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Hydrated and Dehydrated Ca-Coordination Polymers based on Benzene-Dicarboxylates: Mechanochemical Synthesis, Structures Refinement, and Spectroscopic Characterization.

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Supporting Information

Table S1. Elemental analysis and BET surface areas (S_{BET}) of compounds [Ca(*o*BDC)(H_2O)] (**1**), [Ca(*o*BDC)] (**1-H_2O**), [Ca(*m*BDC)(H_2O)$_{3.4}$] (**2**), and [Ca(*m*BDC)] (**2-H_2O**). For BET measurements, the samples were degassed for 24 h at room temperature (r.t.) and after thermal pretreatments at different temperatures. All samples were measured by liquid N_2.

	1	**1-H_2O** (at 290 ˚C)	**2**	**2-H_2O** (at 240 ˚C)	**2-H_2O** (at 260 ˚C)
C% found (calc.)	43.1 (43.2)	46.5 (47.01)	36.9 (35.9)	41.03 (47.01)	-
H% found (calc.)	2.7 (2.7)	2.02 (1.96)	3.9 (4.1)	3.09 (1.96)	-
S_{BET} ($m^2.g^{-1}$)	4.2 ± 0.02	14.3 ± 0.08	3.3 ± 0.04	4.2 ± 0.02	4.2 ± 0.03
Relative pressure (BET)	0.05 ≤ p/p˚ ≤ 0.20	0.05 ≤ p/p˚ ≤ 0.20	0.10 ≤ p/p˚ ≤ 0.30	0.05 ≤ p/p˚ ≤ 0.20	0.05 ≤ p/p˚ ≤ 0.20

