Supporting Information

Tolerance of flexible MOFs towards repeated adsorption stress

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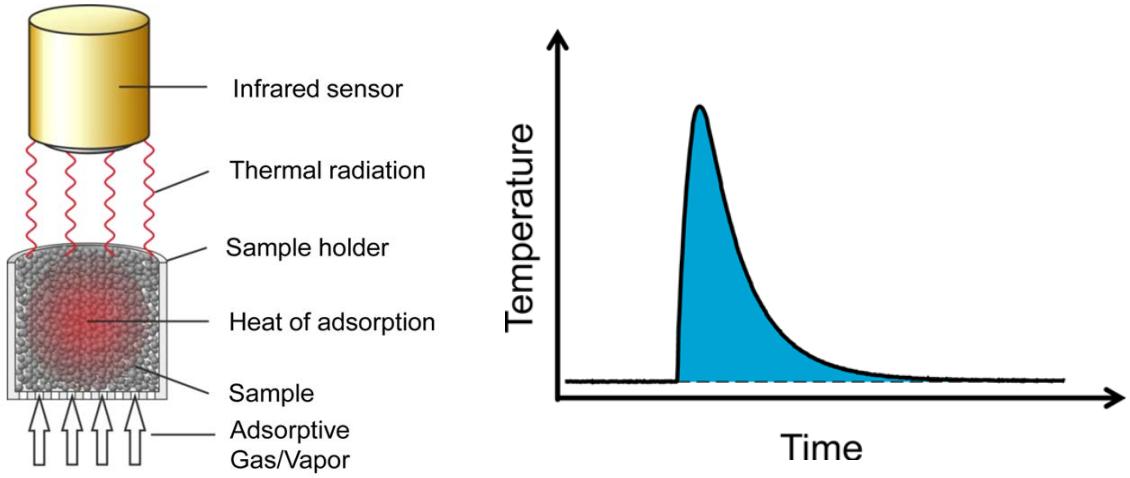
1. Optical calorimeter setup (InfraSORP), used in the thermal response experiments



Scheme S1. Experimental setup of the thermal response measurement (right) and example of a typical thermal response curve during adsorption of test gas (left). (Reprinted with permission from Wollmann et al Chem.Commun., 2011, 47, 5151–5153 Copyright 2011. The Royal Society of Chemistry)

PXRD Patterns

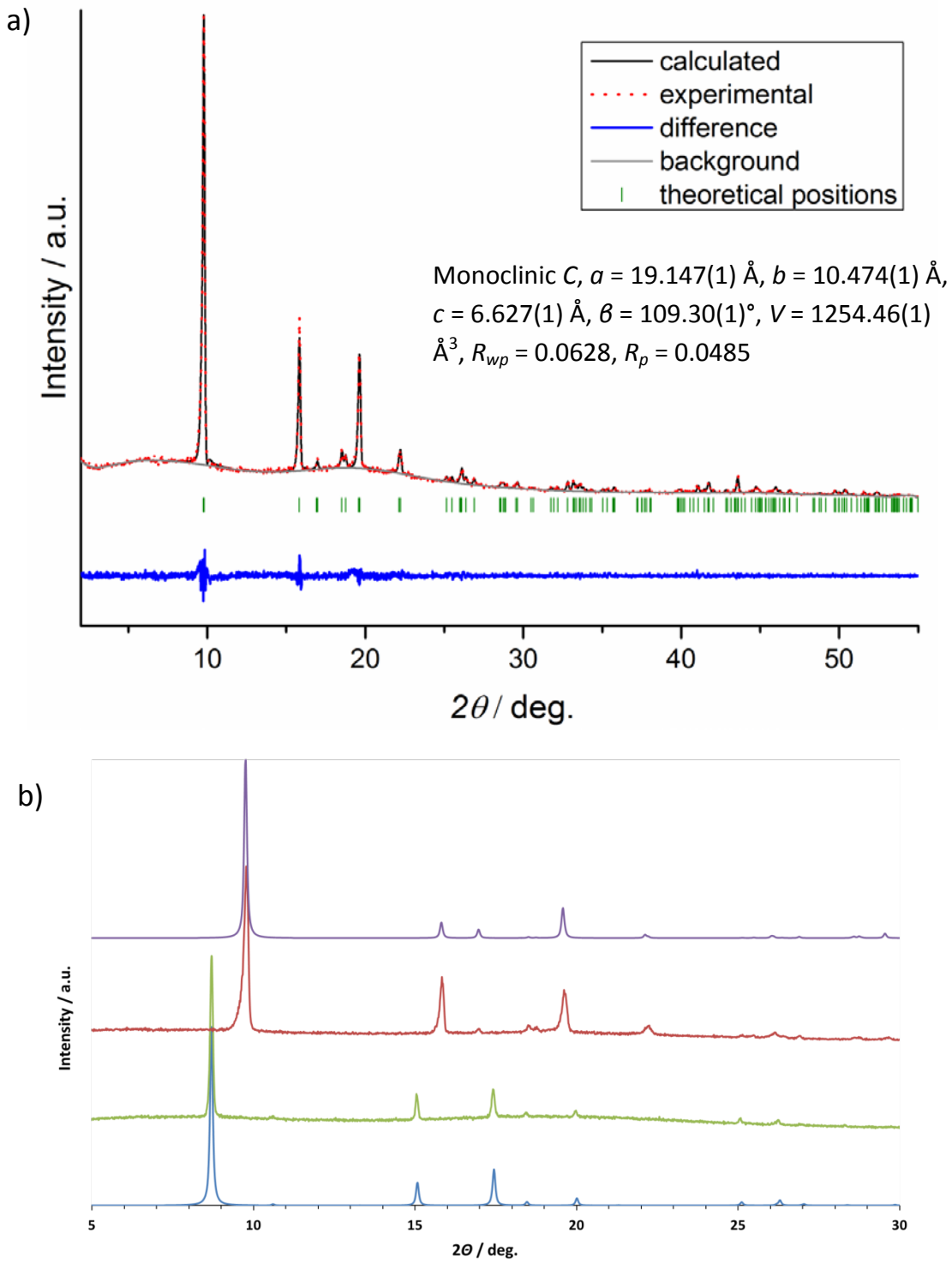


Figure S1. a) Pawley plot for the butane@MIL-53(Al) **np** phase. XRD pattern from the sample, subjected to the butane adsorption and purging with nitrogen; b) PXRD pattern of MIL-53(Al): blue line – calculated PXRD pattern for MIL-53(Al) **lp** phase, light green – experimental PXRD pattern for the activated compound; red line – PXRD pattern measured after 10 *n*-butane adsorption/desorption cycles; violet – calculated PXRD patterns for the structural model, based on the unit cell parameters, obtained from the indexing.

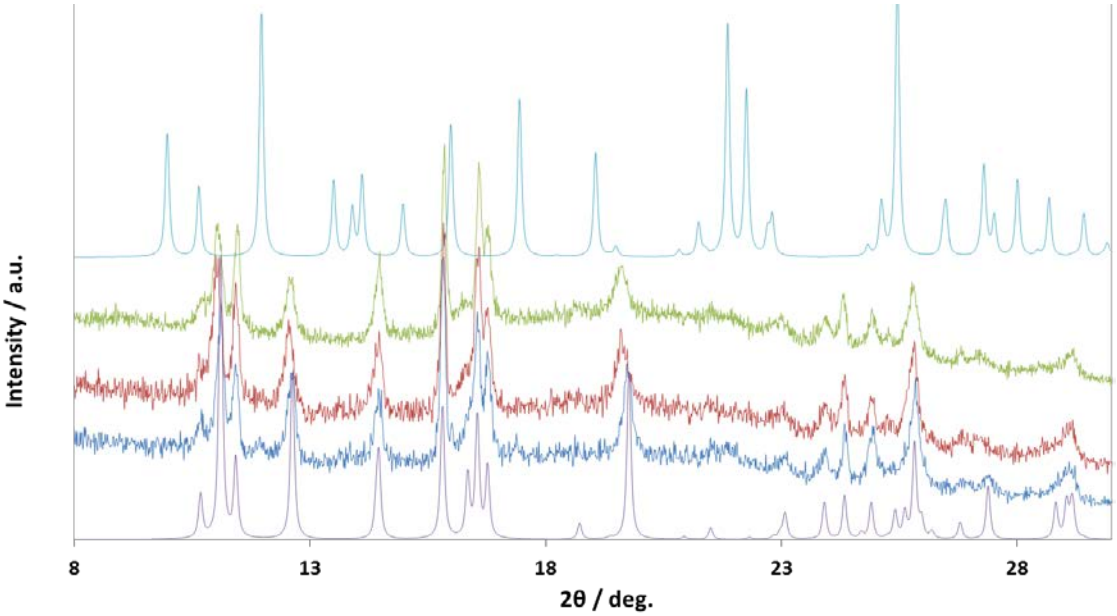


Figure S2. PXRD patterns of ELM-11: violet – theoretical of activated ELM-11, blue – measured for activated ELM-11, red – measured of ELM-11 after 10 n-butane adsorption/desorption cycles, light green – experimental of ELM-11 after 100 *n*-butane adsorption / desorption cycles, navy blue – theoretical of pre-ELM-11.

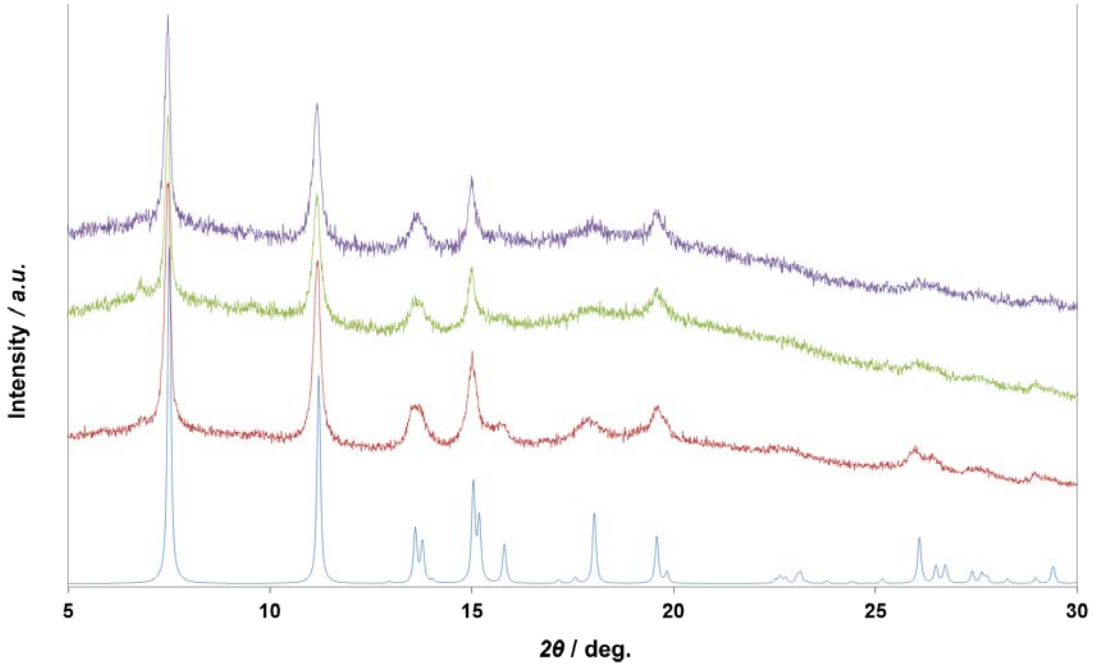


Figure S3. PXRD patterns of DUT-8(Ni): blue – theoretical of activated DUT-8(Ni), red – experimental of activated DUT-8(Ni), light green - experimental of DUT-8(Ni) after 10 *n*-butane adsorption/desorption cycles, violet – experimental of DUT-8(Ni) after 100 *n*-butane adsorption/desorption cycles.

