Supporting Information for:

Strong CO_2 Binding in a Water-Stable, Triazolate-Bridged Metal-Organic Framework Functionalized with Ethylenediamine

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Experimental Details

Water was distilled and deionized prior to use. All other reagents were obtained from commercial vendors, and were used without further purification.

Synthesis of H_3BTTri.[1] Solid 1,3,5-tribromobenzene (9.45 g, 30.0 mmol) was dissolved in 250 mL of freshly distilled diethylamine under a nitrogen atmosphere. Copper(I) iodide (50 mg) and dichlorobis(triphenylphosphine)palladium(II) (400 mg) were added to the stirred solution. Trimethysilylacetylene (10.6 g, 108 mmol) was added, and the mixture was heated at 50 °C for 6 h. After cooling, the resulting precipitate of diethylamine hydrobromide was removed by filtration and washed with ether. The combined filtrates were evaporated to dryness under reduced pressure and the residue was chromatographed on a column (Al_2O_3, light petroleum) to yield 9.5 g (77%) of 1,3,5-tris(trimethylsilylethynyl)benzene as an intermediate. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47 (s, 1 H), 0.21 (s, 9 H) ppm. IR (neat): ν = 2960, 2900, 2165, 2140, 1580, 1410, 1250, 1160, 980, 880, 835, 760, 700, 680 cm^{-1}.

Hydrolysis of this intermediate (9.50 g, 26.0 mmol) was carried out by treatment with a mixture consisting of 20 mL of CH_2Cl_2, 50 mL of methanol, and 30 mL of 1 M $NaOH_{(aq)}$ under stirring at room temperature for 3 h. A standard work-up procedure involving evaporation of the organic solvent, extraction of the residue with ether drying ($MgSO_4$), and removal of the solvent under reduced pressure yielded 2.65 g of white powder containing 1,3,5-triethynylbenzene in essentially pure form. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (s, 1 H), 3.09 (s, 1 H) ppm. IR (neat): ν = 3295, 3280, 3065, 2110, 1790, 1580, 1415, 1260, 935, 885, 800, 755 cm^{-1}.

Under a nitrogen atmosphere, trimethylsilyl azide (9.16 g, 79.5 mmol) was added to a solution of CuI (505 mg, 2.60 mmol) and 1,3,5-triethynylbenzene (2.65 g, 17.6 mmol) in a mixture consisting of 90 mL of DMF and 10 mL of methanol. The reaction mixture was stirred and heated at 100 °C for 36 h. The hot mixture was filtered and concentrated to a volume of ca. 10 mL under reduced pressure. Water (30 mL) was added to the filtrate to afford a pale yellow precipitate. The solid was collected by filtration, washed with diethylether, and dried under reduced pressure to yield 3.74 g (76%) of product. ^{1}H NMR (300 MHz, $(CD_3)_2SO$): δ = 15.21 (s, 1 H), 8.52 (s, 1 H), 8.34 (s, 1 H) ppm. IR (neat): ν = 3135, 2915, 2875, 2825, 2660, 1650, 1615, 1560, 1520, 1435, 1350, 1285, 1225, 1150, 1125, 1105, 1080, 1025, 975, 875, 810, 770, 685 cm^{-1}.

Synthesis of $H_3[(Cu_4Cl)_3(BTTri)_8(DMF)_{12}]\cdot 7DMF\cdot 76H_2O$ (1-DMF). A solution of H_3BTT (225 mg, 0.937 mmol) was dissolved in 40 mL of DMF, and the solution was adjusted to pH 4 using dilute aqueous HCl. Solid $CuCl_2\cdot 2H_2O$ (383 mg, 2.25 mmol) was then added, and the mixture was heated at 100 °C for 72 h in a 125-mL vial. The resulting purple powder was collected by filtration, washed with DMF, and dried under reduced pressure to yield 224 mg (78%) of product. Anal. Calcd. for $C_{129}H_{336}Cl_3Cu_{12}N_{91}O_{95}$ (Mw = 5551.5 g/mol): C 31.37, H 6.33, Cu 12.97, N 17.47. Found: C 31.53, H 6.96, Cu 12.4, N 18.52. Powder X-ray diffraction data showed this compound to be isotypic with the structure of $H[Cu(DMF)_6][(Cu_4Cl)_3(BTT)_8(H_2O)_{12}]\cdot 3.5HCl\cdot 12H_2O\cdot 16CH_3OH$,[2] with a least-squares refinement utilizing the observed peak positions affording a cubic unit cell parameter of a = 18.647(6) Å.

Synthesis of $H_3[(Cu_4Cl)_3(BTTri)_8(MeOH)_{12}]\cdot 12MeOH\cdot 72H_2O$ (1-MeOH). Solid **1-DMF** was washed with methanol via soxhlet extraction for 3 days. Anal. Calcd. for $C_{84}H_{243}Cl_3Cu_{12}N_{72}O_{84}$ (Mw = 4475.2 g/mol): C 27.82, H 6.30, Cu 14.72, N 19.46. Found: C 26.78, H 5.97, Cu 14.3, N 19.32.

Synthesis of $H_3[(Cu_4Cl)_3(BTTri)_8(H_2O)_{12}]\cdot 72H_2O$ (1-H_2O). Solid **1-DMF** was placed in a 20-mL vial containing ca. 15 mL of water and heated at 100 °C for 24 h. The resulting solid was collected by filtration and washed with successive aliquots of water (5 × 5 mL). The washing process was then repeated two times. Anal. Calcd. for $C_{72}H_{168}Cl_3Cu_{12}N_{72}O_{84}$ (Mw = 4306.8 g/mol): C 24.91, H 5.49, Cu 16.48, N 21.79. Found: C 25.15, H 5.26, Cu 16.9, N 20.42.

Synthesis of $H_3[(Cu_4Cl)_3(BTTri)_8]$ (1). Solid **1-MeOH** was heated at 180 °C under dynamic vacuum until an outgas rate of less than 2 mTorr/min (0.27 Pa/min) was achieved (ca. 12 h). During this time, the purple solid changed to a brownish red color indicative of desolvation of the Cu^{II} centers. Anal. Calcd. for $C_{72}H_{96}Cl_3Cu_{12}N_{72}O_{12}$ (Mw = 2961.8 g/mol): 34.61, H 3.27, Cu 22.89, N 30.27. Found: C 34.04, H 4.02, Cu 21.2, N 29.60. Note that the re-adsorption of trace moisture during the elemental analysis procedure accounts for the oxygen present in the formula obtained.

Synthesis of $H_3[(Cu_4Cl)_3(BTTri)_8(en)_5]\cdot 1.5PhMe$ (1-en). A sample of **1** (61.4 mg, 22.0 μmol) was suspended in 5 mL of anhydrous toluene under nitrogen, and 32.8 μL (36.5 mg, 0.607 mmol, 2.3 equivalents per unsaturated Cu^{II} site) of ethylenediamine was added via microsyringe with stirring. The compound immediately turned blue and the suspension was heated at reflux for 12 h under nitrogen. The solid was collected by filtration and washed with successive aliquots of hexane (5 × 5 mL) to remove unreacted ethylenediamine. The solid was then dried

under reduced pressure to remove hexane. Anal. Calcd. for $C_{92.5}H_{103}Cl_3Cu_{12}N_{82}$ (Mw = 3232.2 g/mol): C 34.37, H 3.21, N 35.53. Found: C 35.98, H 3.94, N 35.53.

