Electronic Supplementary Material (ESI) for RSC Advances.

One Pot Synthesis of Zr-Carboxylate Porous Hybrid Materials: Orthogonal C–C Heterocoupling and Carboxylate-Zr Assembly

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Contents

Experimental Procedures

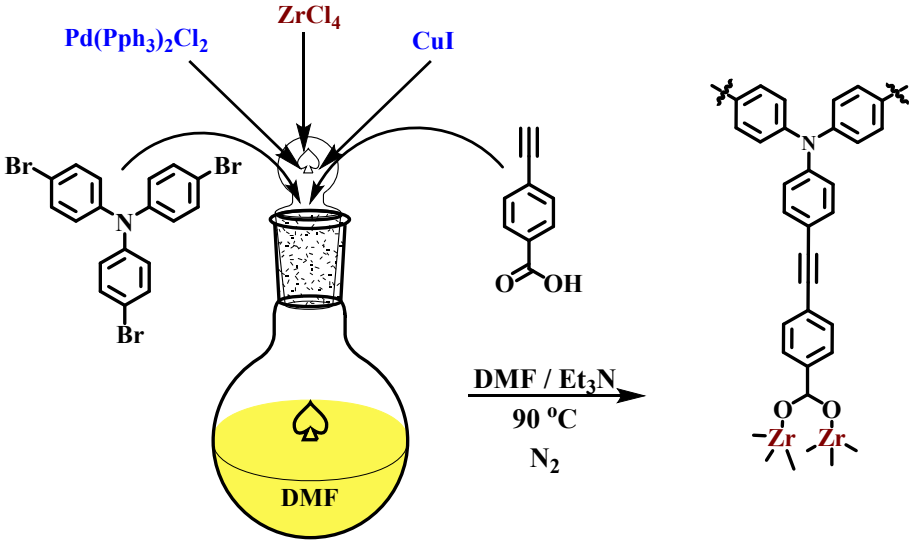
All reagents were used as received without further purification. Solvents, catalysts, and common chemicals were purchased from Sigma-Aldrich or Fisher Scientific-UK. Brominated aromatics were purchased from Combi-Blocks. Nitrogen and CO_2 gases for sorption were purchased from Airliquide (N_2 AlphaGaz2 (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.

Infra-red absorption spectra were recorded on ThermoScientific **Nicolet is-10**. Synthetic reactions were performed under nitrogen atmosphere in oven-dried glassware

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.

SEM images were recorded on FEI-NovaNano SEM 450 equipped with EDAX - Octane Silicon Drift Detector, TEAM™ EDS Analysis Systems for EDX analysis.

Compound 1



In a glass pressure vessel fitted with teflon screw cap (50 mL) charged with a magnetic stirrer a solution of **4-ethynylbenzoic acid** (0.5 mmol, 0.073 g) in **DMF** (15 mL) was prepared and **$ZrCl_4$** (0.25 mmol, 0.0583 g) was then added to the solution and the solution stirred for 1 hour at room temperature (solution turns from clear red to fluorescent orange-red upon addition of the $ZrCl_4$). To this solution was then added **Et_3N** (5 mL) and the vessel was capped with silicon septum, and the solution was degassed through three freeze-pump-thaw cycles and backfilled with nitrogen. To this solution and under nitrogen atmosphere was added **tris-(4-bromophenyl)-amine** (0.165 mmol, 0.079 g), **bis-(triphenylphosphine)palladium(II) dichloride** (0.014 mmol, 10 mg), **CuI** (0.04 mmol, 5 mg) and **triphenylphosphine** (0.02 mmol, 5 mg) and the flask was then evacuated/backfilled with nitrogen and sealed and the mixture was stirred at 90 °C for 24 h to result in yellow-colored precipitate. The reaction vessel was then cooled to room temperature, opened to air and the solid filtered through a fritted funnel, washed with DCM/DMF and kept under Acetonitrile for guest exchange for one week prior to gas sorption measurements. Activation for gas sorption included evacuation under dynamic vacuum at 90°C for 4 hours followed by ramping to 100°C and degassing for additional 6 hours. Note: upon degassing the sample changed color from faint yellow to deep brown. Total dry weight of the product was 0.1053 g, 78% yield based on the sum of masses for reactants excluding counterions and bromine atoms.

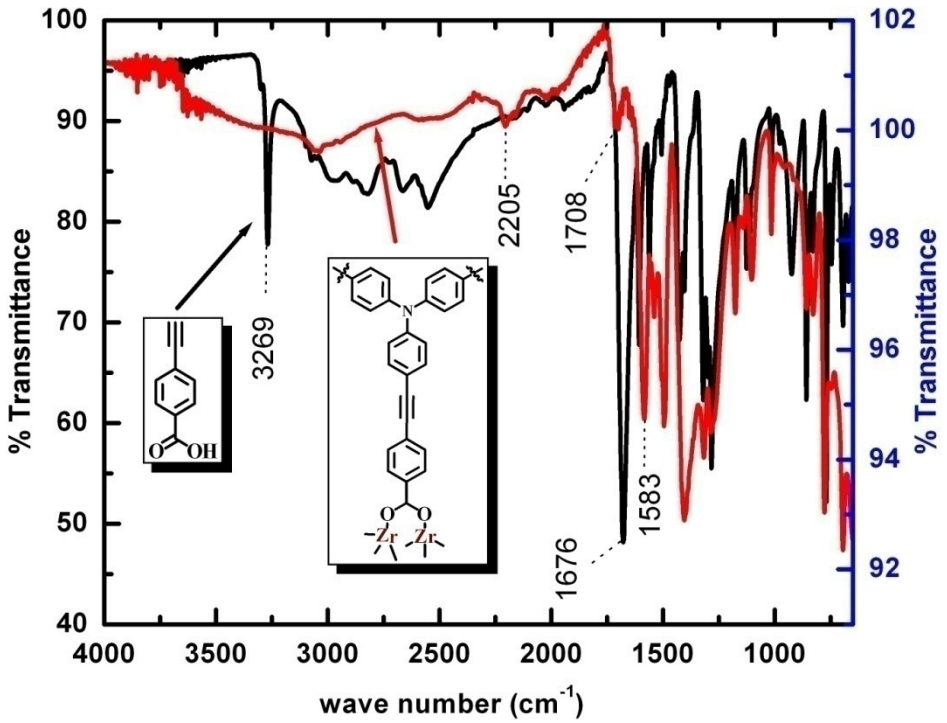


Figure S1. ATR-FTIR spectrum of 4-ethynylbenzoic acid and 1.

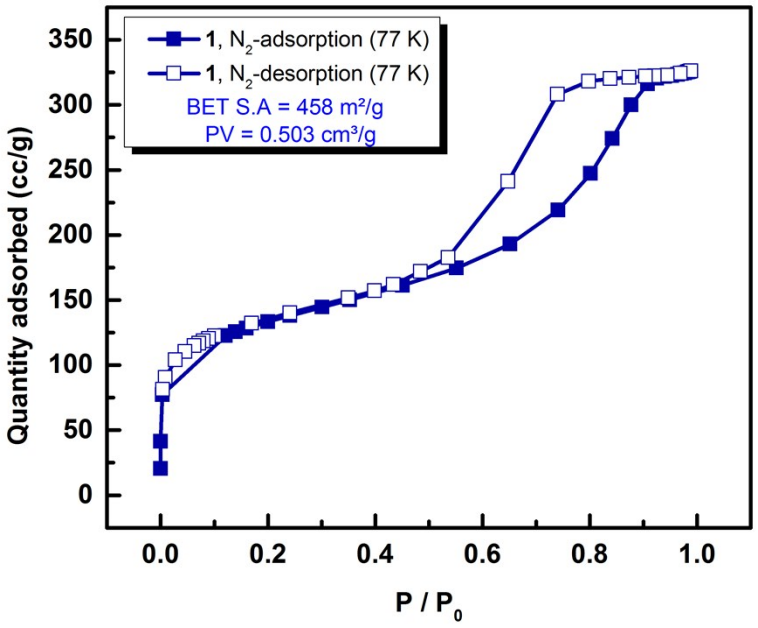


Figure S2. N2 sorption isotherm of 1.

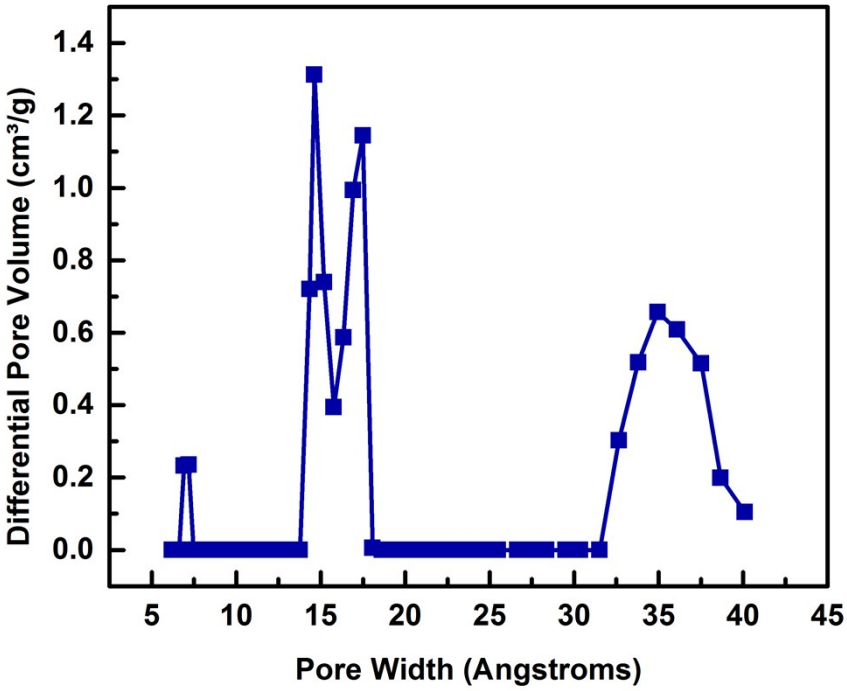


Figure S3. Pore size distribution in 1.

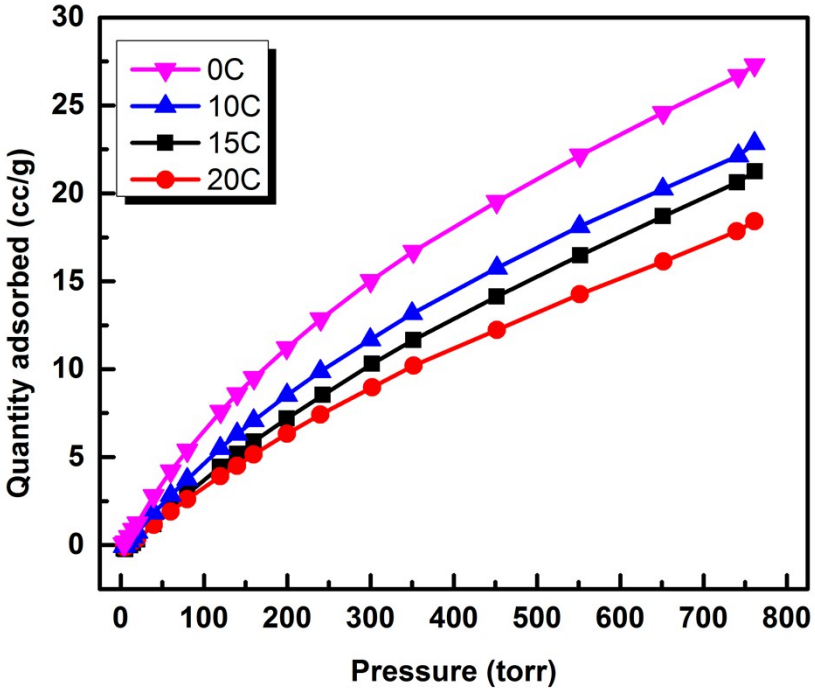


Figure S4. Variable temperature CO_2 isotherms in 1.

