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Ca– and Sr–Tetrafluoroisophthalates: Mechanochemical Synthesis, Characterization, and *ab initio* Structure Determination.

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Supporting Information

Table S1: Selected bonds and H-bonds from the crystal structures of **1** and **2**.

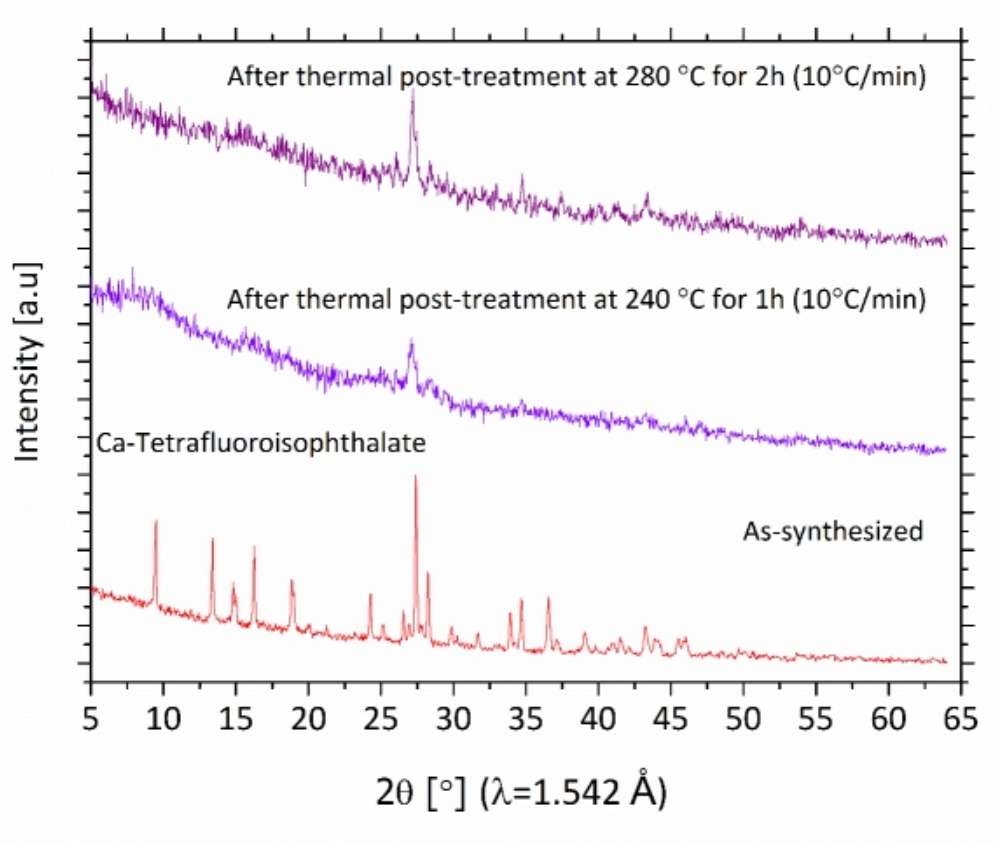
		[{Ca(*m*BDC-F_4)(H_2O)$_2$}·H_2O] (1)	[{Sr(*m*BDC-F_4)(H_2O)$_2$}·H_2O] (2)
M—O (carboxylate) (Å)	M—O1 (chelate)	2.504(7)	2.697(9)
	M—O2 (chelate)	**2.619(8)**	**2.767(1)**
	M—O1’ (bridge)	**2.266(8)**	**2.389(9)**
	M—O2’ (bridge)	2.439(8)	2.472(1)
	M—O3	2.561(8)	2.663(1)
	M—O4	2.398(7)	2.546(1)
M—O (water) (Å)	M—O6w	2.389(6)	2.570(9)
	M—O7w	2.581(6)	2.690(8)
H–Bonds (Å)	O5w ··· O6w	2.679(9)	2.672(1)
	O5w ··· O7w	3.210(8)	3.193(1)
	O5w ··· O3	2.845(1)	2.777(2)
	O5w ··· O4	2.945(9)	2.990(1)
	O6w ··· O2’	3.153(1)	3.434(1) !
	O6w ··· O3	2.906(1)	3.0819(1)
	O6w ··· O7w	2.857(8)	2.919(1)
	O7w ··· O4	2.973(9)	3.247(1)
C—O (carboxyl) (Å)	C4—O1	1.246(7)	1.244(2)
	C4—O2	1.242(7)	1.239(2)
	C8—O3	1.258(7)	1.257(2)
	C8—O4	1.243(7)	1.239(2)
M—(bridging, chain)—M (Å)	M—(O1, O2)—M	3.973(4)	4.181(3)

Table S2: Selected angles from the crystal structures of **1** and **2**.