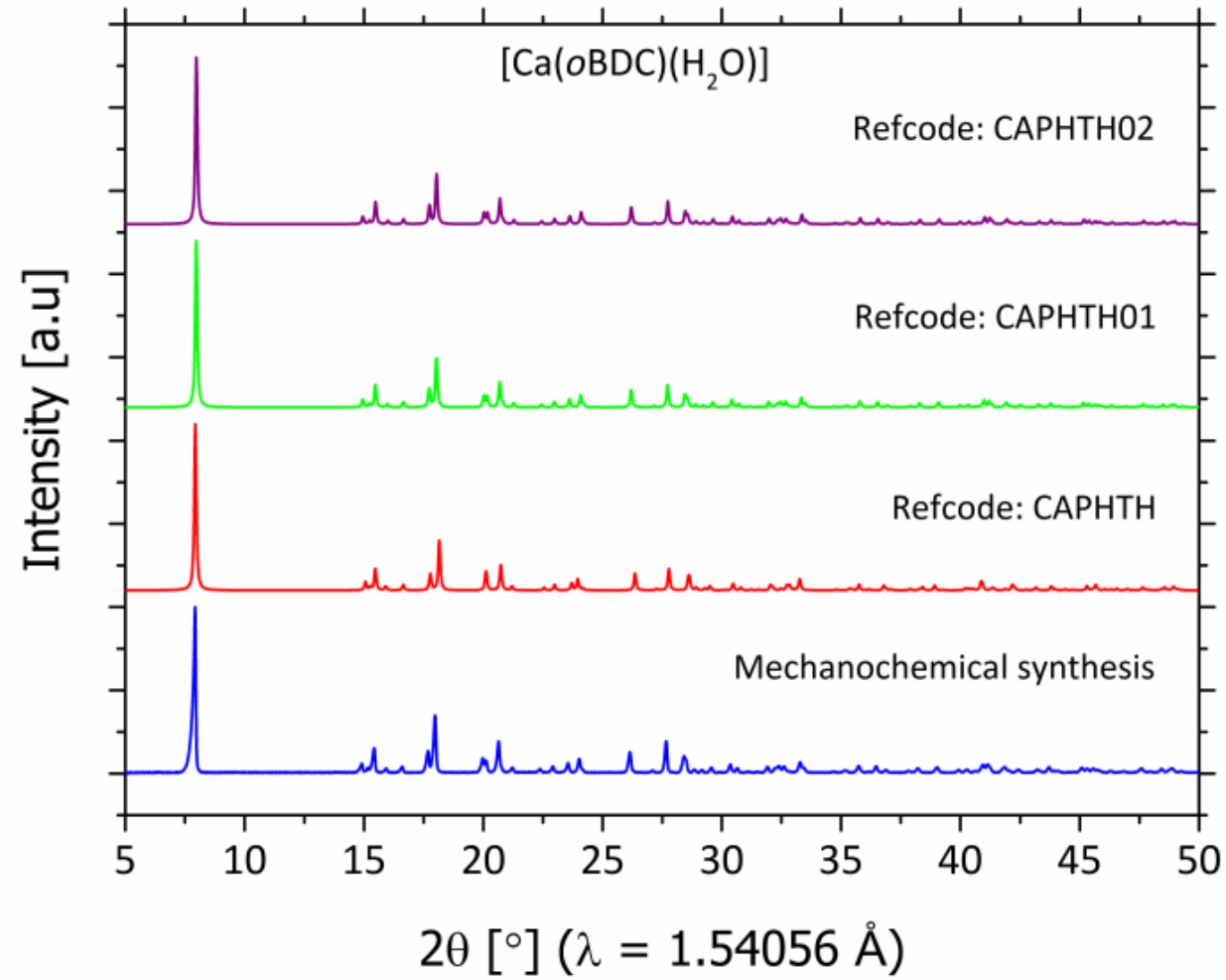


Figure S1. The PXRD patterns of [Ca(*o*BDC)(H_2O)] (**1**). The measured PXRD pattern of **1** obtained after milling (blue PXRD pattern) compared to the simulated PXRD data from the reported crystal structures by Gupta *et al.* (Refcode: CAPHTH, red PXRD pattern), Schuckmann *et al.* (Refcode: CAPHTH01, green PXRD pattern), and Zhang *et al.* (Refcode: CAPHTH02, purple PXRD pattern).

