Electronic Supplementary Material (ESI)

Programming MIL-101Cr for selective and enhanced CO_2 adsorption at low pressure by postsynthetic amine functionalization

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1. Instrumentation

The N_2 sorption isotherms of compounds **1** – **5** were measured in a Quantachrome Autosorb iQ MP instrument at liquid N_2 temperature (77 K). The BET surface area were calculated from data points in the pressure range $p/p_0 = 0.05 – 0.2$. The samples were degassed under high vacuum (10^{-6} Torr) for 8 h prior to sorption measurements. The other gas (CO_2, CH_4, N_2) isotherms were obtained from Micromeritics ASAP 2020 gas sorption analyzer.

Powder X-ray diffraction patterns of each sample was measured on a Bruker D2 Phaser using Cu $K\alpha1/\alpha2$ radiation with $\lambda = 1.5418$ Å.

Thermagravimetric analysis (TGA) were performed at a ramp rate of 5 °C/min in a N2 flow with a Netzsch Thermo – Microbalance Apparatus TG 209 F3 Tarsus.

^1H NMR spectra were recorded in a Bruker Advance DRX 200 MHz NMR instrument. Compounds **2** – **5** were decomposed in conc. NaOH solution and $Cr(OH)_3$ were filtered off. The solution was then acidified with conc. HCl to precipitate the ligands. The ligands were dried and dissolved in $NaOD/D_2O$ mixture for NMR measurement.

2. Materials

Chromium nitrate nonahydrate, $Cr(NO_3)_3\cdot 9H_2O$ (99%) and hydrofluoric acid (analysis grade) were obtained from Acros Organics. Benzene-1,4-dicarboxylic acid (H_2BDC, 99%) was acquired from Aldrich. Dichloromethane (DCM, >99.9%), *N,N'*-dimethylformamide (DMF, 99.9%) and ethanol (99.9%) were purchased from Prolabo. O_2, N_2, CO_2 and CH_4 gas were supplied by Air Liquide (Germany) and used as received (purity 99.99%).

3. Synthesis

MIL-101Cr (**1**) were synthesized from chromium nitrate and benzene-1,4-dicarboxylic acid according to the described literature procedure.[1] The as-synthesized samples were activated through washing with DMF, ethanol and water at room temperature.

MIL-101Cr-NO_2 (**2**): 300 mg of MIL-101Cr (**1**) were added to a mixture of conc. H_2SO_4 (15 mL) and conc. HNO_3 (14 mL), kept in an ice bath. The mixture was stirred at ice temperature for 6 h and then poured into a beaker with 75 mL of crushed ice. The solid material was centrifuged off, washed several times with water and then dried at room temperature.

MIL-101Cr-pNO_2 (**3**): 500 mg of MIL-101Cr was added to a stirred solution of conc. HNO_3 (24 mL) /conc. H_2SO_4 (22 mL) at 0 °C. The solution was stirred for 10 min and then poured into crushed ice. The solid material was filtered and washed several times with water. From test runs we realized that most of the ligand is nitrated quickly. Hence, a short reaction time of only 10 min had to be chosen to stop the nitration at about 78%.

MIL-101Cr-NH_2 (**4**): A mixture of 300 mg MIL-101Cr-NO_2 (**2**) and 2 g $SnCl_2$ were stirred in 20 mL of ethanol at 70 °C for 10 h. 15 mL of conc. HCl (c = 11.65 mol/L) was added to this solution at room temperature and stirred for 30 minutes. The greenish solid was centrifuged off and then washed several times with water. The separated solid is dried at room temperature.

MIL-101Cr-pNH_2 (**5**): 400 mg of MIL-101Cr-pNO_2 (**3**) were stirred with 2.5 g of $SnCl_2$ in 40 mL of ethanol at 70 °C for 16 h. The greenish precipitate was filtered off and suspended in 30 mL of conc. hydrochloric acid (c = 11.65 mol/L). The solid material was separated by centrifugation and then washed several times with water.

