Electronic Supplementary Material (ESI) for Dalton Transactions.

Structure and properties of Al-MIL-53-ADP, a breathing MOF based on the aliphatic linker molecule adipic acid.

Helge Reinsch, Renjith S. Pillai, Renée Siegel, Jürgen Senker, Alexandra Lieb, Guillaume Maurin and Norbert Stock

S1: Comparison of simulated and experimental PXRD data for Al-MIL-53-ADP-H_2O

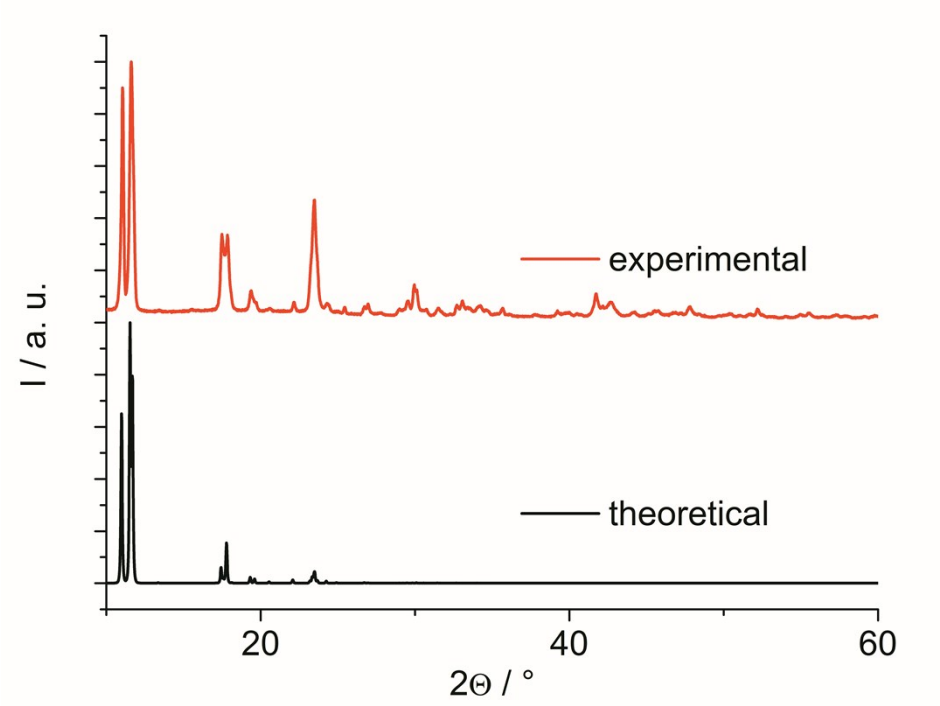

Fig S1: Comparison of the PXRD data simulated for the DFT optimised structure (black line) and the experimental data (red line).