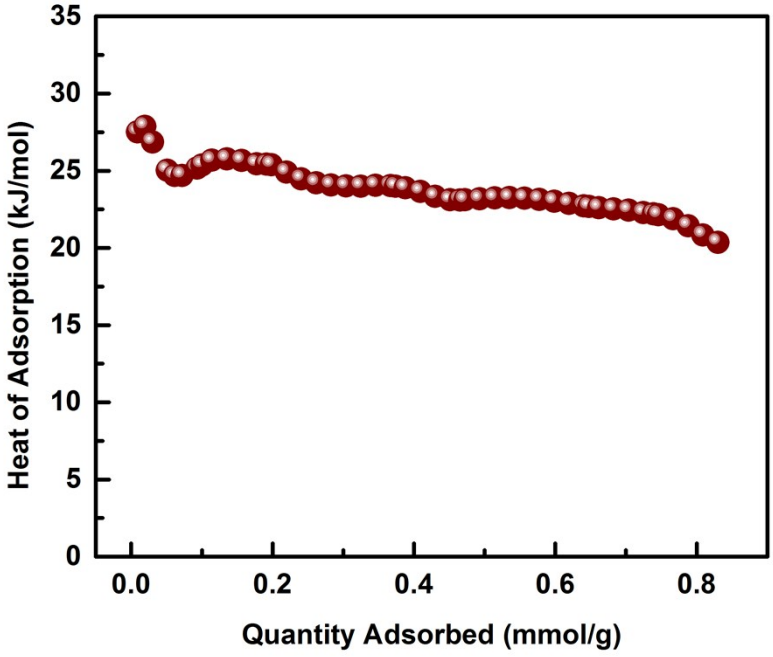
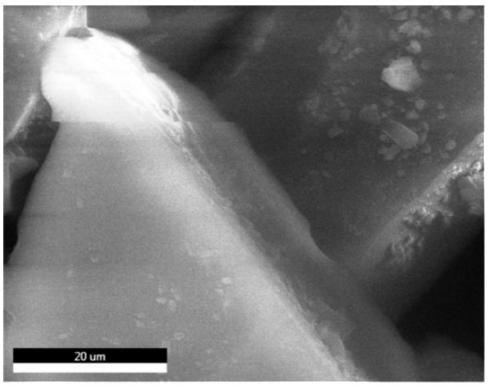
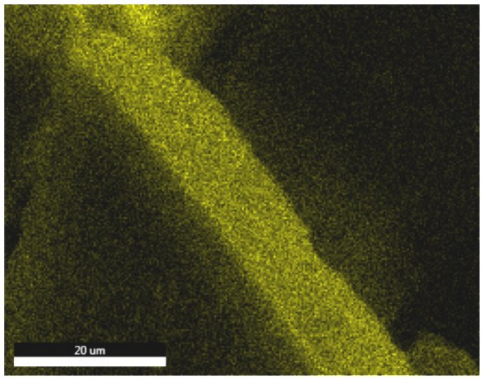


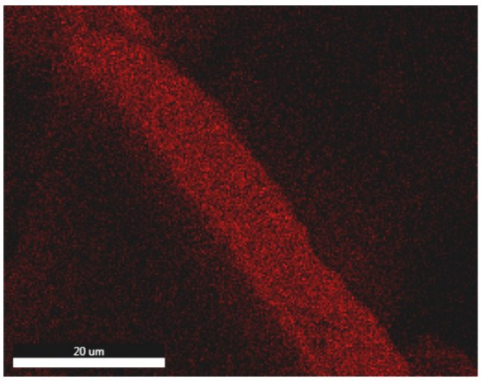
Figure S5. Isosteric heat of adsorption for CO_2 in 1.



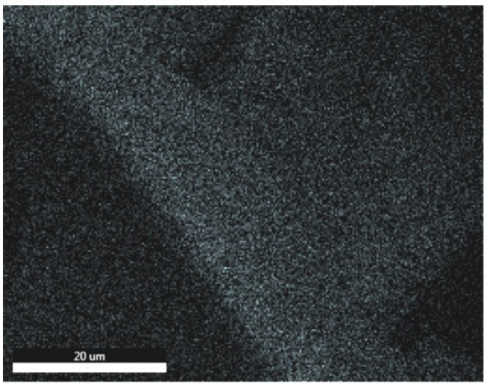
Image



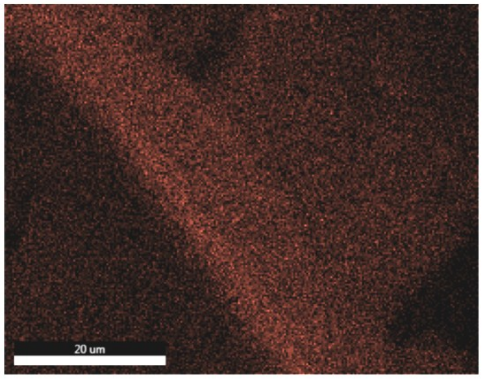
C K



O K

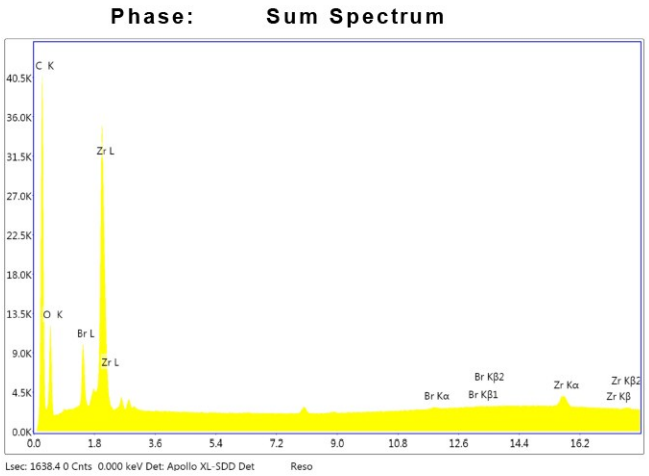


BrK



ZrK

kV: 30 Mag: 3200 Takeoff: 35.7 Live Time(s): 1638.4 Amp Time(µs): 12.8 Resolution:(eV) 135.1

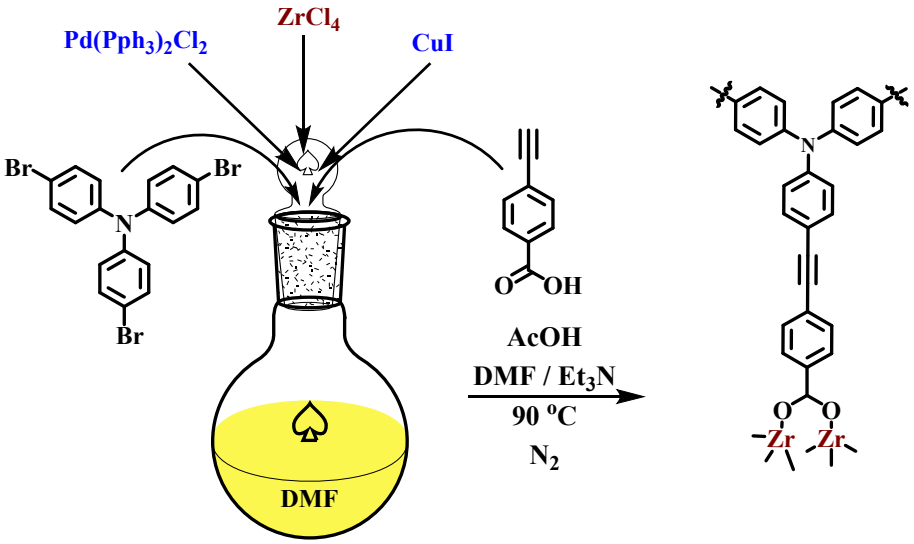


eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Net Int. Error
C K	68.06	79.12	190.2	0
O K	22.19	19.36	46.8	0.01
BrL	1.42	0.25	27.2	0.01
ZrL	8.32	1.27	196.3	0

Figure S6: SEM image and Energy-dispersive X-ray spectroscopy (EDX) for 1 and maps showing the color coded images of the overall elemental distribution, and elemental microanalysis table

Compound 2



In a glass pressure vessel fitted with teflon screw cap (100 mL) charged with a magnetic stirrer a solution of **$ZrCl_4$** (0.25 mmol, 0.0583 g) in **DMF** (10 mL) was prepared and to this solution was added **glacial acetic acid** (0.1 mL, 1.66 mmol). After stirring at 90°C for 1 hr, was then added **Et_3N** (5 mL), and the vessel was capped with silicon septum, and the solution was degassed through three freeze-pump-thaw cycles and backfilled with nitrogen. To this solution and under nitrogen atmosphere was added **4-ethynylbenzoic acid** (0.5 mmol, 0.073 g), **tris-(4-bromophenyl)-amine** (0.165 mmol, 0.079 g), **bis-(triphenylphosphine) palladium(II) dichloride** (0.014 mmol, 10 mg), **CuI** (0.04 mmol, 5 mg) and **triphenylphosphine** (0.02 mmol, 5 mg) and the flask was then evacuated/backfilled with nitrogen and sealed and the mixture was stirred at 90 °C for 24 h to result in yellow-colored precipitate. The reaction vessel was then cooled to room temperature, opened to air and the solid filtered through a fritted funnel, washed with Water/DCM/DMF/Acetone and kept under Acetonitrile for guest exchange for one week prior to gas sorption measurements. Activation for gas sorption included evacuation under dynamic vacuum at 120°C for 6 hours. Total dry weight of the product was 0.0723 g, 54% yield based on the sum of masses for reactants excluding counterions and bromine atoms.

