Electronic Supplementary Material (ESI) for Dalton Transactions.

Strontium-Coordination Polymers based on Tetrafluorophthalic and Phthalic acids: Mechanochemical Synthesis, *ab initio* Structures Determination, and Spectroscopic Characterization.

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Supplementary Materials

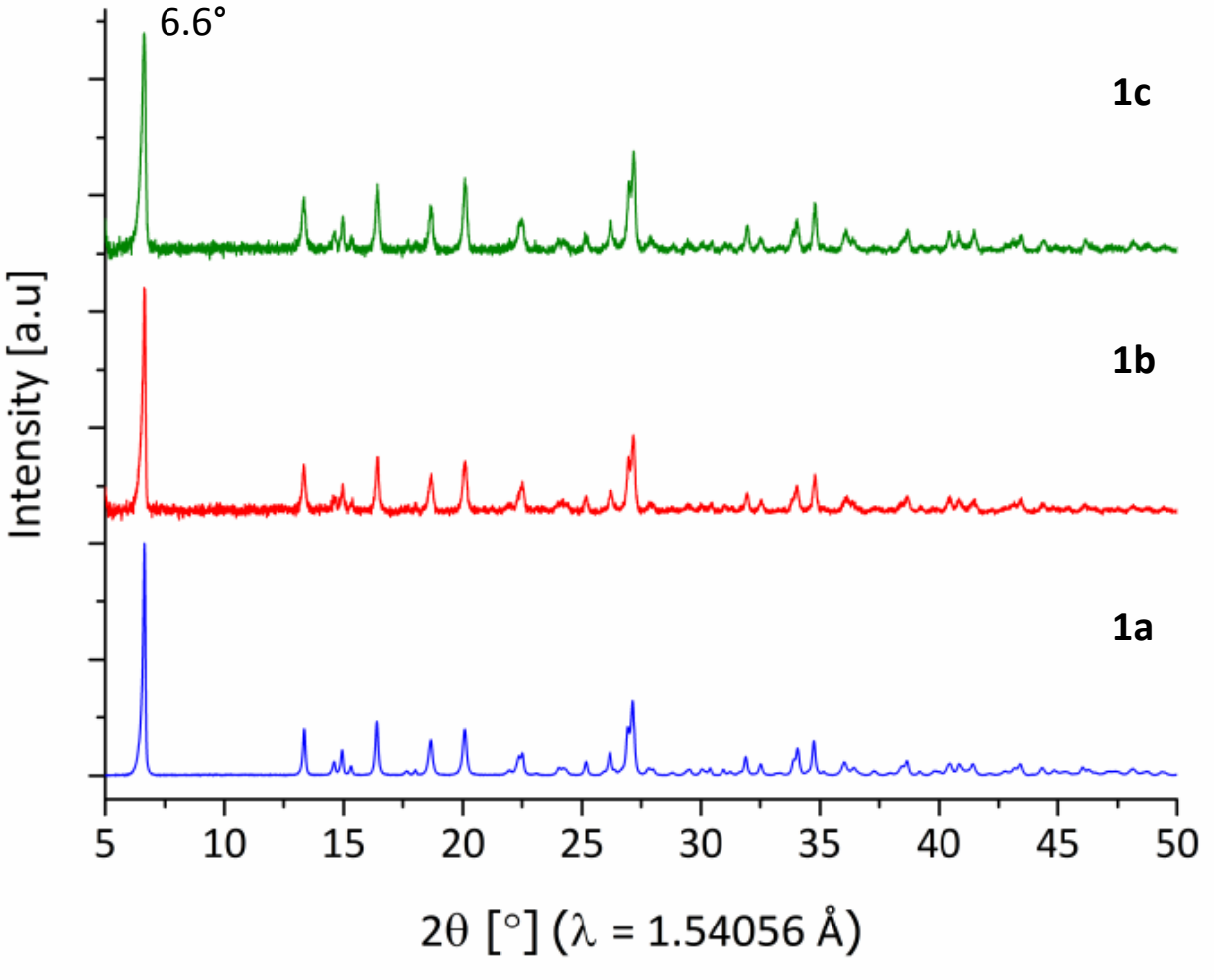


Figure S1. The PXRD patterns of [Sr(*o*BDC-F_4)(H_2O)$_2$] (**1**) obtained by milling the organic ligand H_2*o*BDC-F_4 with (1a) $Sr(OH)_2 \cdot 8H_2O$ for 1h (blue PXRD pattern), (1b) $Sr(OH)_2$ and 130 µL H_2O for 1h (red PXRD pattern), or (1c) $Sr(OH)_2$ for 4h (green PXRD pattern). The molar ratio between organic and inorganic precursors was maintained as 1:1.

