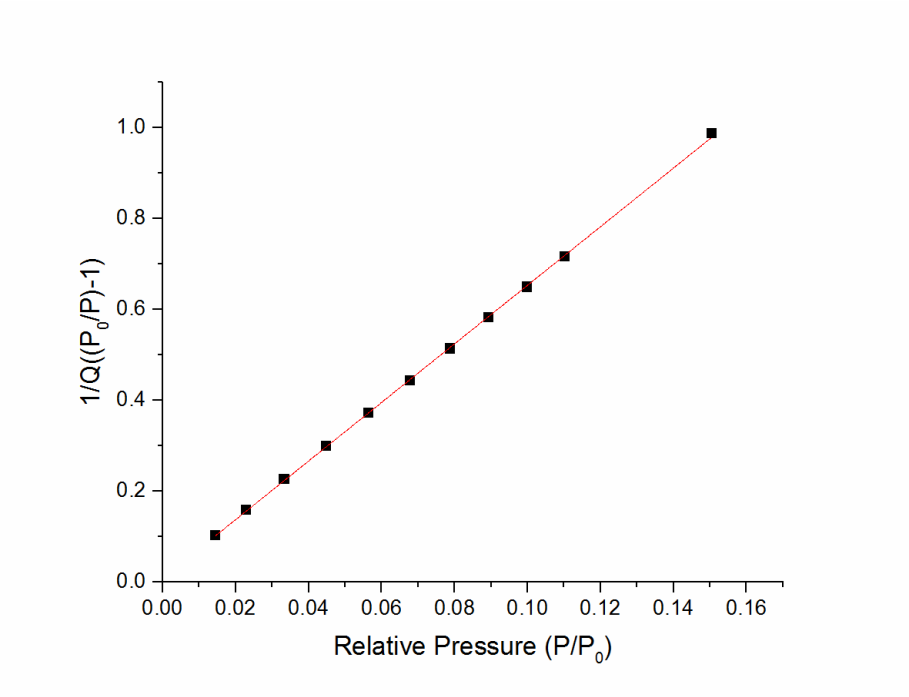

Figure S4: BET plot for CPN-2-Br.