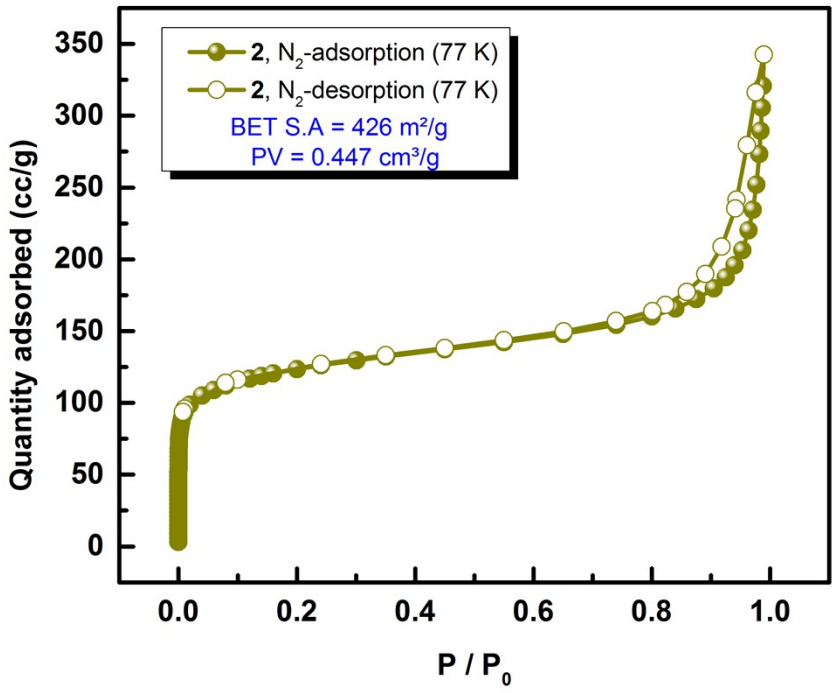


Figure S7. N2 sorption isotherm of 2

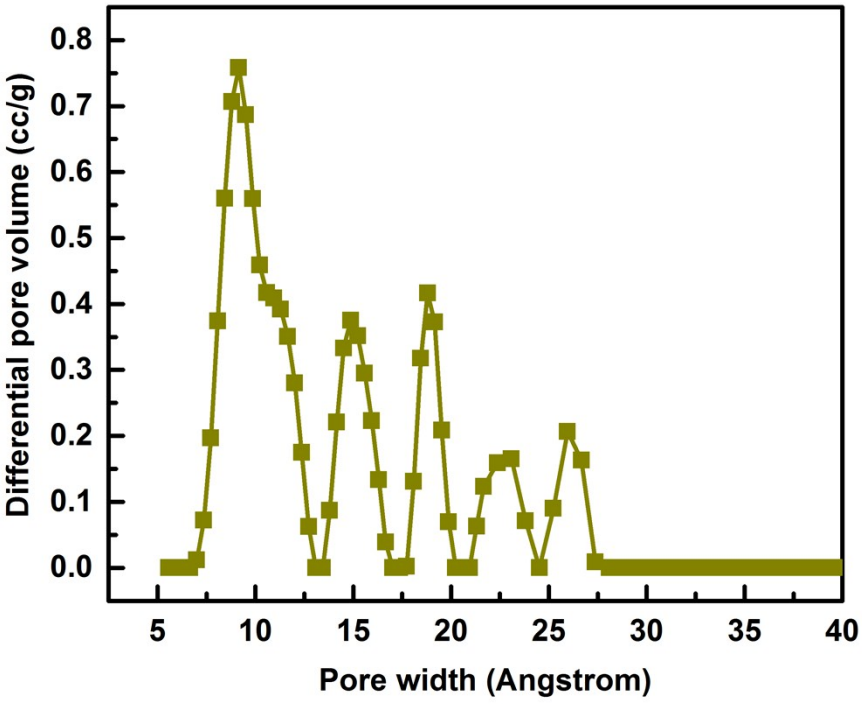


Figure S8. Pore size distribution in 2.

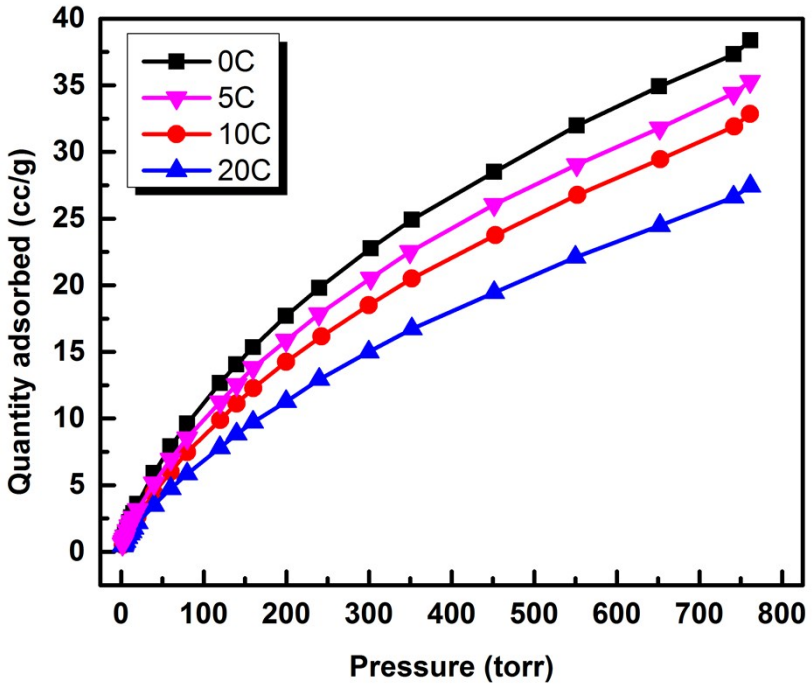


Figure S9. Variable temperature CO_2 isotherms in 2.

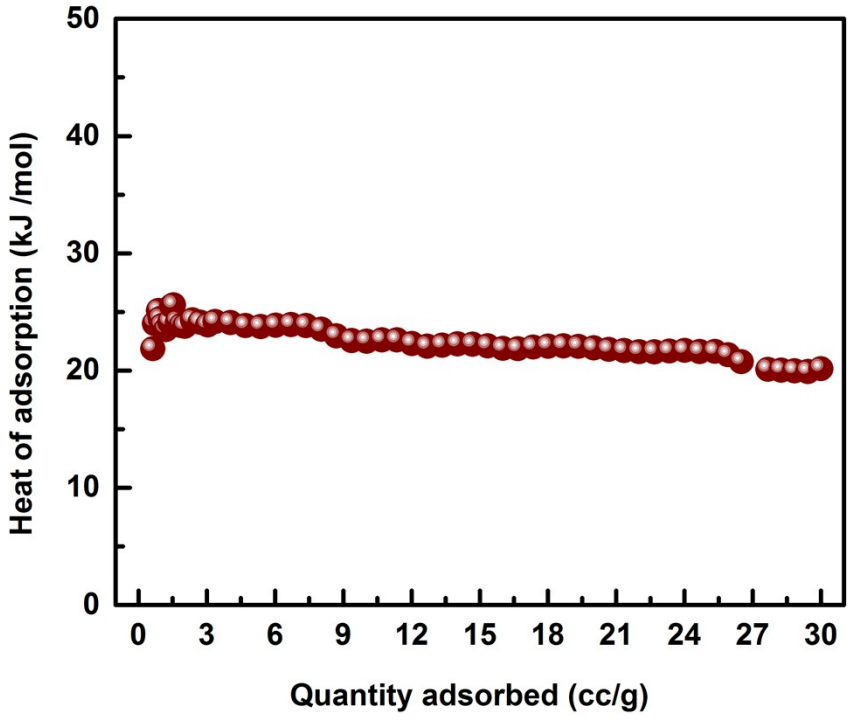
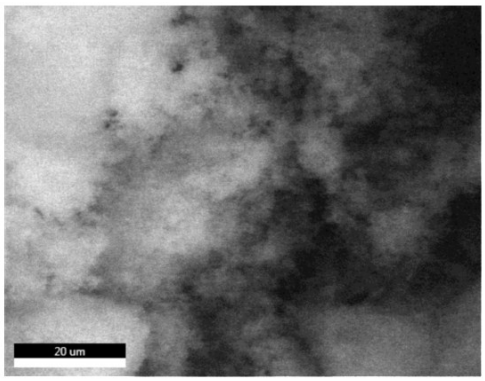
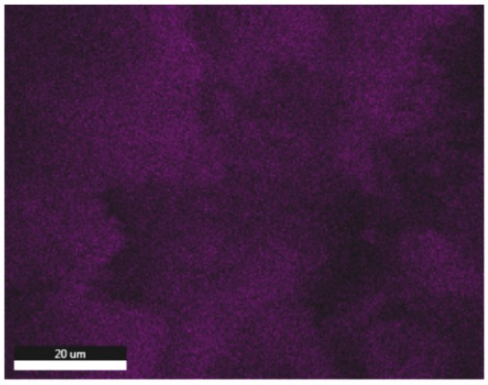
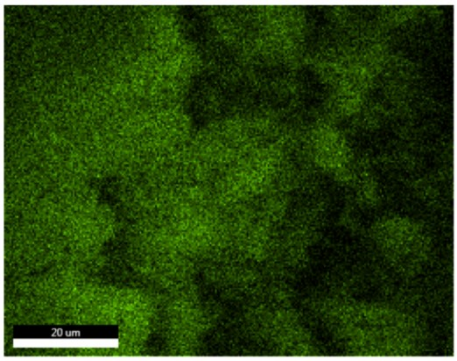


Figure S10. Isosteric heat of adsorption for CO_2 in 2.

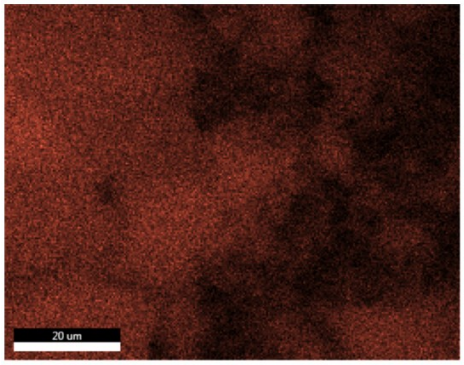




C K

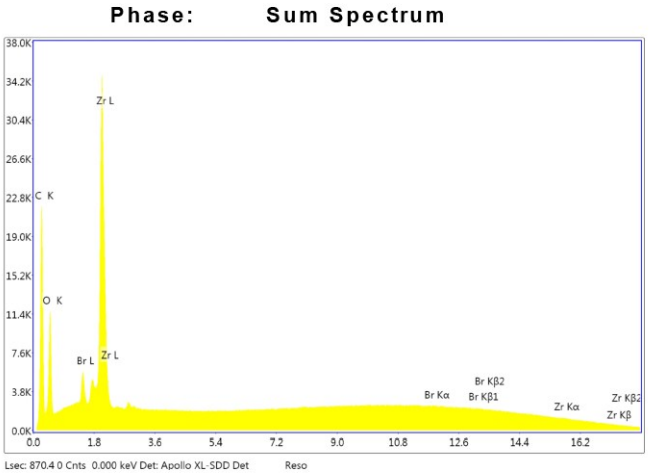


O K



ZrL

kV: 20 Mag: 1600 Takeoff: 36.7 Live Time(s): 870.4 Amp Time(µs): 12.8 Resolution:(eV) 135.1



eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Net Int. Error
C K	55.24	70.9	214.5	0
O K	27.08	26.09	113.9	0
BrL	0.9	0.17	19.8	0.03
ZrL	16.77	2.83	356.9	0

Figure S 11: SEM image and Energy-dispersive X-ray spectroscopy (EDX) for 2 and maps showing the color coded images of the overall elemental distribution, and elemental microanalysis table.