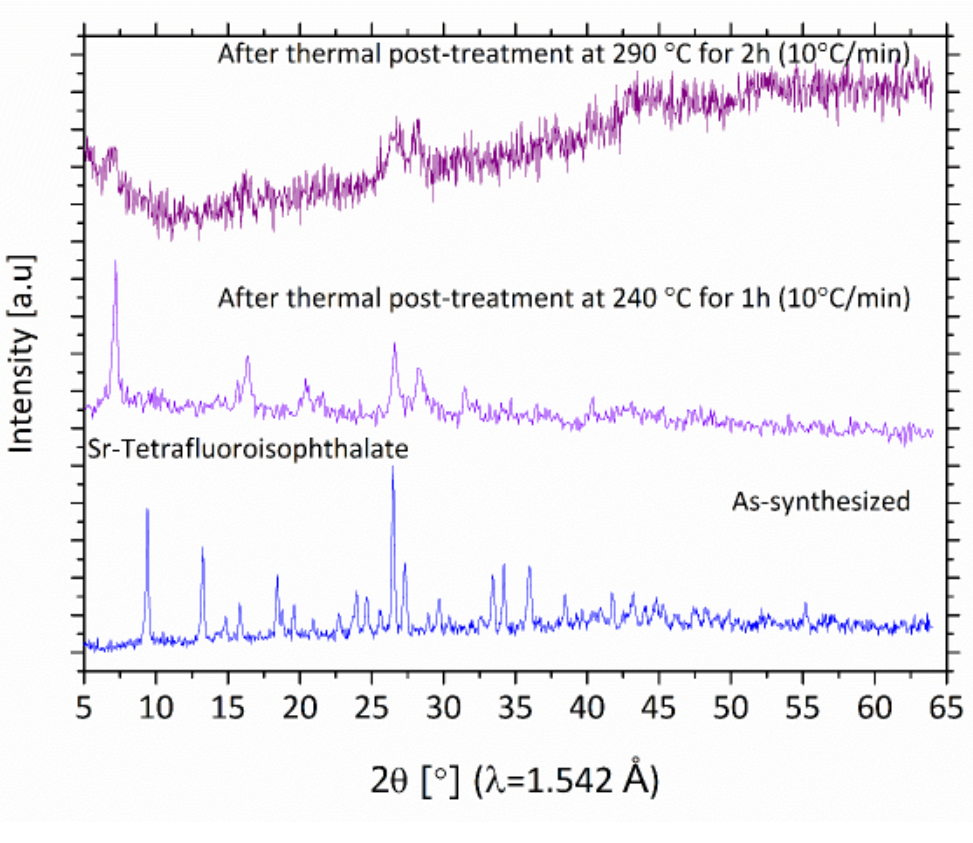
		[{Ca(*m*BDC-F_4)(H_2O)$_2$}•H_2O] (1)	[{Sr(*m*BDC-F_4)(H_2O)$_2$}•H_2O] (2)
O—M—O (°)	O1—M—O1'	119.755(3)	118.134(3)
	O1—M—O2	**51.672(2)**	**48.932(3)**
	O1—M—O2'	68.549(2)	70.223(3)
	O1—M—O3	72.032(2)	72.631(3)
	O1—M—O4	78.232(2)	72.691(2)
	O1—M—O6w	129.027(2)	130.565(3)
	O1—M—O7w	145.159(2)	143.701(3)
	O2—M—O1'	69.048(2)	70.222(2)
	O2—M—O2'	119.171(3)	117.572(3)
	O2—M—O3	76.476(2)	70.677(2)
	O2—M—O4	73.286(2)	75.847(2)
	O2—M—O6w	144.069(2)	139.744(2)
	O2—M—O7w	133.297(2)	143.029(3)
	O1'—M—O2'	**171.690(1)**	**170.452(3)**
	O1'—M—O3	86.054(2)	83.701(3)
	O1'—M—O4	95.987(3)	95.735(3)
	O1'—M—O6w	92.081(3)	91.018(3)
	O1'—M—O7w	83.168(2)	88.622(2)
	O2'—M—O3	96.902(3)	103.823(3)
	O2'—M—O4	85.835(2)	81.582(2)
	O2'—M—O6w	81.532(3)	85.799(4)
	O2'—M—O7w	89.627(3)	81.846(4)
	O3—M—O4	146.615(2)	144.601(1)
	O3—M—O6w	71.805(2)	72.124(1)
	O3—M—O7w	139.814(2)	138.574(2)
	O4—M—O6w	141.067(2)	143.137(2)
	O4—M—O7w	73.211(2)	76.591(2)
	O6w—M—O7w	70.048(2)	67.369(2)
O—C—O (carboxyl) (°)	O1—C4—O2	127.851(5)	127.920(2)
	O3—C8—O4	126.804(5)	126.876(2)
M—(bridging)—M (°)	M—(O1)—M	112.682(3)	110.446(3)
	M—(O2)—M	103.472(3)	105.737(4)