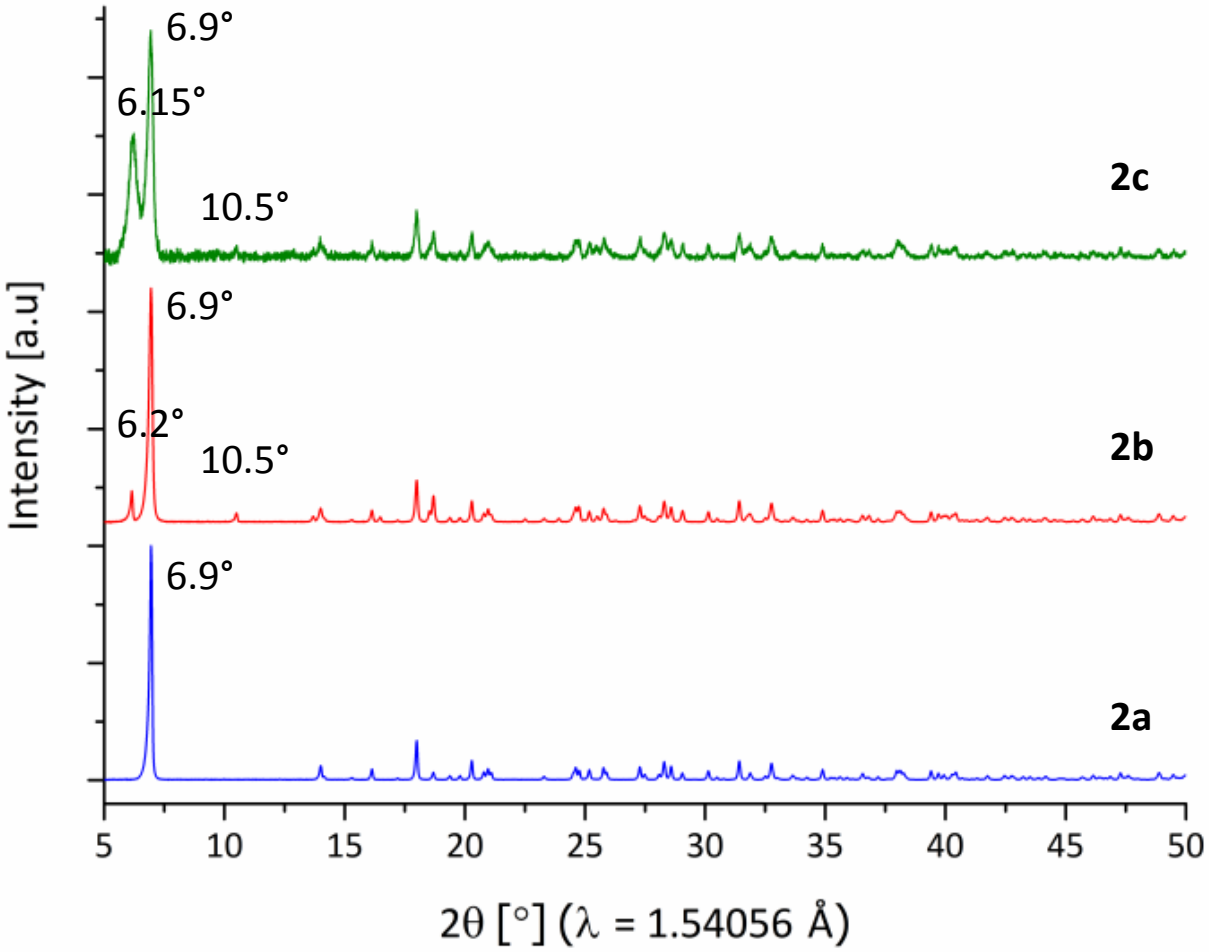


Figure S2. The PXRD patterns of [Sr(*o*BDC-F_4)(H_2O)$_2$] (**1**), 2a, obtained by milling the organic ligand H_2*o*BDC with Sr(OH)$_2$·8H_2O for 1h (blue PXRD pattern). (2b) Product obtained after milling H_2*o*BDC with Sr(OH)$_2$ and 130 µL H_2O for 1h (red PXRD pattern). Product 2c obtained after milling H_2*o*BDC with Sr(OH)$_2$ for 4h (green PXRD pattern). The molar ratio between organic and inorganic precursors was maintained as 1:1.

Table S1. Elemental analysis results of products 1a, 1b and 1c as depicted in Figure S1, products 2a, 2b, and 2c as depicted in Figure S2, and the samples after thermal post-treatments of compounds 1 and 2 at 300 ˚C and 400 ˚C, respectively.

	1a	1b	1c	1 (300 ˚C)	2a	2b	2c	2 (400 ˚C)
C% found (calc.)	26.5 (26.7)	27.1	26.9	26.8 (29.7)	30.4 (31.4)	33.4	34.7	37.4 (38.1)
H% found (calc.)	0.95 (1.1)	0.9	0.91	0.5 (0)	3.1 (3.3)	3.1	2.6	1.5 (1.6)
F% found (calc.)	19.4 (21.1)	-	-	26.7 (23.5)	-	-	-	-

Table S2: Selected bonds, distances, and H-bonds from the crystal structures of **1** and **2**.

		[Sr(*o*BDC-F_4)(H_2O)$_2$] (1)	[{Sr(*o*BDC)(H_2O)$_2$}·H_2O] (2)	
Sr—O (carboxylate) (Å)	Sr—O1	**2.426(2)**	Sr—O1	2.968(1)
	Sr—O1’	**2.774(1)**	Sr—O2	**2.443(1)**
	Sr—O2	2.437(2)	Sr—O2‘	**2.800(1)**
	Sr—O2’	2.667(1)	Sr—O3	2.603(1)
	Sr—O3	2.671(1)	Sr—O3’	2.685(1)
	Sr—O4	2.573(1)	Sr—O4	2.550(1)
Sr—O (water) (Å)	Sr—O1w	2.732(1)	Sr—O1w	2.628(1)
	Sr—O2w	2.688(1)	Sr—O1w’	2.720(1)
	Sr—O2w’	3.183(2)	Sr—O2w	2.687(1)
H–Bonds (Å)	O2w ··· O3	2.670(1)	O3w ··· O1	2.829(1)
	O2w ··· O4	2.738(1)	O3w ··· O1w	2.913(1)
	-	-	O2w ··· O1	2.539(1)
	-	-	O2w ··· O4	2.492(1)
C—O (carboxyl) (Å)	C8—O1	**1.209(2)**	C1—O1	1.272
	C8—O2	**1.253(2)**	C1—O2	1.256
	C7—O3	**1.250(2)**	C7—O3	1.251
	C7—O4	**1.228(1)**	C7—O4	1.265
Sr—(bridging, chain)—Sr (Å)	Sr—(O1, O1’)—Sr	4.229(1)	Sr—(O3, O1w)—Sr	4.238(2)
	Sr—(O2, O2’)—Sr	3.992(1)	Sr—(O2, O2’)—Sr	4.167(2)
	Sr—(O2w, O2w’) ··· Sr	5.080(2)	-	-
	Interlayer distance	13.294(6)	Interlayer distance	12.612(2)

Table S3: Selected angles from the crystal structures of **1** and **2**.

		[Sr(*o*BDC-F_4)(H_2O)$_2$] (1)		[{Sr(*o*BDC)(H_2O)$_2$}·H_2O] (2)
	O1—Sr—O1′	69.62(5)	**O1—Sr—O2**	**45.106(2)**
	O1—Sr—O2	**49.434(4)**	O1—Sr—O2‘	110.006(4)
	O1—Sr—O2′	125.172(8)	O1—Sr—O3	136.014(5)
	O1—Sr—O3	89.429(6)	O1—Sr—O3‘	125.254(5)
	O1—Sr—O4	81.212(5)	O1—Sr—O4	105.091(4)
	O1—Sr—O1w	144.329(7)	O1—Sr—O1w	67.352(3)
	O1—Sr—O2w	124.110(7)	O1—Sr—O1w‘	78.270(3)
	O1—Sr···O2w′	65.003(4)	O1—Sr—O2w	53.060(2)
	O1′—Sr—O2	116.526(8)	O2—Sr—O2′	74.960(3)
	O1′—Sr—O2′	162.084(1)	O2—Sr—O3	146.892(5)
	O1′—Sr—O3	88.781(6)	O2—Sr—O3′	131.647(5)
	O1′—Sr—O4	124.614(8)	O2—Sr—O4	71.198(3)
	O1′—Sr—O1w	81.633(6)	O2′—Sr—O3	113.700(5)
O—Sr—O (°)	O1′—Sr—O2w	79.834(5)	O2′—Sr—O3‘	66.834(3)
	O1′—Sr···O2w′	68.865(44)	O2′—Sr—O4	78.913(3)
	O2—Sr—O2′	76.061(5)	**O2′—Sr—O1w**	**150.260(54)**
	O2—Sr—O3	76.049(5)	O2′—Sr—O1w′	138.287(5)
	O2—Sr—O4	66.853(4)	O2′—Sr—O2w	79.242(4)
	O2—Sr—O1w	140.031(7)	O3—Sr—O3‘	78.033(3)
	O2—Sr—O2w	146.083(7)	O3—Sr—O4	125.745(5)
	O2—Sr··O2w′	96.112(6)	O3—Sr—O1w	140.382(5)
	O3—Sr—O4	138.076(7)	O3—Sr—O1w′	75.169(3)
	O3—Sr—O1w	68.728(4)	O3—Sr—O2w	73.841(3)
	O3—Sr—O2w	136.446(7)	O4—Sr—O1w	73.684(3)
	O3—Sr··O2w′	**150.287(7)**	O4—Sr—O1w‘	140.186(5)
	O4—Sr—O1w	133.831(7)	O4—Sr—O2w	139.855(5)
	O4—Sr—O2w	79.374(5)	O1w—Sr—O1w‘	71.34(3)
	O4—Sr··O2w′	56.164(4)	O1w—Sr—O2w	115.331(4)

Table S3: Selected angles from the crystal structures of **1** and **2**.