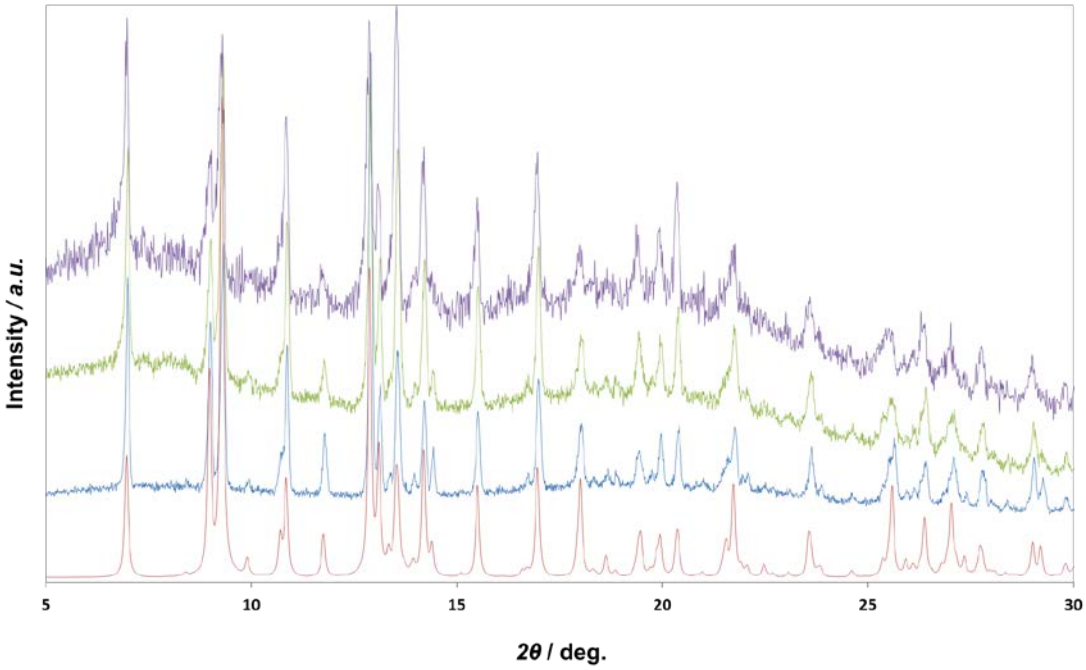


Figure S4. PXRD patterns of SNU-9: red – theoretical of SNU-9 **cp**, blue – experimental of activated SNU-9, light green – experimental of SNU-9 after 10 *n*-butane adsorption/desorption cycles, violet – experimental of SNU-9 after 100 *n*-butane adsorption/desorption cycles.

InfraSORP data

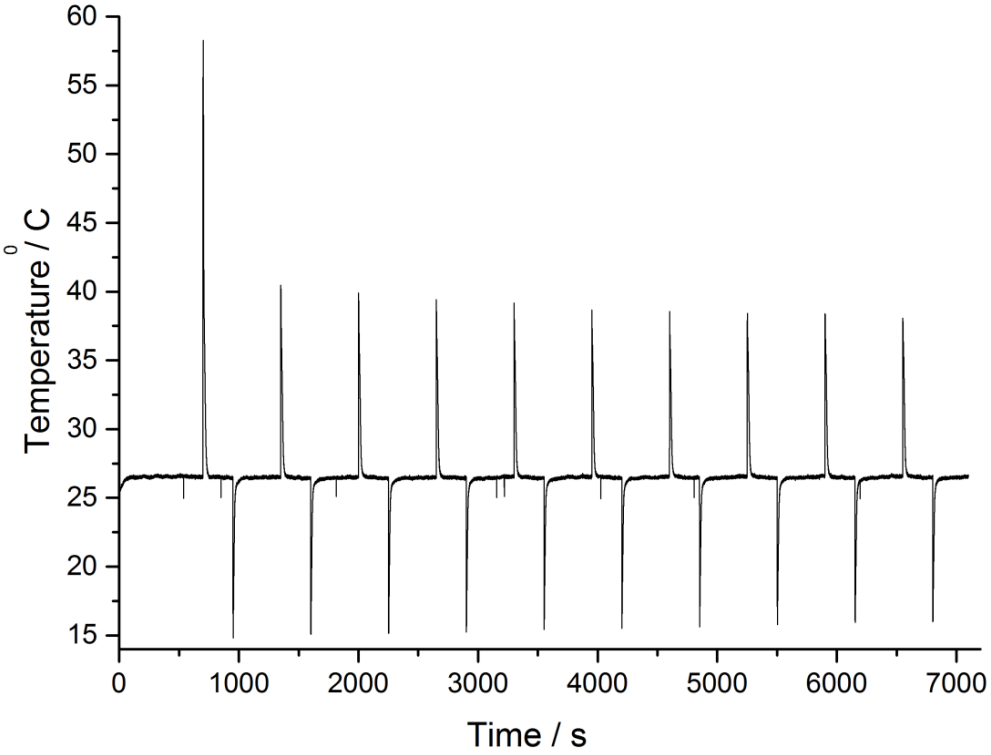


Figure S5. Thermal response curve for 10 *n*-butane adsorption/desorption cycles on MIL-53(Al).

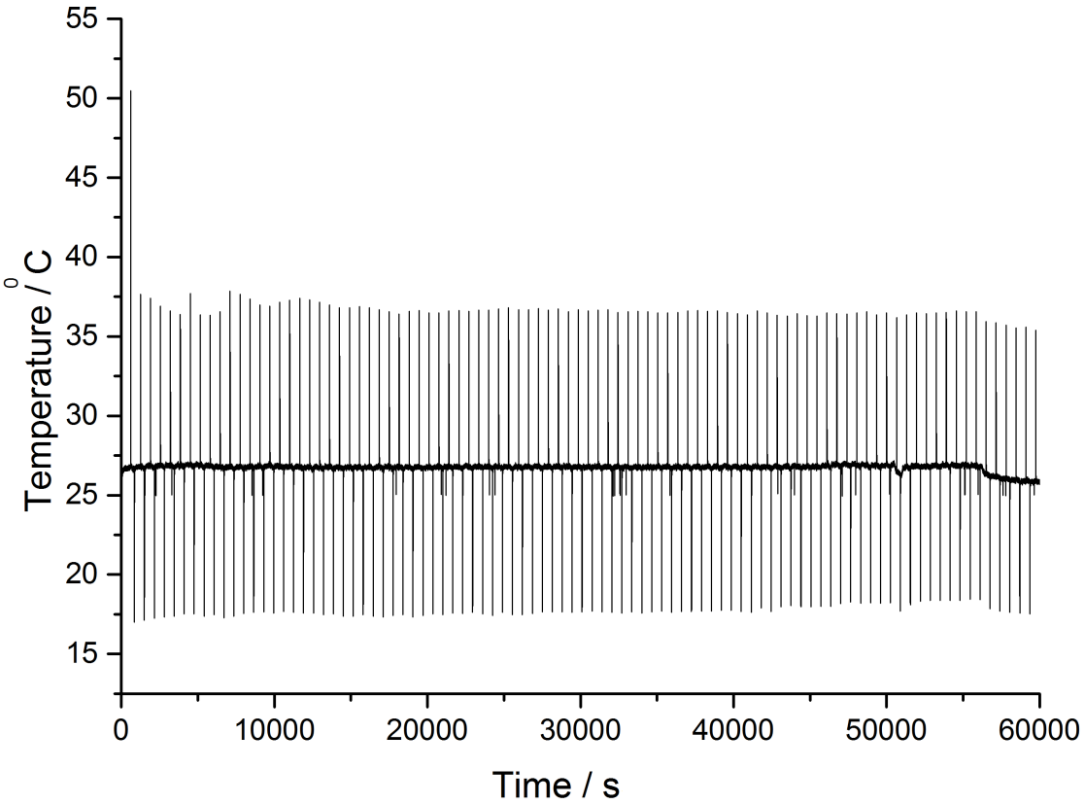


Figure S6. Thermal response curve for 100 *n*-butane adsorption/desorption cycles on MIL-53(Al).