Low-Pressure Gas Adsorption Measurements. Gas adsorption isotherms for pressures in the range 0-1.2 bar were measured by a volumetric method using a Micromeritics ASAP2020 instrument. A sample of ca. 60 mg of **1-MeOH** was transferred to a pre-weighed analysis tube, which was capped with a transeal and evacuated by heating at 180 °C under dynamic vacuum until an outgas rate of less than 2 mTorr/min (0.27 Pa/min) was achieved (ca. two days). The evacuated analysis tube containing the degassed sample of **1** was then carefully transferred to an electronic balance and weighed again to determine the mass of sample (50.7 mg). The tube was then transferred back to the analysis port of the gas adsorption instrument. The outgas rate was again confirmed to be less than 2 mTorr/min (0.27 Pa/min). For all isotherms, warm and cold free space correction measurements were performed using ultra-high purity He gas (UHP grade 5.0, 99.999% purity); N_2 and H_2 isotherms at 77 and 87 K were measured in liquid nitrogen and liquid argon baths, respectively, using UHP-grade gas sources. CO_2 isotherms at 298, 303, 308, 313 and 318 K were measured using a Micromeritics heating mantle with a UHP-grade gas source. Oil-free vacuum pumps and oil-free pressure regulators were used for all measurements to prevent contamination of the samples during the evacuation process or of the feed gases during the isotherm measurements.

An identical procedure was employed for the measurement of the N_2 and CO_2 isotherms for **1-en**. To determine the optimum conditions for degassing, a sample of ca. 60 mg of **1-en** was transferred to a pre-weighed analysis tube and evacuated by heating (at 80, 100, and 120 °C) under dynamic vacuum until an outgas rate of less than 2 mTorr/min (0.27 Pa/min) was achieved (ca. two days). The N_2 isotherms at 77 K were measured following degassing at each temperature, from which it was determined that the sample degassed at 100 °C exhibited the highest surface area. A second sample of **1-en** was subsequently degassed at 100 °C prior to performing the CO_2 sorption measurements.

Isosteric Heat of Adsorption (Q_{st}) Calculations.[3] The Clausius-Clapeyron equation was employed to calculate the enthalpies of adsorption for H_2 on **1** (at 77 and 87 K) and CO_2 on **1** and **1-en** (at 303, 308, and 313 K). In each case, the data were fit using the equation:

$$(\ln P)_n = -(Q_{st}/R)(1/T) + C \qquad \text{(S-1)}$$

where P is the pressure, n is the amount adsorbed, T is the temperature, R is the universal gas constant and C is a constant. The isosteric heat of adsorption Q_{st} was subsequently obtained from the slope of plots of $(\ln P)_n$ as a function of $1/T$.

Thermogravimetric Analysis and Gas Cycling Measurements. Thermogravimetric analyses were carried out at a ramp rate of 2 °C/min under a nitrogen flow with a TA Instruments TGA Q5000 V3.1 Build 246. CO_2 cycling experiments were performed using 15% CO_2/N_2 (Praxair Certified standard NI-CD15C-K) and N_2 (Praxair, 99.99%). A flow rate of 25 mL/min was employed for both gases. Prior to cycling, the sample was activated by heating at 100 ºC for 2 h, followed by cooling to 30 °C under a nitrogen atmosphere. An empty sample pan was employed to compensate for buoyancy effects arising from the switching of gases.

Other Physical Measurements. Infrared spectra were collected on a Nicolet Avatar 360 FTIR spectrometer equipped with an attenuated total reflectance accessory (ATR). Powder X-ray diffraction data was collected using Cu Kα (λ = 1.5406 Å) radiation on a Bruker D8 Advance diffractometer. Diffuse reflectance spectra were recorded on a CARY5000 UV/visible/NIR spectrophotometer over the range 5000-50000 cm^{-1} using an air-free cell. Carbon, hydrogen, and nitrogen analyses were obtained from the Microanalytical Laboratory of the University of California, Berkeley. The determination of the quantity of Cu was performed by oxidizing pyrolysis (heating in air to 700 °C at 2 °C/min to transform into CuO, as confirmed by powder X-ray diffraction, and cooling to 20 °C at 10 °C/min).

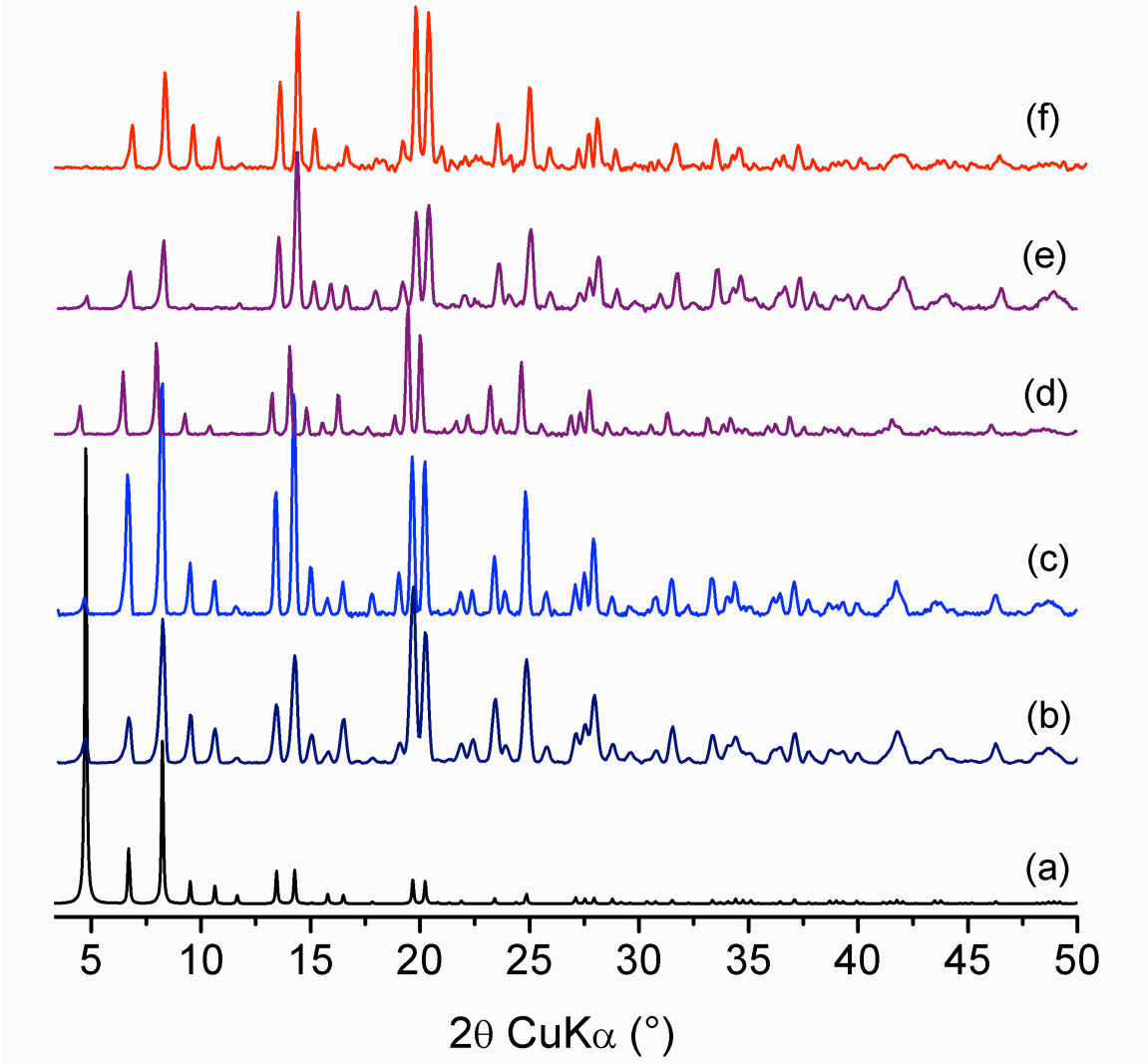

Figure S1. Powder X-ray diffraction patterns: (a) simulated from the X-ray crystal diffraction file for $H[Cu(DMF)_6][(Cu_4Cl)_3(BTT)_8(H_2O)_{12}]\cdot 3.5HCl\cdot 12H_2O\cdot 16CH_3OH$ (BTT^{3-} = 1,3,5-tris(tetrazol-5-ate)benzene)),[2] (b) for as-synthesized **1-DMF**, (c) for **1** after 3 days in boiling water, (d) for **1** after 1 day in a 0.001 M solution of HCl (pH = 3) at room temperature, (e) for **1** after heating at 270 °C under reduced pressure, and (f) for **1-en**.