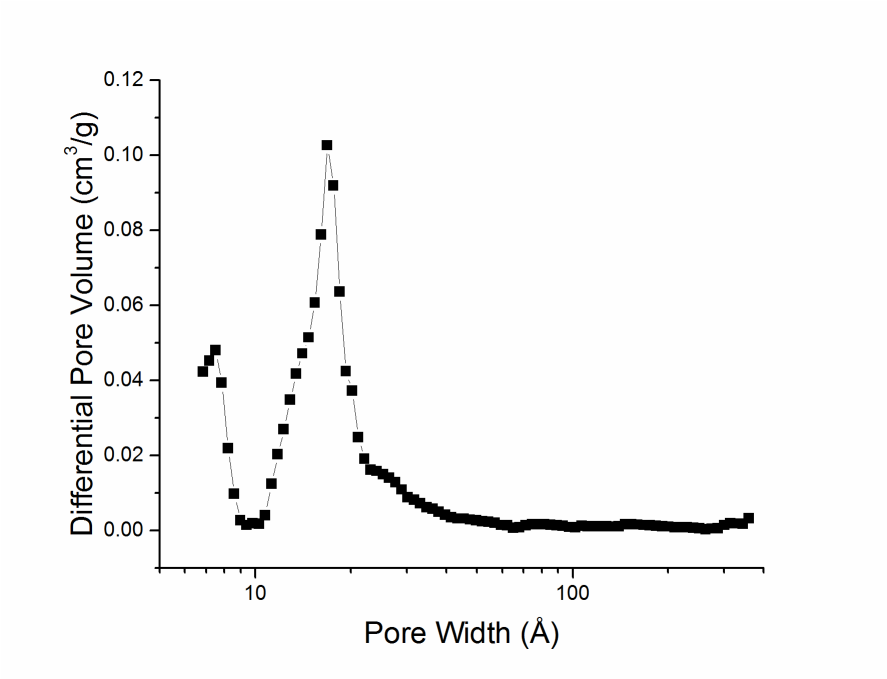

Figure S5: NLDFT pore size distribution for CPN-1-Br

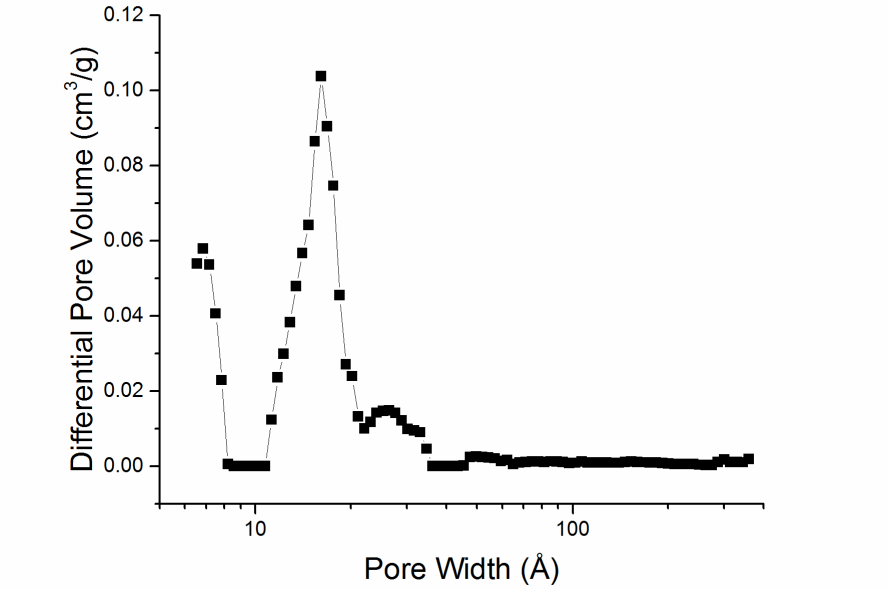

Figure S6: NLDFT pore size distribution for CPN-1-Cl

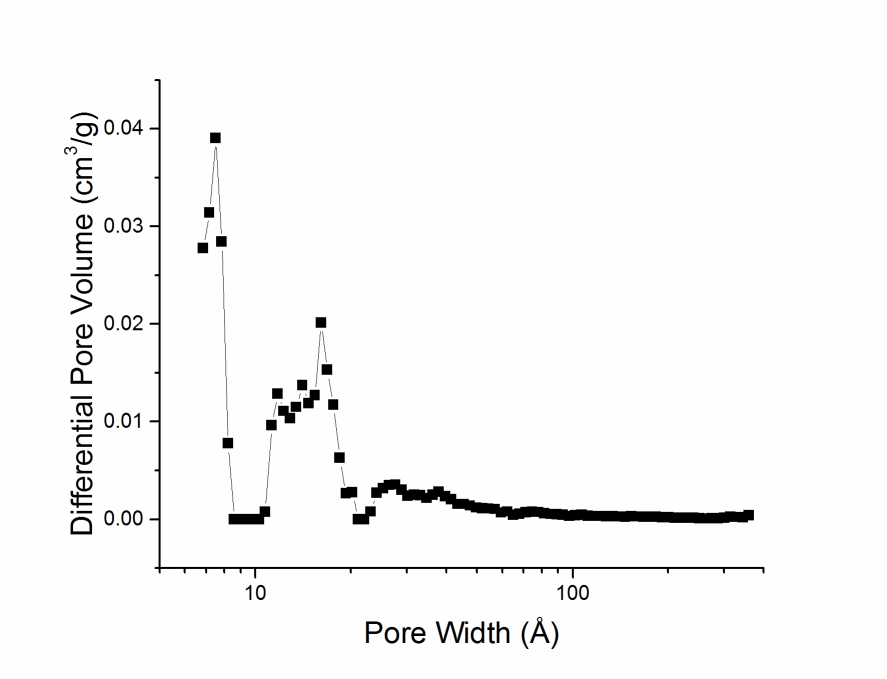