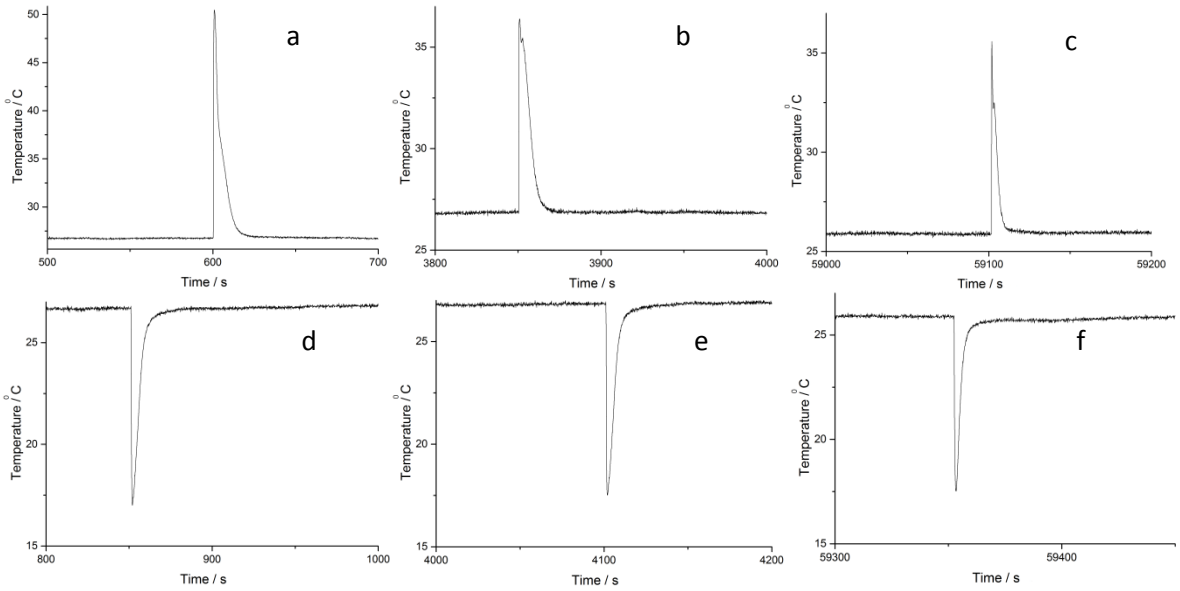


Figure S7. Selected thermal response curves for MIL-53(Al): a – cycle 1 adsorption, b – cycle 6 adsorption, c – cycle 89 adsorption, d – cycle 1 desorption, e – cycle 6 desorption, f – cycle 89 desorption.

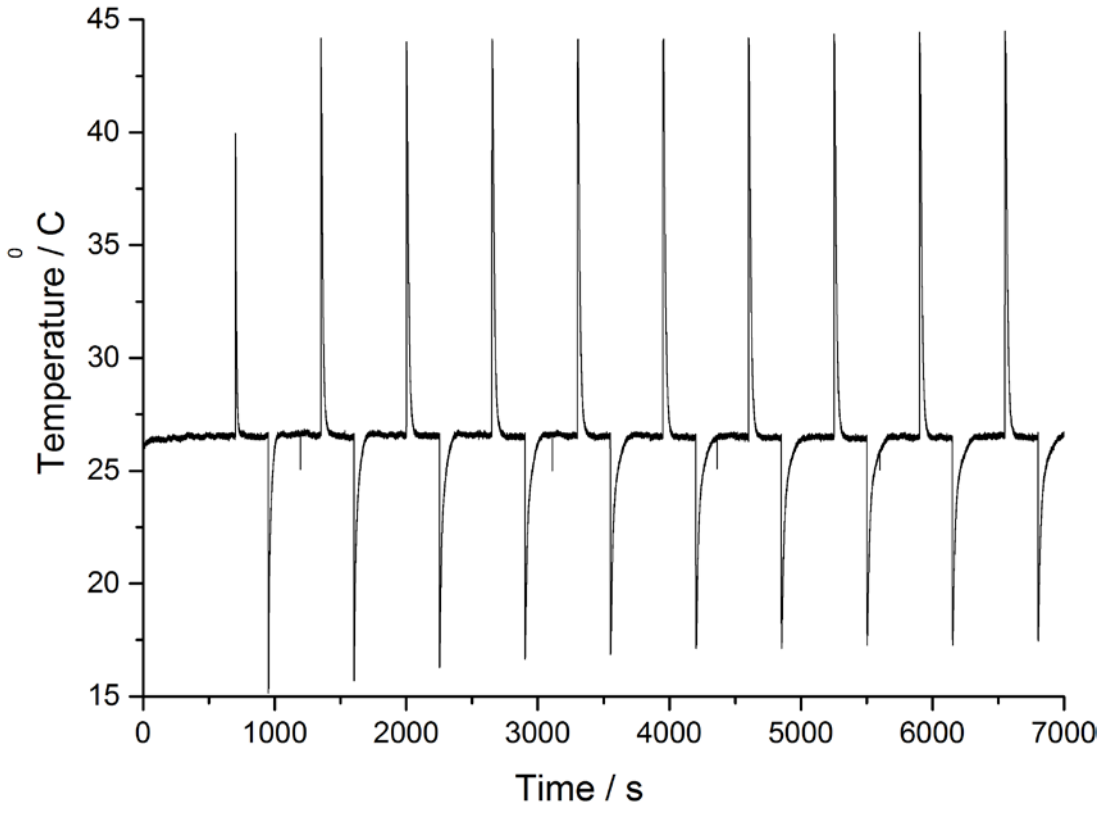


Figure S8. Thermal response curves for 10 adsorption/desorption cycles of *n*-butane on ELM-11.

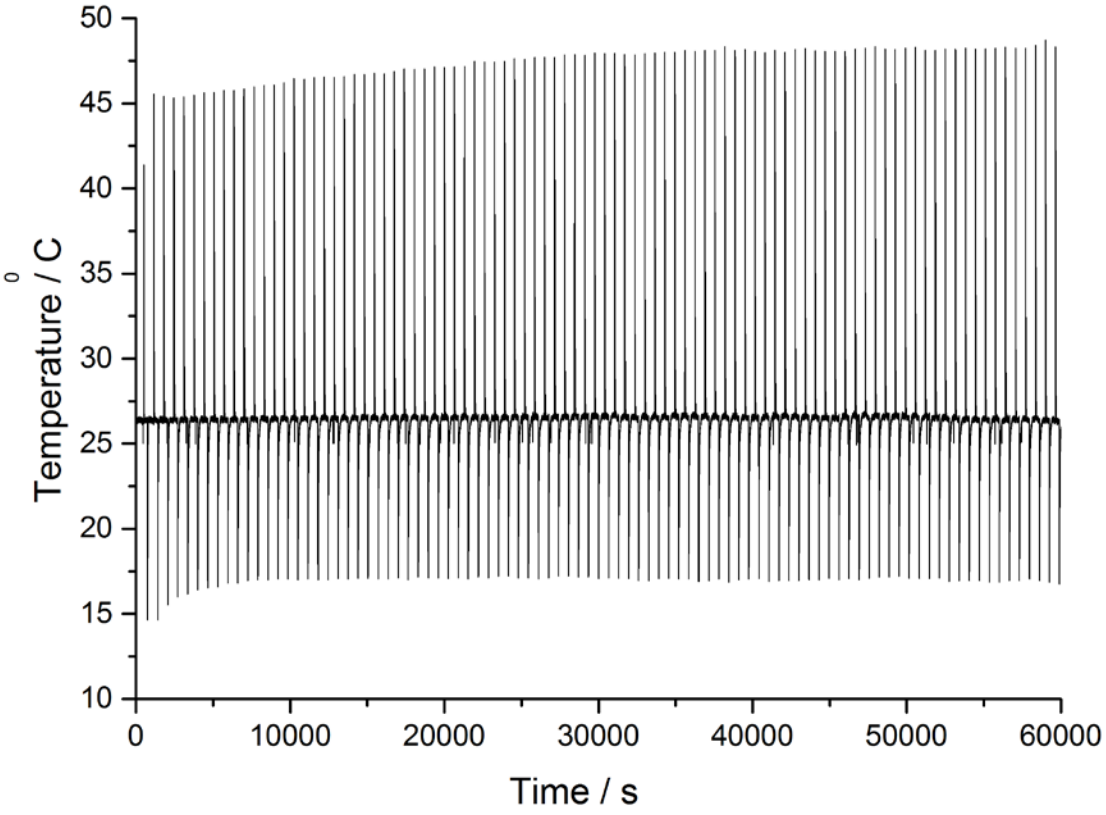


Figure S9. Thermal response curves for 100 adsorption/desorption cycles of *n*-butane on ELM-11.

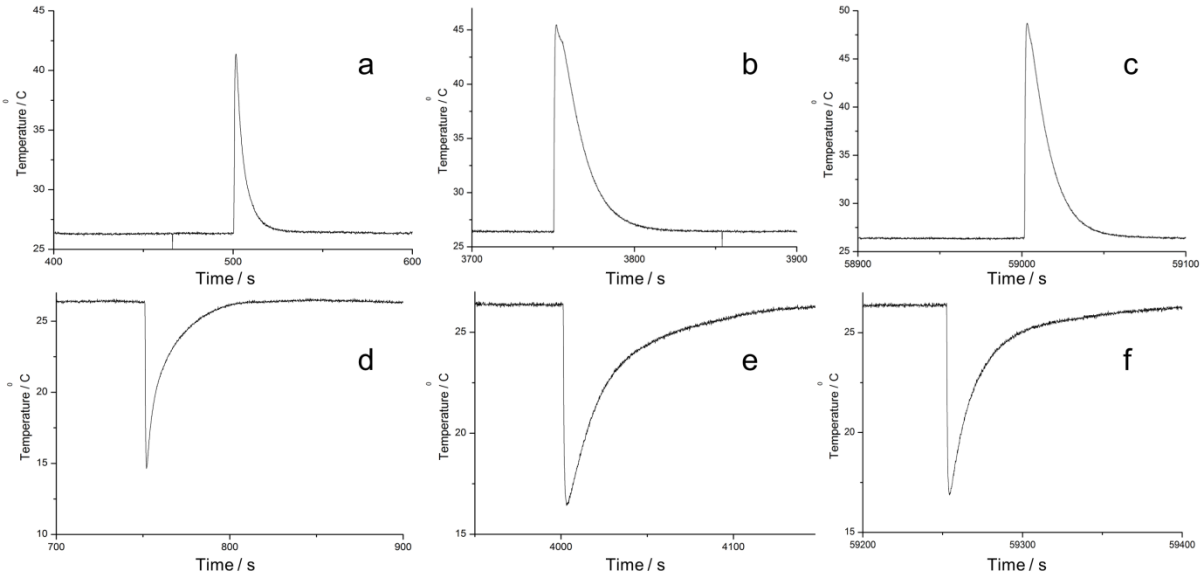


Figure S10. Selected thermal response adsorption/desorption curves of ELM-11: a – cycle 1 adsorption, b – cycle 6 adsorption, c – cycle 89 adsorption, d – cycle 1 desorption, e – cycle 6 desorption, f – cycle 89 desorption.