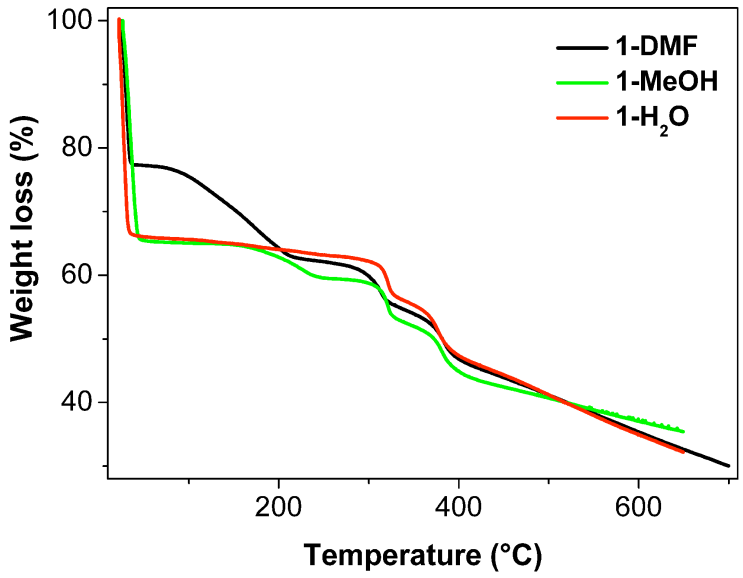

Figure S2. Thermogravimetric analysis of **1-DMF**, **1-MeOH**, and **1-H_2O** under a nitrogen flow.

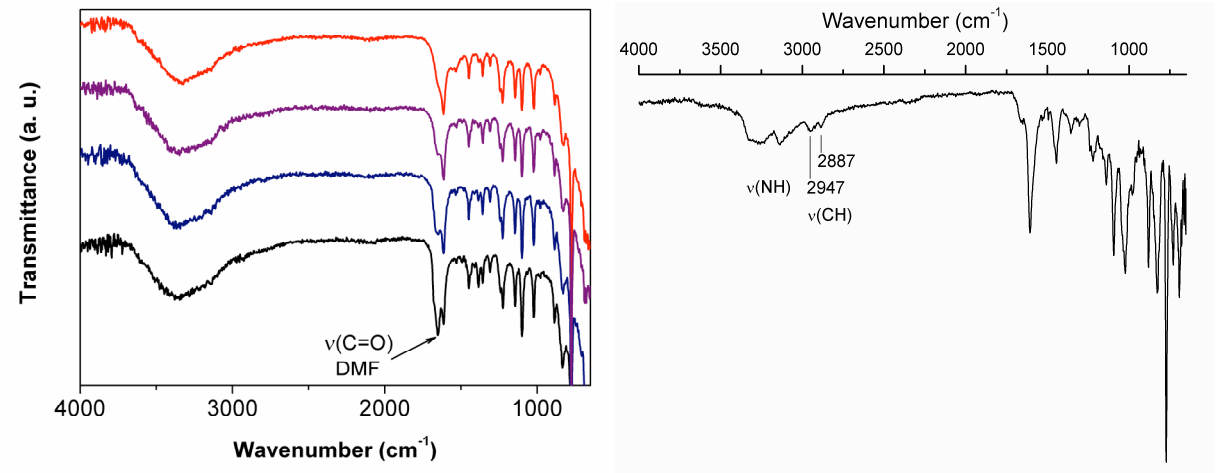

Figure S3. Infrared spectra. Left: Spectra of as-synthesized **1-DMF** (black) and after soaking in methanol at room temperature for 1 day (blue), for 2 days (purple), and for 3 days (red). Note the absence of the ν(CO) vibration of the coordinated DMF molecule in the completely-exchanged sample, **1-MeOH** (red). Right: Spectra of as-synthesized **1-en** showing ν(CH) and ν(NH) stretching frequencies for en molecule coordinated to the Cu^{2+} sites.

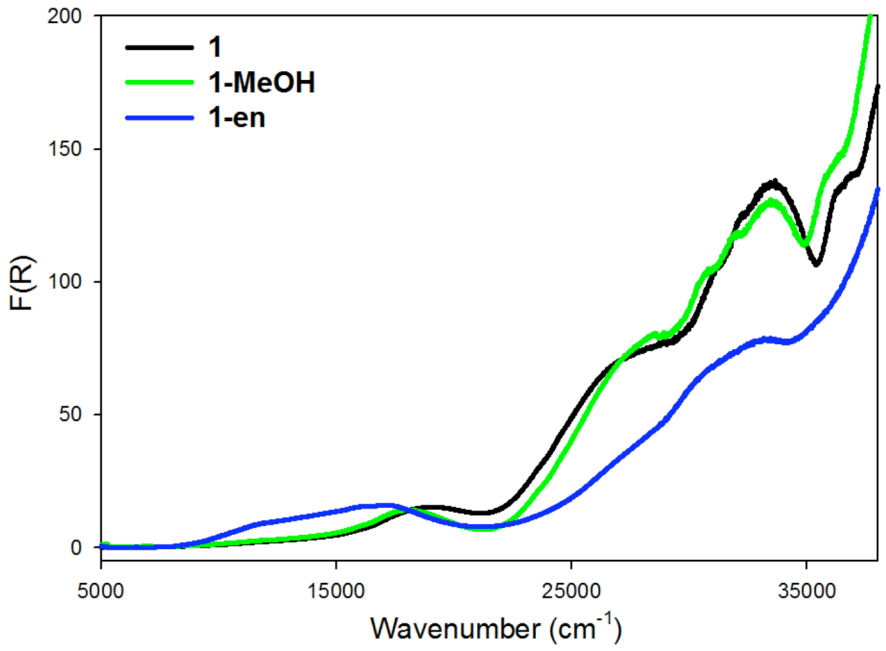

Figure S4. Diffuse reflectance spectra of **1-MeOH** (green), the desolvated framework **1** (black), and the ethylenediamine-appended framework **1-en** (blue).

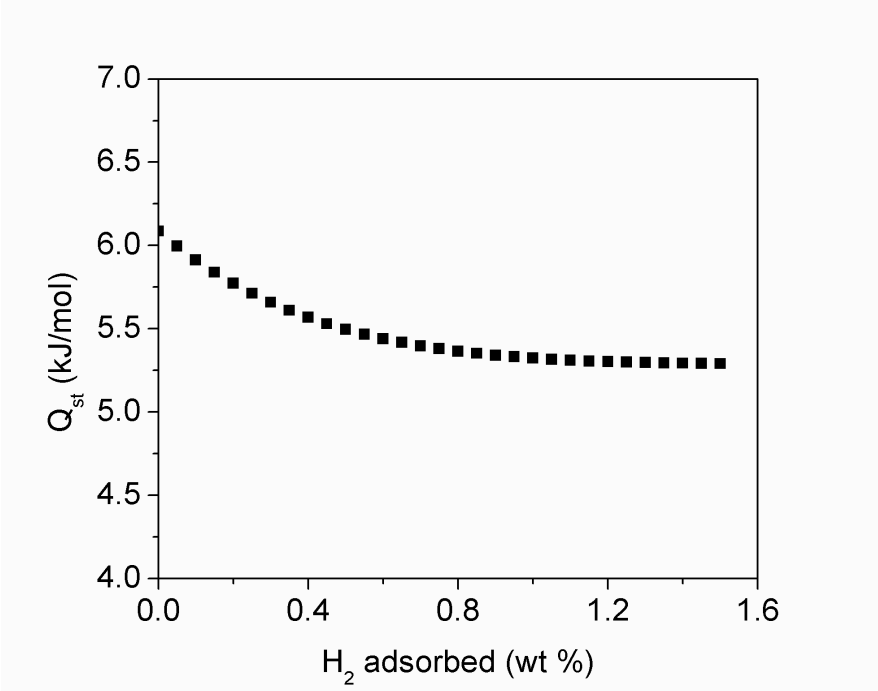

Figure S5. Isosteric heat of adsorption as a function of H_2 uptake for **1**.