Figure S7: NLDFT pore size distribution for CPN-2-Br

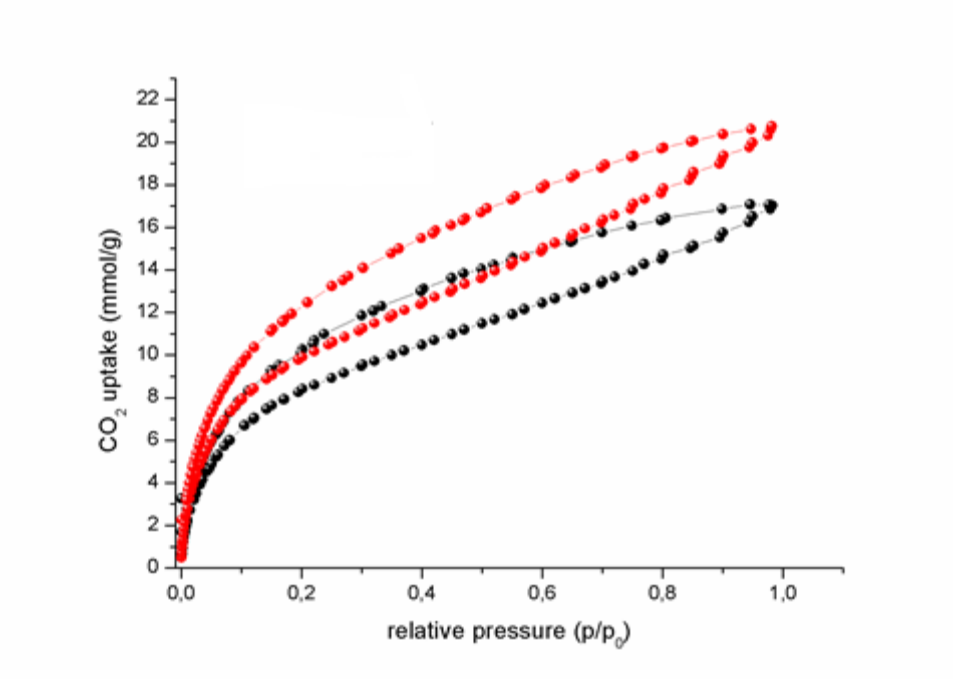

Figure S8: CO_2 sorption at 195 K of CPN-1-Br (black) and CPN-1-Cl (red).

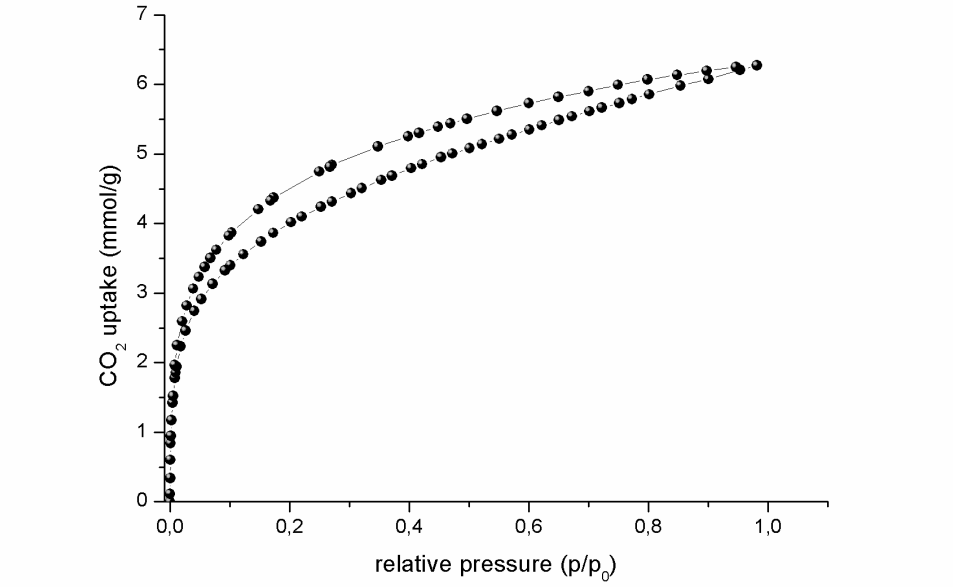

Figure S9: CO_2 sorption at 195 K of CPN-2-Br.