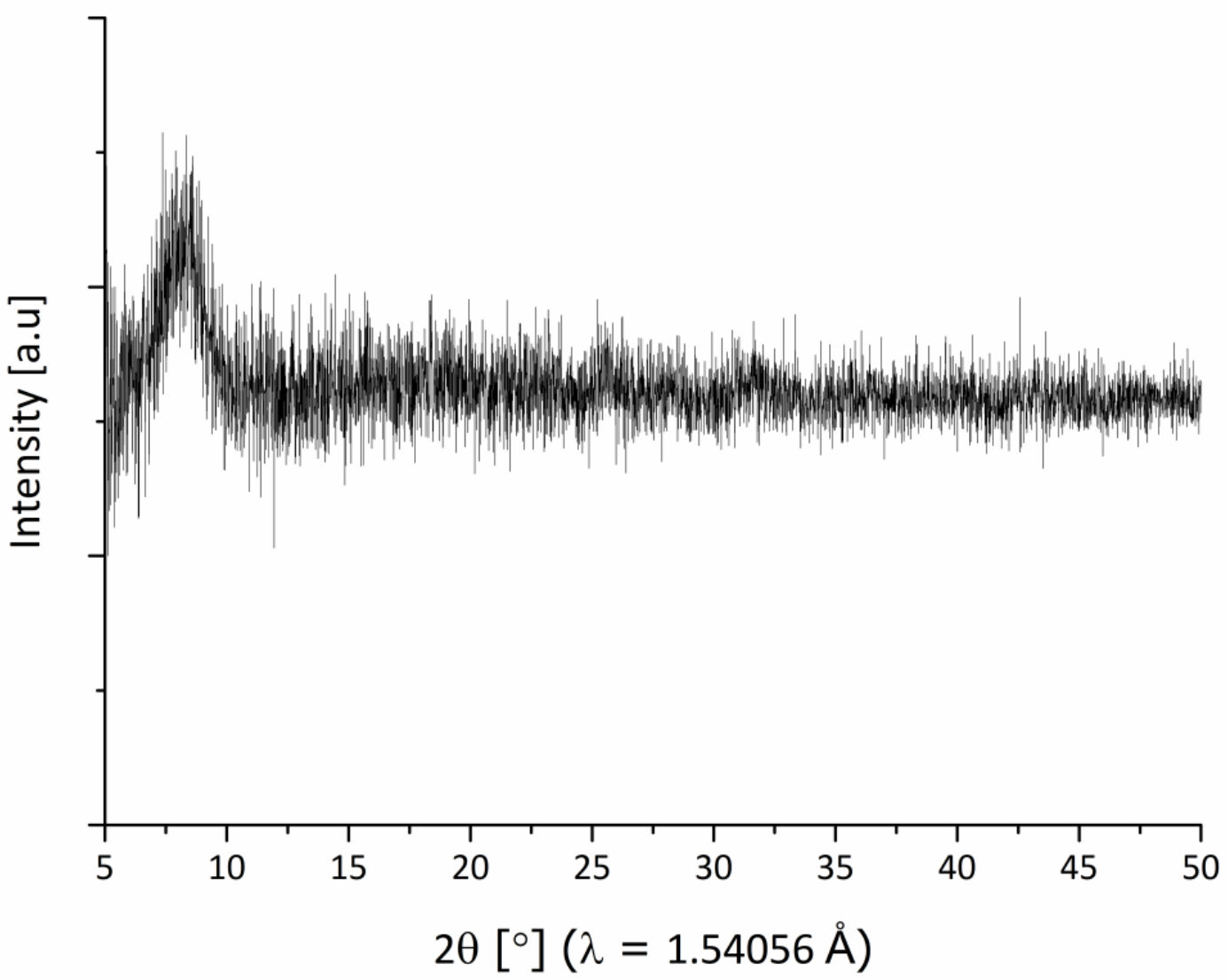


Figure S2. PXRD pattern of the amorphous product obtained by milling H_2*m*BDC and $Ca(OH)_2$ without adding water. Milling time = 4h. The molar ratio between organic and inorganic reactants was 1:1.

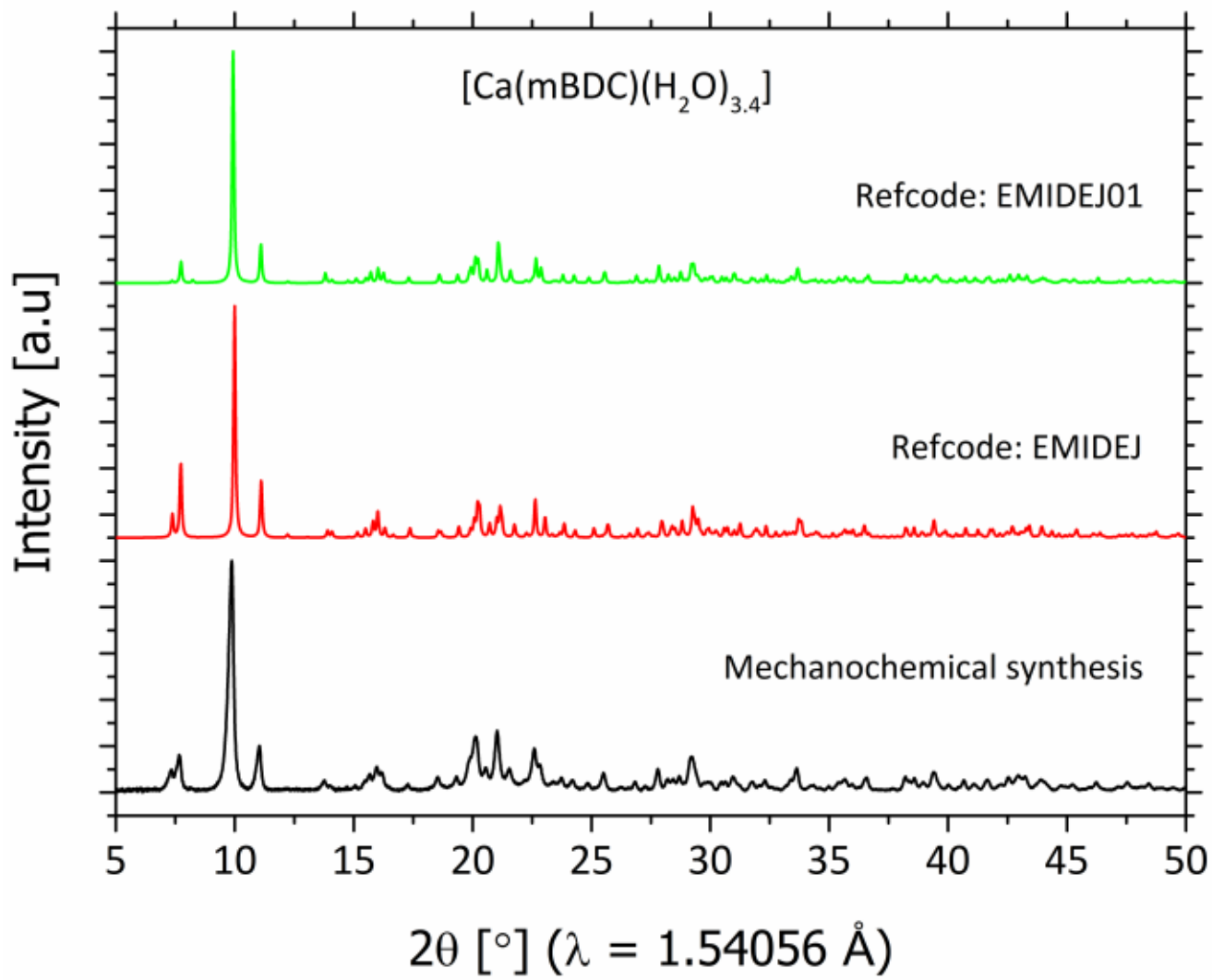


Figure S3. The PXRD patterns of [Ca(*m*BDC)(H_2O)$_{3.4}$] (**2**). The measured PXRD pattern of the mechanochemically synthesized compound (red PXRD pattern) compared to the calculated PXRD data from the two reported structure by Elsegood and coworkers (Refcode: EMIDEJ01, black PXRD pattern) and by Li and coworkers (Refcode: EMIDEJ01 , green PXRD pattern).