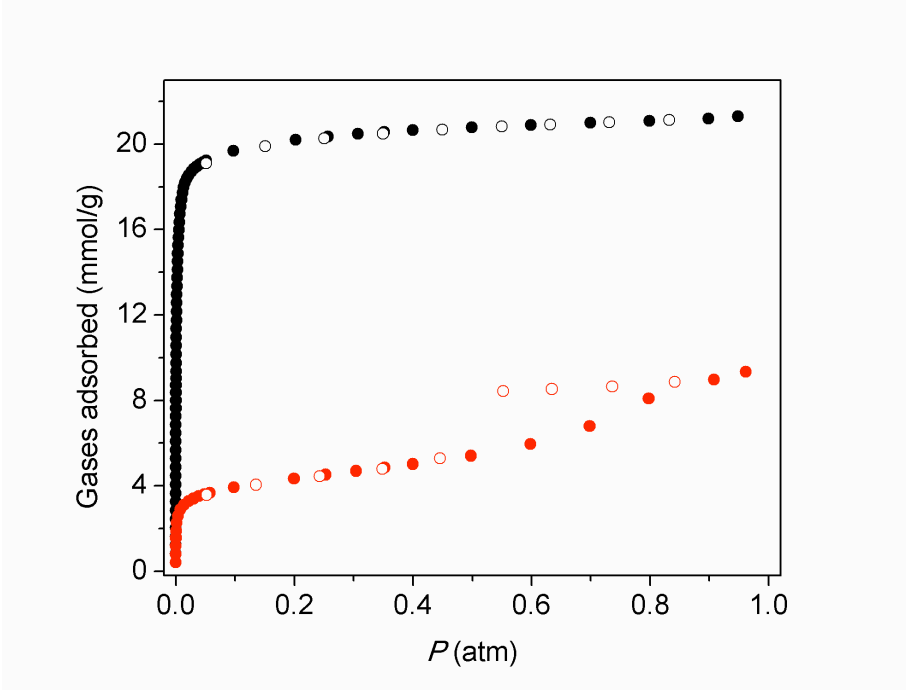

Figure S6. N_2 adsorption isotherms at 77 K in **1** (black) and in **1-en** (red) and corresponding desorption curves (open circles).

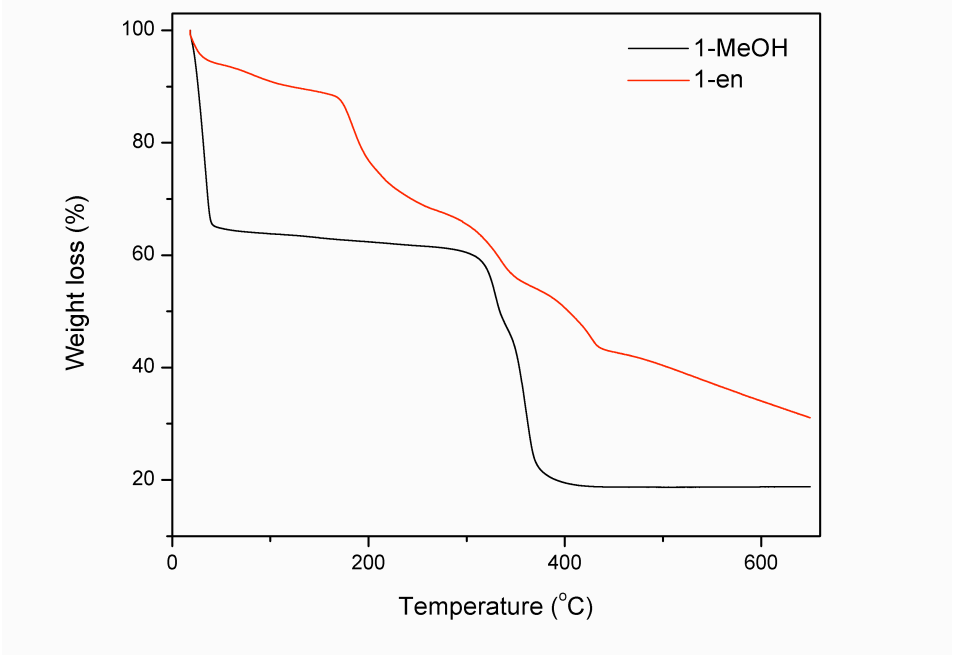

Figure S7. Thermogravimetric analyses of **1-en** and **1-MeOH** (for comparison) under a nitrogen flow.

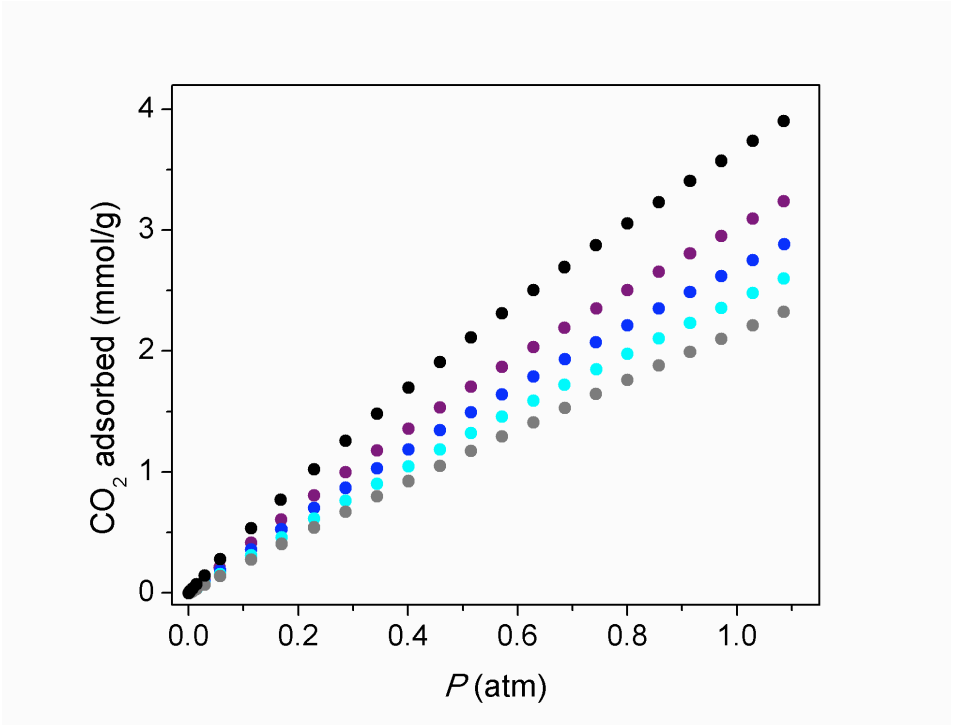

Figure S8. CO_2 adsorption isotherms at 298 (black), 303 (purple), 308 (blue), 313 (cyan), and 318 (grey) K in **1**.