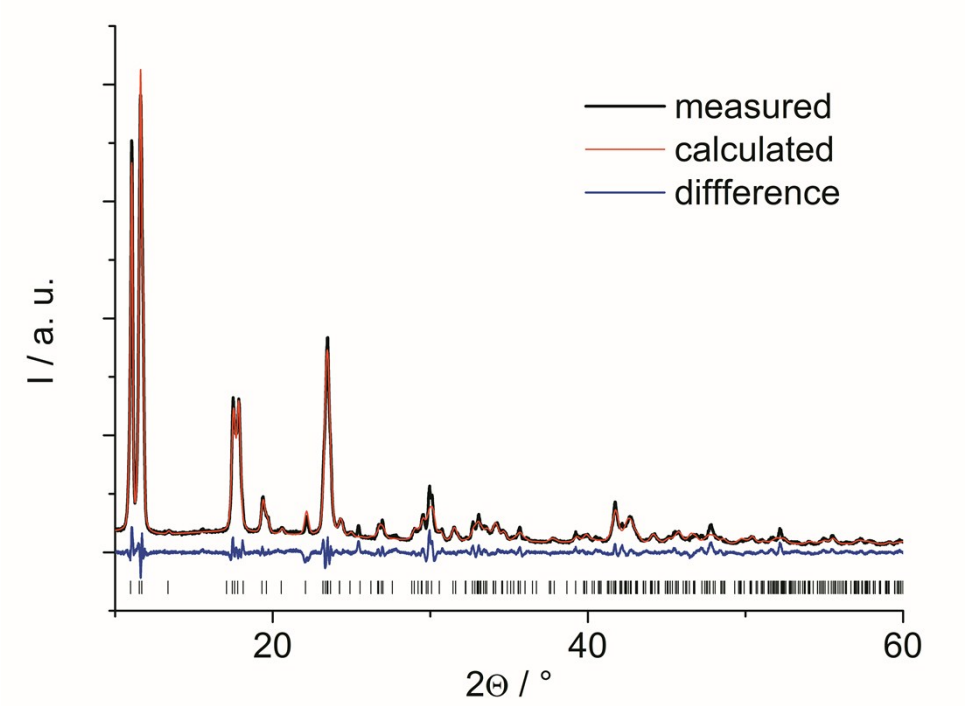

Fig S2: Initial Rietveld fit achieved without refining any structural parameters of the DFT optimised structure and only accounting for deviating intensities using the spherical harmonics correction.

The pore size distributions (PSD) of the crystal structures of both MIL-53-ADP np and lp forms were calculated by Gelb and Gubbins methodology[1] and shown in Figure S3. In these calculations the van der Waals parameter for the framework atoms were adopted from UFF forcefield.[2]

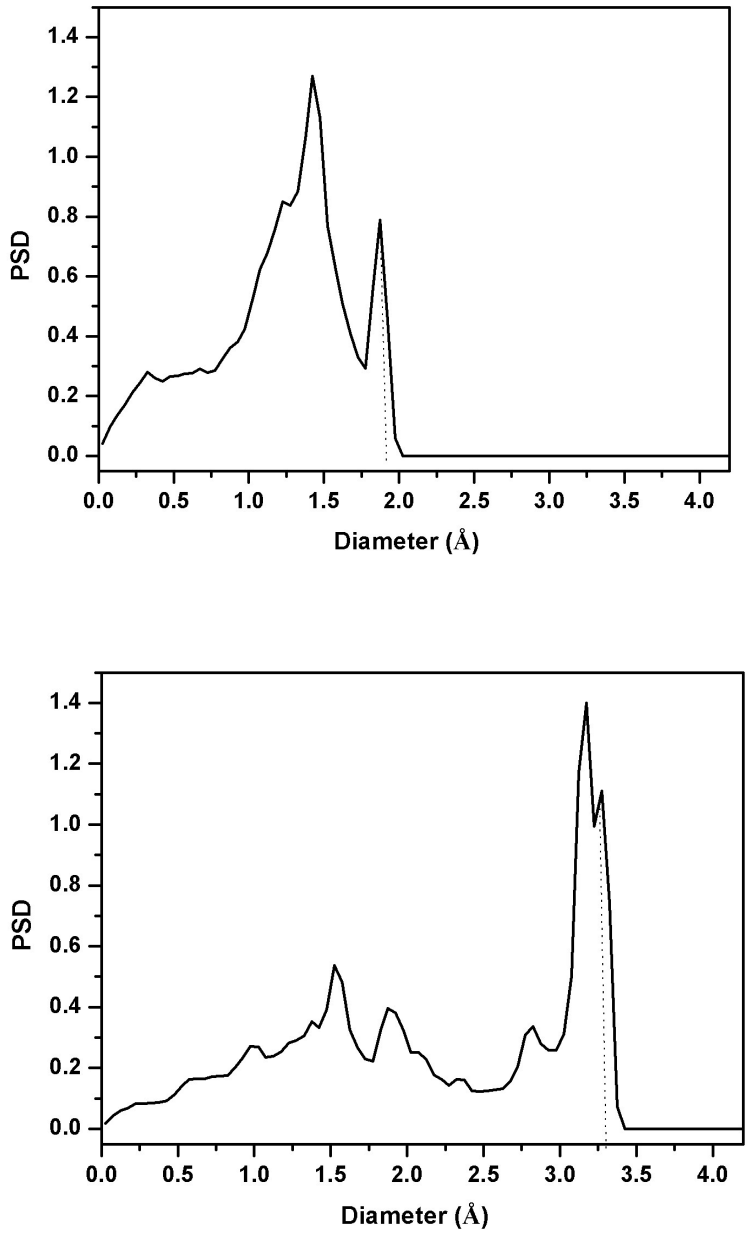

Fig S3: Top: pore size distribution (PSD) calculated form the crystal structure of [Al(OH)(O_2C-C_4H_8-CO_2)] (Al-MIL-53-ADP-*np*). Bottom: pore size distribution (PSD) calculated form the crystal structure of [Al(OH)(O_2C-C_4H_8-CO_2)]·H_2O (Al-MIL-53-ADP-*lp*).