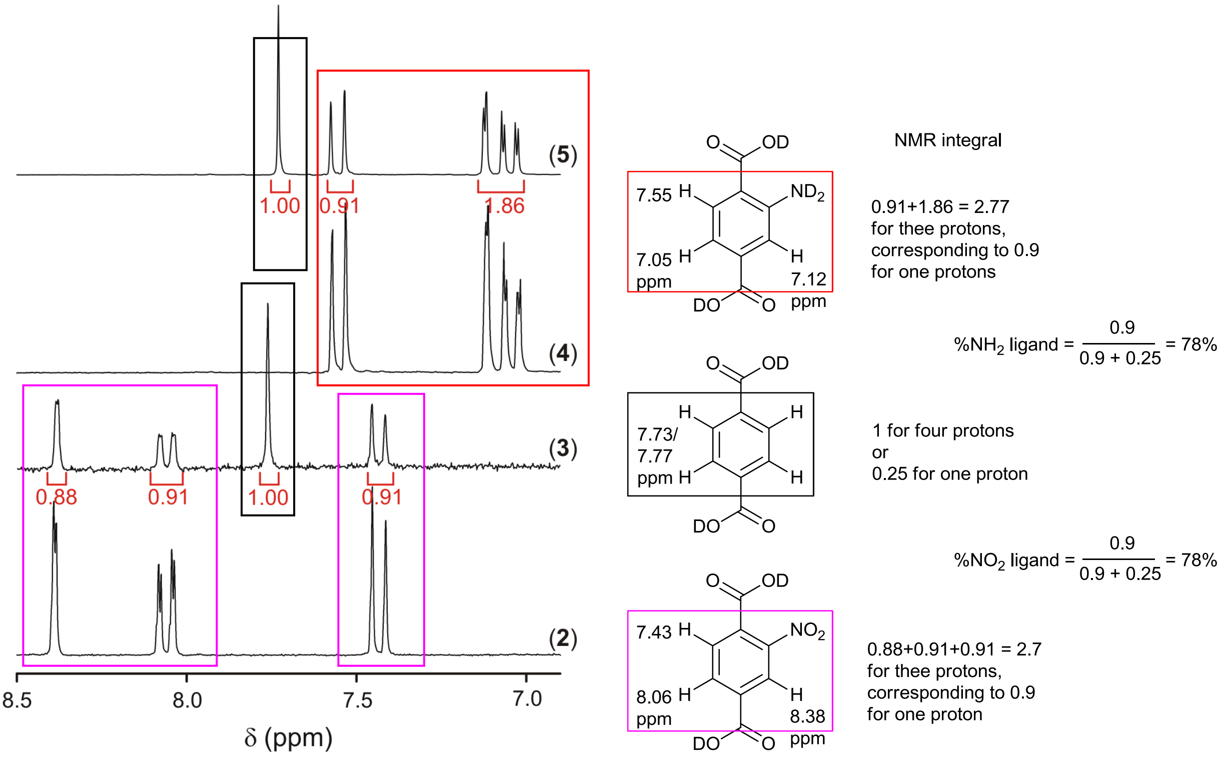


Figure S1. ^{1}H NMR spectra of the organic linkers in D_2O/NaOD solution after decomposition of **2-2-5** in NaOD/D_2O. The relative intensities are provided for partially nitrated/aminated mixed-ligand materials **3** and **5**. The assignments of individual (pH dependent) resonances are provided with the formula drawings.

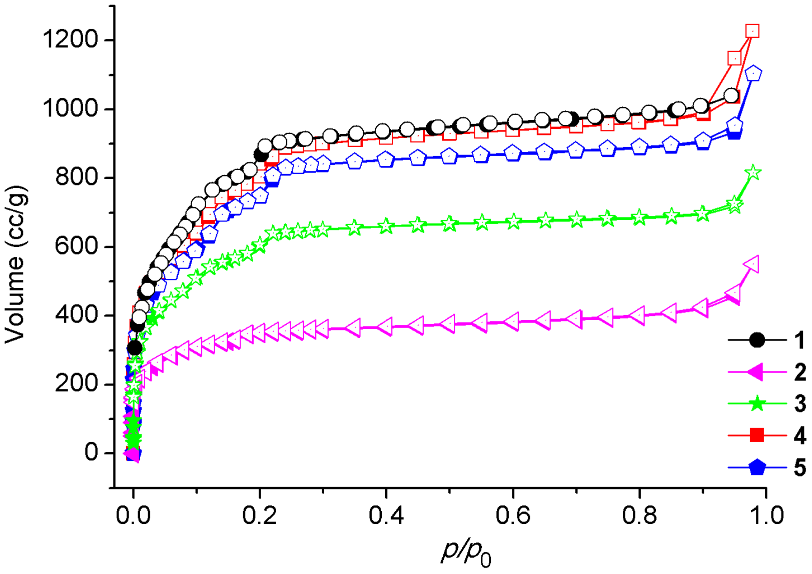


Figure S2. N_2 sorption isotherms of compounds **1** – **5** at 77 K. Closed and open symbols refer to adsorption and desorption respectively.