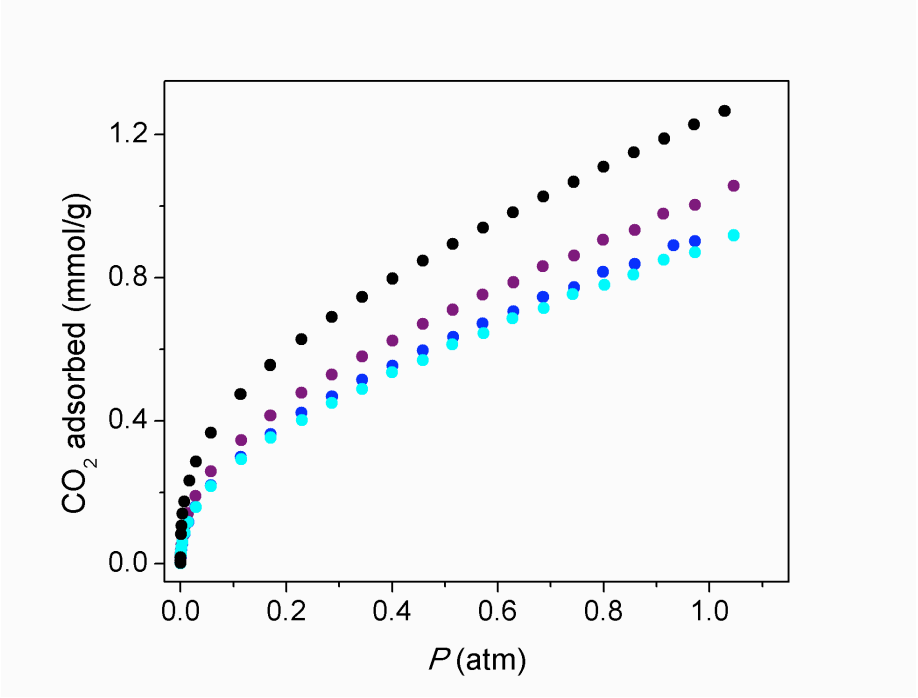

Figure S9. CO_2 adsorption isotherms at 298 (black), 303 (purple), 308 (blue), and 313 (cyan) K in **1-en**.

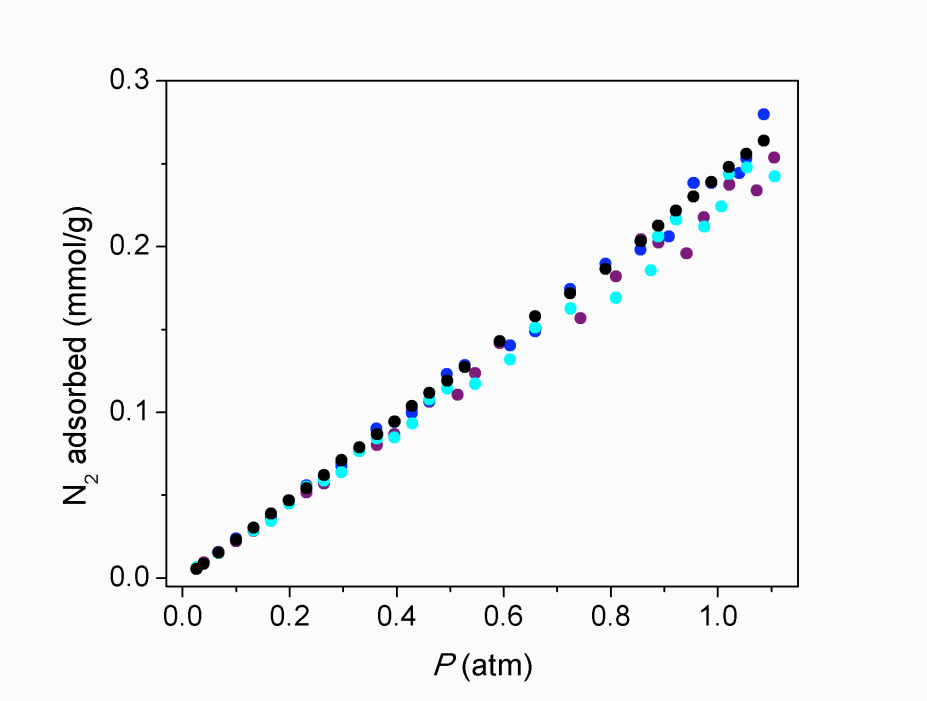

Figure S10. N_2 adsorption isotherms at 298 (black), 303 (purple), 308 (blue) and 313 K (cyan) in **1**.

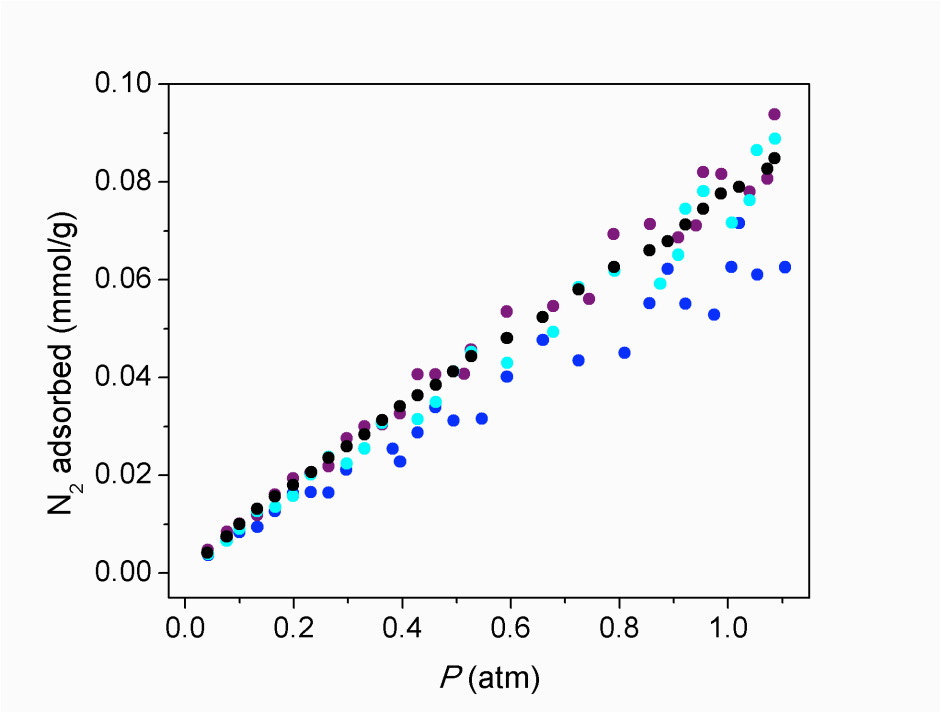

Figure S11. N_2 adsorption isotherms at 298 (black), 303 (purple), 308 (blue) and 313 K (cyan) in **1-en**.

Table S1. Adsorption and desorption data for N_2 and H_2 uptake at 77 K, for H_2 uptake at 87 K and for CO_2 gas at 195 K in **1**.