		[Sr(*o*BDC-F_4)(H_2O)$_2$] (1)		[{Sr(*o*BDC)(H_2O)$_2$}·H_2O] (2)
O—C—O (carboxyl) (°)	O1—C8—O2	127.308(2)	O1—C1—O2	122.670(1)
	O3—C7—O4	123.910(2)	O3—C7—O4	123.911
	O1—Sr—O2 (chelate)	49.434(4)	O1—Sr—O2 (chelate)	45.106(2)
	Sr—O1—Sr (bridge)	110.374(6)		
Sr—(bridging)—Sr (°)	Sr—O2—Sr (bridge)	103.939(6)	Sr—O2—Sr (bridge)	105.04(4)
	Sr—C7(O3,O4)—Sr (bridge)	67.575(4)	Sr—O3—Sr (bidentate)	106.531(4)
			Sr—C7(O3,O4)—Sr (bridge)	73.375(3)
			Sr—C7(O3,O4)—Sr (bridge)	118.741(3)

Table S4. EXAFS fit parameters for the compounds **1** and **2**. The root mean square error (RMSE) is 0.03 For **1** and 0.0002 for **2.**

	[Ca(*o*BDC-F_4)(H_2O)$_2$] (**1**)				[{Sr(*o*BDC)(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)
Sr—O1	**2.426(2)**	2.259	0.028	Sr—O1	2.968(1)	2.976	0.000064
Sr—O1’	**2.774(1)**	2.601	0.030	Sr—O2	**2.443(1)**	2.451	0.000064
Sr—O2	2.437(2)	2.259	0.032	Sr—O2‘	**2.800(1)**	2.808	0.000064
Sr—O2’	2.667(1)	2.502	0.027	Sr—O3	2.603(1)	2.623	0.0004
Sr—O3	2.671(1)	2.502	0.029	Sr—O3’	2.685(1)	2.694	0.000081
Sr—O4	2.573(1)	2.400	0.030	Sr—O4	2.550(1)	2.558	0.000064
Sr—O1w	2.732(1)	2.560	0.030	Sr—O1w	2.628(1)	2.623	0.000025
Sr—O2w	2.688(1)	2.502	0.035	Sr—O1w’	2.720(1)	2.728	0.000064
Sr—O2w’	3.183(2)	3.010	0.030	Sr—O2w	2.687(1)	2.694	0.000049
Average (Å)	2.683	2.510			2.676	2.684	
RMSE			0.030				0.00018
R-Factor			0.007				0.014
Reduced chi-square (X^2)			858.893				6800.510

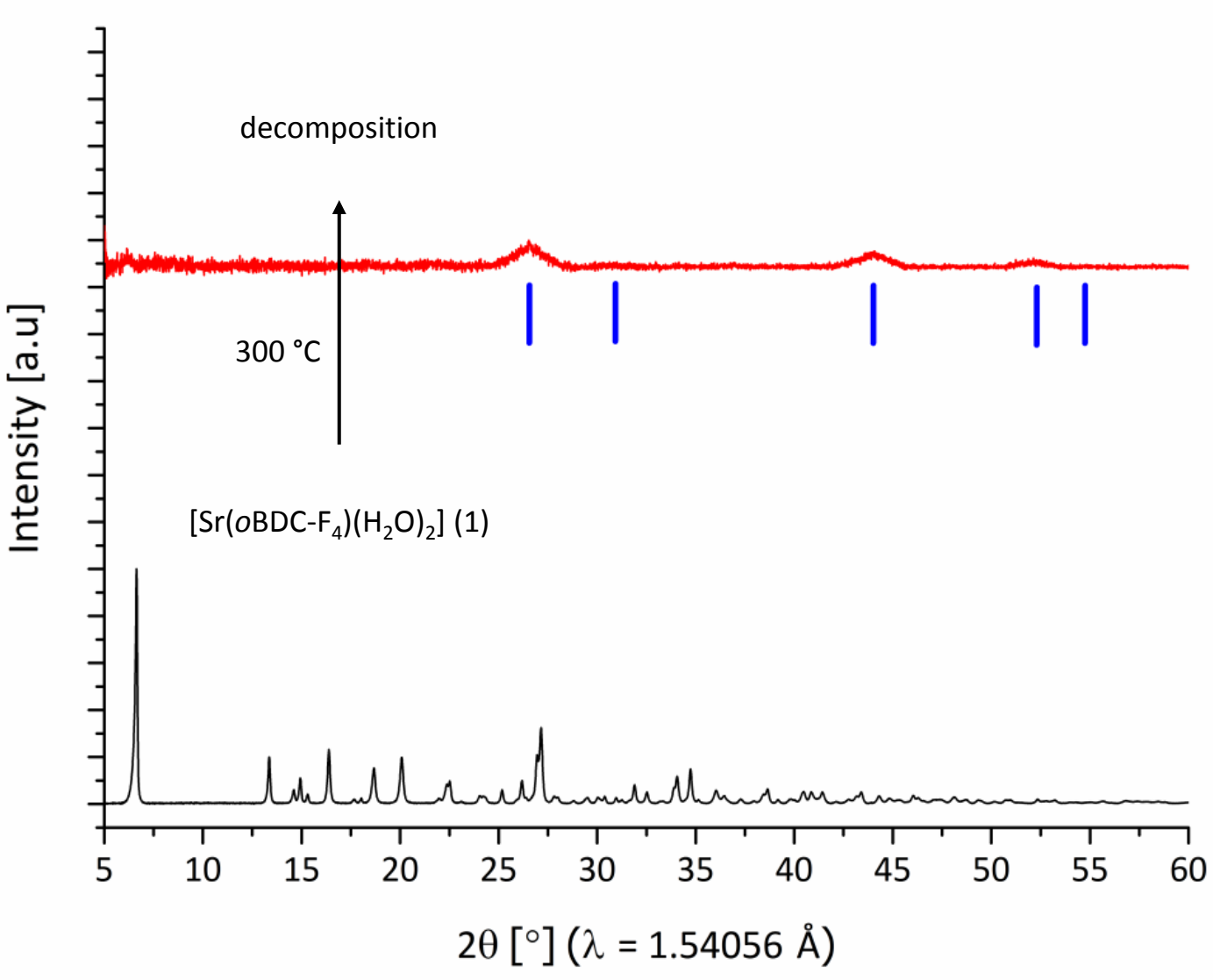


Figure S3. PXRD patterns of compound **2** as-synthesized (black PXRD pattern) and the decomposed compound after thermal post-treatment at 300 °C (red PXRD pattern). The PXRD pattern of sample of **1** after decomposition is compared to the standard X-ray lines for SrF2 from the 00-001-0644 card (blue vertical lines).