S2: Crystallographic Data for Al-MIL-53-ADP-*np*

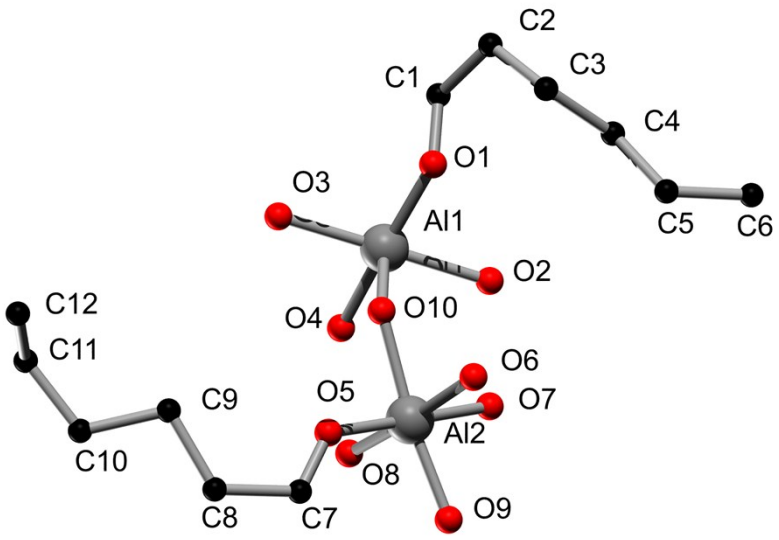

Fig S4: Asymmetric Unit of Al-MIL-53-ADP-*np* with numbering scheme used in Table S1.

Table S1: Most important bond lengths in the structure of Al-MIL-53-ADP-*np*.

Al1	O4	1.847(20)	O5	C7	1.226(19)
	O9	1.862(20)	O6	C1	1.303(20)
	O10	1.863(21)	O7	C6	1.263(20)
	O1	1.932(21)	O8	C12	1.282(17)
	O2	1.945(17)	C1	C2	1.558(25)
	O3	1.950(18)	C2	C3	1.527(25)
Al2	O9	1.842(19)	C3	C4	1.588(37)
	O7	1.849(20)	C4	C5	1.519(27)
	O5	1.851(19)	C5	C6	1.509(21)
	O6	1.892(20)		C4	1.519(27)
	O8	1.894(20)	C7	C8	1.528(23)
	O10	1.938(21)	C8	C9	1.568(32)
O1	C1	1.273(19)	C9	C10	1.567(33)
O2	C6	1.293(17)	C10	C11	1.523(27)
O3	C7	1.250(17)	C11	C12	1.567(25)
O4	C12	1.297(19)			