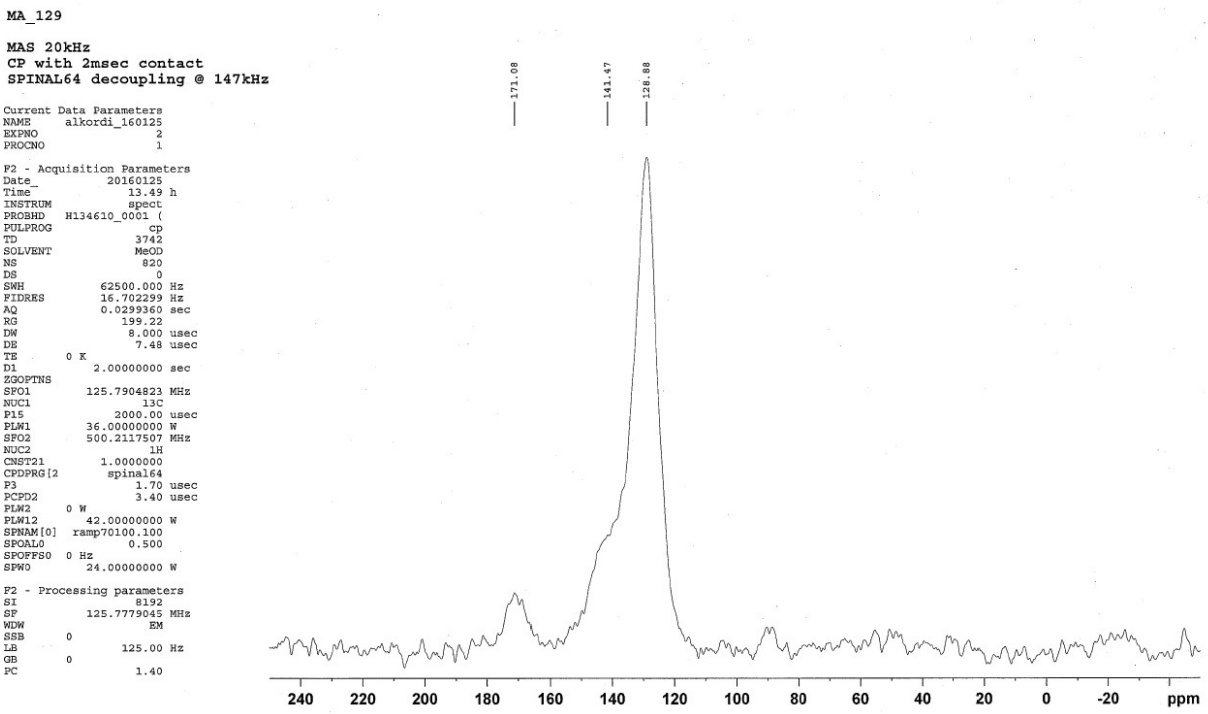
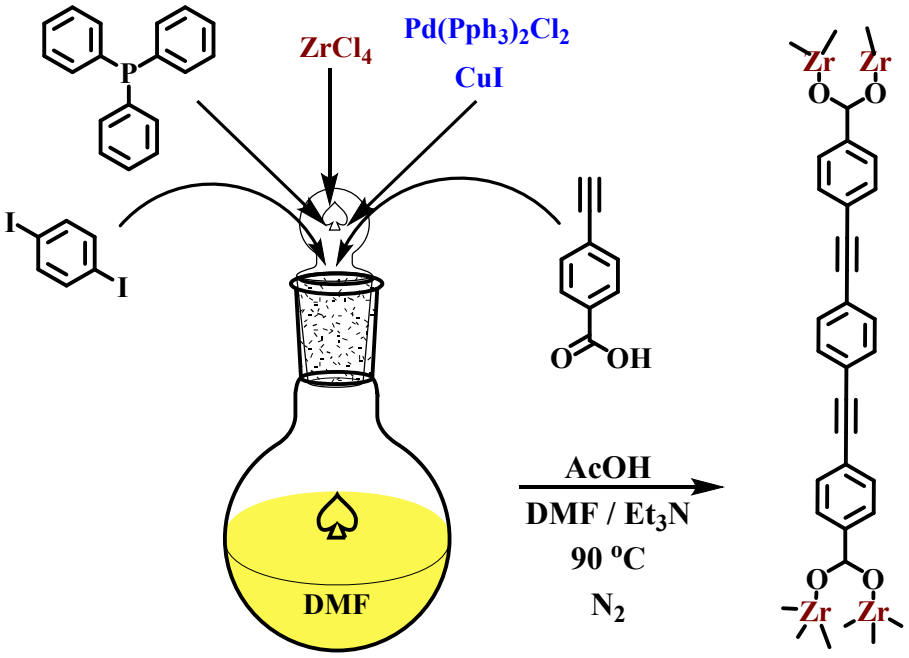


Figure S12 : 13C-CPMAS NMR spectrum of 2

Compound 3



In a glass pressure vessel fitted with teflon screw cap (100 mL) charged with a magnetic stirrer a solution of **$ZrCl_4$** (0.25 mmol, 0.0583 g) in **DMF** (10 mL) was prepared and to this solution was added **glacial acetic acid** (0.1 mL, 1.66 mmol). After brief stirring at room temperature was then added **Et_3N** (2 mL), and the vessel was capped with silicon septum, and the solution was degassed through three freeze-pump-thaw cycles and backfilled with nitrogen. To this solution and under nitrogen atmosphere was added **4-ethynylbenzoic acid** (0.5 mmol, 0.073 g), **1,4-diiodobenzene** (0.23 mmol, 0.075 g), **bis-(triphenylphosphine) palladium(II) dichloride** (0.014 mmol, 10 mg), **CuI** (0.04 mmol, 5 mg) and **triphenylphosphine** (0.02 mmol, 5 mg) and the flask was then evacuated/backfilled with nitrogen and sealed and the mixture was stirred at 90 °C for 24 hours to result in yellow-colored precipitate. The reaction vessel was then cooled to room temperature, opened to air and the solid filtered through a fritted funnel, washed with DMF/Acetone/MeOH and kept under Acetone for guest exchange for one week prior to gas sorption measurements. Activation for gas sorption included evacuation under dynamic vacuum at 120°C for 6 hours. Total dry weight of the product was 0.0927 g, 81.5% yield based on the sum of masses for reactants excluding counterions and bromine atoms.

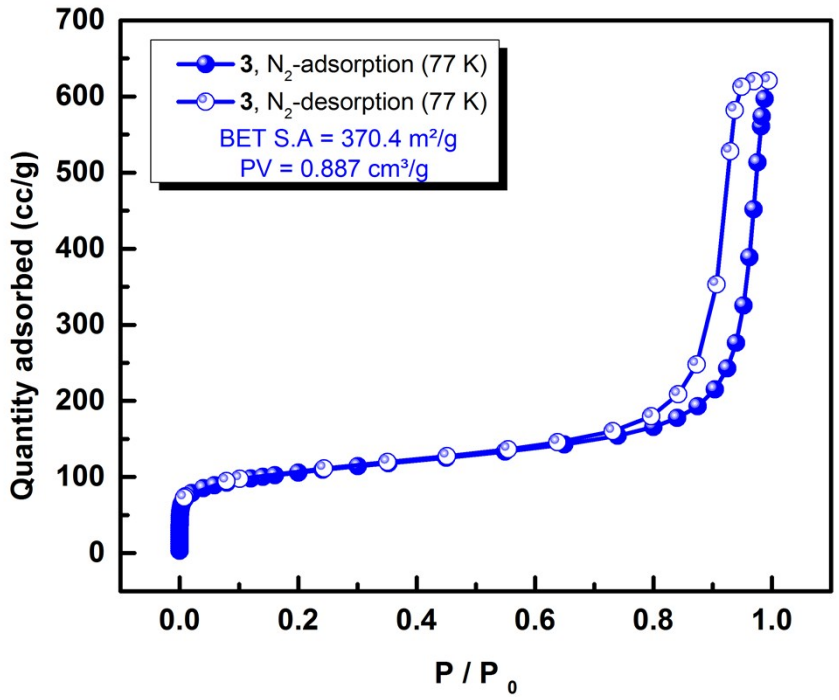


Figure S13. N2 sorption isotherm of 3

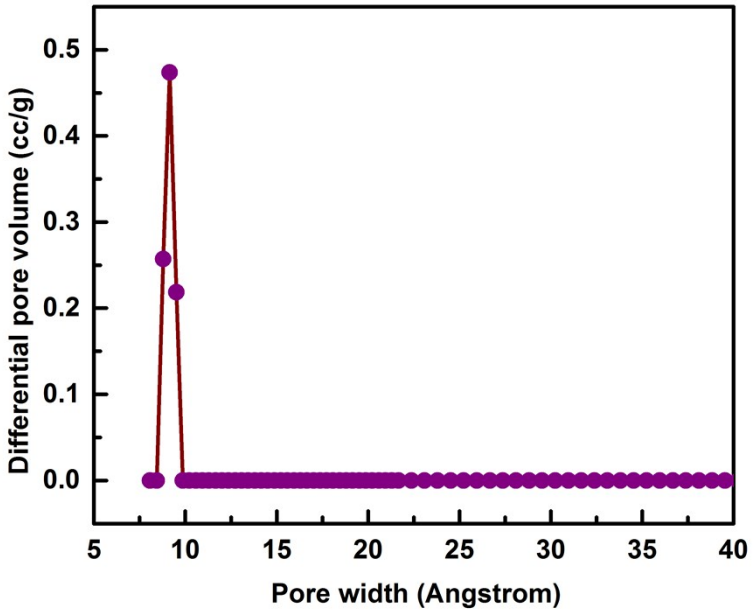
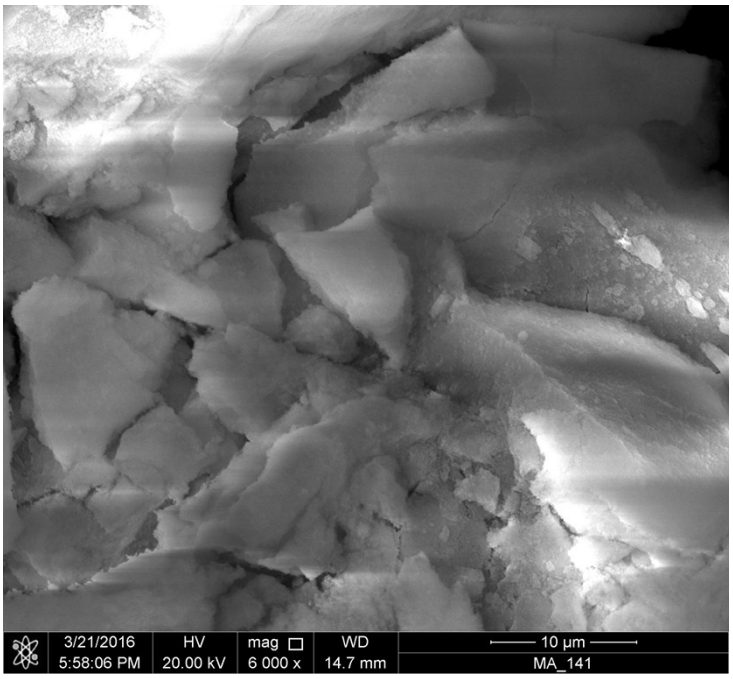


Figure S14. Pore size distribution in 3.


3/21/2016
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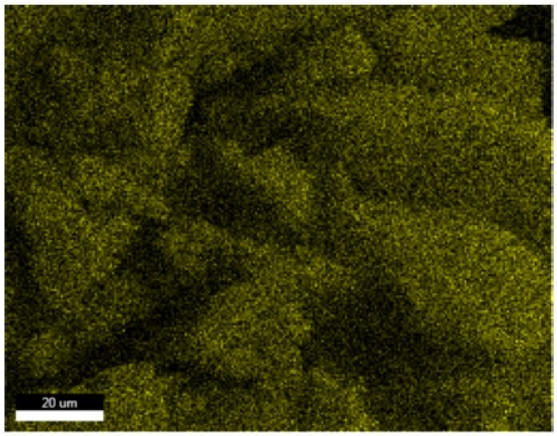
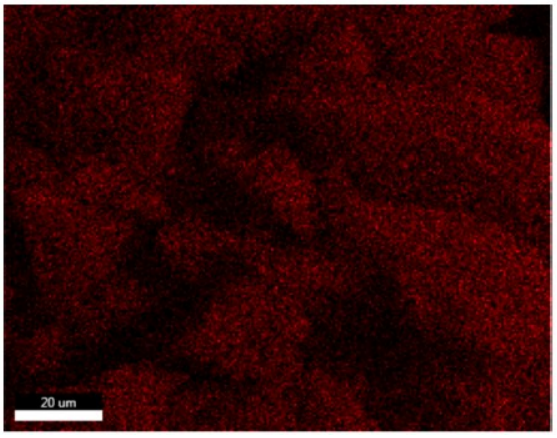
HV
20.00 kV
mag
6 000 x
WD
14.7 mm
10 µm
MA_141