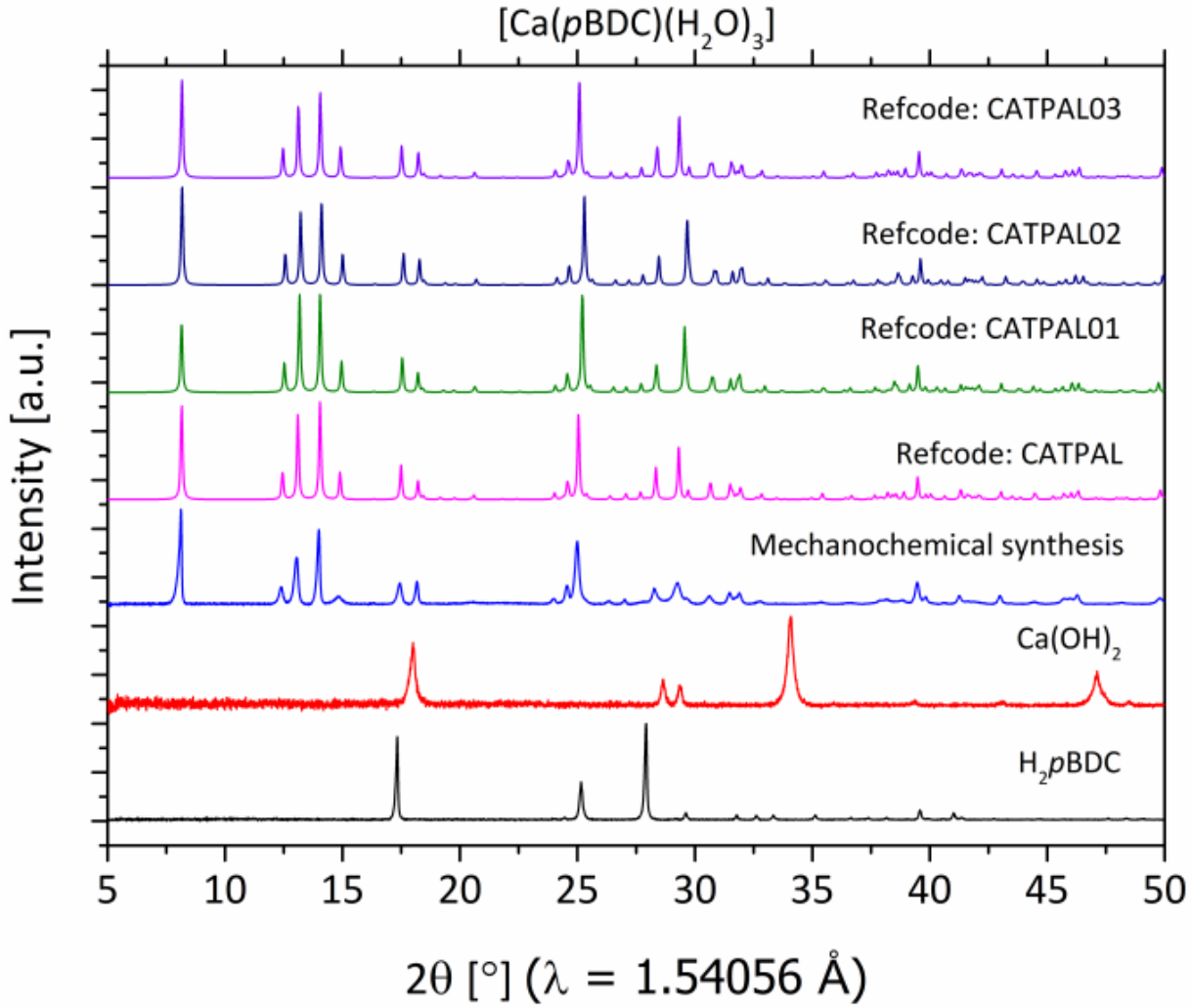


Figure S4. The PXRD patterns of the reactants H_2*p*BDC (black PXRD pattern), $Ca(OH)_2$ (red PXRD pattern), and compound [Ca(*p*BDC)(H_2O)$_3$] (**3**). The measured PXRD pattern of **3** (blue PXRD pattern) is compared to the simulated PXRD patterns from the reported crystal structures by Matsuzka *et al.* (Refcode: CAPTAL, magenta PXRD pattern), Groeneman *et al.* (Refcode: CAPTAL01, green PXRD pattern), Dale *et al.* (Refcode: CAPTAL02, dark blue PXRD pattern), and Zhang *et al.* (Refcode: CAPTAL03, dark purple PXRD pattern).