N_2 at 77 K		H_2 at 77 K		H_2 at 87 K		CO_2 at 195 K	
P (atm)	Q (mmol/g)	P (atm)	Q (mmol/g)	P (atm)	Q (mmol/g)	P (atm)	Q (mmol/g)
1.52632e-6	0.40783	2.07066e-4	0.02916	2.83028e-4	0.00696	7.73684e-6	0.0208
2.67105e-6	0.81536	3.25211e-4	0.04403	4.9087e-4	0.01304	1.47368e-5	0.03986
3.97368e-6	1.22261	4.05118e-4	0.05316	7.98141e-4	0.02181	2.40132e-5	0.05703
5.25E-6	1.62965	8.15474e-4	0.09018	0.00106	0.02921	4.14079e-5	0.07861
6.55263e-6	2.03642	0.00172	0.14866	0.00135	0.03686	6.11974e-5	0.09996
7.84211e-6	2.44296	0.00281	0.19955	0.00159	0.04333	8.27763e-5	0.12118
9.36842e-6	2.84921	0.00438	0.25839	0.00184	0.04966	1.05421e-4	0.14206
1.11053e-5	3.25519	0.01043	0.43548	0.00208	0.05584	1.30171e-4	0.16289
1.31316e-5	3.66076	0.02268	0.72935	0.00233	0.06182	1.54303e-4	0.18361
1.57237e-5	4.06592	0.03251	0.9445	0.00309	0.07857	1.78829e-4	0.20414
1.9E-5	4.47047	0.04955	1.27938	0.00405	0.0982	2.03605e-4	0.22445
2.31053e-5	4.87427	0.06579	1.57735	0.00727	0.14702	2.28789e-4	0.24473
2.85395e-5	5.27705	0.09474	2.05912	0.0099	0.18413	2.54053e-4	0.26481
3.56711e-5	5.6785	0.13151	2.60782	0.01267	0.22013	2.79303e-4	0.28474
4.53553e-5	6.07808	0.19746	3.44011	0.01772	0.27865	3.04789e-4	0.30452
5.89605e-5	6.47506	0.26401	4.13865	0.02277	0.33275	3.30158e-4	0.32412
7.83684e-5	6.86823	0.32971	4.72286	0.02803	0.39233	3.55526e-4	0.34355
1.06368e-4	7.2558	0.39692	5.23537	0.03359	0.44431	3.80947e-4	0.36278
1.45908e-4	7.63542	0.46376	5.68116	0.0491	0.57393	4.06289e-4	0.38188
1.97434e-4	8.00475	0.52653	6.05363	0.06618	0.70925	4.31553e-4	0.40077
2.59066e-4	8.36203	0.59289	6.40628	0.09626	0.91958	4.56697e-4	0.41945
3.2725e-4	8.70627	0.65848	6.72145	0.13145	1.1517	4.81855e-4	0.43799
3.98289e-4	9.03717	0.72421	7.01128	0.19673	1.54731	5.06618e-4	0.45628
4.70224e-4	9.35468	0.7901	7.27749	0.26258	1.91448	5.31592e-4	0.47442
5.75566e-4	9.75731	0.8557	7.52524	0.32867	2.25358	5.56342e-4	0.49237
6.84855e-4	10.15972	0.92132	7.75202	0.39486	2.57161	5.80908e-4	0.51014
7.98118e-4	10.56061	0.98696	7.96646	0.46143	2.87018	6.0554e-4	0.52774
9.15368e-4	10.96266	1.05281	8.17361	0.52645	3.13965	6.29724e-4	0.54511
0.00104	11.36439	1.10494	8.32685	0.59209	3.39864	6.54092e-4	0.56229
0.00117	11.76547	1.16488	8.50279	0.6579	3.64077	6.78224e-4	0.57934
0.00132	12.16547	0.96345	7.92328	0.72374	3.86596	7.02171e-4	0.59619
0.00149	12.56411	0.8149	7.41716	0.7893	4.08263	7.26079e-4	0.61273
0.00169	12.96096	0.56204	6.27486	0.85532	4.28899	7.49645e-4	0.62921
0.00192	13.35534	0.2964	4.45653	0.9209	4.48342	7.73171e-4	0.64552
0.0022	13.74633	0.22093	3.71333	0.98665	4.66981	7.96684e-4	0.66159
0.00254	14.13308	0.15728	2.95314	1.0524	4.84747	8.20066e-4	0.67755
0.00294	14.51435	0.08172	1.83462	1.1067	4.99041	8.43e-4	0.69324
0.00342	14.88931	0.0181	0.58755	1.16744	5.14831	8.65974e-4	0.70874
0.00398	15.25771	0.00131	0.10645			8.885e-4	0.7241
0.00463	15.62755					9.10895e-4	0.73916
0.00534	15.99041					9.33053e-4	0.75402
0.00612	16.34567					9.55276e-4	0.76884
0.00709	16.73798					9.82158e-4	0.79133
0.00815	17.08451					0.00101	0.81367
0.00945	17.40886					0.01389	4.72303
0.01109	17.7163					0.02699	6.51769
0.01307	17.97385					0.03932	8.24964
0.01561	18.2081					0.05296	10.57839
0.01847	18.39445					0.06753	13.26944
0.02168	18.5517					0.08297	15.43304
0.02591	18.70948					0.10144	16.59986
0.03055	18.84467					0.11366	17.00743
0.03531	18.9592					0.12891	17.35068
0.04032	19.05985					0.14205	17.57359

cont.. N_2 at 77 K	
P (atm)	Q (mmol/g)
0.04569	19.15182
0.05098	19.23153
0.09696	19.68863
0.20205	20.19744
0.25634	20.36018
0.30675	20.48096
0.35167	20.56912
0.39948	20.6538
0.49956	20.79216
0.59917	20.90399
0.69897	21.00104
0.79894	21.09166
0.8986	21.19907
0.94849	21.30136
0.8319	21.13412
0.73141	21.03015
0.63133	20.92398
0.54994	20.82876
0.44988	20.67411
0.34954	20.49449
0.25059	20.26179
0.1508	19.89651
0.05087	19.10772

cont... CO_2 at 195 K	
P (atm)	Q (mmol/g)
0.15454	17.74769
0.16565	17.88172
0.178	18.0129
0.19049	18.13074
0.20393	18.24564
0.21715	18.34881
0.23061	18.44412
0.24382	18.53202
0.25726	18.61433
0.27049	18.68934
0.28386	18.76246
0.29705	18.8294
0.31059	18.89486
0.32392	18.9563
0.33714	19.01627
0.35055	19.073
0.36395	19.12756
0.37723	19.1816
0.39069	19.23314
0.40405	19.28273
0.41733	19.3307
0.43071	19.37817
0.44399	19.42451
0.45761	19.46991
0.47034	19.51408
0.48409	19.55908
0.49736	19.60195
0.51056	19.64378
0.52405	19.68533
0.53753	19.72749
0.55091	19.76609
0.56435	19.80459
0.57783	19.84377
0.59111	19.88148
0.60453	19.91833
0.61793	19.95591
0.63142	19.99125
0.64474	20.02818
0.65819	20.0644
0.70827	19.83268
0.99827	20.38872

Table S2. Adsorption and desorption data for N_2 uptake at 77 K in **1-en**.

P (atm)	Q (mmol/g)
0.000014567	0.40426
0.000050335	0.80447
0.000115612	1.19757
0.000298675	1.56855
0.000682435	1.89271
0.001709564	2.26708
0.003905212	2.59916
0.007813858	2.88920
0.014014979	3.11670
0.021430533	3.27692
0.029787578	3.40385
0.038914855	3.51051
0.048082154	3.59931
0.057299646	3.67544
0.097867456	3.92639
0.199368852	4.34277
0.252506498	4.52369
0.303679755	4.69067
0.352512662	4.85061
0.399886136	5.01529
0.497499981	5.40400
0.598362985	5.96235
0.698056324	6.80368
0.797758997	8.09036
0.907905422	8.97467
0.961726289	9.34978
0.841389046	8.87135
0.736186101	8.65274
0.634152192	8.53047
0.552608179	8.43563
0.445203974	5.28196
0.348205711	4.79783
0.242883127	4.44571
0.135367929	4.04573
0.052244444	3.57306

Table S3. Adsorption data for CO_2 gas at 298, 303, 308, 313 and 318 K in **1**.