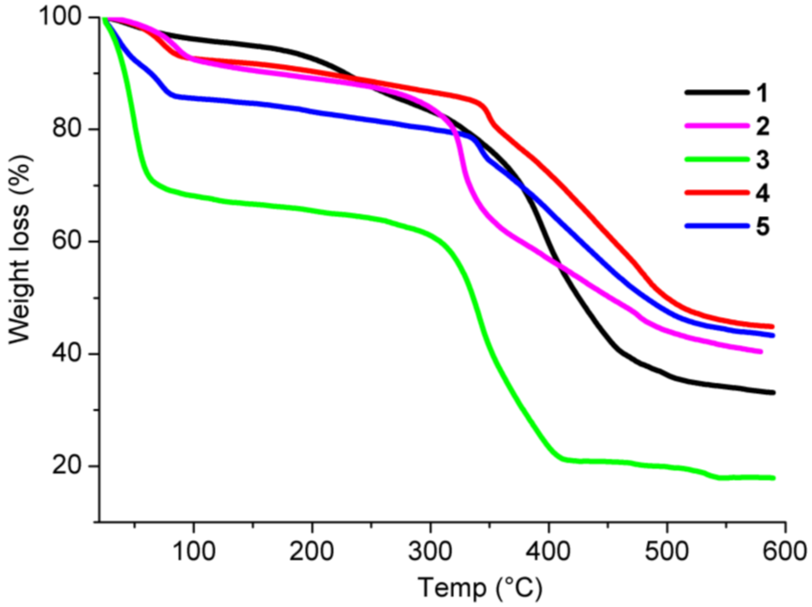


Figure S3. Thermogravimetric analysis (TGA) of compounds **1** – **5**.

3. Gas uptake

Gas uptakes are given in Table S1 at P = 750 Torr determined from the gas adsorption isotherms in Figure S4 – Figure S8.

Table S1 CO_2, CH_4 and N_2 gas uptake of compounds **1** – **5** at different temperature and 1 bar.

Compounds	CO_2 uptake (**wt%**)[c]		CH_4 uptake (**wt%**)[c]		N_2 uptake (**wt%**)[c]	
	273 K	293 K	273 K	293 K	273 K	293 K
MIL-101Cr (**1**)	15.5	10.5	1.27	0.89	0.84	0.59
MIL-101Cr-NO_2 (**2**)	12.7	7.8	1.25	0.67	1.20	0.49
MIL-101Cr-pNO_2 (**3**)	12.2	7.3	1.15	0.71	1.23	0.53
MIL-101Cr-NH_2 (**4**)	22.2	15.9	1.67	0.87	2.27	0.92
MIL-101Cr-pNH_2 (**5**)	19.9	13.7	1.46	0.83	1.68	1.12

Compounds	CO_2 uptake (**mmol g^{-1}**)[c]		CH_4 uptake (**mmol g^{-1}**)[c]		N_2 uptake (**mmol g^{-1}**)[c]	
	273 K	293 K	273 K	293 K	273 K	293 K
MIL-101Cr (**1**)	3.51	2.38	0.79	0.21	0.30	0.56
MIL-101Cr-NO_2 (**2**)	2.89	1.79	0.78	0.16	0.43	0.42
MIL-101Cr-pNO_2 (**3**)	2.74	1.63	0.72	0.19	0.44	0.44
MIL-101Cr-NH_2 (**4**)	5.08	3.6	1.04	0.33	0.81	0.54
MIL-101Cr-pNH_2 (**5**)	4.5	3.12	0.91	0.4	0.60	0.52

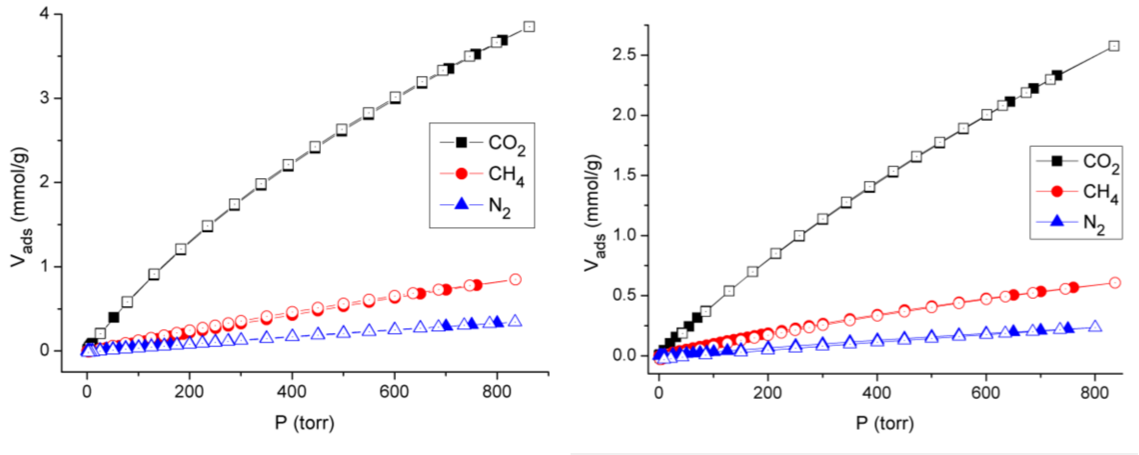


Figure S4. CO_2, CH_4 and N_2 sorption isotherms of MIL-101Cr (**1**) at 273 K (left) and 293 K (right).