20 um

C K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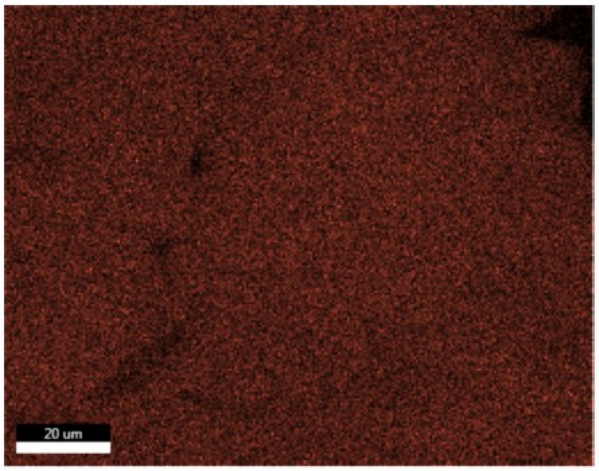
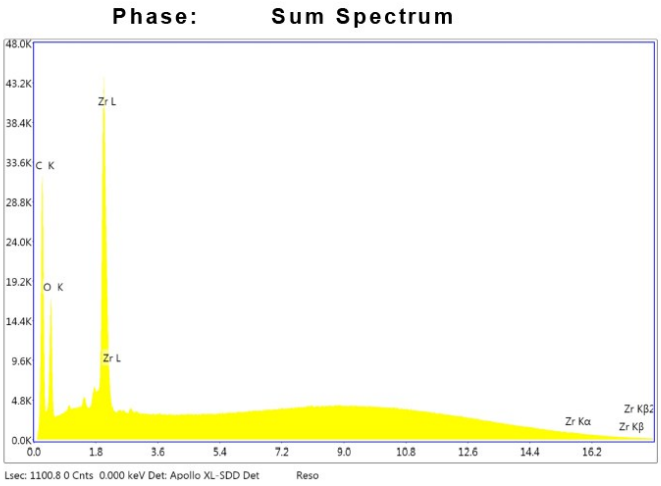
O K


20 um

ZrL

kV: 20 Mag: 1600 Takeoff: 36.7 Live Time(s): 1100.8 Amp Time(µs): 12.8 Resolution:(eV) 135.1



eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Net Int. Error
C K	57.6	72.93	222.2	0
O K	25.52	24.26	99.9	0
ZrL	16.87	2.81	348.1	0

Figure S 15 SEM image and Energy-dispersive X-ray spectroscopy (EDX) for 3 and maps showing the color coded images of the overall elemental distribution, and elemental microanalysis table.

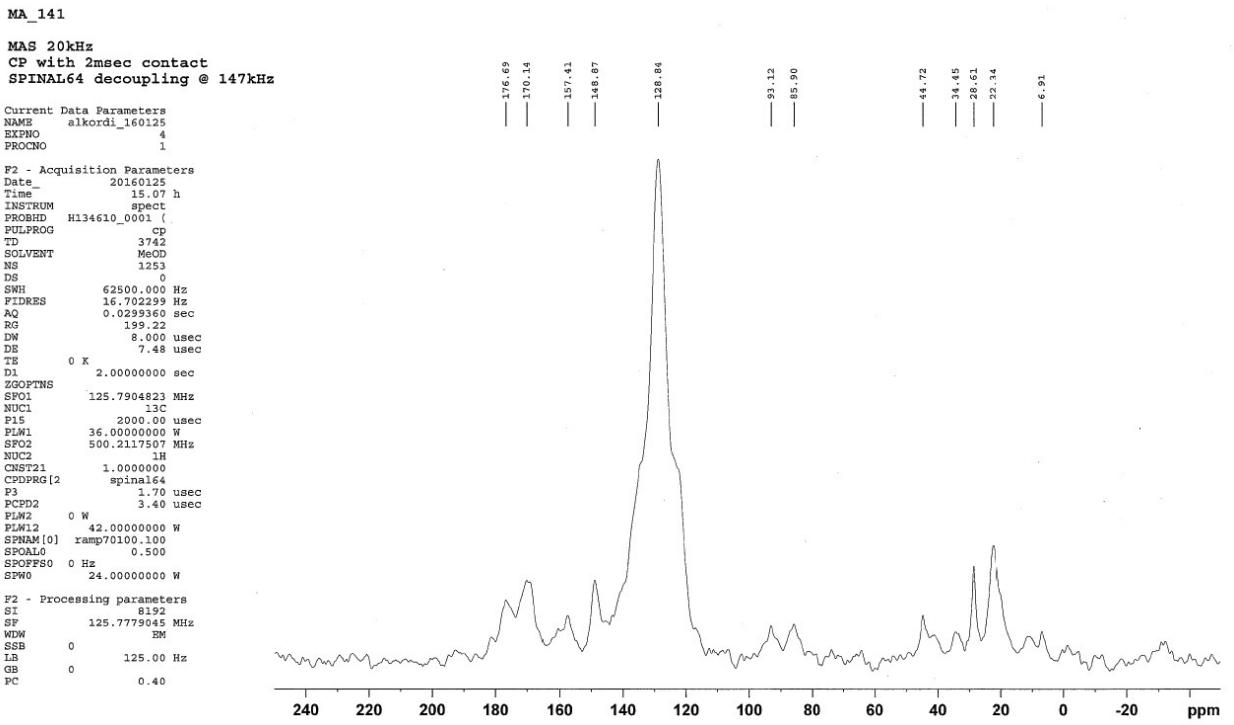
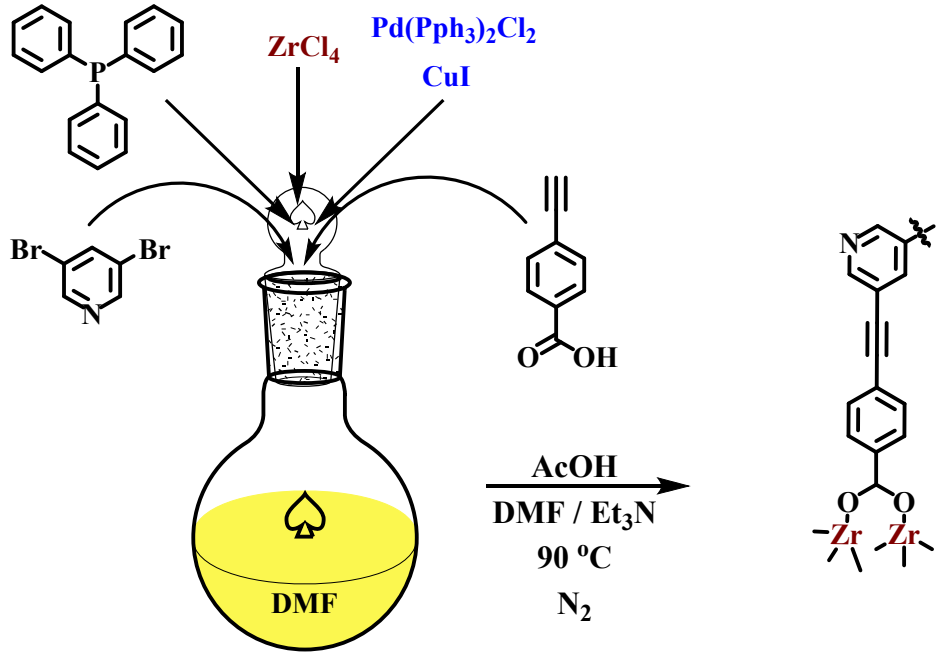


Figure S16 : 13C-CPMAS NMR spectrum of 3

Compound 4



In a glass pressure vessel fitted with teflon screw cap (100 mL) charged with a magnetic stirrer a solution of **$ZrCl_4$** (0.25 mmol, 0.0583 g) in **DMF** (10 mL) was prepared and to this solution was added **glacial acetic acid** (0.1 mL, 1.66 mmol). After brief stirring at room temperature was then added **Et_3N** (5 mL), and the vessel was capped with silicon septum, and the solution was degassed through three freeze-pump-thaw cycles and backfilled with nitrogen. To this solution and under nitrogen atmosphere was added **4-ethynylbenzoic acid** (0.5 mmol, 0.073 g), **3,5-dibromopyridine** (0.25 mmol, 0.0545 g), **bis-(triphenylphosphine) palladium(II) dichloride** (0.014 mmol, 10 mg), **CuI** (0.04 mmol, 5 mg) and **triphenylphosphine** (0.02 mmol, 5 mg) and the flask was then evacuated/backfilled with nitrogen and sealed and the mixture was stirred at 90 °C for 24 h to result in yellow-colored precipitate. The reaction vessel was then cooled to room temperature, opened to air and the solid filtered through a fritted funnel, washed with Water/DCM/DMF/Acetone and kept under Acetonitrile for guest exchange for one week prior to gas sorption measurements. Activation for gas sorption included evacuation under dynamic vacuum at 120°C for 6 hours. Total dry weight of the product was 0.0577 g, 50% yield based on the sum of masses for reactants excluding counterions and bromine atoms.

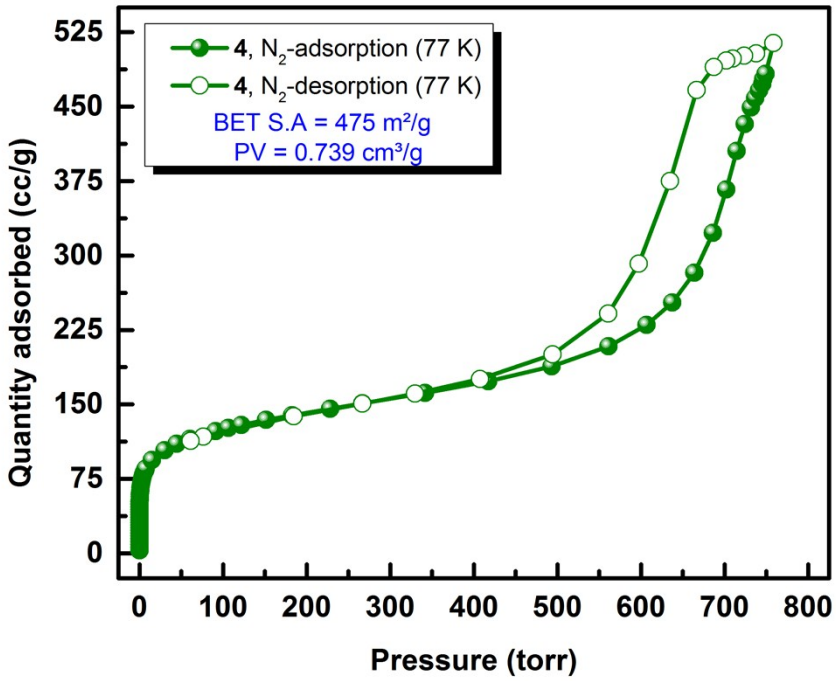


Figure S17: N_2 gas sorption isotherms in 4.

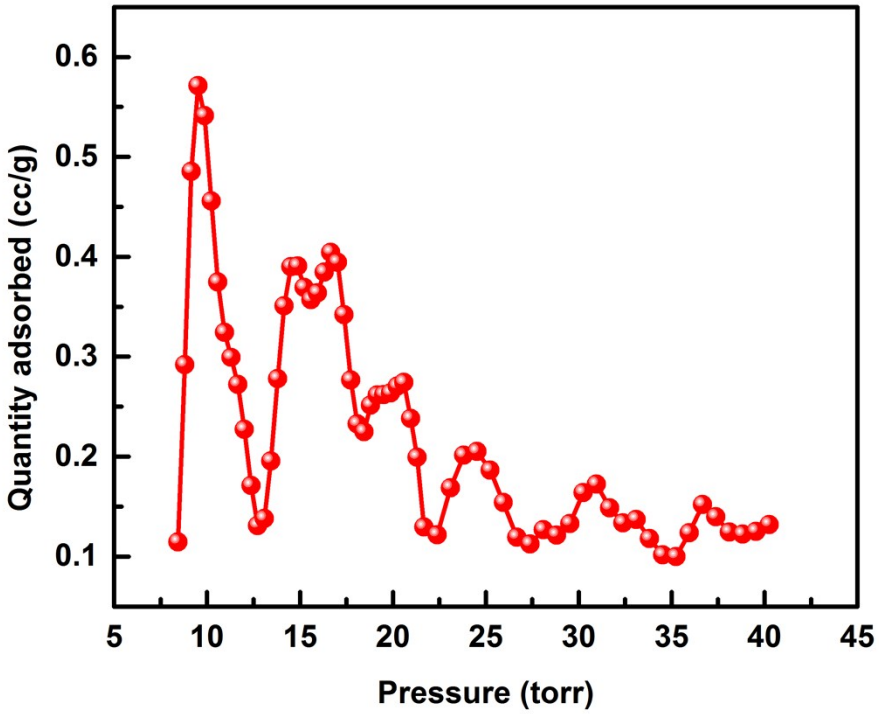


Figure S18. Pore size distribution in 4.