Table S3. EXAFS fit parameters for the compounds **1** and **2**. The root mean square error (RMSE) is 0.032 For **1** and 0.00005 for **2.**

	[{Ca(*m*BDC-F_4)(H_2O)$_2$}·H_2O] (**1**)			[{Sr(*m*BDC-F_4)(H_2O)$_2$}·H_2O] (**2**)		
Scattering path	R_{model} (Å)	R_{fit} (Å)	R_{diff}^2 (Å)	R_{model} (Å)	R_{fit} (Å)	R_{diff}^2 (Å)
M^{II}–O1 (chelate)	2.50	2.32	0.0324	2.70	2.70	0
M^{II}–O2 (chelate)	2.62	2.44	0.0324	2.77	2.77	0
M^{II}–O1 (bridge)	2.27	2.09	0.0324	2.39	2.40	0.0001
M^{II}–O2 (bridge)	2.44	2.26	0.0324	2.47	2.48	0.0001
M^{II}–O3	2.56	2.39	0.0289	2.68	2.68	0
M^{II}–O4	2.40	2.22	0.0324	2.56	2.56	0
M^{II}–O6w	2.39	2.22	0.0289	2.57	2.56	0.0001
M^{II}–O7w	2.58	2.39	0.0361	2.69	2.68	0.0001
Average (Å)	2.47	2.58		2.6	2.60	
RMSE			0.032			0.00005
R-Factor			0.0052			0.0008
Reduced chi-square (X^2)			38.5922			67.5069