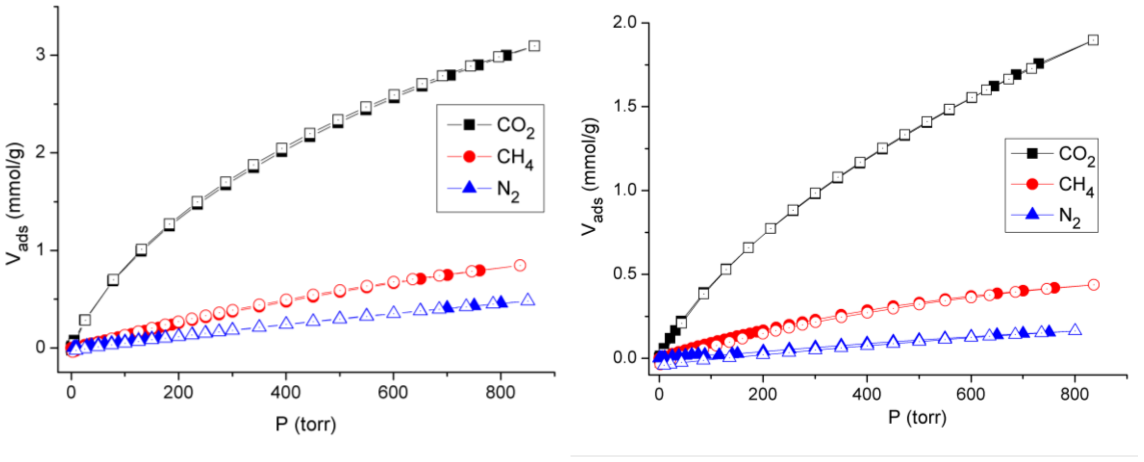


Figure S5. CO_2, CH_4 and N_2 sorption isotherms of MIL-101Cr-NO_2 (**2**) at 273 K (left) and 293 K (right).

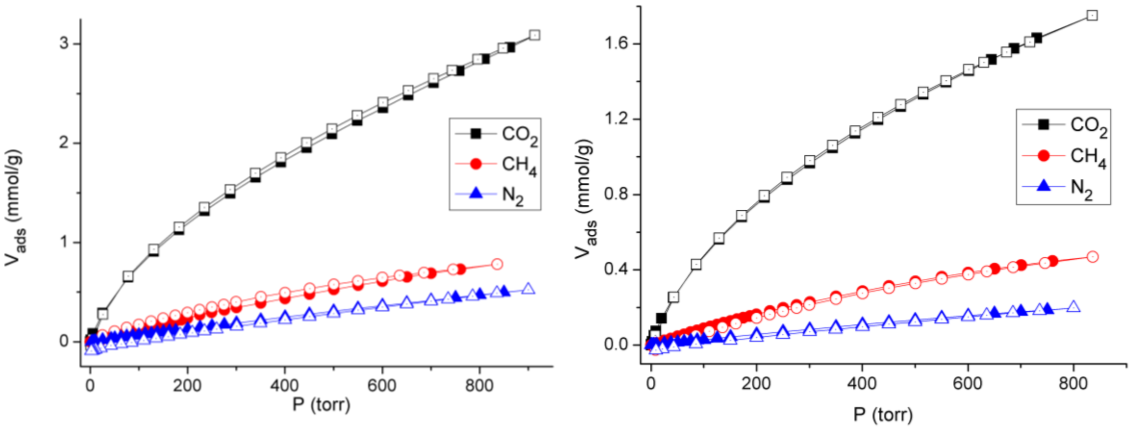


Figure S6. CO_2, CH_4 and N_2 sorption isotherms of MIL-101Cr-pNO_2 (**3**) at 273 K (left) and 293 K (right).