At 298 K		At 303 K		At 308 K	
P (atm)	Q (mmol/g)	P (atm)	Q (mmol/g)	P (atm)	Q (mmol/g)
0.00116	0.00343	0.00373	0.0045	0.00374	0.00424
0.002	0.00745	0.00775	0.01964	0.00818	0.02012
0.00375	0.01634	0.01529	0.04851	0.01521	0.04402
0.00777	0.0355	0.02912	0.1015	0.02924	0.09056
0.01497	0.07032	0.05728	0.20779	0.05802	0.18355
0.02918	0.14034	0.11417	0.41342	0.11418	0.35849
0.05754	0.27732	0.16932	0.6056	0.16954	0.52591
0.11411	0.53299	0.22927	0.80557	0.2292	0.70073
0.16847	0.76821	0.28639	0.99469	0.28646	0.86645
0.22924	1.02089	0.34371	1.17764	0.34367	1.02655
0.2863	1.25494	0.40097	1.35668	0.40085	1.18554
0.34357	1.4794	0.45838	1.5334	0.4582	1.34305
0.40113	1.6967	0.51485	1.70271	0.51467	1.49269
0.4584	1.90901	0.57189	1.86945	0.57179	1.63876
0.51481	2.11227	0.62886	2.03115	0.62873	1.78698
0.57173	2.30992	0.68591	2.19256	0.68614	1.93136
0.6288	2.5027	0.74335	2.3491	0.74311	2.0706
0.68597	2.69292	0.80015	2.5034	0.80013	2.21221
0.74317	2.876	0.85751	2.65612	0.85742	2.35168
0.80023	3.05582	0.91442	2.80553	0.91446	2.48723
0.85746	3.23118	0.97146	2.95261	0.97154	2.61919
0.91441	3.40411	1.02881	3.09311	1.02861	2.75176
0.97168	3.57234	1.08564	3.23663	1.08585	2.88309
1.02856	3.73678				
1.08575	3.90006				

At 313 K		At 318K	
P (atm)	Q (mmol/g)	P (atm)	Q (mmol/g)
0.00374	0.00149	0.00375	9.6E-4
0.00779	0.01303	0.00773	0.01145
0.0154	0.03532	0.01493	0.02975
0.02909	0.07429	0.02939	0.06744
0.05761	0.15545	0.05749	0.13675
0.11438	0.3109	0.11445	0.27315
0.16973	0.45904	0.17029	0.40308
0.22931	0.61323	0.22903	0.53957
0.28635	0.75994	0.28645	0.66931
0.34358	0.90239	0.34358	0.79674
0.40093	1.04408	0.40088	0.92294
0.45823	1.18309	0.4582	1.04874
0.51469	1.3189	0.51481	1.17196
0.57169	1.45568	0.57173	1.29044
0.62906	1.58718	0.62876	1.40939
0.68583	1.71893	0.68613	1.52946
0.74333	1.84889	0.74327	1.64593
0.80026	1.97477	0.80017	1.76146
0.85719	2.10368	0.85741	1.87937
0.91466	2.23192	0.91448	1.98993
0.97144	2.35403	0.97132	2.10123
1.02851	2.47742	1.02867	2.21257
1.08572	2.59822	1.08567	2.32384

Table S4. Adsorption and desorption data for CO_2 gas at 298, 303, 308 and 313 K in **1-en**.

At 298 K		At 303 K		At 308 K		At 313 K	
P (atm)	Q (mmol/g)	P (atm)	Q (mmol/g)	P (atm)	Q (mmol/g)	P (atm)	Q (mmol/g)
4.40395E-05	0.00182	7.31711E-05	0.00121	9.03158E-05	0.00086	6.46316E-05	0.00151
8.34737E-05	0.00832	0.000101342	0.00341	0.000131697	0.00282	9.36053E-05	0.00377
0.000129474	0.01759	0.000130474	0.00545	0.000342316	0.01281	0.000154211	0.00811
0.001066921	0.08231	0.000363526	0.01923	0.000587487	0.01945	0.000337974	0.01694
0.001849039	0.10578	0.000577711	0.02639	0.001106395	0.02964	0.000575145	0.02392
0.003826408	0.14073	0.001061289	0.03829	0.001941447	0.04100	0.001133197	0.03532
0.007328	0.17354	0.001940066	0.05331	0.003668974	0.05739	0.00194225	0.04572
0.016783211	0.23290	0.003656158	0.07359	0.007483737	0.08383	0.003556947	0.06096
0.028888289	0.28605	0.007536382	0.10445	0.015199566	0.11728	0.007824724	0.08704
0.057486671	0.36637	0.014663408	0.14098	0.028370342	0.15950	0.014604737	0.11634
0.113453579	0.47399	0.028606263	0.18942	0.057806513	0.21952	0.029007961	0.15816
0.169841605	0.55533	0.057497197	0.25806	0.11371925	0.29858	0.057453882	0.21685
0.228836013	0.62782	0.114498855	0.34524	0.170188526	0.36307	0.114748474	0.29202
0.286333329	0.68951	0.170029026	0.41391	0.228874329	0.42219	0.170310026	0.35278
0.343584	0.74572	0.228935224	0.47888	0.286496395	0.46700	0.229299539	0.40193
0.401035105	0.79747	0.286310776	0.52867	0.343274329	0.51444	0.286012829	0.44994
0.458493842	0.84729	0.343469645	0.57973	0.400831079	0.55405	0.343533079	0.48893
0.51461375	0.89395	0.40081775	0.62369	0.458055671	0.59668	0.400474303	0.53531
0.571792355	0.93956	0.458041539	0.67031	0.515159645	0.63435	0.458240632	0.56902
0.62887625	0.98244	0.515039461	0.71020	0.571566697	0.67219	0.513578632	0.61350
0.686044711	1.02669	0.571582105	0.75280	0.629280737	0.70599	0.572950908	0.64423
0.743319618	1.06792	0.629320526	0.78703	0.68567425	0.74620	0.627870132	0.68648
0.799923066	1.10974	0.685020039	0.83158	0.743925882	0.77285	0.687142224	0.71439
0.857296434	1.15043	0.744078382	0.86176	0.798875513	0.81583	0.741863618	0.75461
0.914488776	1.18887	0.798864829	0.90620	0.858845434	0.83866	0.801442197	0.78049
0.971359737	1.22891	0.858860211	0.93298	0.932111	0.89058	0.856711461	0.80850
1.028841921	1.26570	0.912694829	0.97898	0.973151118	0.90159	0.914098724	0.84942
1.08551475	1.30438	0.973335421	1.00355			0.972716408	0.87067
1.010545829	1.27793	1.046154303	1.05693			1.046533763	0.91844
0.954002868	1.25850	1.087214579	1.07143			1.086799868	0.93583
0.897588145	1.23638	1.009294855	1.06302				
0.860082447	1.22284	0.953173105	1.03335				
0.803857579	1.19804	0.895322934	1.02677				
0.747296947	1.17046	0.839266645	0.99360				
0.690790513	1.14235	0.798981513	0.98616				
0.634508711	1.11075	0.725330316	0.94773				
0.577945987	1.07851	0.685471711	0.93150				
0.521618013	1.04262	0.629777842	0.90361				
0.464934539	1.00564	0.572531934	0.86914				
0.4086425	0.96501	0.514754039	0.84201				
0.352130974	0.92155	0.459121263	0.80358				
0.295912474	0.87386	0.400425434	0.77161				
0.239481276	0.82024	0.345015921	0.72793				
0.183410066	0.75592	0.286453934	0.68704				
0.126691658	0.67415	0.230910658	0.63164				
0.070733276	0.56159	0.172541947	0.57055				
0.013654474	0.34019	0.116287697	0.50012				
		0.059773158	0.39194				
		0.050819263	0.39120				
		0.049403789	0.39580				
		0.049281382	0.39619				

Table S5. Adsorption and desorption data for N_2 gas at 298, 303, 308 and 313 K in **1**.