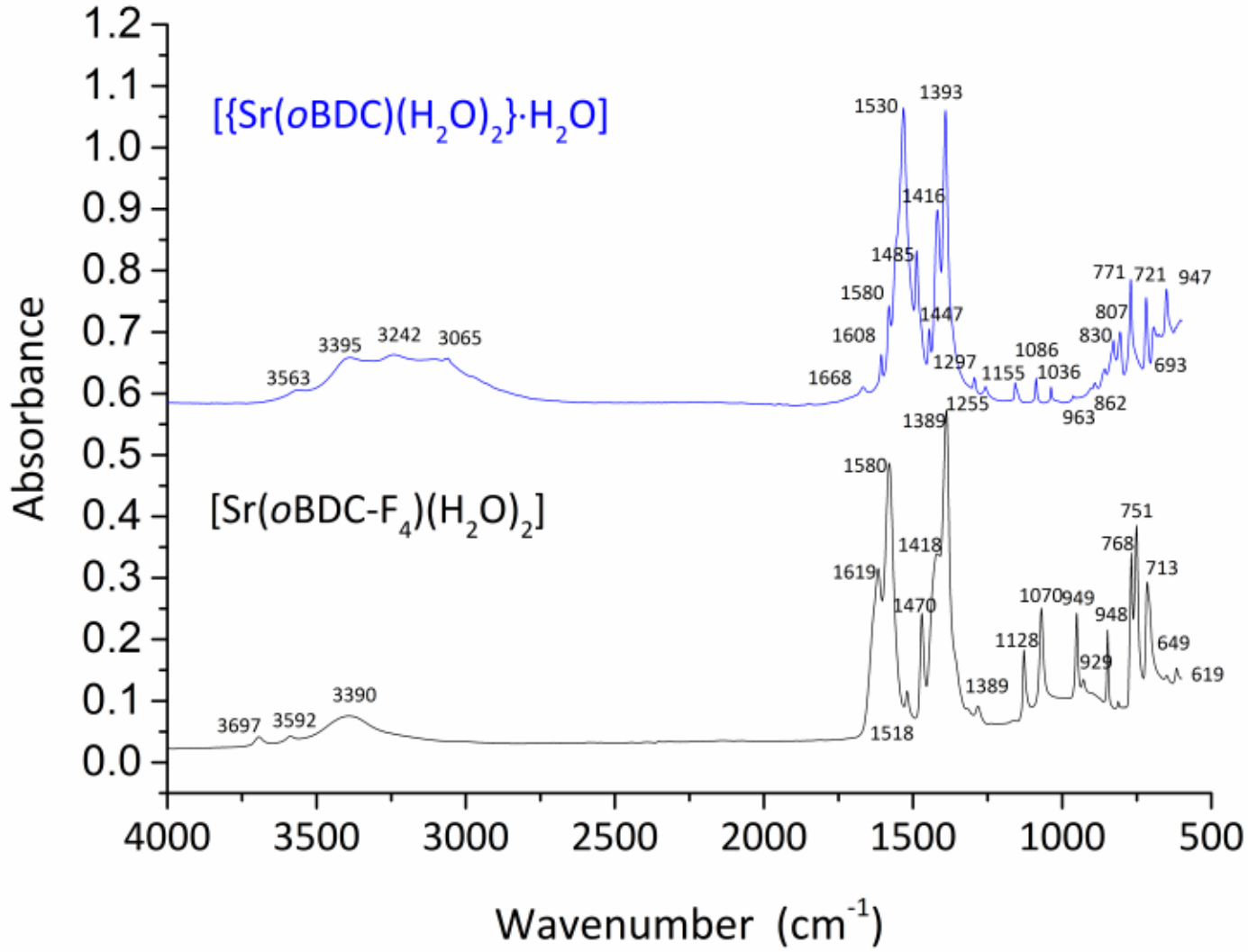
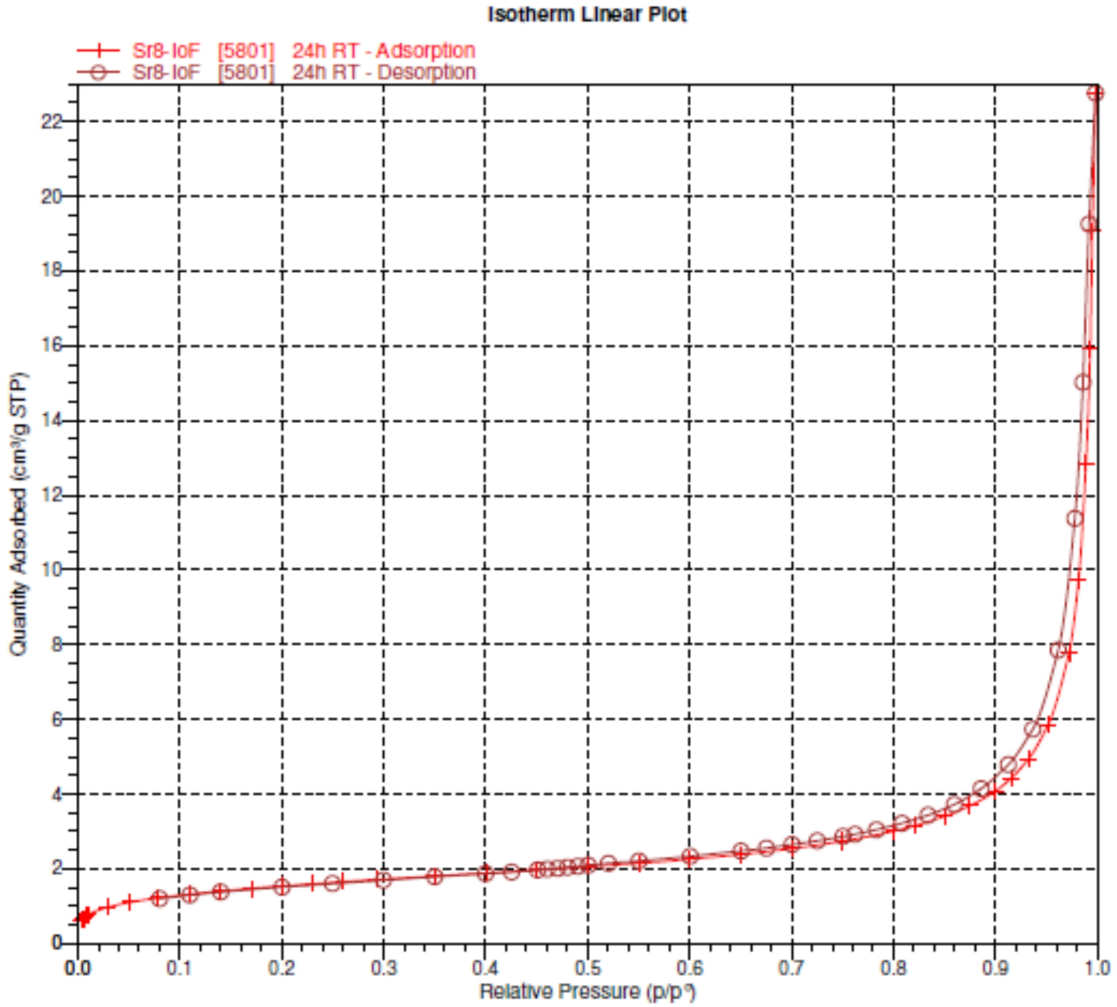
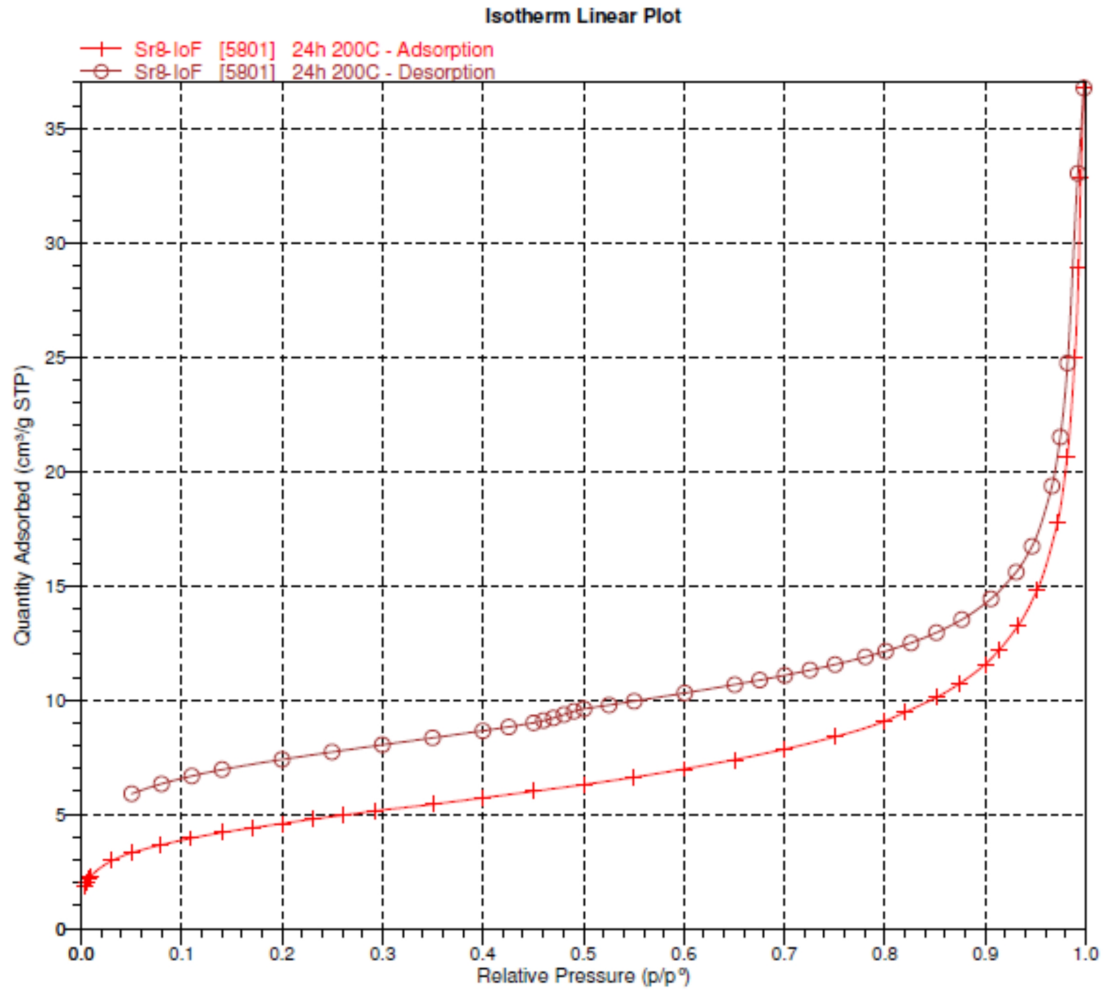