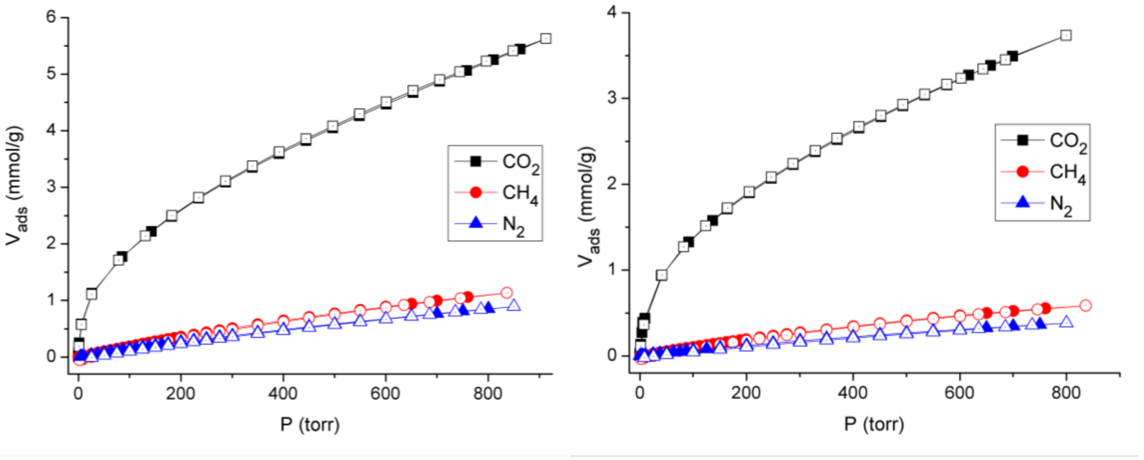


Figure S7. CO_2, CH_4 and N_2 sorption isotherms of MIL-101Cr-NH_2 (**4**) at 273 K (left) and 293 K (right).

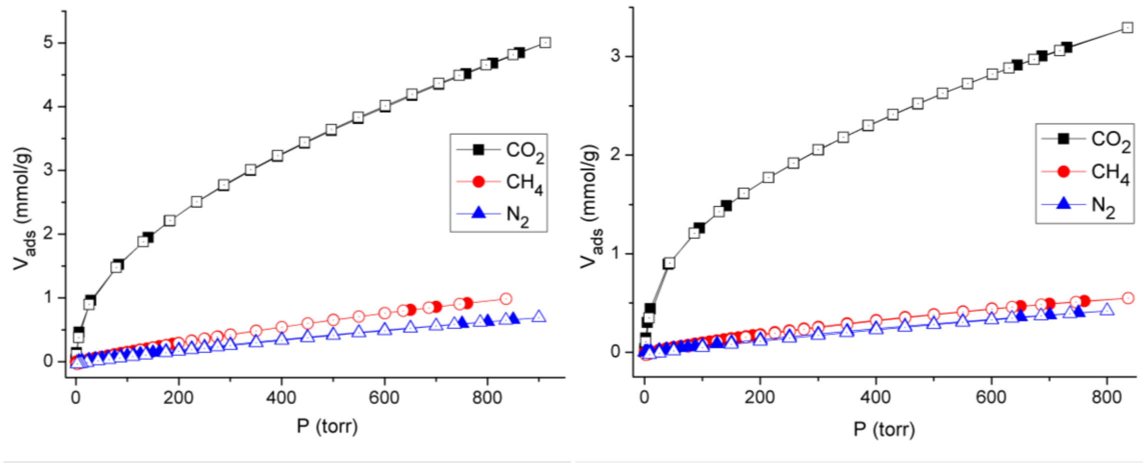


Figure S8. CO_2, CH_4 and N_2 sorption isotherms of MIL-101Cr-pNH$_2$ (**5**) at 273 K (left) and 293 K (right).

4. Gas selectivity

Selectivities were estimated from the ratio of the initial slopes in the Henry region of the adsorption isotherms.

Table S2 Initial slopes of adsorption isotherms for CO_2, N_2 and CH_4 at 273 and 293 K.

	initial slopes for gas adsorption isotherms (10^{-3})					
	CO_2		N_2		CH_4	
Compounds	at 273 K	at 293 K	at 273 K	at 293 K	at 273 K	at 293 K
MIL-101Cr (**1**)	7.32	4.37	0.47	0.927	0.977	1.03
MIL-101Cr-NO$_2$ (**2**)	11.29	5.25	0.65	0.315	1.25	0.958
MIL-101Cr-pNO$_2$ (**3**)	11.23	7.19	0.725	0.294	1.12	0.921
MIL-101Cr-NH$_2$ (**4**)	104.48	66.3	1.43	0.66	1.97	1.05
MIL-101Cr-pNH$_2$ (**5**)	115.6	61.78	0.969	0.719	1.55	1.01

Table S3. Gas selectivities for CO_2/N_2, CO_2/CH_4 and CH_4/N_2 of compounds **1–5**.