At 298 K		At 303 K		At 308 K		At 313 K	
P (atm)	Q (mmol/g)	P (atm)	Q (mmol/g)	P (atm)	Q (mmol/g)	P (atm)	Q (mmol/g)
0.025355	0.00540	0.02628	0.00595	0.026254	0.00650	0.026179	0.00662
0.039028	0.00861	0.039357	0.00940	0.038853	0.00870	0.038834	0.00855
0.067067	0.01538	0.066729	0.01574	0.066589	0.01545	0.067112	0.01516
0.099376	0.02318	0.09942	0.02216	0.09958	0.02395	0.09973	0.02321
0.132613	0.03049	0.132677	0.02853	0.132313	0.03026	0.132653	0.02861
0.165513	0.03890	0.165448	0.03829	0.165094	0.03661	0.165568	0.03453
0.198588	0.04681	0.1982	0.04681	0.198393	0.04486	0.19858	0.04496
0.231339	0.05433	0.231368	0.05161	0.231041	0.05593	0.231043	0.05506
0.264325	0.06225	0.264151	0.05700	0.264294	0.06139	0.264143	0.05886
0.296656	0.07114	0.29693	0.06983	0.296942	0.06773	0.296928	0.06386
0.330406	0.07898	0.330033	0.07825	0.330265	0.07670	0.329831	0.07670
0.363335	0.08676	0.362787	0.08034	0.362253	0.09004	0.362803	0.08437
0.396055	0.09452	0.395634	0.08693	0.395702	0.09415	0.395457	0.08492
0.428571	0.10374	0.428459	0.10145	0.428344	0.09963	0.42911	0.09349
0.461249	0.11167	0.461077	0.10628	0.461121	0.10692	0.461297	0.10779
0.49456	0.11908	0.514289	0.11070	0.493704	0.12313	0.494571	0.11441
0.527049	0.12723	0.546506	0.12362	0.527341	0.12843	0.546531	0.11726
0.592564	0.14307	0.59271	0.14188	0.612096	0.14046	0.611991	0.13191
0.658625	0.15794	0.658948	0.15082	0.658207	0.14872	0.658345	0.15128
0.724294	0.17179	0.743735	0.15671	0.724128	0.17451	0.724699	0.16266
0.789969	0.18663	0.809326	0.18211	0.790575	0.18977	0.809651	0.16911
0.855831	0.20329	0.856192	0.20441	0.855618	0.19817	0.874989	0.18577
0.888697	0.21258	0.889232	0.20239	0.908251	0.20607	0.888594	0.20615
0.921757	0.22168	0.941497	0.19585	0.921438	0.21701	0.922108	0.21640
0.954428	0.23034	0.973554	0.21777	0.954796	0.23847	0.974241	0.21204
0.987401	0.23896	0.98789	0.23879	0.987746	0.23837	1.006755	0.22431
1.020285	0.24801	1.020972	0.23746	1.039919	0.24447	1.02062	0.24383
1.052913	0.25588	1.072755	0.23391	1.053159	0.25321	1.053706	0.24784
1.085752	0.26407	1.105292	0.25379	1.085558	0.27983	1.105927	0.24224
1.118827	0.27519	1.118862	0.27788	1.119439	0.28014	1.138322	0.25701
1.151787	0.28547	1.152464	0.28696	1.171461	0.28519	1.151872	0.28029
1.006288	0.25838	1.006712	0.24417	1.006278	0.25461	1.006152	0.26036
0.879868	0.23392	0.879708	0.21773	0.879284	0.24627	0.880415	0.22403
0.75338	0.20831	0.753088	0.21055	0.753137	0.22565	0.753377	0.20904
0.646038	0.18553	0.626796	0.19031	0.645979	0.19779	0.62725	0.19473
0.519652	0.15481	0.520037	0.15705	0.519624	0.16779	0.520365	0.16611
0.393536	0.12298	0.393145	0.12549	0.393135	0.14259	0.392805	0.13335
0.267303	0.08995	0.266773	0.10168	0.267205	0.11563	0.37445	0.15612
0.140518	0.05474	0.141164	0.07098	0.140678	0.07843	0.372714	0.13226
0.01287	-0.01315	0.013657	0.02257	0.013812	0.01197	0.37234	0.12929

Table S6. Adsorption and desorption data for N_2 gas at 298, 303, 308 and 313 K in **1-en**.

At 298 K		At 303 K		At 308 K		At 313 K	
P (atm)	Q (mmol/g)	P (atm)	Q (mmol/g)	P (atm)	Q (mmol/g)	P (atm)	Q (mmol/g)
0.04068	0.00422	0.042041	0.00472	0.042523	0.00367	0.042756	0.00390
0.07663	0.00754	0.076905	0.00852	0.07657	0.00696	0.076472	0.00657
0.099616	0.01003	0.100031	0.01016	0.09977	0.00839	0.099895	0.00906
0.13246	0.01314	0.132805	0.01188	0.132967	0.00945	0.132191	0.01267
0.165462	0.01571	0.165086	0.01605	0.165322	0.01268	0.16604	0.01357
0.198343	0.01803	0.198736	0.01944	0.198512	0.01637	0.198455	0.01583
0.231825	0.02065	0.23087	0.02044	0.231547	0.01653	0.23109	0.02021
0.263736	0.02355	0.26378	0.02189	0.264253	0.01652	0.263816	0.02373
0.297328	0.02595	0.297357	0.02761	0.29665	0.02110	0.297286	0.02243
0.330256	0.02840	0.329948	0.03006	0.330113	0.02553	0.330158	0.02550
0.362743	0.03131	0.362834	0.03040	0.382139	0.02541	0.362535	0.03069
0.395549	0.03416	0.395467	0.03267	0.396064	0.02281	0.395681	0.03408
0.42821	0.03635	0.428135	0.04063	0.428009	0.02876	0.428402	0.03146
0.461683	0.03850	0.461312	0.04066	0.460842	0.03392	0.461974	0.03499
0.494009	0.04125	0.514197	0.04073	0.494694	0.03116	0.494363	0.04123
0.527172	0.04432	0.52669	0.04572	0.546647	0.03155	0.527078	0.04528
0.592715	0.04812	0.592608	0.05347	0.592726	0.04017	0.593273	0.04298
0.658597	0.05235	0.678172	0.05460	0.659075	0.04765	0.677973	0.04935
0.724429	0.05799	0.744288	0.05612	0.725086	0.04350	0.724498	0.05850
0.790085	0.06259	0.789398	0.06930	0.809669	0.04505	0.790673	0.06186
0.855586	0.06604	0.856481	0.07139	0.855568	0.05514	0.875466	0.05916
0.888726	0.06785	0.908609	0.06865	0.888906	0.06222	0.908131	0.06510
0.921318	0.07132	0.94118	0.07107	0.921831	0.05513	0.921374	0.07450
0.954469	0.07450	0.954066	0.08205	0.974361	0.05285	0.954831	0.07808
0.987385	0.07760	0.987932	0.08159	1.006713	0.06260	1.007355	0.07171
1.020369	0.07901	1.040158	0.07805	1.020277	0.07157	1.039871	0.07623
1.072593	0.08269	1.072837	0.08070	1.054104	0.06100	1.052943	0.08653
1.085781	0.08486	1.085605	0.09384	1.105648	0.06254	1.086531	0.08881
1.119042	0.08738	1.119564	0.09354	1.118662	0.07205	1.139031	0.08134
1.171558	0.08929	1.171758	0.08977	1.152033	0.08121	1.171487	0.08436
1.00601	0.07979	1.006131	0.07756	1.006505	0.06316	1.005475	0.08588
0.879499	0.07408	0.879002	0.08004	0.879894	0.05507	0.879552	0.07615
0.753553	0.06663	0.753626	0.06867	0.75269	0.05823	0.753576	0.06009
0.646271	0.05834	0.646228	0.05557	0.626801	0.05189	0.645672	0.05793
0.519766	0.04897	0.519881	0.04695	0.520322	0.03712	0.500287	0.05003
0.393632	0.03908	0.393751	0.04007	0.393314	0.03102	0.393781	0.03607
0.267214	0.02766	0.267589	0.02568	0.24794	0.02249	0.267045	0.02388
0.140486	0.01470	0.140889	0.01163	0.140864	0.01255	0.140976	0.01329
0.012599	-0.00544	0.01237	-0.00704	0.012264	-0.00398	0.012599	-0.00654

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