Figure S4. The ATR-IR spectra of compound **1** (black spectrum) and compound **2** (blue spectrum).

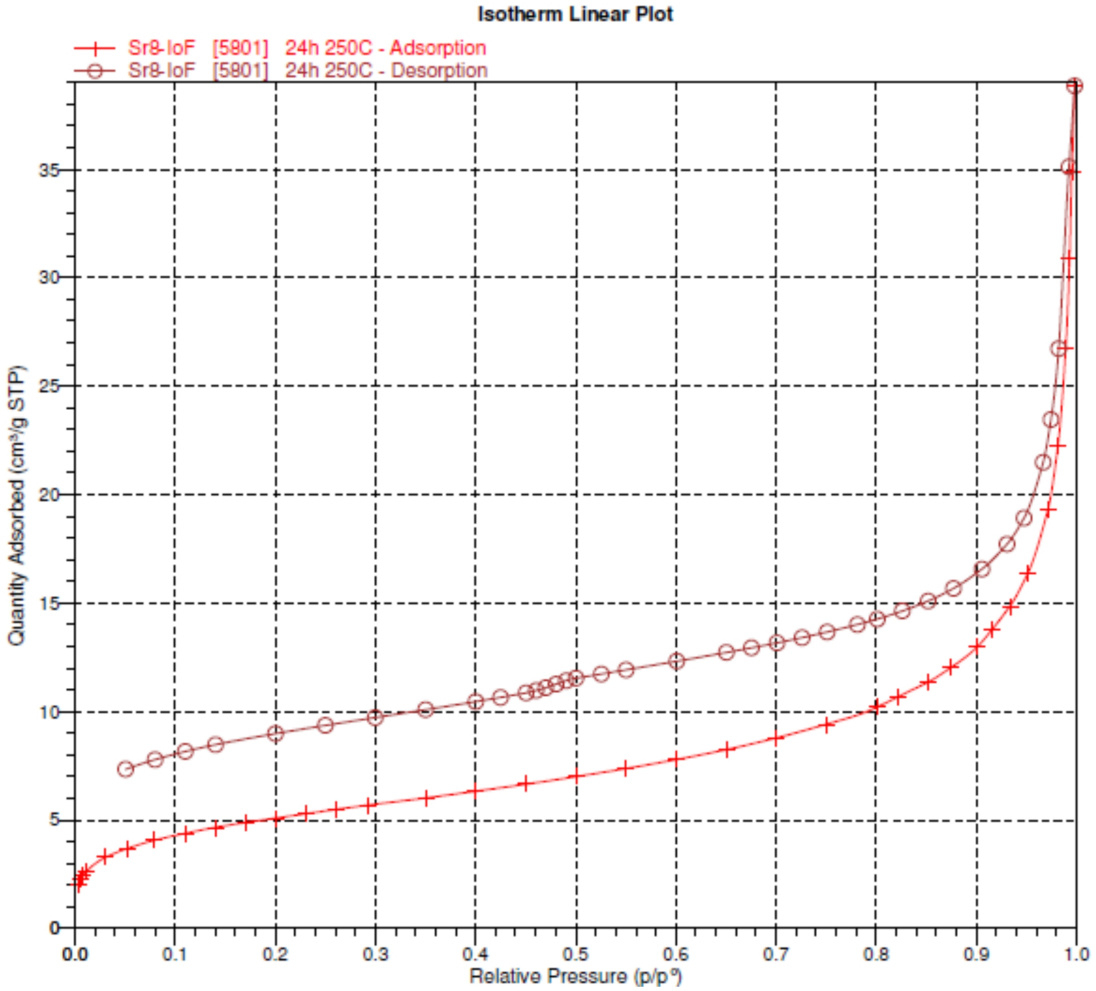


a



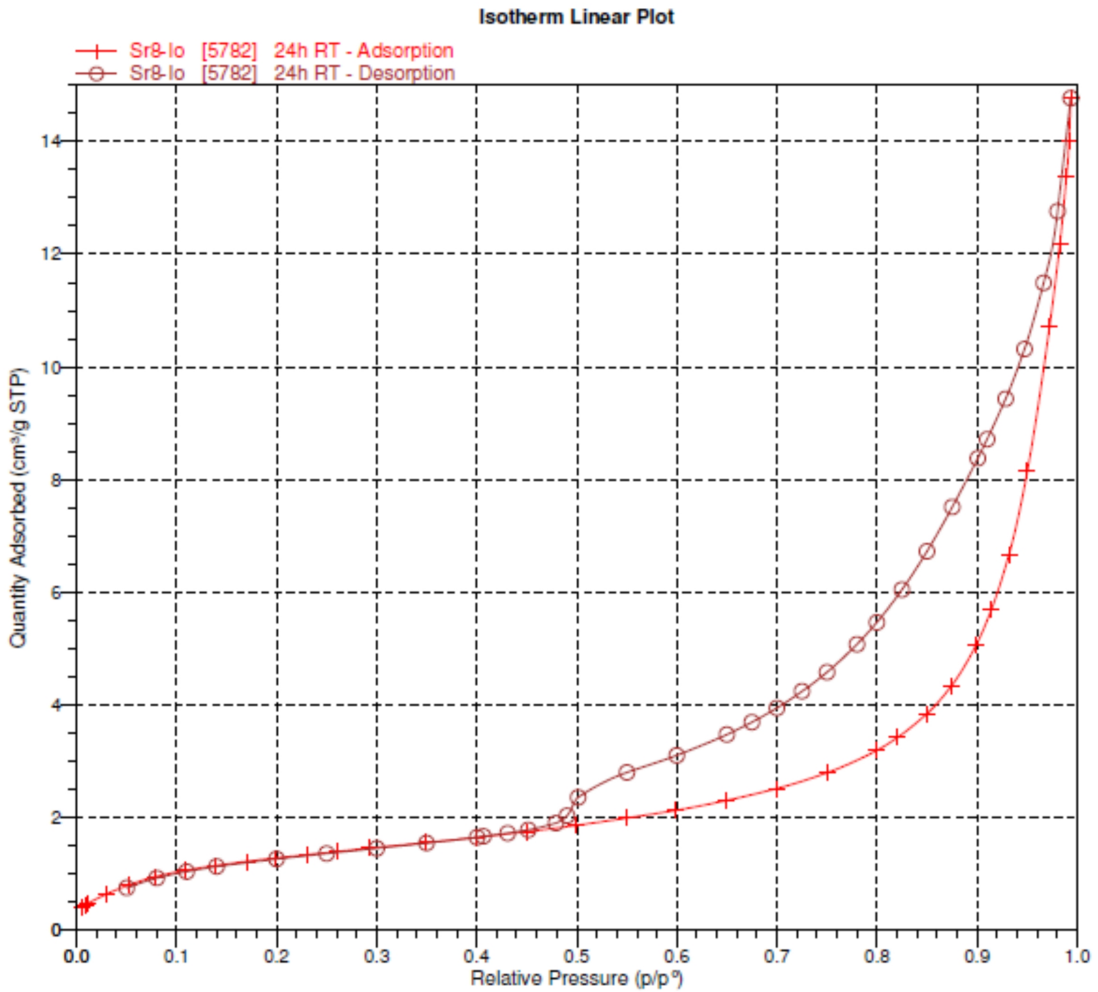
b

Figure S5. Isotherm curves of the compound **1**. Adsorption (crosses) and desorption pore volume (circles) isotherm for nitrogen at room temperature (a), at 200 °C (b), and at 250 °C (c).