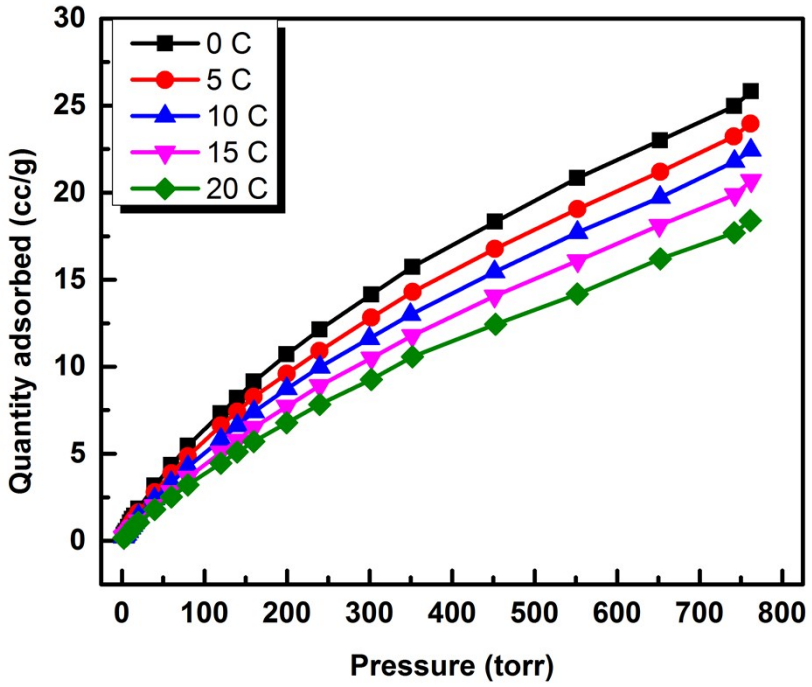


Figure S19. Variable temperature CO_2 isotherms in 4.

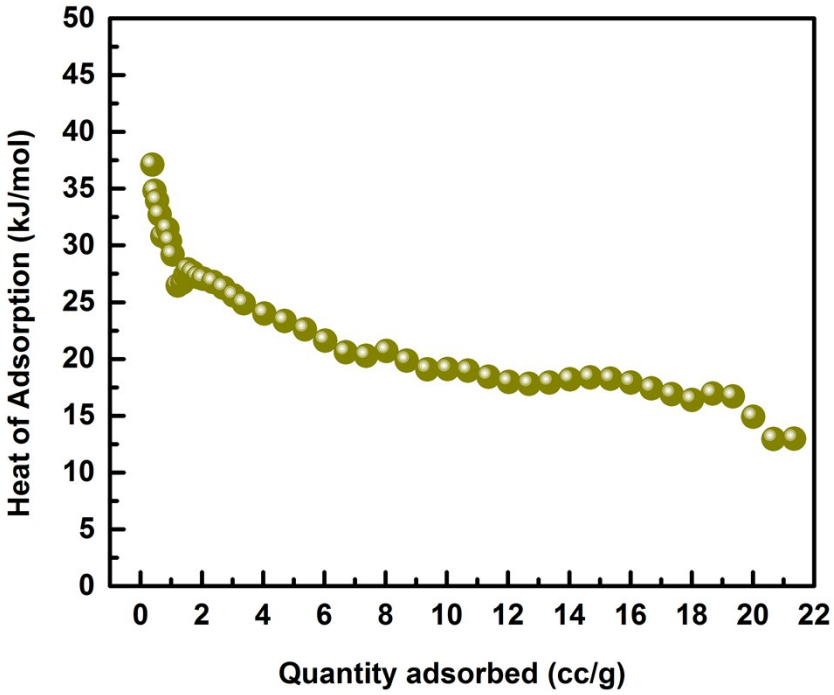
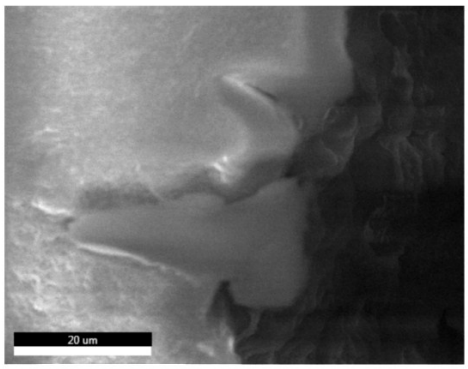
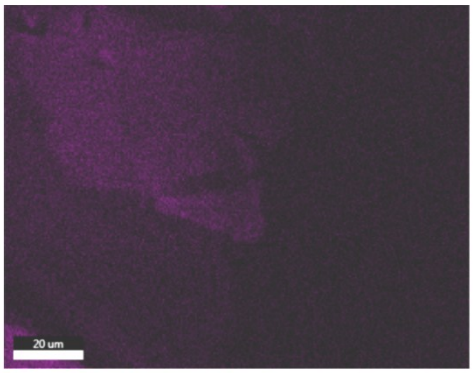
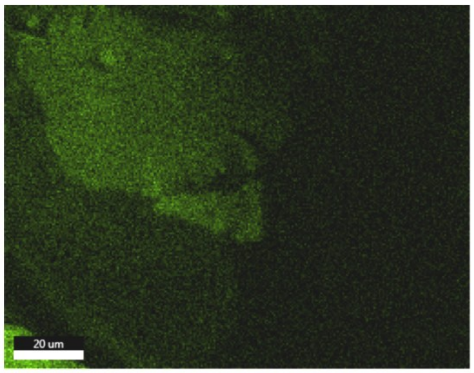


Figure S20. Isosteric heat of adsorption for CO_2 in 4.

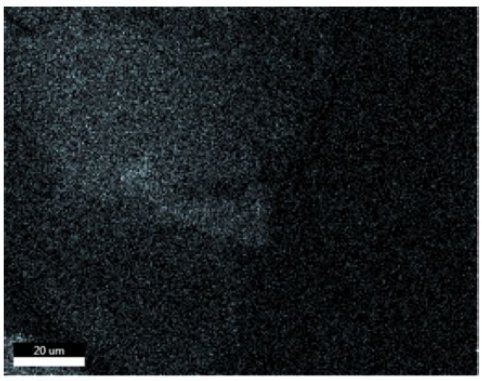




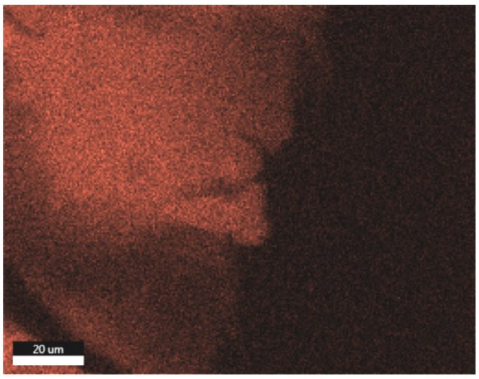
C K



O K



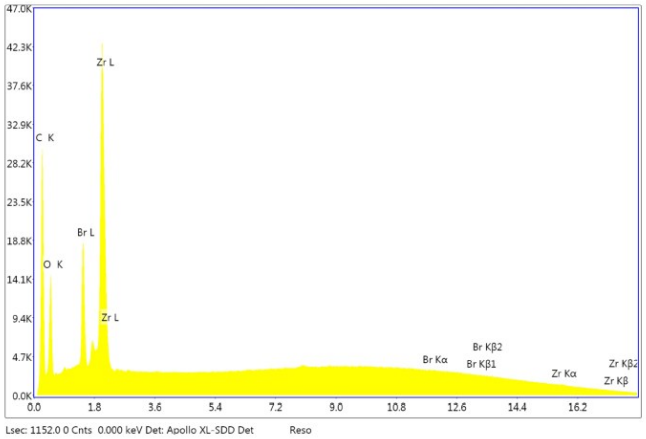
BrL



ZrL

kV: 20	Mag: 1600	Takeoff: 36.7	Live Time(s): 1152	Amp Time(µs): 12.8	Resolution:(eV) 135.1

Phase: Sum Spectrum



eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Net Int. Error
C K	54.27	70.01	226.4	0
O K	27.72	26.85	131.8	0
BrL	3.49	0.68	84.6	0.01
ZrL	14.51	2.46	330.8	0

SEM image and Energy-dispersive X-ray spectroscopy (EDX) for 4 and maps showing the color coded images of the overall elemental distribution, and elemental microanalysis table

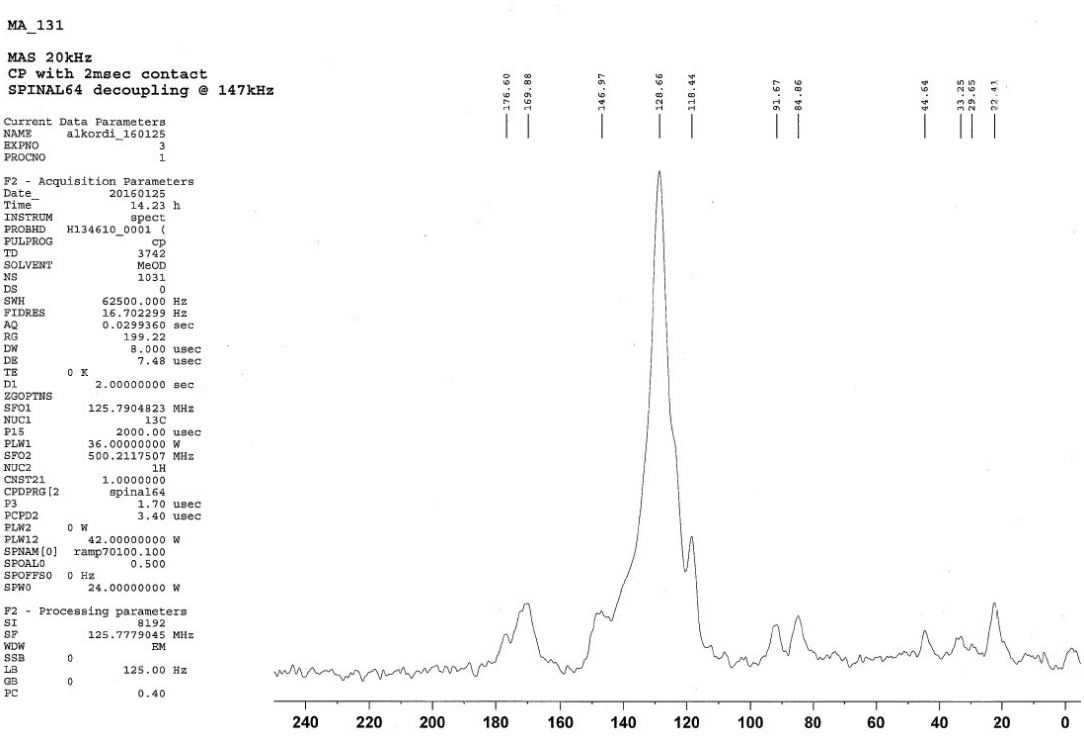
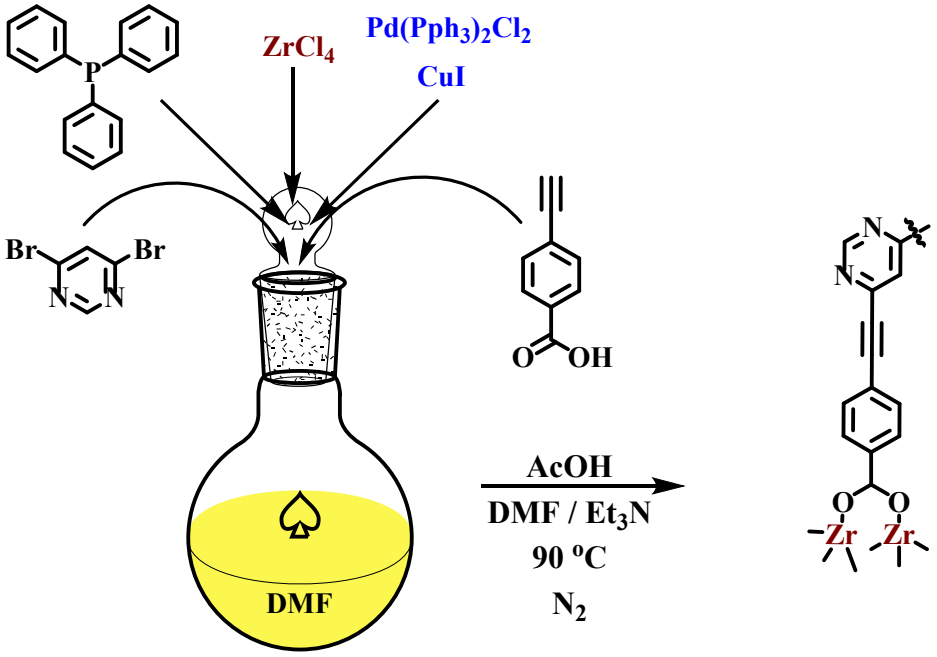