Compounds	**273 K**			**293 K**		
	CO_2/N_2	CO_2/CH_4	CH_4/N_2	CO_2/N_2	CO_2/CH_4	CH_4/N_2
MIL-101Cr (**1**)	16	8	2	5	4	1
MIL-101Cr-NO$_2$ (**2**)	17	9	2	17	6	3
MIL-101Cr-pNO$_2$ (**3**)	15	10	1.5	24	8	3
MIL-101Cr-NH$_2$ (**4**)	73	53	1.4	100	63	1.6
MIL-101Cr-pNH$_2$ (**5**)	119	75	1.6	86	61	1.7

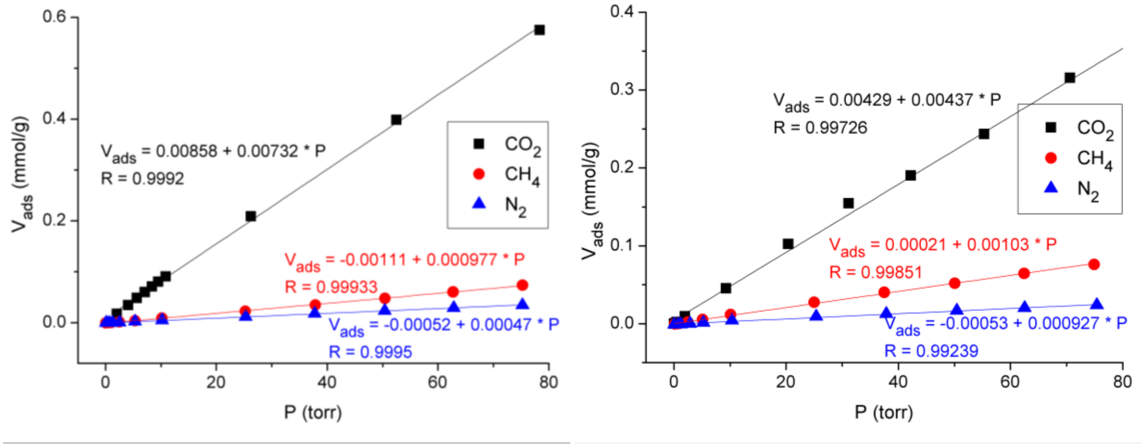


Figure S9. Initial slope calculation for CO_2, CH_4 and N_2 isotherms of MIL-101Cr (**1**) collected at 273 K (left) and 293 K (right).

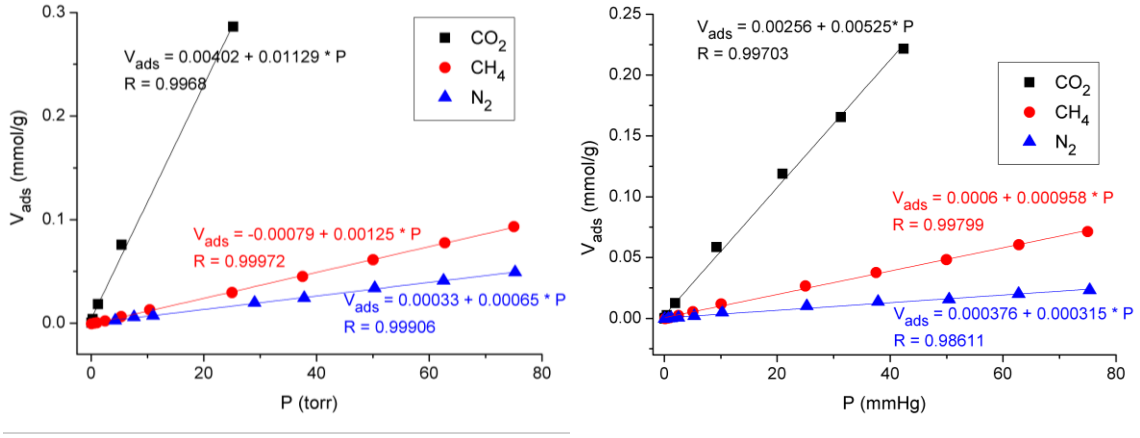


Figure S10. Initial slope calculation for CO_2, CH_4 and N_2 isotherms of MIL-101Cr-NO_2 (**2**) collected at 273 K (left) and 293 K (right).

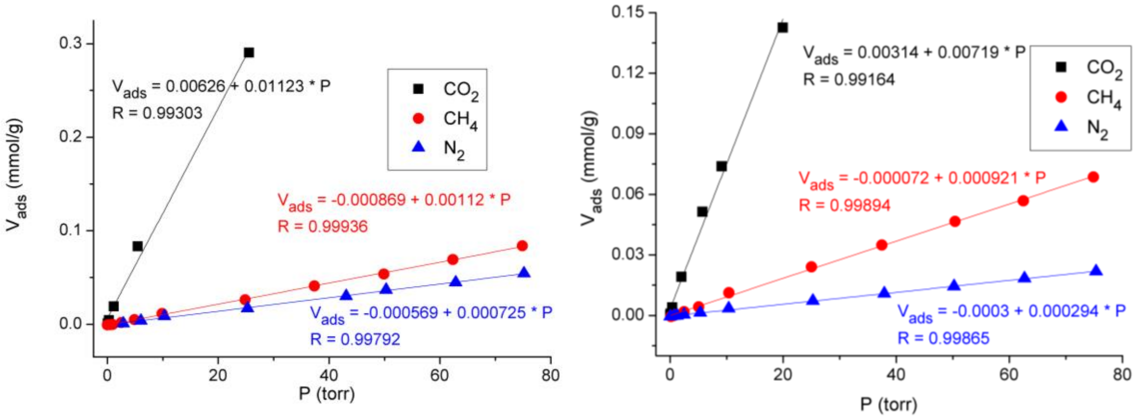


Figure S11. Initial slope calculation for CO_2, CH_4 and N_2 isotherms of MIL-101Cr-pNO_2 (**3**) collected at 273 K (left) and 293 K (right).