c

Figure S5. Isotherm curves of the compound **1**. Adsorption (crosses) and desorption pore volume (circles) isotherm for nitrogen at room temperature (a), at 200 °C (b), and at 250 °C (c).



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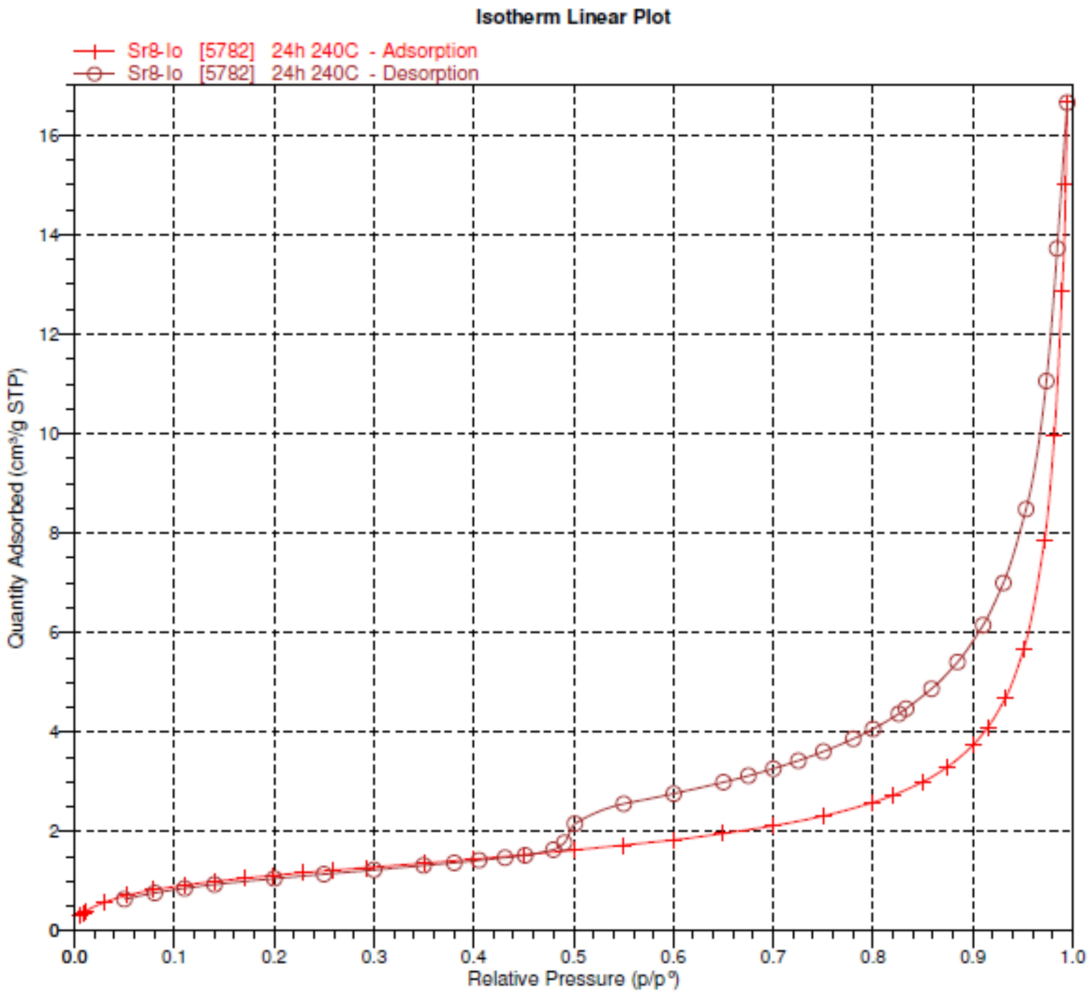
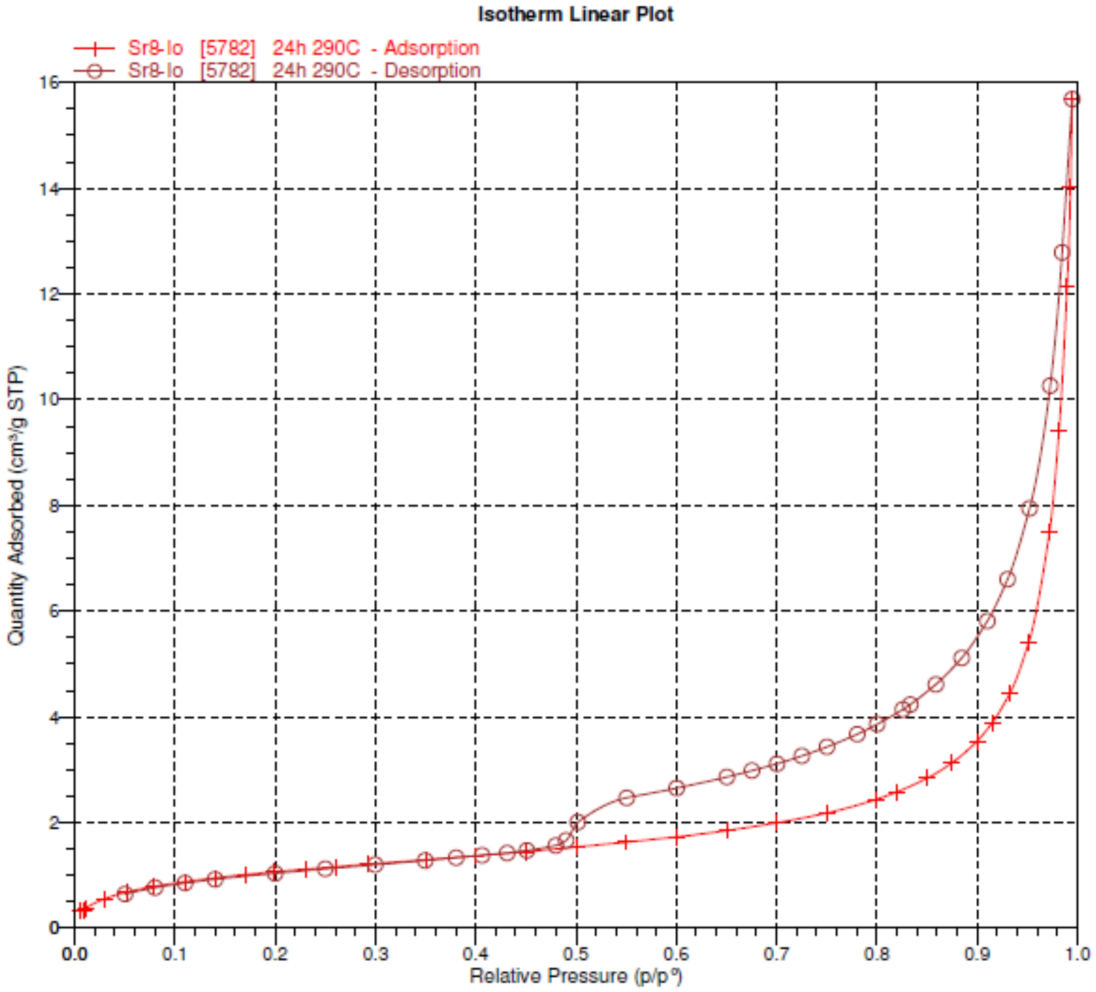