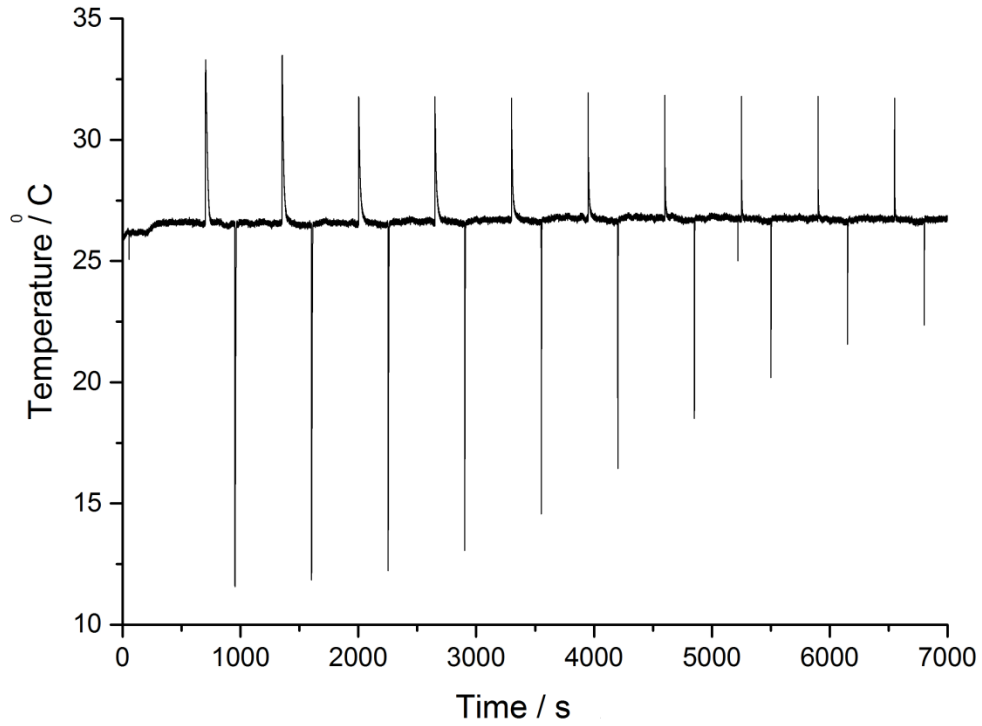


Figure S11. Thermal response curves for 10 adsorption/desorption cycles of *n*-butane on DUT-8(Ni).

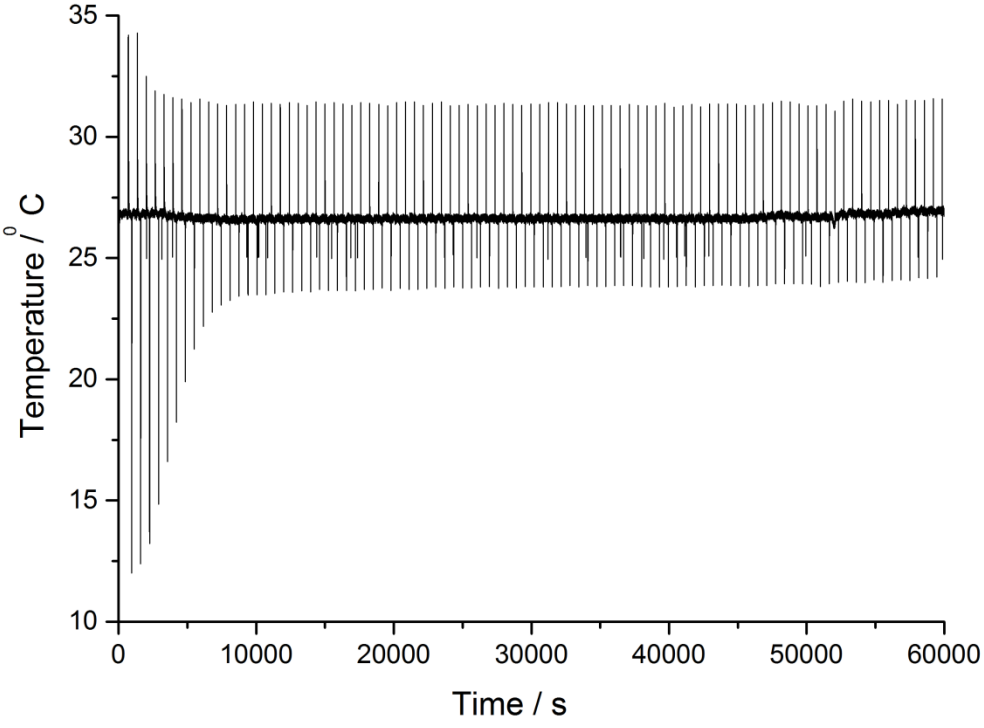


Figure S12. Thermal response curves for 100 *n*-butane adsorption/desorption cycles on DUT-8(Ni).

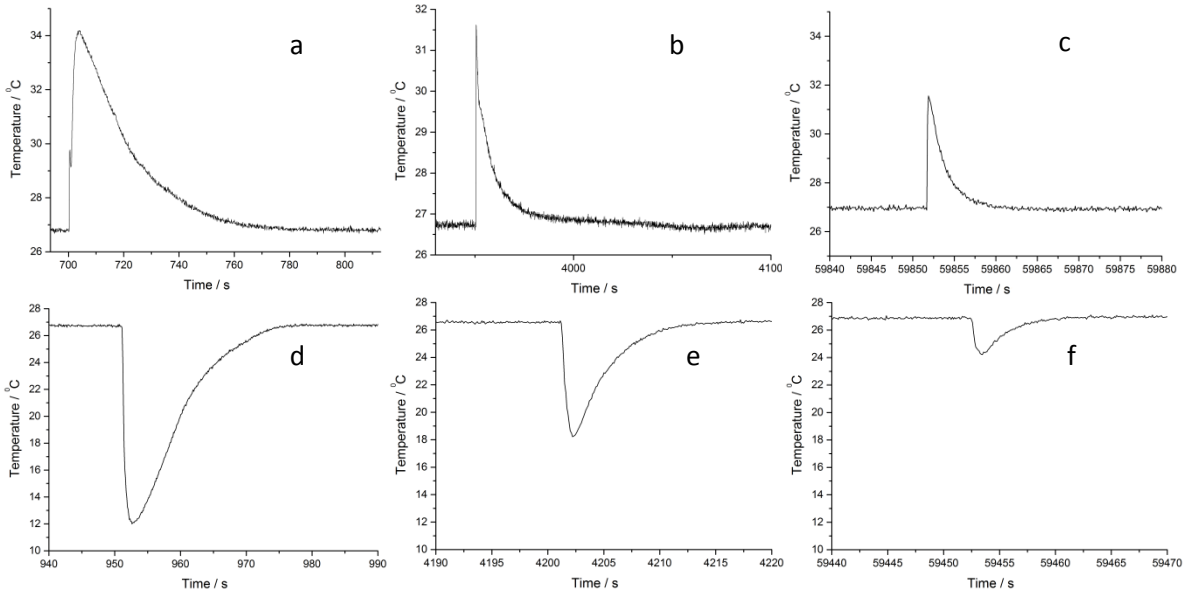


Figure S13. Selected adsorption/desorption thermal response curves of DUT-8(Ni): a – cycle 1 adsorption, b – cycle 6 adsorption, c – cycle 90 adsorption, d – cycle 1 desorption, e – cycle 6 desorption, f – cycle 89 desorption.

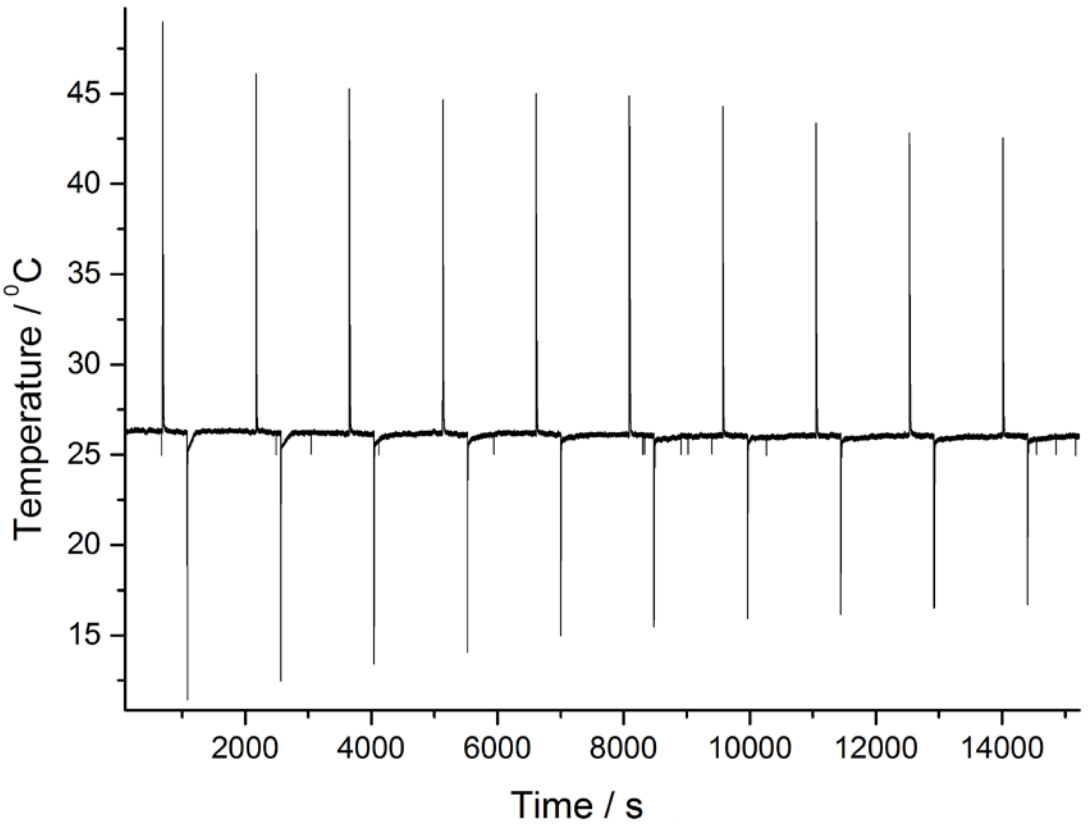


Figure S14. Thermal response curves for 10 *n*-butane adsorption/desorption cycles on SNU-9.