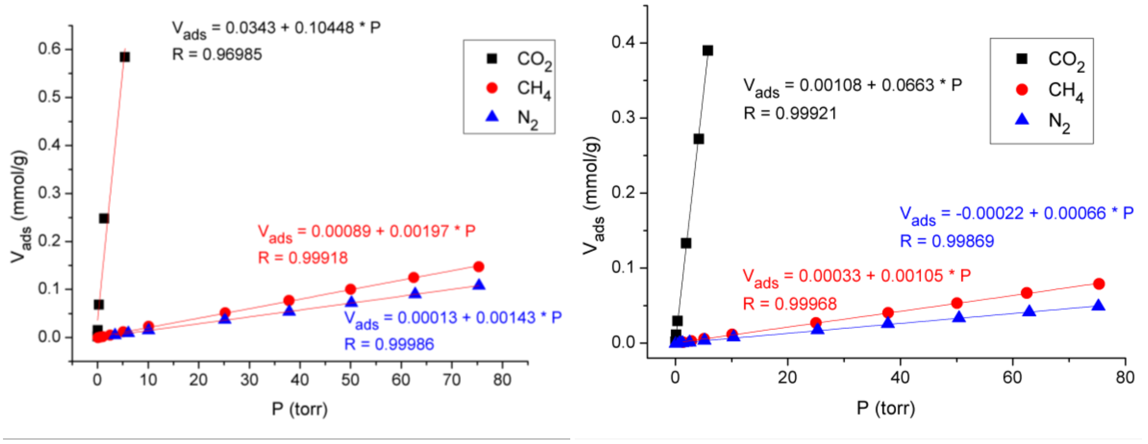


Figure S12. Initial slope calculation for CO_2, CH_4 and N_2 isotherms of MIL-101Cr-NH_2 (**4**) collected at 273 K (left) and 293 K (right).