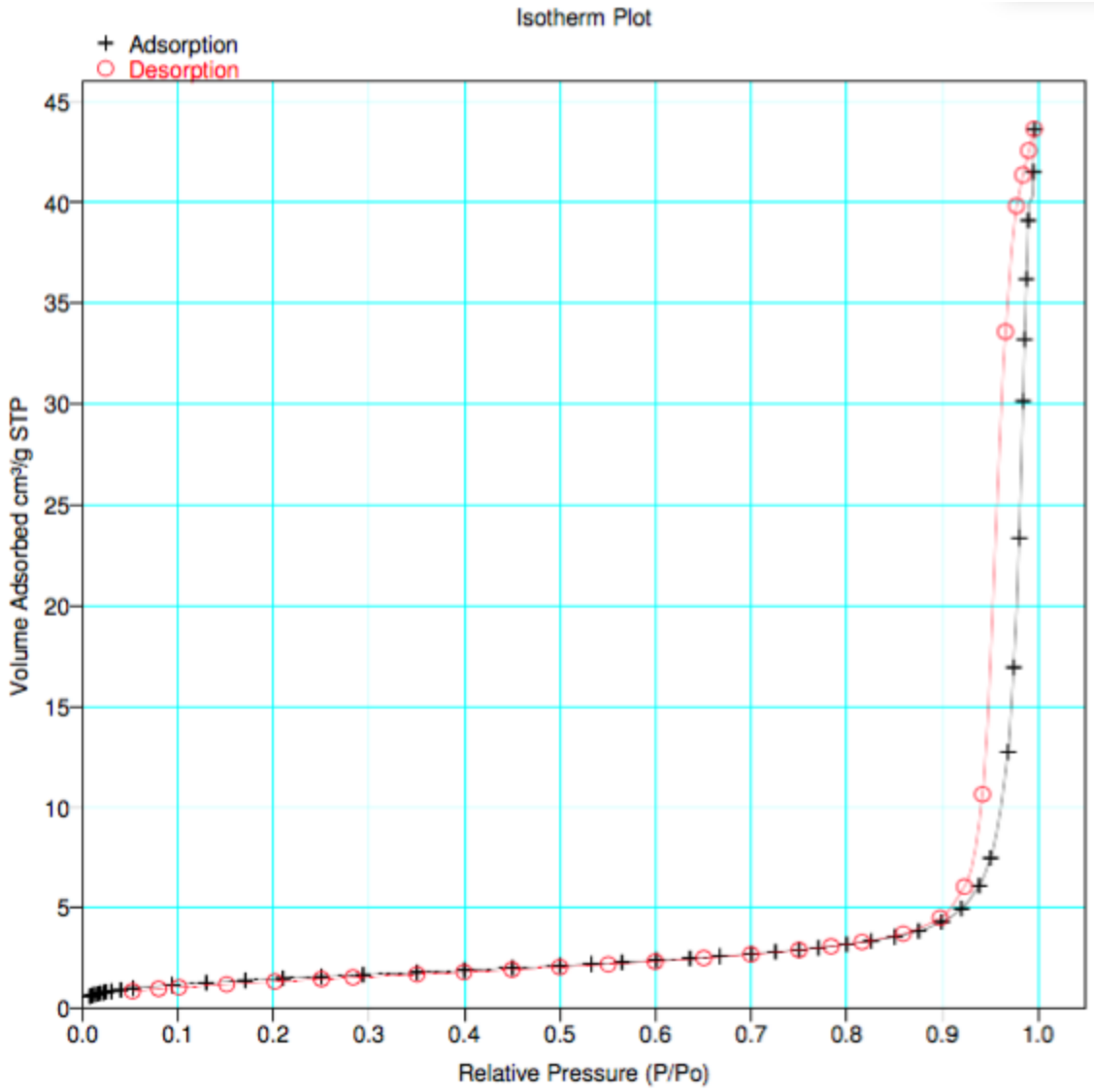


a



b

Figure S1. The PXRD patterns for compound **1** (a) and **2** (b). The compounds as-synthesized (red and blue PXRD patterns) and after the thermal post-treatment (violet and purple PXRD patterns). All samples were measured for comparison with the same diffractometer.