Crystallographic Information Files

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_cell_length_b  7.96457(33)
_cell_length_c  6.61867(33)
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_cell_angle_beta  93.6699(49)
_cell_angle_gamma 90
_cell_volume 835.086(69)
_symmetry_space_group_name_H-M P21
loop_
_symmetry_equiv_pos_as_xyz
            '-x, y+1/2, -z'
            'x, y, z'
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_symmetry_multiplicity
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_B_iso_or_equiv
Al1 Al   0 0.25604(78) 0.0789(20) 0.2327(19) 1 0.50(17)
Al2 Al   0 0.24989(77) 0.0560(18) 0.7450(21) 1 0.50(17)
O1 O   0 0.28999(96) 0.3014(17) 0.1546(21) 1 0.50(17)
O2 O   0 0.37295(74) 0.0476(13) 0.3322(18) 1 0.50(17)
O3 O   0 0.13854(87) 0.1089(23) 0.1347(20) 1 0.50(17)
O4 O   0 0.22799(69) -0.1372(15) 0.3042(23) 1 0.50(17)
O5 O   0 0.14345(80) 0.1203(25) 0.8141(19) 1 0.50(17)
O6 O   0 0.2917(11) 0.2758(17) 0.7931(24) 1 0.50(17)
O7 O   0 0.35499(93) -0.0113(14) 0.6705(23) 1 0.50(17)
O8 O   0 0.21322(87) -0.1628(18) 0.6695(19) 1 0.50(17)
O9 O   0 0.2856(13) -0.0263(27) 0.9962(17) 1 0.50(17)
O10 O   0 0.2245(12) 0.1576(28) 0.4820(22) 1 0.50(17)
C1 C   0 0.3050(12) 0.3395(18) -0.0264(18) 1 0.50(17)
C2 C   0 0.3425(11) 0.5200(25) -0.0331(26) 1 0.50(17)
C3 C   0 0.3828(11) 0.5894(25) 0.1653(27) 1 0.50(17)
C4 C   0 0.4656(10) 0.4907(73) 0.2426(25) 1 0.50(17)
C5 C   0 0.5077(10) 0.5196(20) 0.4523(31) 1 0.50(17)
C6 C   0 0.60277(83) 0.5176(14) 0.4811(18) 1 0.50(17)
C7 C   0 0.10390(79) 0.0861(34) 0.9619(16) 1 0.50(17)
C8 C   0 0.0075(12) 0.0916(38) 0.9405(34) 1 0.50(17)
C9 C   0 -0.03701(91) 0.1508(67) 0.7345(29) 1 0.50(17)
C10 C   0 -0.1262(12) 0.0661(26) 0.7132(31) 1 0.50(17)
C11 C   0 -0.1806(10) 0.1166(25) 0.5252(31) 1 0.50(17)
C12 C   0 -0.21226(81) 0.3030(19) 0.5199(17) 1 0.50(17)
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_cell_length_c     9.0811
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_cell_angle_beta             87.743
_cell_angle_gamma            88.372
_cell_volume       461.0
_symmetry_space_group_name_H-M          'P 1'
loop_
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1 x,y,z
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_symmetry_multiplicity
_atom_site_Wyckoff_symbol
_atom_site_attached_hydrogens
_atom_site_calc_flag
_atom_site_thermal_displace_type
_atom_site_u_iso_or_equiv
Al1 Al -0.9813 -0.9241  0.0121  1.000 1 a ? d Uiso  1
Al2 Al -0.4955 -0.9262  0.0022  1.000 1 a ? d Uiso  1
O17 O -0.2452 -0.8346  0.0033  1.000 1 a ? d Uiso   1
H213 H -0.2558 -0.7212 0.0005  1.000 1 a ? d Uiso   1
O18 O -0.3926 -0.1366  0.1704  1.000 1 a ? d Uiso   1
O19 O -0.0545 -0.1396  0.1988  1.000 1 a ? d Uiso   1
O20 O -0.9293 -0.8486  0.1778  1.000 1 a ? d Uiso   1
O21 O -0.5906 -0.8590  0.1739  1.000 1 a ? d Uiso   1
O22 O -0.7374 -0.0222  0.0050  1.000 1 a ? d Uiso   1
O23 O -0.5688 -0.6908  0.8435  1.000 1 a ? d Uiso   1
O24 O -0.9085 -0.7006  0.8473  1.000 1 a ? d Uiso   1
O25 O -0.0885 -0.0534  0.8960  1.000 1 a ? d Uiso   1
O26 O -0.4276 -1.0049  0.8413  1.000 1 a ? d Uiso   1
C113 C -0.2265 -0.2004  0.2357  1.000 1 a ? d Uiso  1
C114 C -0.2383 -0.3856  0.3705  1.000 1 a ? d Uiso  1
H225 H -0.1167 -0.4263  0.4610  1.000 1 a ? d Uiso  1
H226 H -0.2513 -0.4753  0.3135  1.000 1 a ? d Uiso  1
C115 C -0.4390 -0.3984  0.4624  1.000 1 a ? d Uiso  1
H223 H -0.5647 -0.3172  0.3839  1.000 1 a ? d Uiso  1
H224 H -0.4368 -0.3665  0.5691  1.000 1 a ? d Uiso  1
C116 C -0.7381 -0.6497  0.7775  1.000 1 a ? d Uiso  1
C117 C -0.7380 -0.5634  0.5888  1.000 1 a ? d Uiso  1
H221 H -0.7697 -0.4205  0.5382  1.000 1 a ? d Uiso  1
H222 H -0.8637 -0.6064  0.5398  1.000 1 a ? d Uiso  1
C118 C -0.5199 -0.5789  0.5270  1.000 1 a ? d Uiso  1
H219 H -0.4381 -0.6723  0.6395  1.000 1 a ? d Uiso  1
H220 H -0.4956 -0.6350  0.4396  1.000 1 a ? d Uiso  1
C119 C -0.7581 -0.8555  0.2421  1.000 1 a ? d Uiso  1
C120 C -0.7530 -0.8165  0.3889  1.000 1 a ? d Uiso  1
H217 H -0.6966 -0.6840  0.3536  1.000 1 a ? d Uiso  1
H218 H -0.6545 -0.9188  0.4826  1.000 1 a ? d Uiso  1
C121 C -0.0325 -0.0243  0.5595  1.000 1 a ? d Uiso  1
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H229 H -0.0560 -0.0404 0.4466 1.000 1 a ? d Uiso 1
C122 C -0.2361 -0.0109 0.7912 1.000 1 a ? d Uiso 1
C123 C -0.2342 -0.0621 0.6489 1.000 1 a ? d Uiso 1
H228 H -0.2922 -0.1888 0.6679 1.000 1 a ? d Uiso 1
C124 C -0.9548 -0.8416 0.4917 1.000 1 a ? d Uiso 1
H216 H -0.9219 -0.8260 0.6046 1.000 1 a ? d Uiso 1
H230 H -0.9146 -0.1216 0.6323 1.000 1 a ? d Uiso 1
H227 H -0.3377 -0.9507 0.5730 1.000 1 a ? d Uiso 1
H214 H -0.7341 -0.1229 0.9844 1.000 1 a ? d Uiso 1
H215 H -0.0794 -0.7436 0.4330 1.000 1 a ? d Uiso 1
O27 O -0.7783 -0.3435 0.9315 1.000 1 a ? d Uiso 1
H209 H -0.7439 -0.4362 1.0519 1.000 1 a ? d Uiso 1
H210 H -0.9350 -0.3500 0.9417 1.000 1 a ? d Uiso 1
O28 O -0.3692 -0.4880 0.0034 1.000 1 a ? d Uiso 1
H211 H -0.3319 -0.5820 0.1213 1.000 1 a ? d Uiso 1
H212 H -0.5261 -0.4932 0.0056 1.000 1 a ? d Uiso 1