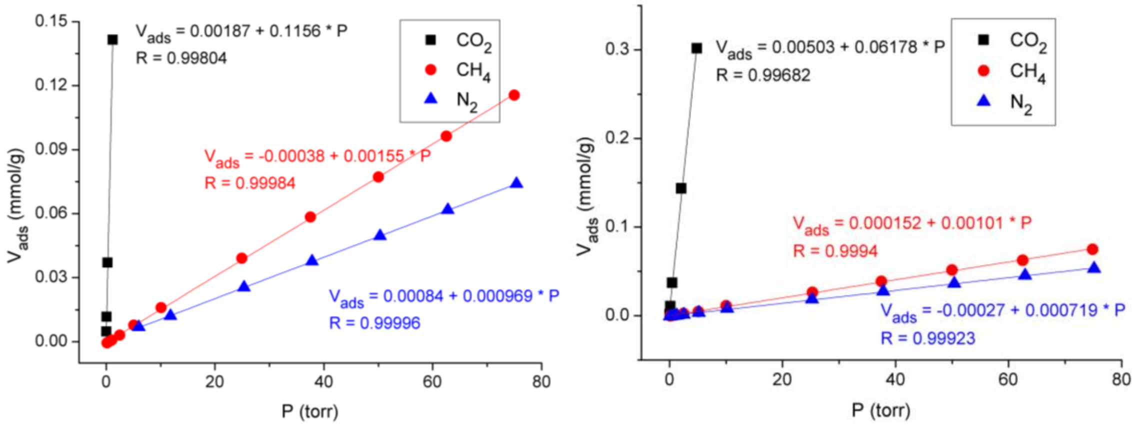
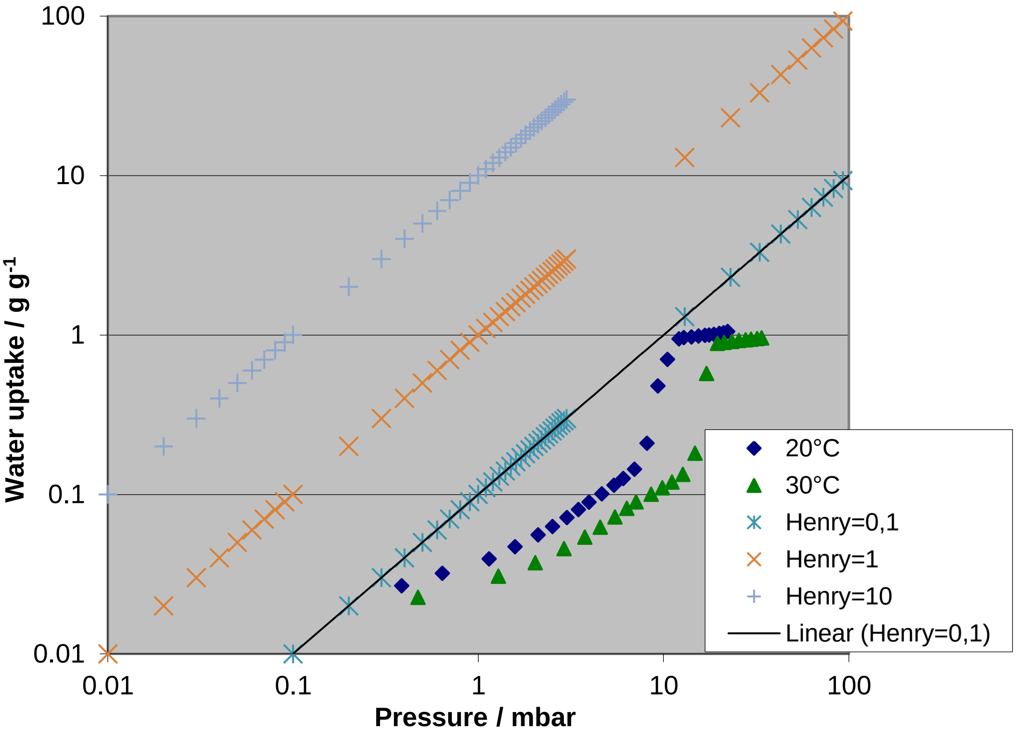
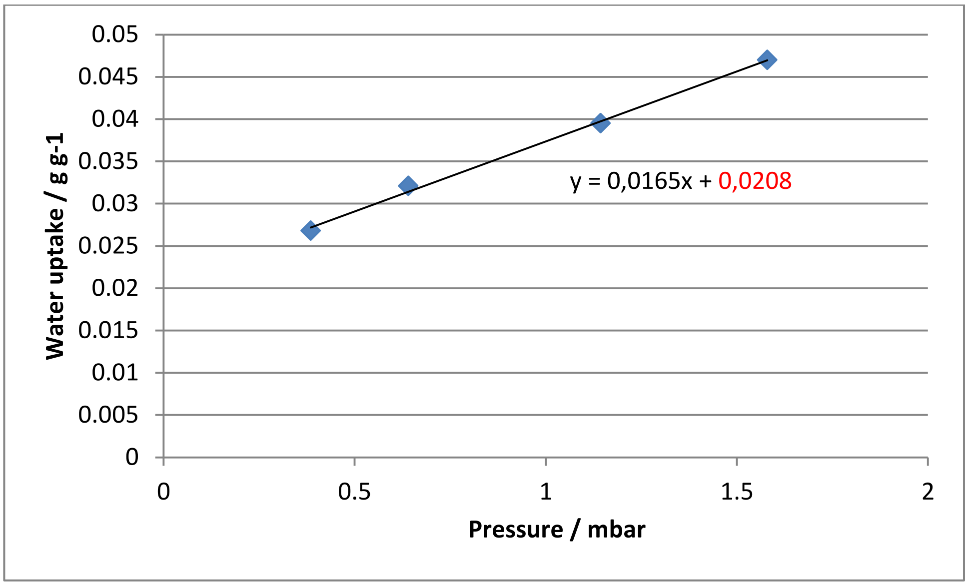


Figure S13. Initial slope calculation for CO_2, CH_4 and N_2 isotherms of MIL-101Cr-pNH_2 (**5**) collected at 273 K (left) and 293 K (right).



(a)



(b)

Figure S14. (a) Water isotherms of MIL-101Cr-pNH$_2$ (**5**) at 20 and 30 °C in a log-log plot together with three arbitrary Henry isotherms with Henry constants of 0.1, 1 and 10. It can be seen that Henry isotherms run parallelt in a log-log plot independent of the Henry constant. It is evident that the first values of the water isotherms of MIL-101Cr-pNH$_2$ (**5**) do not run parallel to the Henry isotherms, hence, they already lie out of the Henry region.

(b) Also, for $p \rightarrow 0$ the value of the Henry isotherm has to converge to zero. When the first values of the water adsorption isotherm for **5** at 20 °C are plotted the y-section is 0.0208 for p = 0 which is in the range of the Henry constant (slope) itself.

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[1] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surble, and I. Margiolaki, *Science*, **2005**, *309*, 2040-2042.