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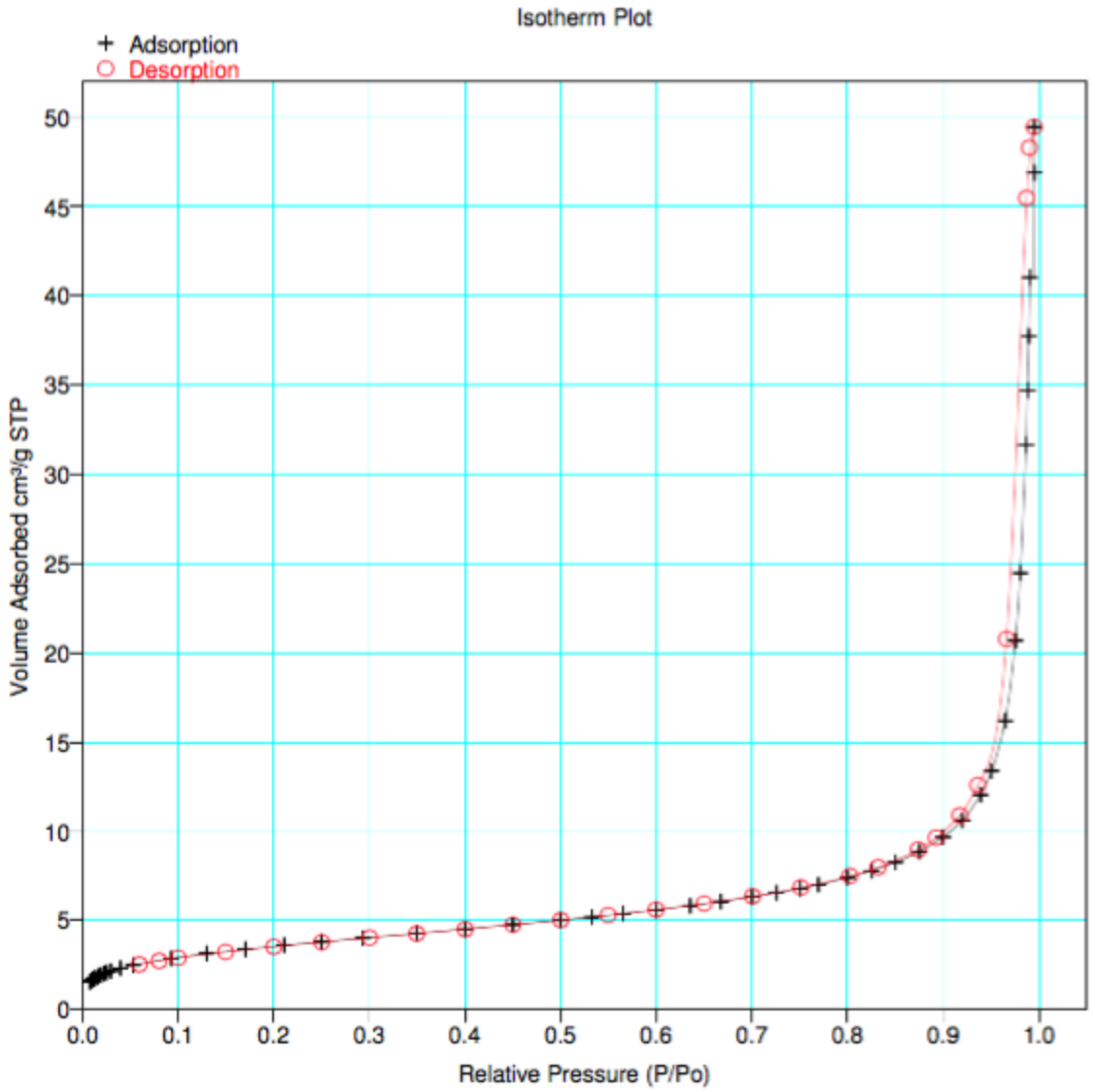
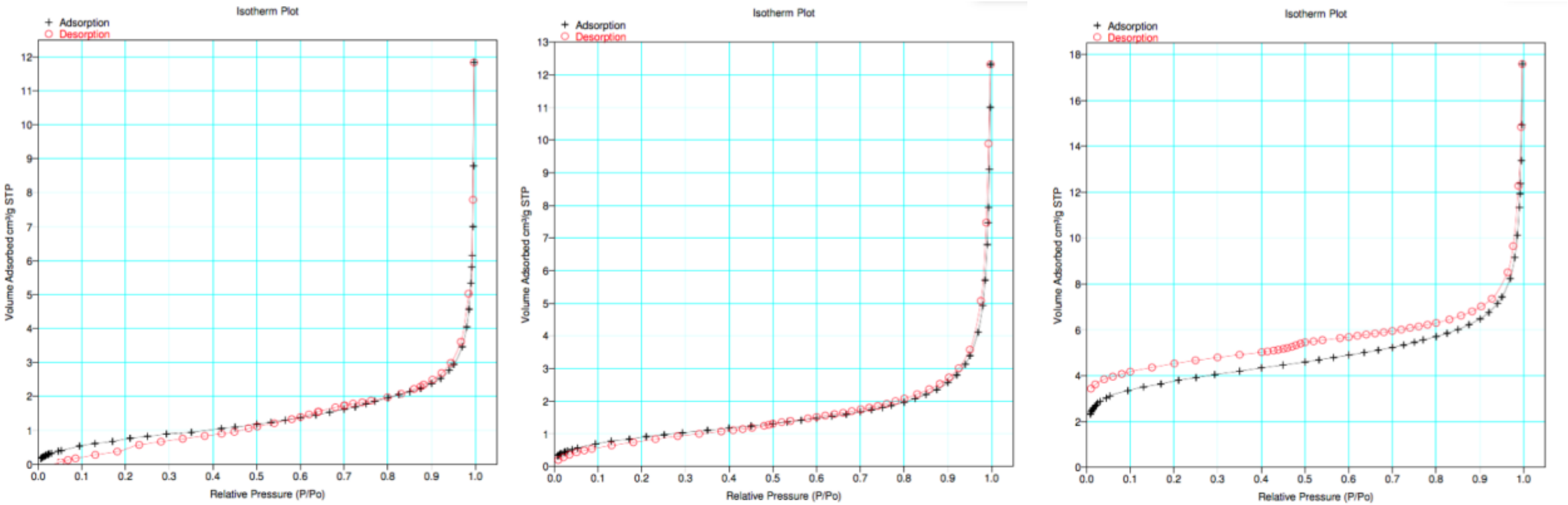


b

Figure S2. Isotherm curves of the compound **1**. Adsorption (crosses) and desorption pore volume (circles) isotherm for nitrogen (a) at room temperature, S_{BET} = 5.4 ± 0.04 m^2/g. (b) at 240 °C, S_{BET} = 12.9 ± 0.12 m^2/g.



a b c

Figure S3. Isotherm curves of the compound **2**. Adsorption (crosses) and desorption pore volume (circles) isotherm for nitrogen (a) at room temperature, S_{BET} = 3.1 ± 0.04 m^2/g. (b) at 200 °C, S_{BET} = 3.4 ± 0.03 m^2/g. (c) at 240 °C, S_{BET} = 13.6 ± 0.023 m^2/g.