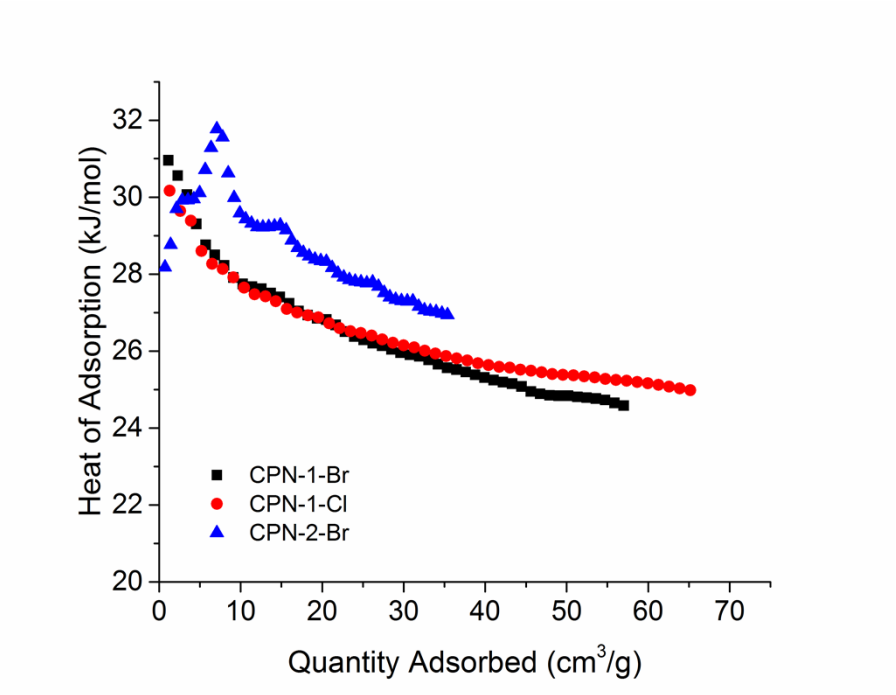

Figure S10: CO_2 heats of adsorption for CPN-1-Br (black squares), CPN-1-Cl (red circles) and CPN-2-Br (blue triangles).

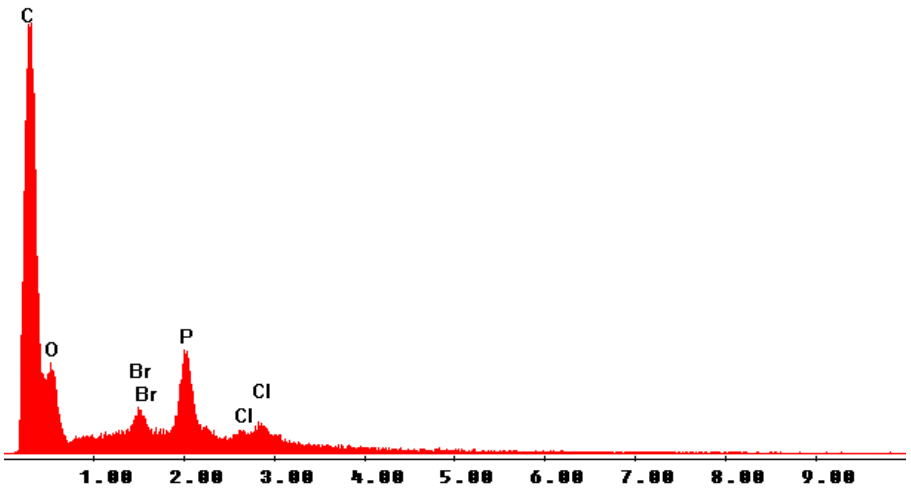

Figure S11: EDX analysis of CPN-1-Br.

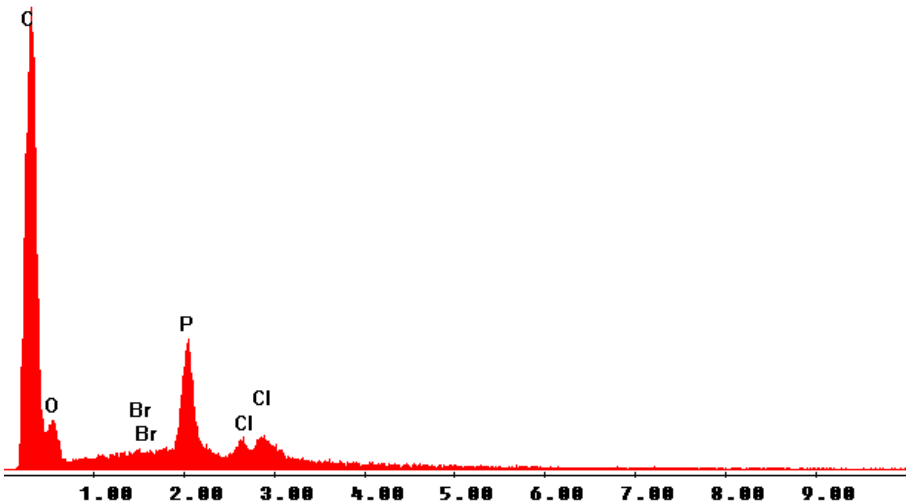

Figure S12: EDX analysis of CPN-1-Cl.