Figure S21 : 13C-CPMAS NMR spectrum of 4

Compound 5



In a glass pressure vessel fitted with teflon screw cap (100 mL) charged with a magnetic stirrer a solution of **$ZrCl_4$** (0.25 mmol, 0.0583 g) in **DMF** (10 mL) was prepared and to this solution was added **glacial acetic acid** (0.1 mL, 1.66 mmol). After brief stirring at room temperature was then added **Et_3N** (5 mL), and the vessel was capped with silicon septum, and the solution was degassed through three freeze-pump-thaw cycles and backfilled with nitrogen. To this solution and under nitrogen atmosphere was added **4-ethynylbenzoic acid** (0.5 mmol, 0.073 g), **3,5-dibromopyrimidine** (0.23 mmol, 0.055 g), **bis-(triphenylphosphine) palladium(II) dichloride** (0.014 mmol, 10 mg), **CuI** (0.04 mmol, 5 mg) and **triphenylphosphine** (0.02 mmol, 5 mg) and the flask was then evacuated/backfilled with nitrogen and sealed and the mixture was stirred at 90 °C for 24 h to result in yellow-colored precipitate. The reaction vessel was then cooled to room temperature, opened to air and the solid filtered through a fritted funnel, washed with Water/DCM/DMF/Acetone and kept under Acetonitrile for guest exchange for one week prior to gas sorption measurements. Activation for gas sorption included evacuation under dynamic vacuum at 120°C for 6 hours. Total dry weight of the product was 0.105 g, 93% yield based on the sum of masses for reactants excluding counterions and bromine atoms.

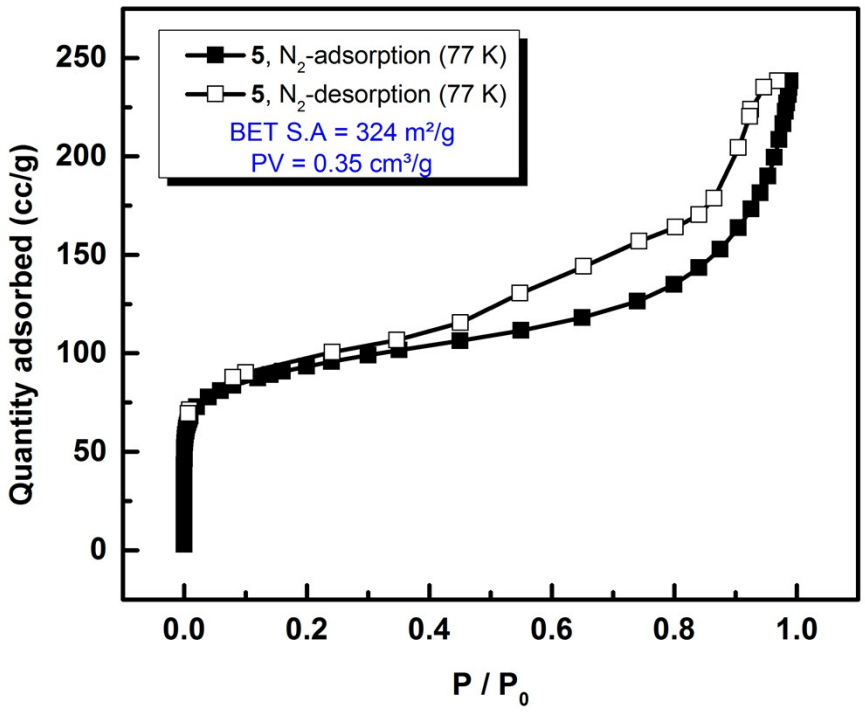


Figure S22: N_2 gas sorption isotherms in 5.

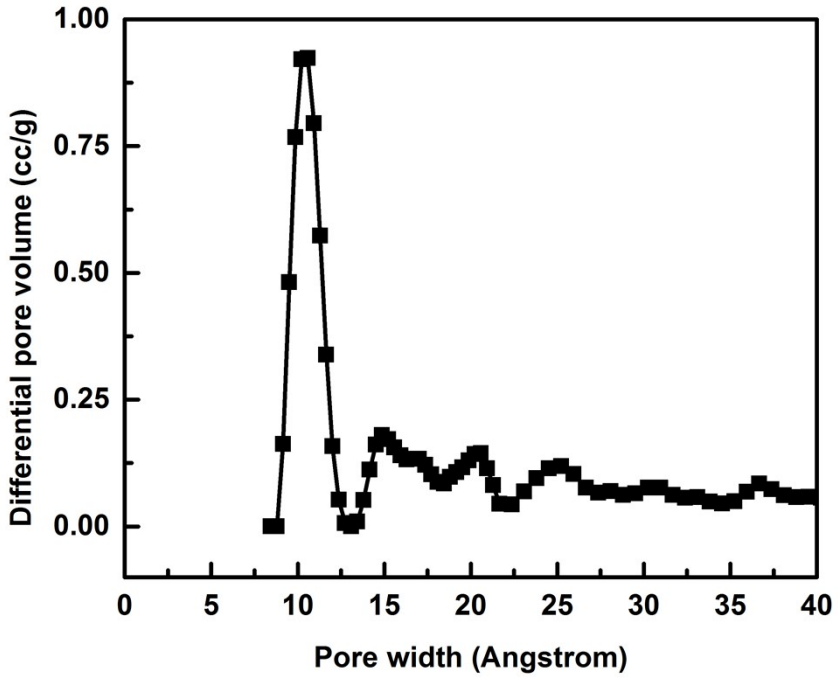


Figure S23. Pore size distribution in 5.

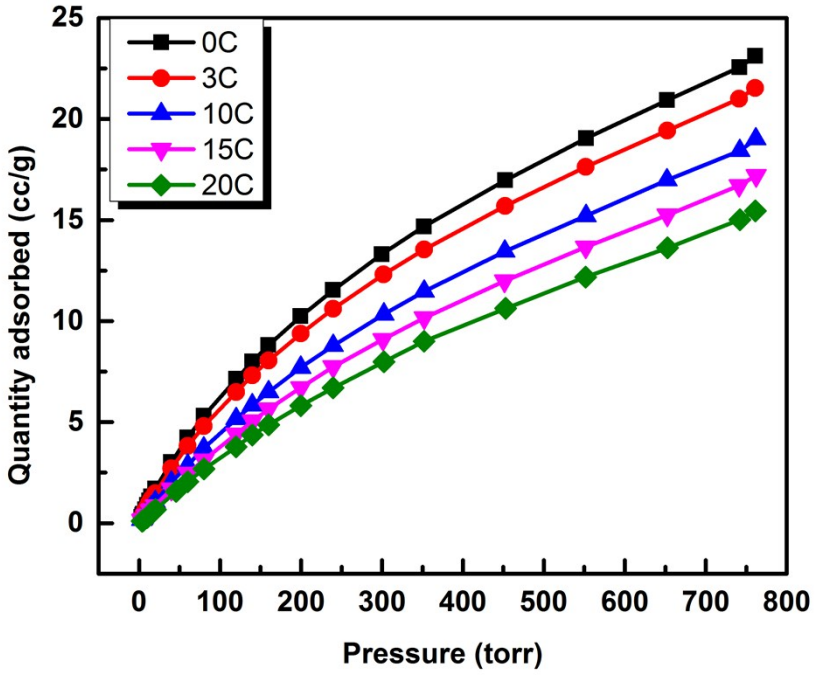


Figure S24. Variable temperature CO_2 isotherms in 5.

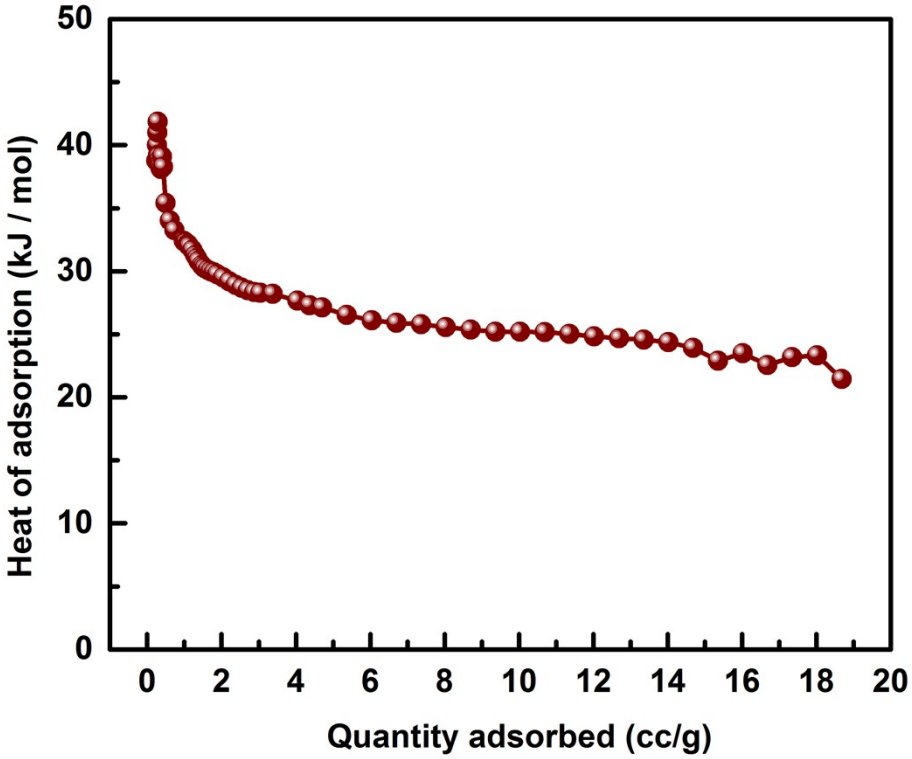
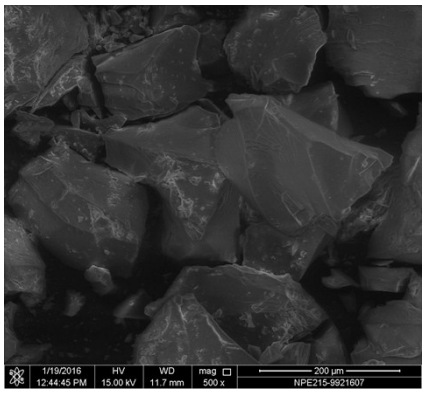
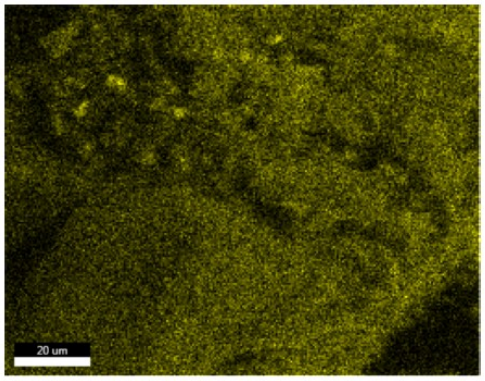
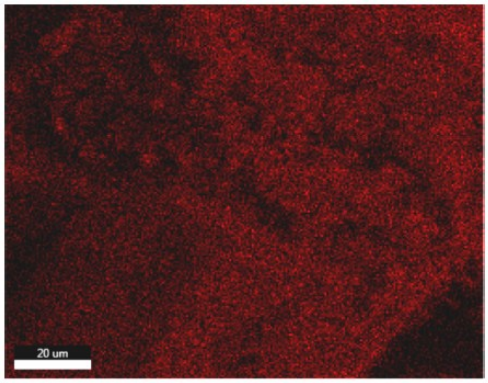