b

Figure S6. Isotherm curves of the compound **2**. Adsorption (crosses) and desorption pore volume (circles) isotherm for nitrogen at room temperature (a), at 240 °C (b), 290 °C (c), and at 390 °C (d)



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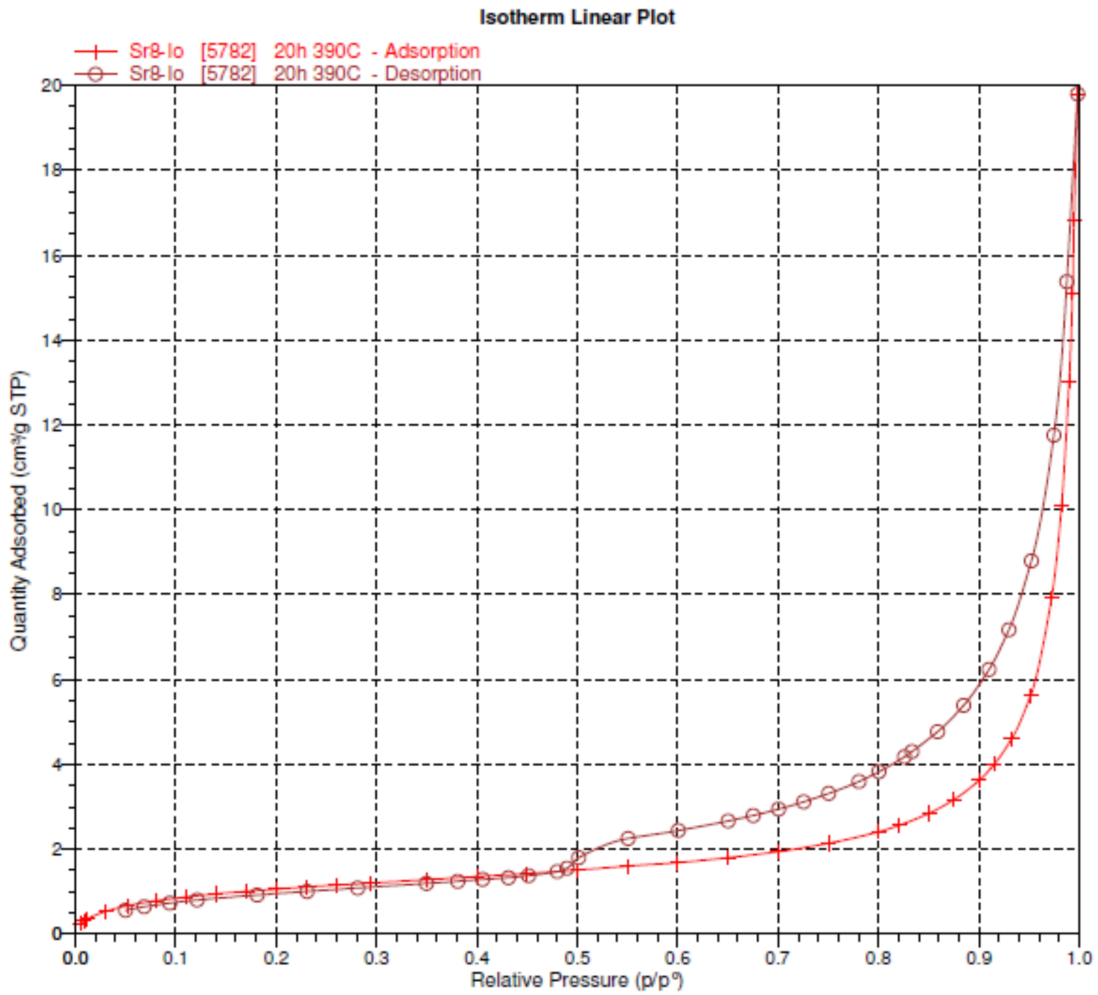
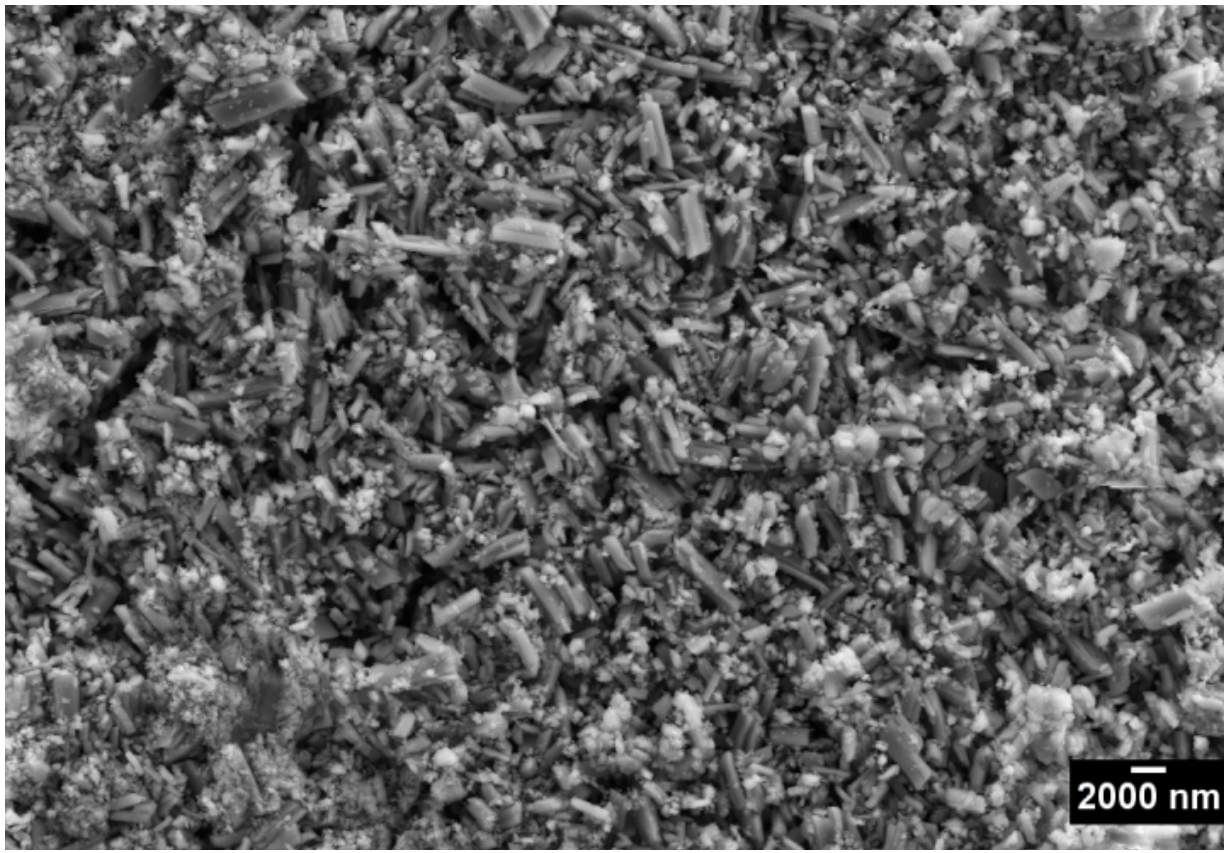