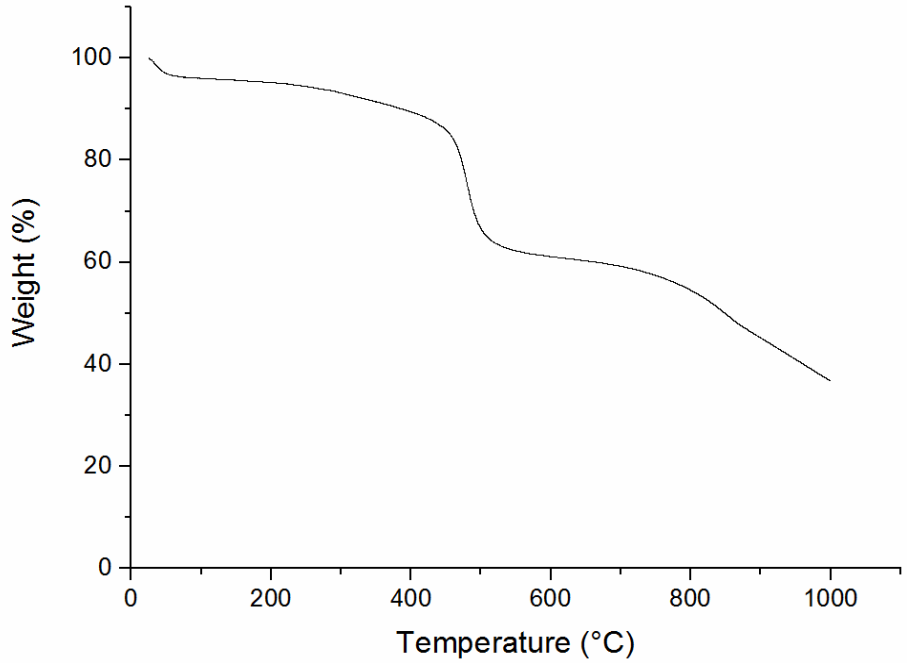

Figure S13: TGA analysis of CPN-1-Br.

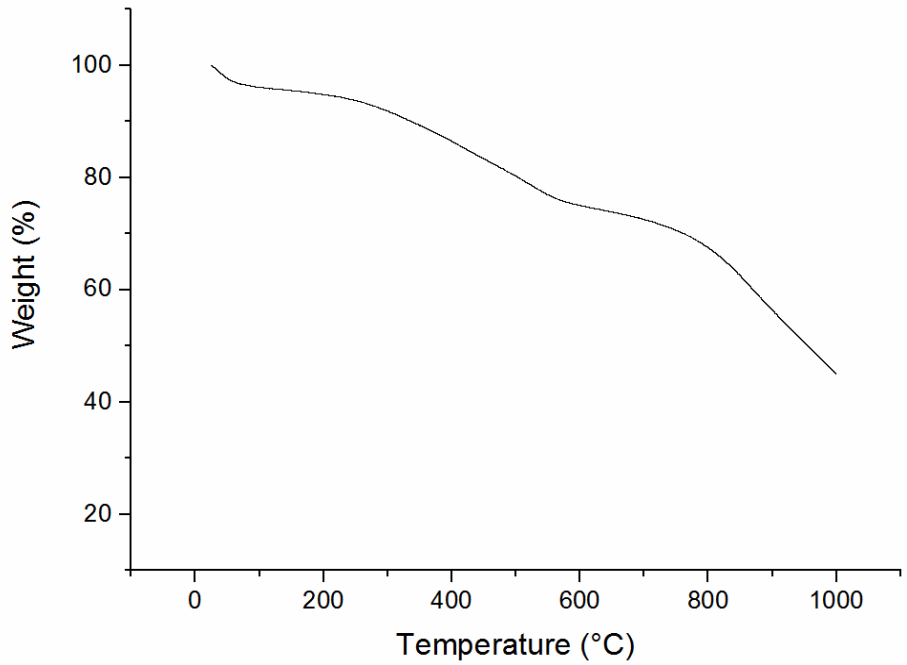

Figure S14: TGA analysis of CPN-2-Br.