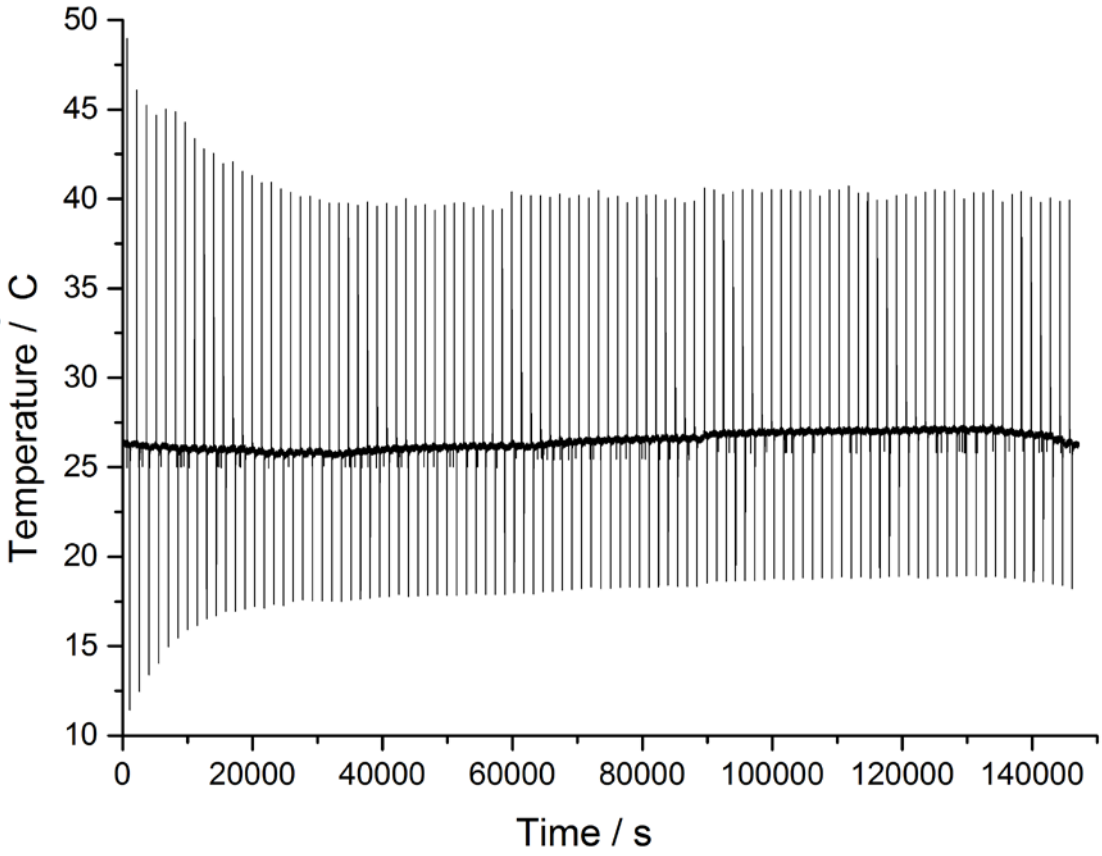


Figure S15. Thermal response curve for 100 *n*-butane adsorption/desorption cycles on SNU-9.

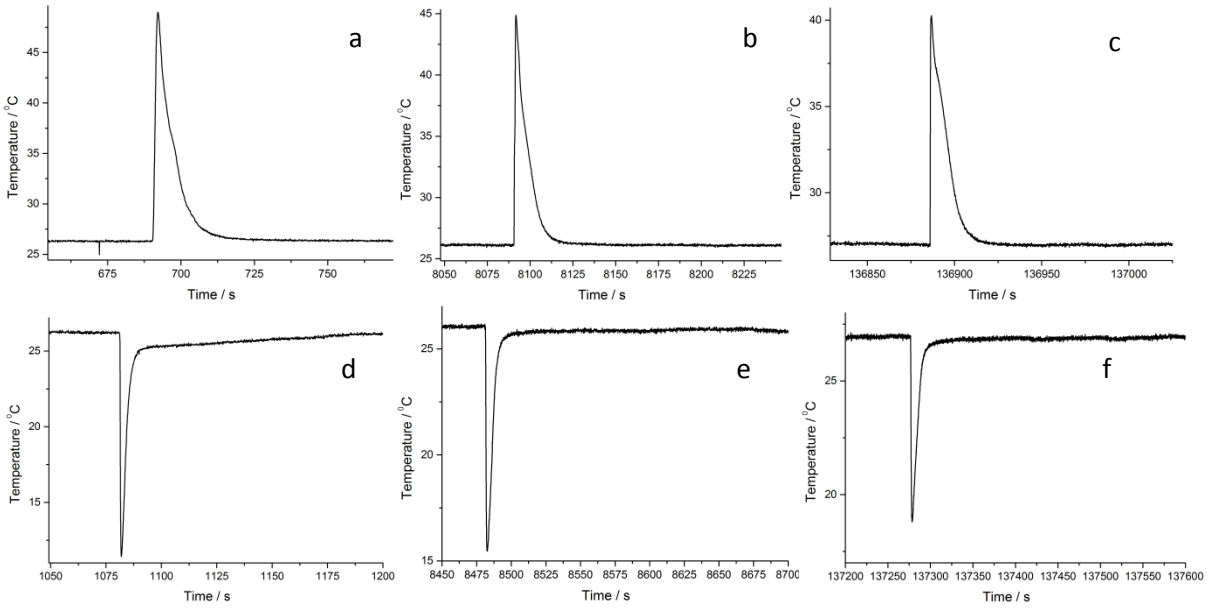


Figure S16. Selected adsorption/desorption thermal response curves of SNU-9: a – cycle 1 adsorption, b – cycle 6 adsorption, c – cycle 90 adsorption, d – cycle 1 desorption, e – cycle 6 desorption, f – cycle 89 desorption.

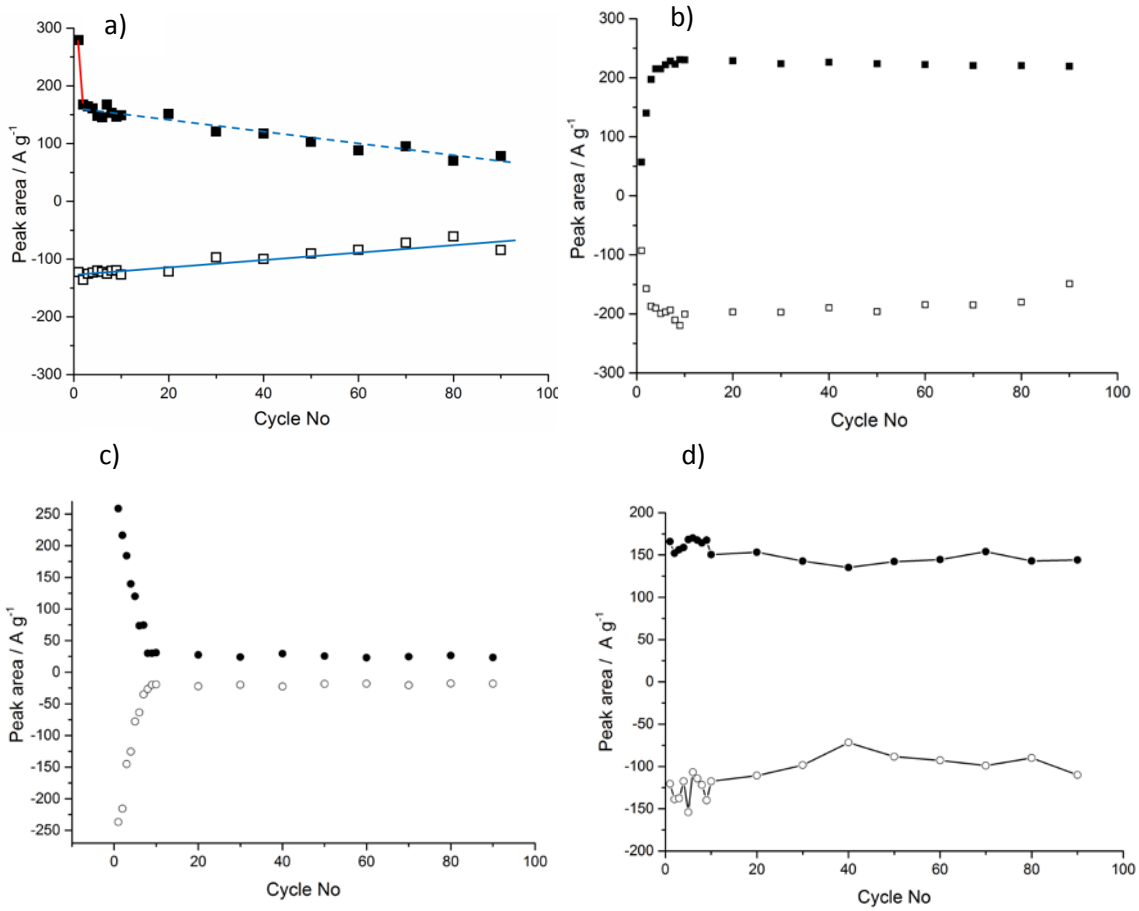


Figure S17. Integrated peak area for adsorption (close symbols) and desorption (open symbols) peaks for MIL-53 (a), ELM-11 (b), DUT-8 (c), and SNU-9 (d).

Table S1. Integrated InfraSORP data for MIL-53(Al).

	Adsorption			Desorption		
Cycle No	Peak area A·g^{-1}	FWHM*	Δt, °C	Peak area A·g^{-1}	FWHM	Δt, °C
1	279.0	3.08	23.7	-122.9	4.60	-9.7
2	167.5	6.29	14.0	-136.2	4.68	-9.6
3	164.3	6.35	10.6	-125.7	4.74	-9.6
4	160.7	6.65	10.0	-123.5	4.67	-9.4
5	147.8	6.51	9.8	-120.1	4.71	-9.3
6	145.4	6.48	9.7	-122.6	4.68	-9.3
7	167.5	6.15	10.9	-125.8	4.72	-9.3
8	152.9	6.49	9.5	-120.4	4.69	-9.4
9	146.2	6.38	9.5	-119.5	4.69	-9.3
10	148.8	6.22	9.8	-127.8	4.68	-9.4
20	151.3	5.60	10.5	-121.6	4.57	-9.2
30	120.8	5.17	9.8	-97.3	4.17	-9.3
40	117.2	4.67	9.9	-100.1	3.87	-9.2
50	102.7	4.23	9.7	-90.5	3.61	-9.3
60	88.2	3.78	9.8	-84.1	3.30	-9.0
70	94.9	3.45	9.6	-71.8	2.94	-8.8
80	70.0	3.04	9.6	-61.1	2.70	-8.5
90	78.2	2.88	8.7	-84.5	2.52	-8.4

*FWHM - Full Width at Half Maximum

Table S2. Integrated InfraSORP data for ELM-11.