Figure S25. Isosteric heat of adsorption for CO_2 in 5.

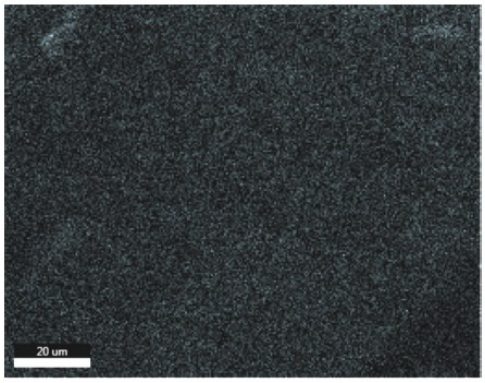

1/19/2016
12:44:45 PM
HV
15.00 kV
WD
11.7 mm
mag
500 x
200 µm
NPE215-9921607


20 um

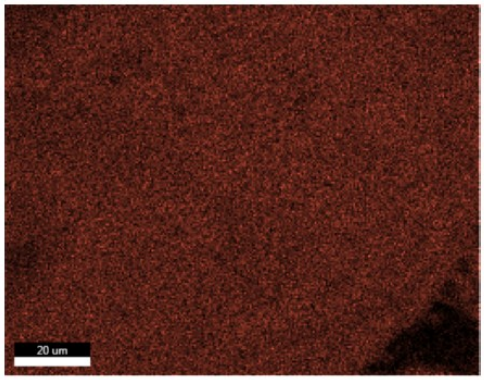
C K


20 um

O K

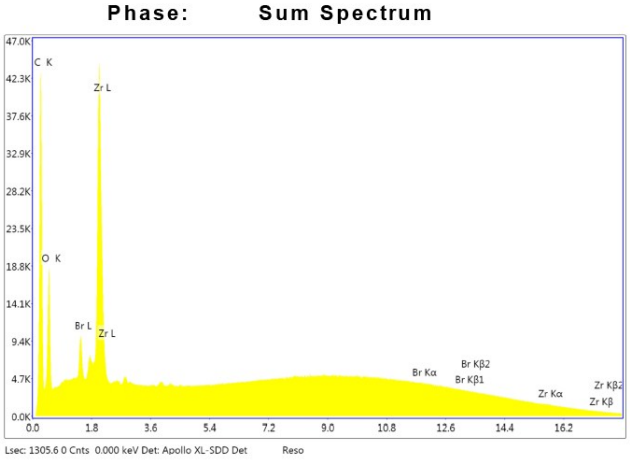

20 um

BrL


20 um

ZrL

kV: 20 Mag: 1600 Takeoff: 36.7 Live Time(s): 1305.6 Amp Time(µs): 12.8 Resolution:(eV) 135.1



eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Net Int. Error
C K	61.05	75.43	258.6	0
O K	23.81	22.09	94.2	0
BrL	1.11	0.21	24.4	0.01
ZrL	14.03	2.28	295.9	0

Figure S 26: SEM image and Energy-dispersive X-ray spectroscopy (EDX) for 5 and maps showing the color coded images of the overall elemental distribution, and elemental microanalysis table

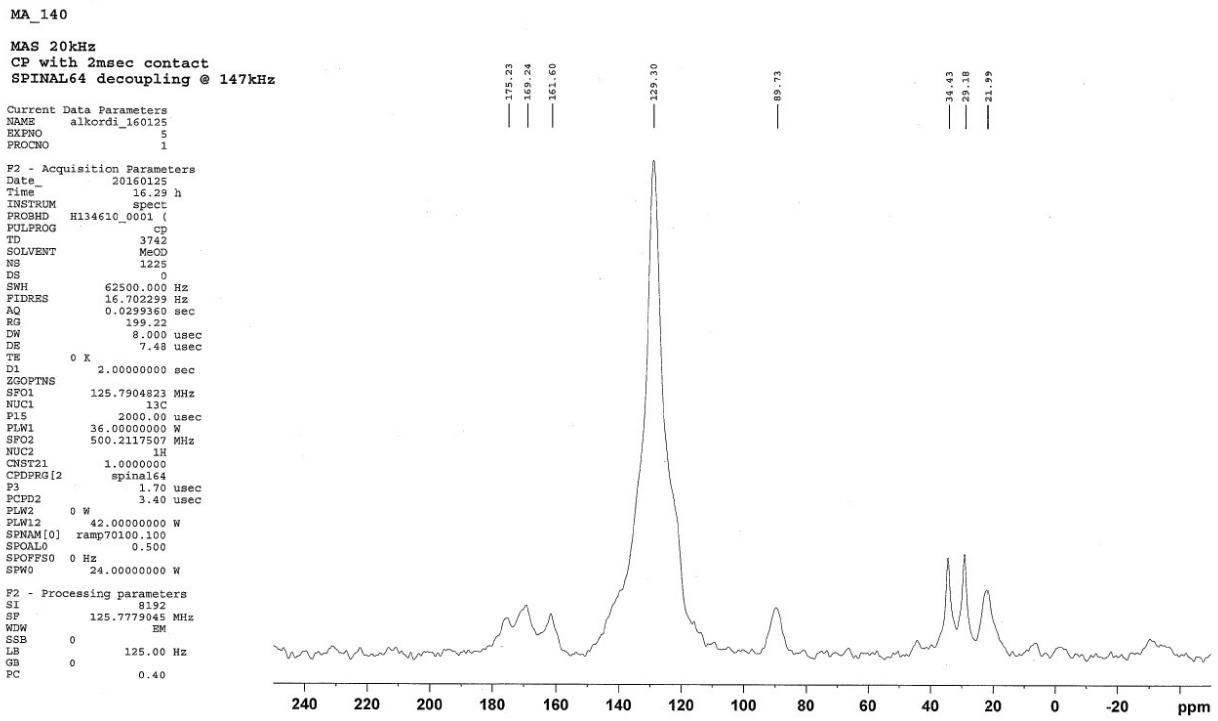


Figure S27 : 13C-CPMAS NMR spectrum of 5

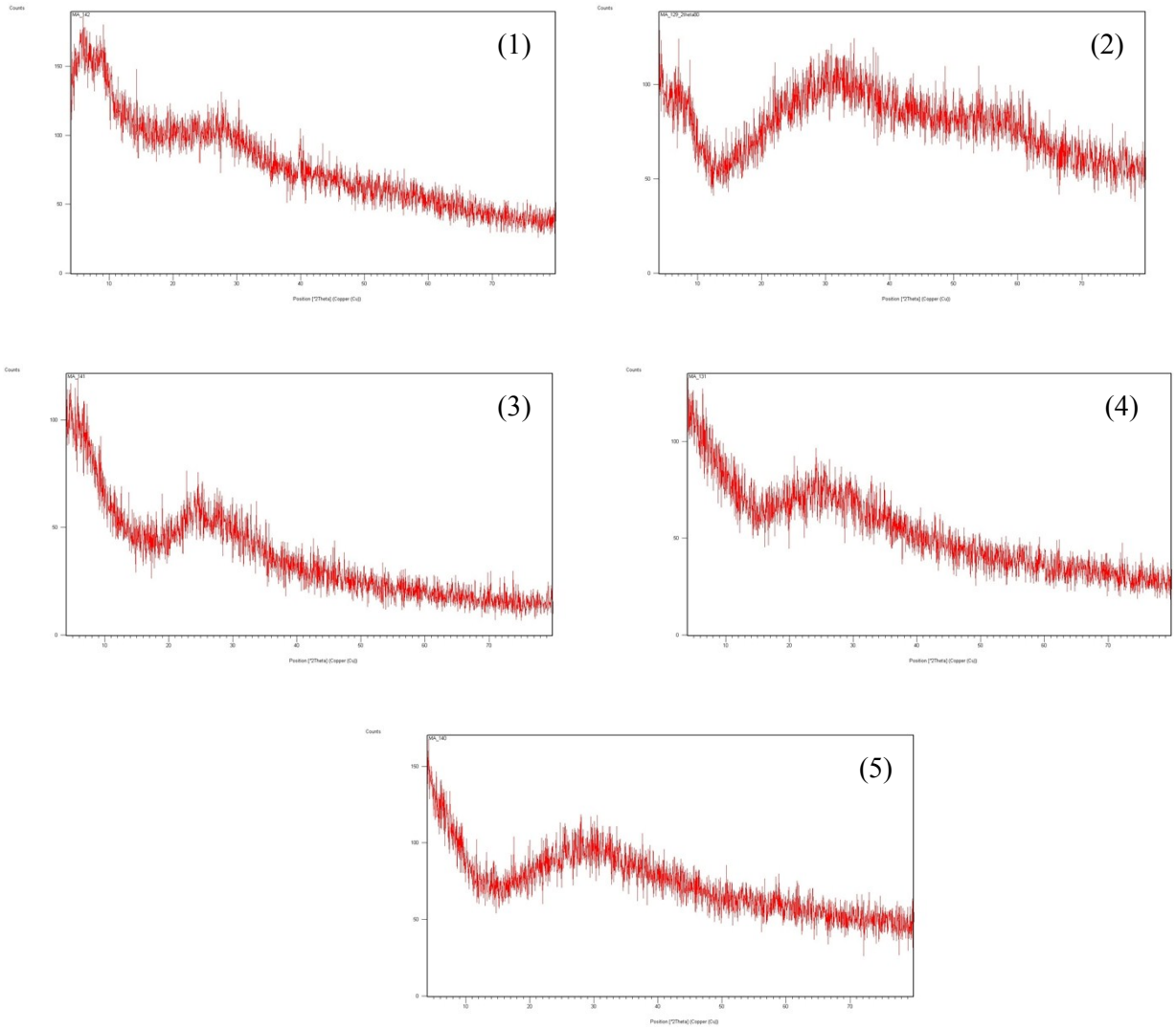


Figure S28: X-ray powder diffraction patterns for compounds 1-5.