Table S2. ^{27}Al quadrupolar parameters: quadrupolar coupling constant C_Q (MHz) and asymmetry parameter η; isotropic chemical shifts δ_{iso} (ppm) of the various protons (^{1}H) and carbon (^{13}C) atoms calculated at the DFT-level from the elucidated crystal structure of the anhydrous Al-MIL-53-ADP-*np* and hydrated Al-MIL-53-ADP-*lp* solids

^{27}Al			
	C_Q, η		
Al-MIL-53-ADP-*np*	8.6, 0.11; 7.9, 0.31		
Al-MIL-53-ADP-*lp*	8.3, 0.13; 12.5, 0.25		
^{1}H			
	δ_{iso}, Al-O**H**	δ_{iso}, $\mathbf{H}_{CH2}$	δ_{iso}, $\mathbf{H}_{H2O}$
Al-MIL-53-ADP-*np*	2.0	1.8	
Al-MIL-53-ADP-*lp*	3.2	2.0	2.7; 3.7
^{13}C			
	δ_{iso}, **C**=O	δ_{iso}, **C**-H $_{CH2}$	
Al-MIL-53-ADP-*np*	183.4	37.2; 36,4; 25,2; 22.5	
Al-MIL-53-ADP-*lp*	183.4	38.1; 24.5	

[1] L. D. Gelb, K. E. Gubbins, Pore Size Distributions in Porous Glasses: A Computer Simulation Study, .*Langmuir* **1998,** *15* (2), 305-308.

[2] A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard, W. M. Skiff, UFF, a Full Periodic-Table Force-Field for Molecular Mechanics and Molecular-Dynamics Simulations. *J. Am. Chem. Soc.* **1992,** *114* (25), 10024-10035.