	Adsorption			Desorption		
Cycle No	Peak area A ·g^{-1}	FWHM	Δt, °C	Peak area A·g^{-1}	FWHM	Δt, °C
1	57.1	4.00	15.1	-92.8	6.97	-11.8
2	140.2	8.75	19.3	-157.3	13.00	-11.8
3	196.9	11.94	19.0	-187.0	16.85	-10.9
4	214.9	14.40	18.9	-190.5	17.98	-10.4
5	215.0	14.60	19.0	-199.6	10.21	-10.2
6	221.8	15.13	19.1	-196.8	18.87	-10.0
7	228.0	12.71	19.3	-193.7	19.51	-9.9
8	222.9	15.13	19.3	-210.3	19.87	-9.8
9	230.4	15.15	19.4	-219.4	20.36	-9.6
10	229.9	15.29	19.4	-200.7	19.73	-9.6
20	228.6	14.64	20.1	-196.8	20.10	-9.4
30	223.8	14.17	20.6	-196.9	20.00	-9.4
40	226.1	13.45	21.2	-189.6	19.32	-9.5
50	223.6	13.11	21.4	-196.1	18.71	-9.5
60	222.2	13.02	21.6	-184.3	18.51	-9.5
70	220.6	12.78	21.6	-184.6	18.02	-9.6
80	220.6	12.93	21.8	-180.0	31.46	-9.5
90	219.2	12.88	22.4	-148.8	14.14	-9.5

Table S3. Integrated InfraSORP data for DUT-8(Ni).

	Adsorption			Desorption		
Cycle No	Peak area $A \cdot g^{-1}$	FWHM	Δt, °C	Peak area $A \cdot g^{-1}$	FWHM	Δt, °C
1	258.7	15.08	6.8	-236.9	5.70	-14.9
2	216.3	11.85	6.9	-215.4	5.03	-14.6
3	184.1	10.97	5.2	-145.2	4.41	-14.21
4	139.7	7.24	5.3	-125.6	3.34	-13.4
5	120.1	5.04	5.2	-77.7	2.54	-11.9
6	73.7	1.26	5.4	-63.6	1.87	-10.1
7	74.5	1.43	5.3	-35.1	1.51	-8.2
8	30.0	1.24	5.1	-26.5	1.46	-6.5
9	30.0	1.21	5.1	-20.1	1.42	-5.1
10	30.8	1.29	5.0	-19.3	1.46	-4.4
20	27.5	1.68	4.8	-22.1	2.60	-2.9
30	24.0	1.63	4.7	-20.0	2.49	-2.9
40	29.5	1.67	4.4	-22.6	2.50	-2.8
50	25.4	1.53	4.4	-18.4	2.46	-2.8
60	23.0	1.57	4.4	-17.9	2.45	-2.8
70	24.5	1.51	4.4	-20.5	2.36	-2.8
80	26.4	1.63	4.6	-17.9	2.46	-2.8
90	23.3	1.54	4.6	-18.0	2.39	-2.6

Table S4. Integrated InfraSORP data for SNU-9.

	Adsorption			Desorption		
Cycle No	Peak area $A \cdot g^{-1}$	FWHM	Δt, °C	Peak area $A \cdot g^{-1}$	FWHM	Δt, °C
1	165.8	4.89	22.7	-120.6	2.65	-14.5
2	152.1	5.34	19.9	-139.0	2.90	-13.8
3	156.3	5.75	19.1	-137.7	3.45	-12.8
4	158.9	6.39	18.5	-117.5	3.84	-12.1
5	168.2	6.38	18.9	-154.1	4.44	-11.2
6	170.0	6.17	18.8	-106.7	4.89	-10.6
7	167.6	6.33	18.2	-114.3	5.21	-10.1
8	164.2	6.88	17.4	-121.7	5.38	-9.8
9	167.5	6.96	16.8	-140.0	5.89	-9.5
10	150.4	6.76	16.5	-117.7	6.02	-9.3
20	153.3	8.41	14.3	-110.8	7.40	-8.4
30	142.8	8.58	13.9	-98.4	7.42	-8.3
40	135.1	8.74	13.3	-71.8	7.29	-8.3
50	142.2	8.65	13.6	-88.4	7.34	-8.3
60	144.5	8.53	13.4	-92.7	7.36	-8.3
70	153.9	8.46	13.5	-99.0	7.43	-8.3
80	143.0	9.18	12.9	-89.9	7.56	-8.1
90	144.1	9.07	13.2	-110.0	7.56	-8.2

2. Adsorption isotherms

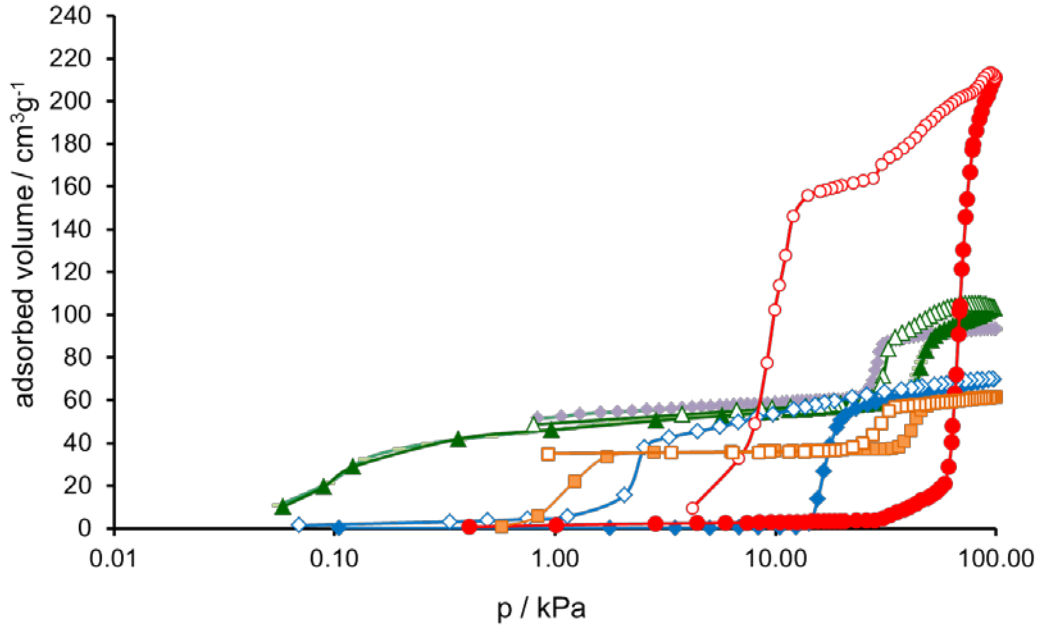


Figure S18. *n*-Butane physisorption isotherms on ELM-11 (blue), MIL-53 (green), DUT-8 (red), and SNU-9 (orange) at 298 K (close symbols – adsorption, open symbols – desorption, circles – fresh activated sample, diamonds – sample after 10 cycles adsorption of *n*-butane, triangles – sample after 100 cycles adsorption of *n*-butane).

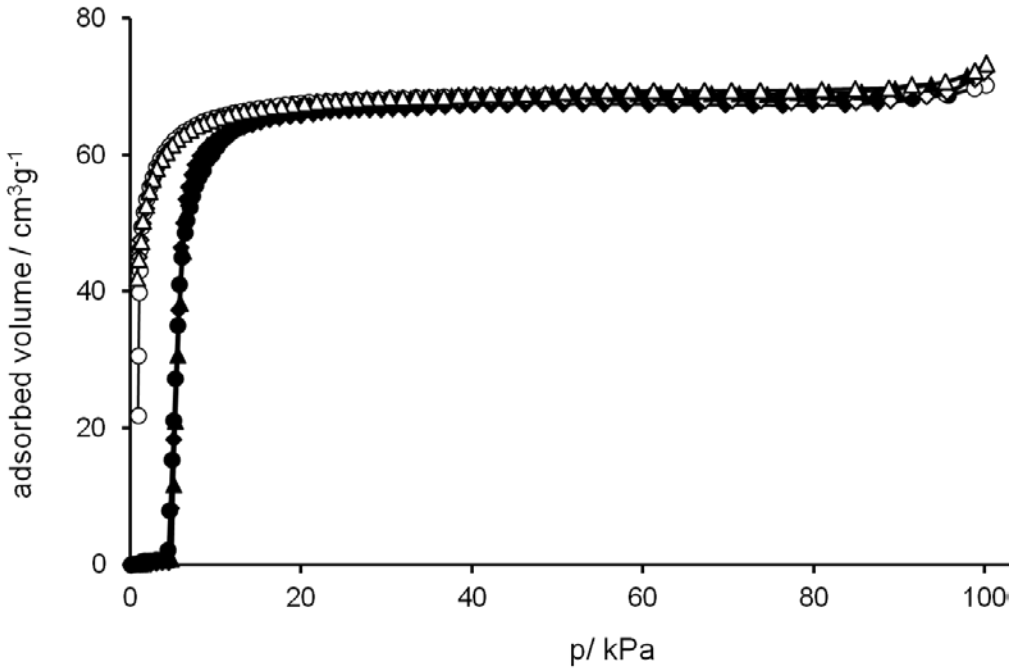


Figure S19. *n*-Butane physisorption isotherms on ELM-11 at 273 K (p_0 = 102.64 kPa) (close symbols – adsorption, open symbols – desorption, circles – fresh activated sample, diamonds – sample after 10 cycles adsorption of *n*-butane, triangles – sample after 100 cycles adsorption of *n*-butane).