d

Figure S6. Isotherm curves of the compound **2**. Adsorption (crosses) and desorption pore volume (circles) isotherm for nitrogen at room temperature (a), at 240 °C (b), 290 °C (c), and at 390 °C (d)



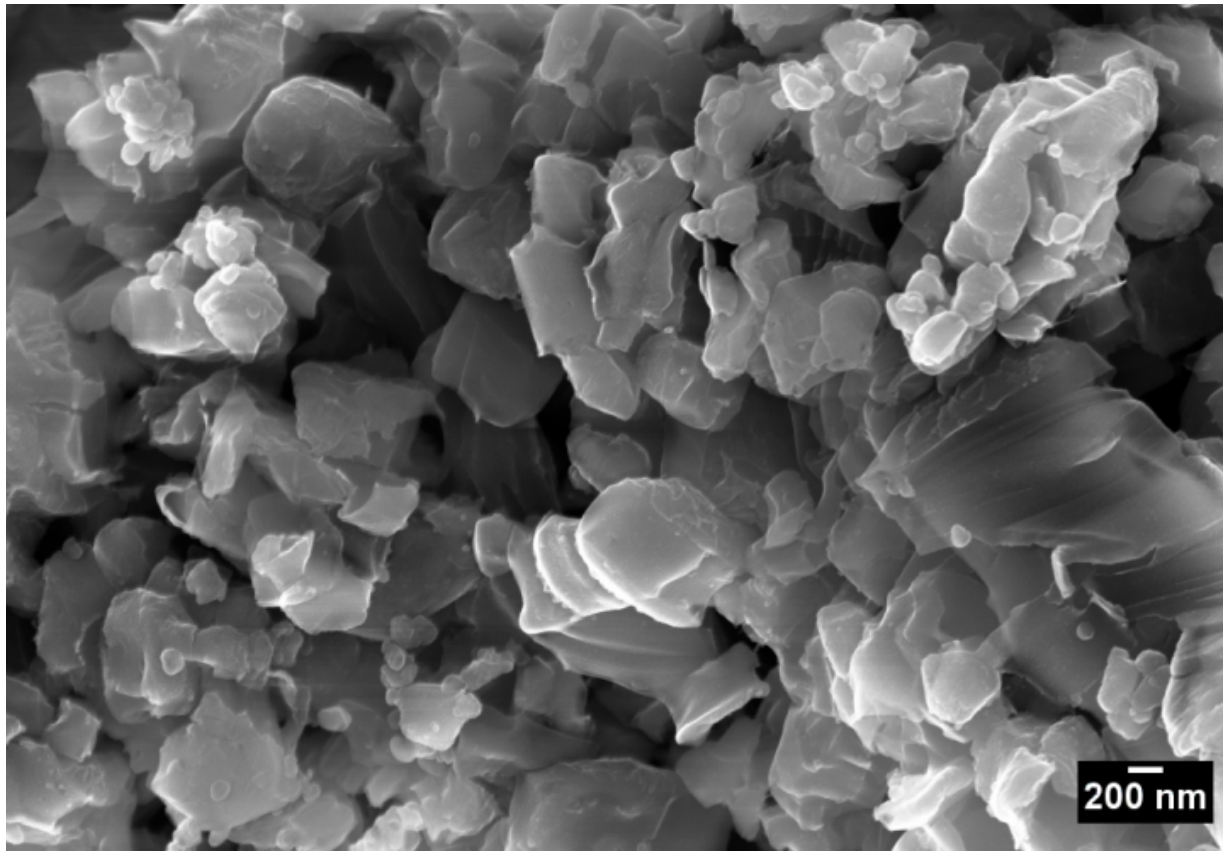


Figure S7. SEM images for [Sr(*o*BDC-F_4)(H_2O)$_2$] (**1**).

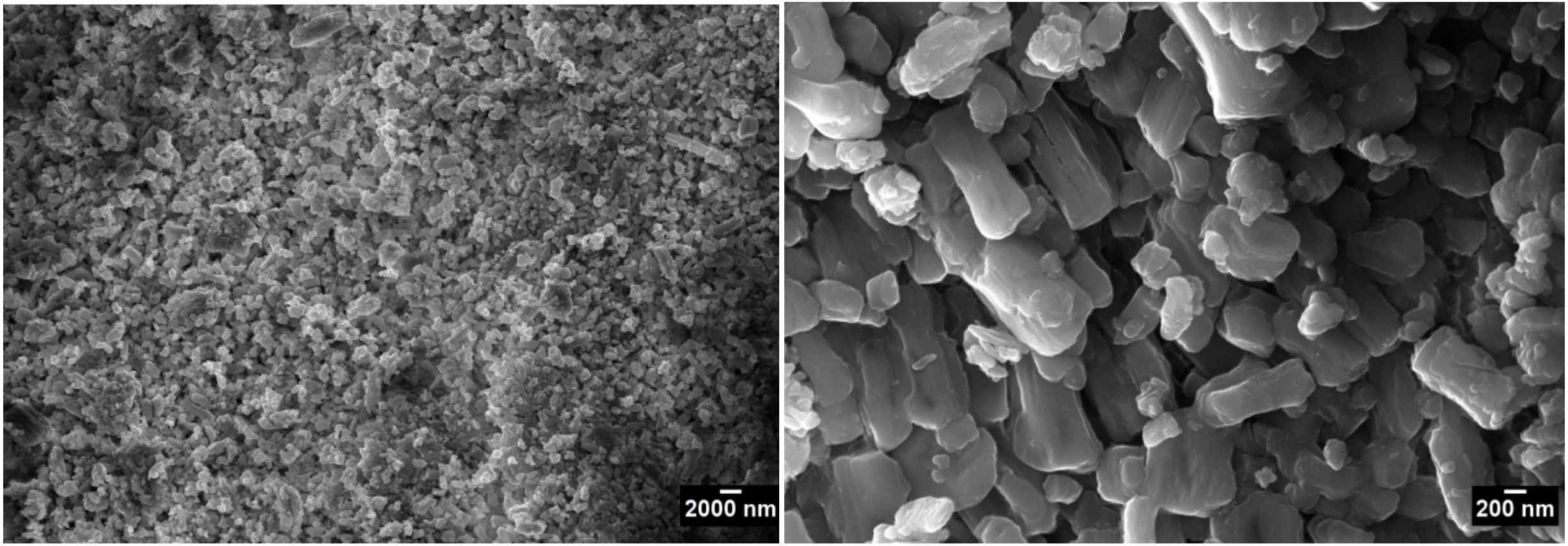


Figure S8. SEM images for [{Sr(*o*BDC)(H_2O)$_2$}·H_2O] (**2**).