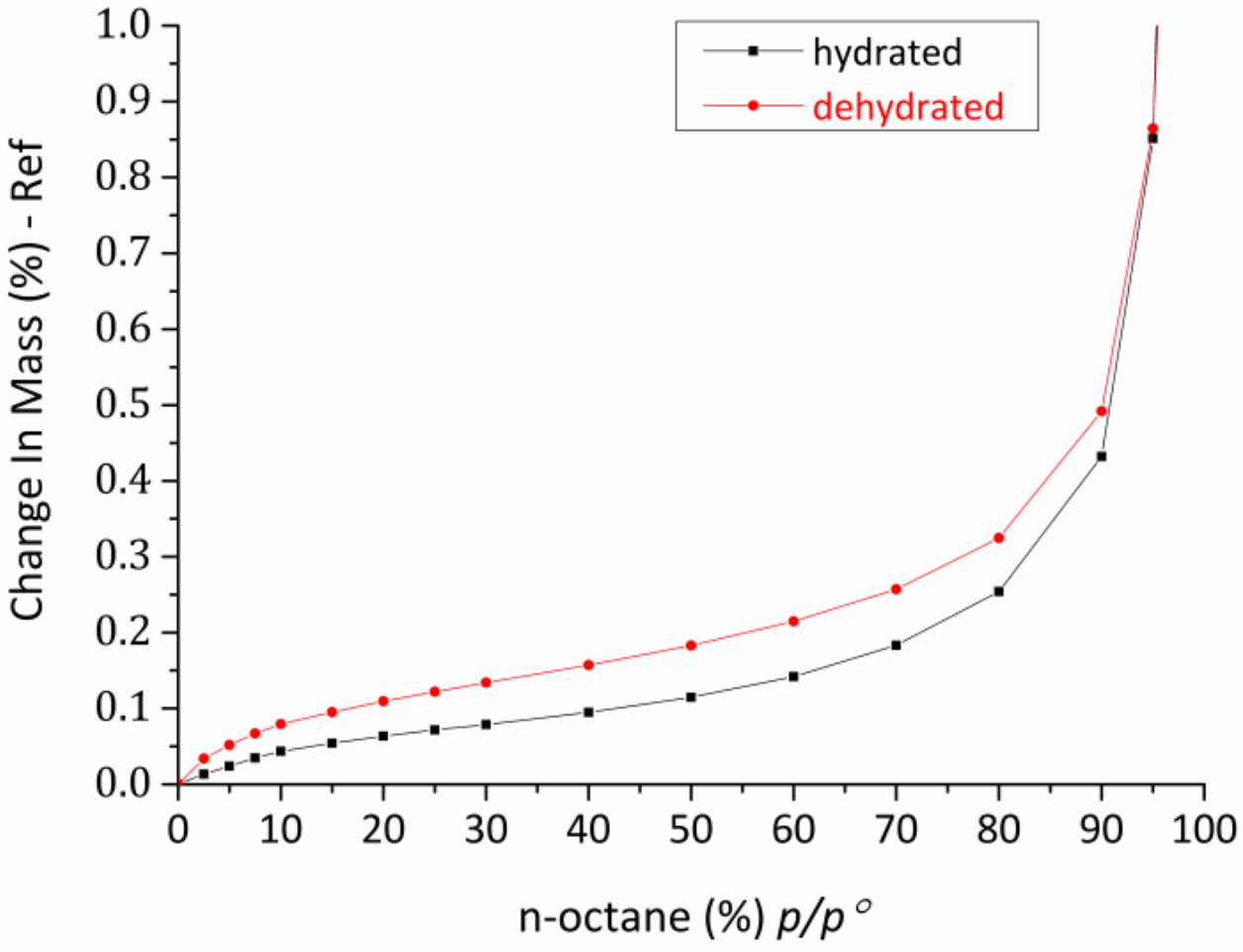


Figure S4. Isotherm curves for the dynamic vapor adsorption of *n*-octane on samples of compound **2** as synthesized (black curve) and after thermal post-treatment (red curve).