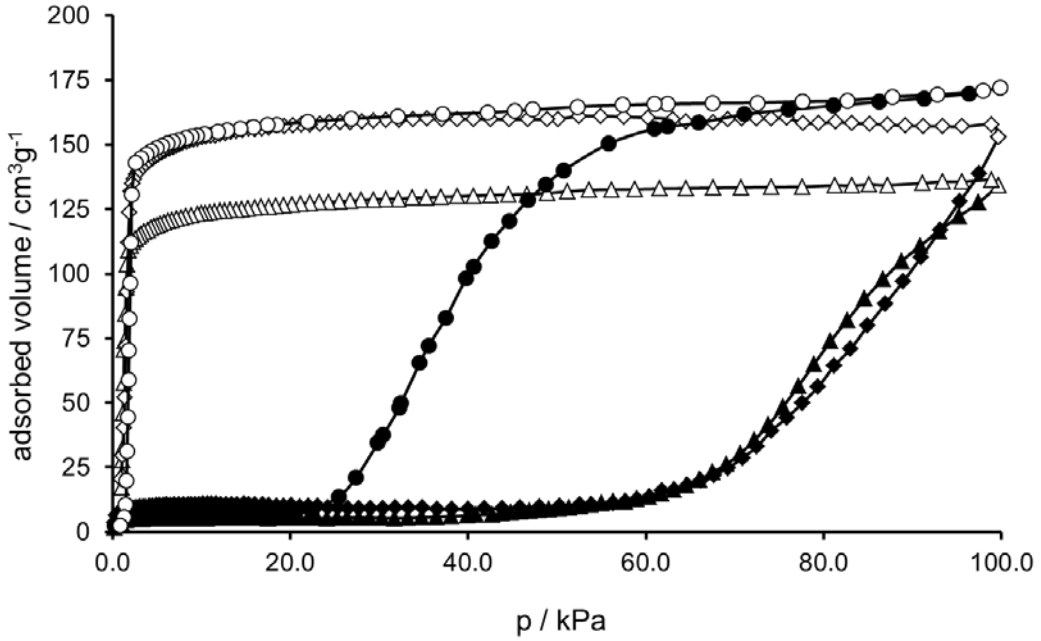


Figure S20. *n*-Butane physisorption isotherms on DUT-8(Ni) at 273 K (p_0 = 102.64 kPa). (close symbols – adsorption, open symbols – desorption, circles – fresh activated sample, diamonds – sample after 10 cycles adsorption of *n*-butane, triangles – sample after 100 cycles adsorption of *n*-butane).

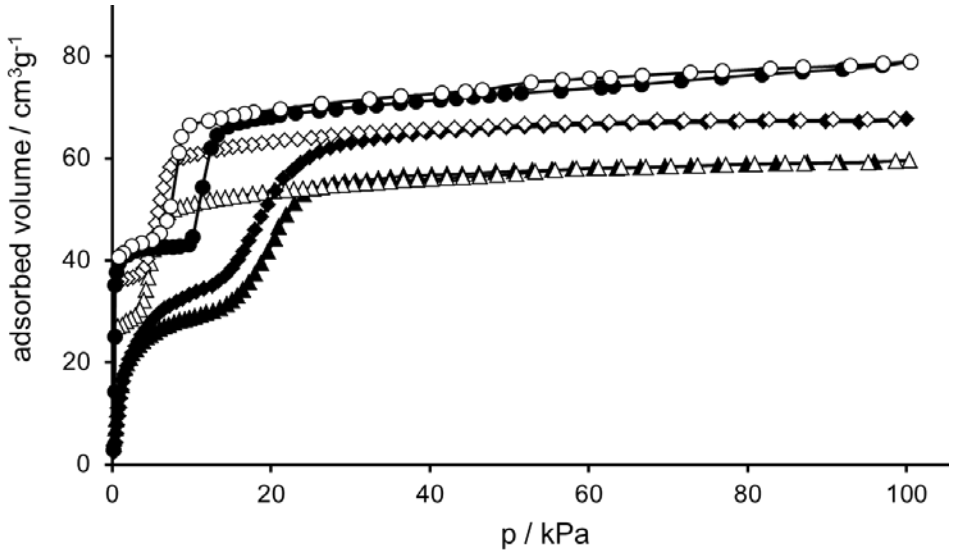


Figure S21. *n-B*utane physisorption isotherms on SNU-9 at 273 K (p_0 = 102.64 kPa). (close symbols – adsorption, open symbols – desorption, circles – fresh activated sample, diamonds – sample after 10 cycles adsorption of n-butane, triangles – sample after 100 cycles adsorption of *n*-butane).

SEM images

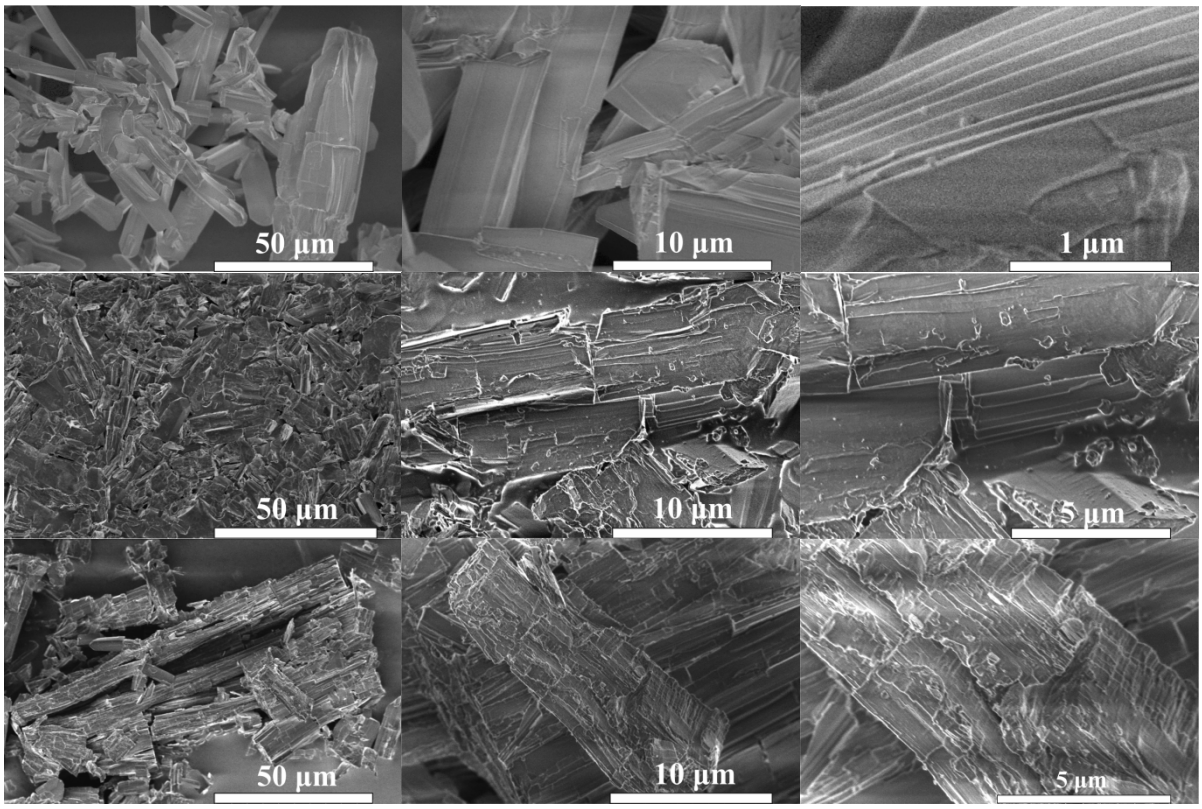


Figure S22. SEM images of DUT-8(Ni) before adsorption (top row), after 10 cycles (middle row) and 100 cycles (bottom row) of adsorption/desorption of *n*-butane at 298 K.

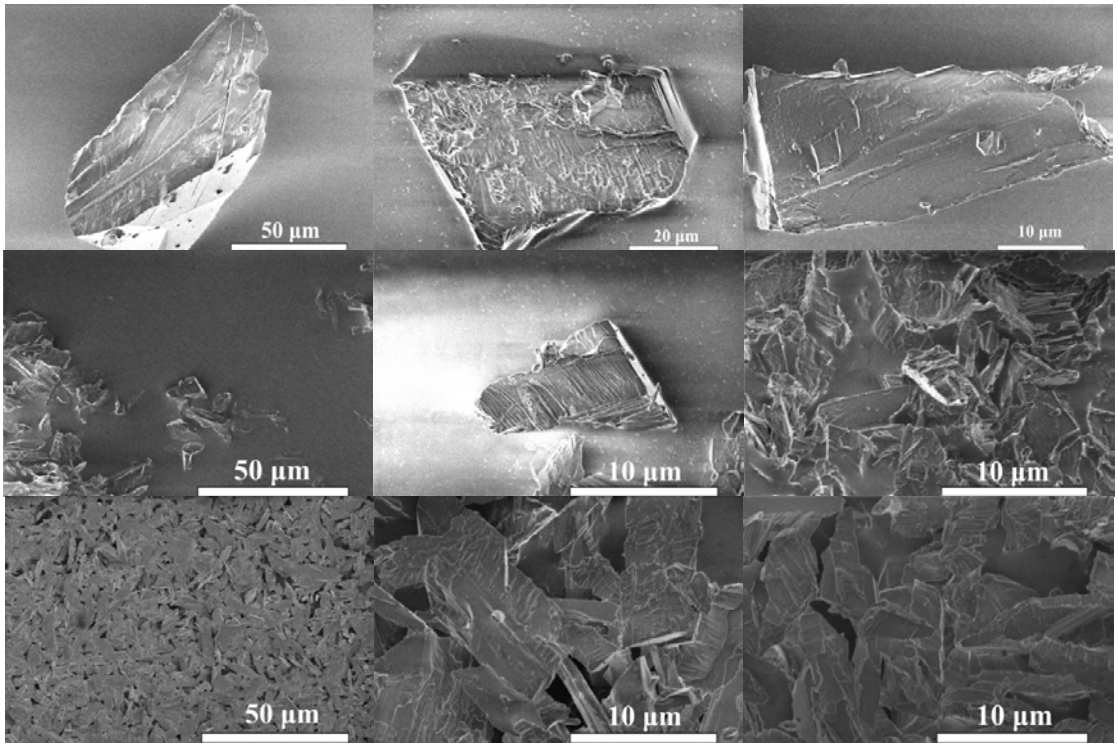


Figure S23. SEM images of SNU-9 before adsorption (top row), after 10 cycles (middle row) and 100 cycles (bottom row) of adsorption/desorption of *n*-butane at 298 K.

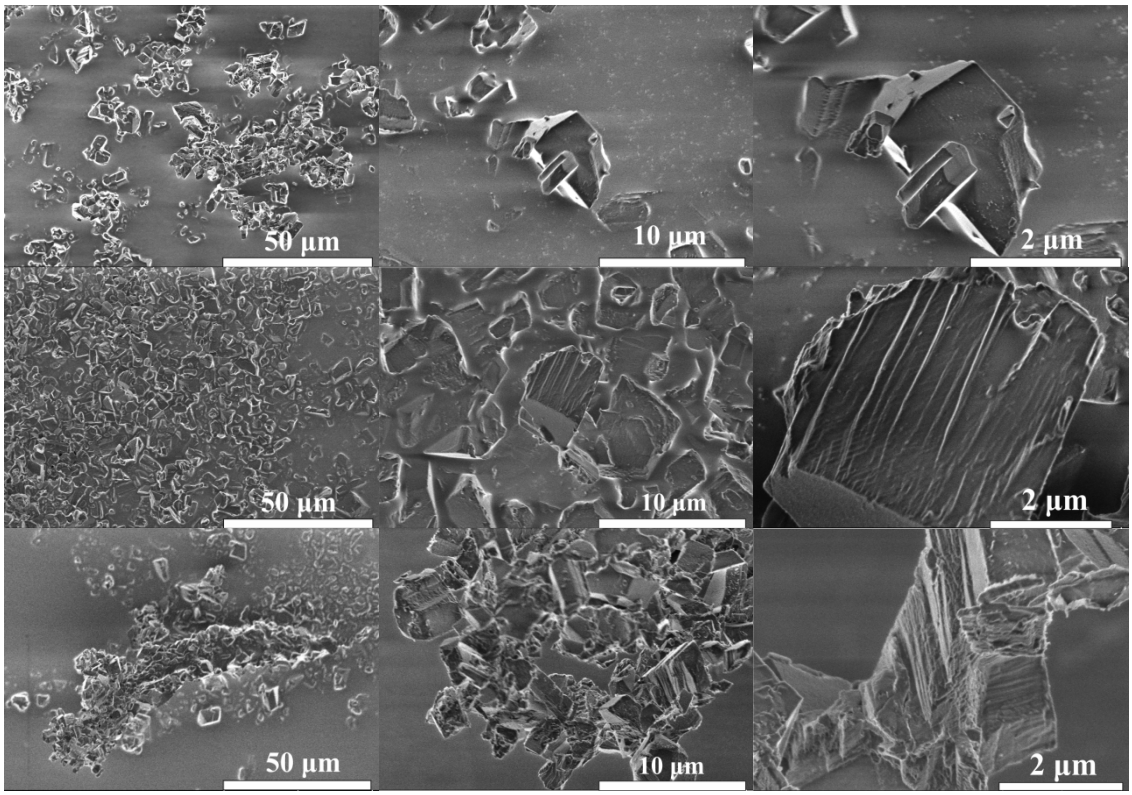


Figure S24. SEM images of MIL-53(Al) before adsorption (top row), after 10 cycles (middle row) and 100 cycles (bottom row) of adsorption/desorption of *n*-butane at 298 K.

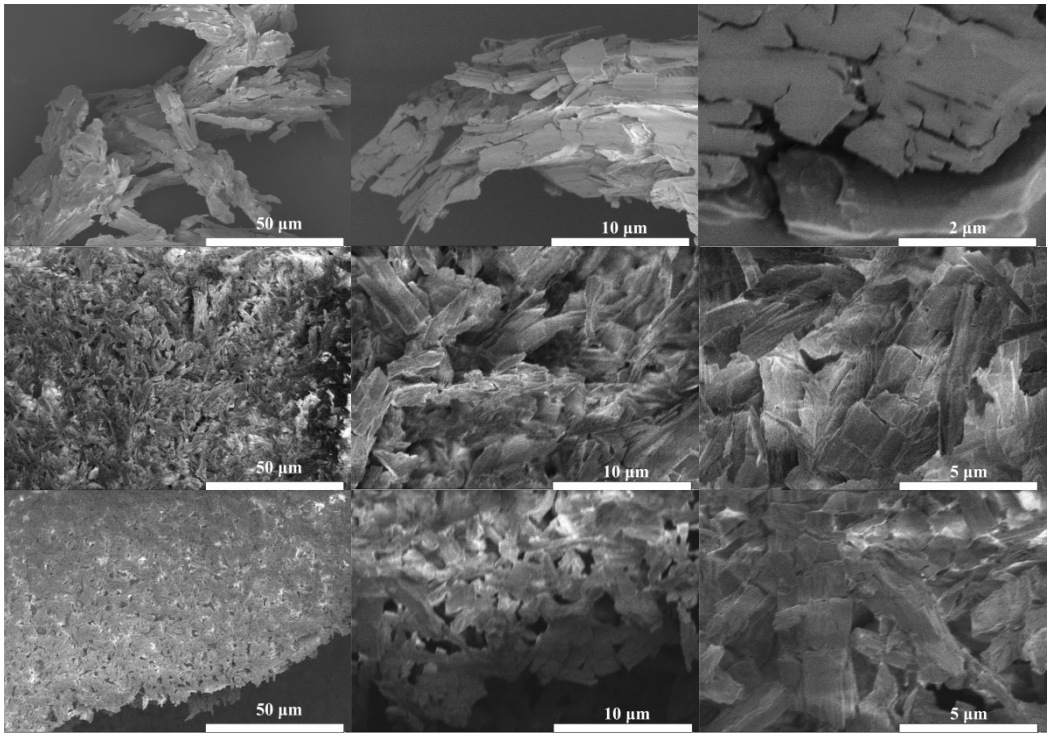


Figure S25. SEM images of ELM-11 before adsorption (top row), after 10 cycles (middle row) and 100 cycles (bottom row) of adsorption/desorption of *n*-butane at 298 K.

DRIFT spectra

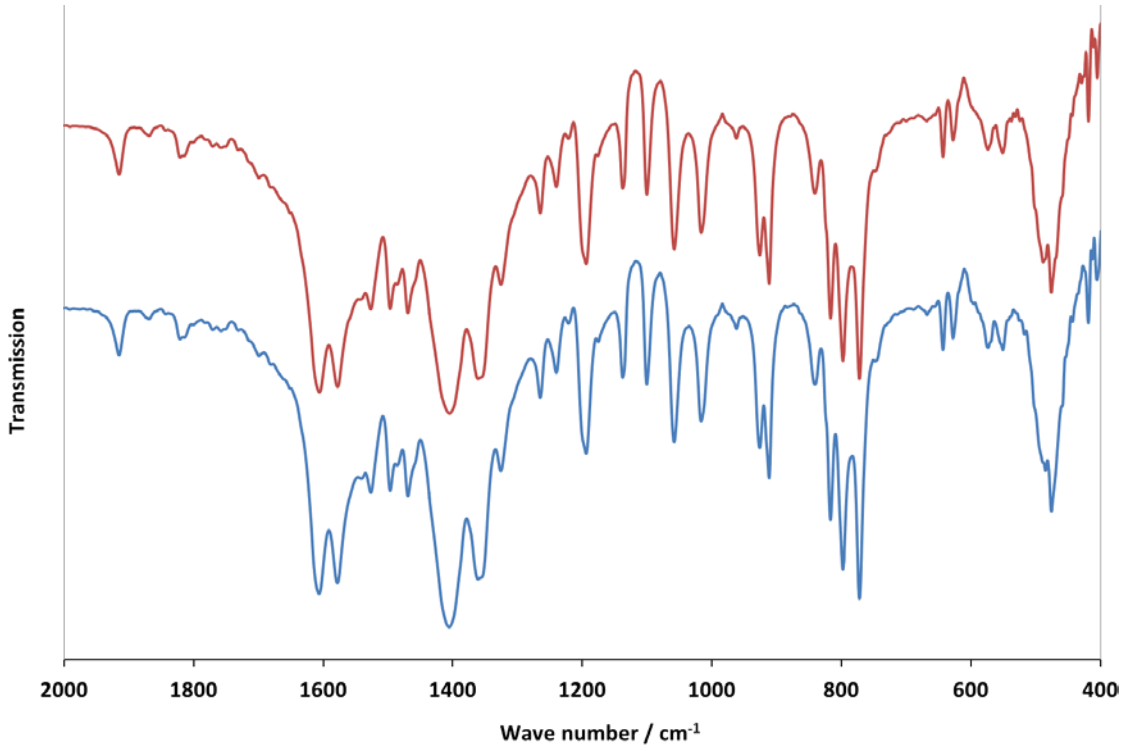


Figure S26. DRIFT spectra for freshly activated DUT-8(Ni) (blue line) and DUT-8(Ni) after 100 adsorption/desorption cycles of *n*-butane at 298 K (red line).

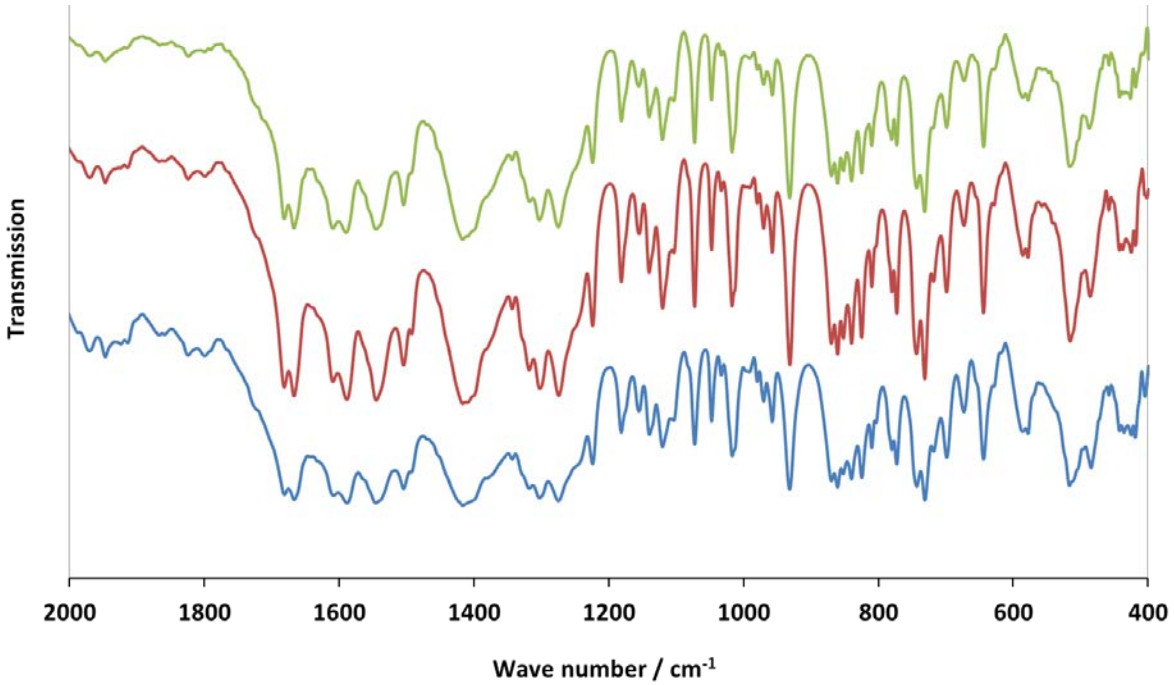


Figure S27. DRIFT spectra for freshly activated SNU-9 (blue line), material after 10 (red line) and 100 (light green line) cycles of adsorption/desorption of *n*-butane at 298 K.