Table S2: Selected bonds, H-bonds, and distances derived from the crystal structures of **1, 1-H_2O**, **2**, and **3**.

	[Ca(*o*BDC)(H_2O)] (1)		[Ca(*o*BDC)] (1-H_2O)				[Ca(*m*BDC)(H_2O)$_{3.4}$] (2)				[Ca(*p*BDC)(H_2O)$_3$] (3)	
M—O (carboxylate) (Å)	Ca1—O1	**2.595(5)**	Ca1—O1	2.478(8)	Ca1—O1	**2.657(1)**	Ca2—O7	2.557(1)	Ca3—O12	2.549(1)	Ca1—O1	2.530(1)
	Ca1—O1′	**2.307(5)**	Ca1—O1′	**2.350(1)**	Ca1—O1′	**2.363(1)**	Ca2—O15	**2.456(1)**	Ca3—O13	**2.770(1)**	Ca1—O1′	2.351(1)
	Ca1—O2	2.486(5)	Ca1—O2	**2.633(9)**	Ca1—O2	2.525(1)	Ca2—O8	**2.452(1)**	Ca3—O12′	2.549(1)	Ca1—O2	2.492(1)
	Ca1—O2′	2.327(5)	Ca1—O2′	2.283(8)	Ca1—O5	2.535(1)	Ca2—O9	2.572(1)	Ca3—O13′	**2.770(1)**	Ca1—O2′	2.350(1)
	Ca1—O3	3.389(5)	Ca1—O3	2.662(9)	Ca1—O6	2.565(1)	Ca2—O6	2.407(1)	Ca3—O8	2.411(1)		
	Ca1—O4	2.335(4)	Ca1—O3′	2.375(1)	Ca1—O7	2.374(1)	Ca2—O12	2.330(1)	Ca3—O8′	2.411(1)		
			Ca1—O4	2.431(1)								
			Ca1—O4′	2.356(1)								
M—O (water) (Å)	Ca1—O1w	2.381(5)			Ca1—O3	2.371(1)	Ca2—O10	2.389	Ca3—O11	2.637(1)	Ca1—O1w	2.375(1)
					Ca1—O4	2.426(1)	Ca2—O11	2.463(1)	Ca3—O11′	2.637(1)	Ca1—O2w	2.637(1)
									Ca3—O14	2.345(1)	Ca1—O2w′	2.525(1)
											Ca1—O3w	2.398(1)
C—O (carboxyl) (Å)	C7—O1	1.256(5)	C7—O1	1.254(10)	C1—O1	1.271(1)	C8—O5	1.268(1)	C15—O7	1.266(1)	C7—O1	1.255(1)
	C7—O2	1.261(5)	C7—O2	1.278(9)	C1—O2	1.263(1)	C8—O6	1.263(1)	C15—O15	1.253(1)	C7—O2	1.265(1)
	C8—O3	1.262(5)	C8—O3	1.245(9)	C21—O12	1.251(1)	C20—O8	1.256(1)	C15—O7′	1.266(1)	C8—O3	1.260(1)
	C8—O4	1.252(4)	C8—O4	1.266(1)	C21—O13	1.264(1)	C20—O9	1.254(1)	C15—O15′	1.253(1)	C8—O4	1.260(1)
H–Bonds (Å)	O1w ··· O3	2.959(8)			O1w ··· O2	2.782(1)	O3w ··· O11	2.751(1)			O1 ··· O2w	2.834(1)
	O1w ··· O4	2.899(9)			O1w ··· O3	2.795(1)	O3w ··· O13	2.805(1)			O2 ··· O1w	2.812(1)
					O1w ··· O10	2.713(1)	O4w ··· O14	2.958(1)			O2 ··· O2w	2.770(1)
					O2w ··· O5	2.726(1)	O4w ··· O15	2.959(1)			O2 ··· O3w	2.816(1)
											O3 ··· O1w	2.755(1)
											O4 ··· O1w	2.762(1)
Ca ··· Ca	Ca1—(O1, O2)—Ca	3.898(3)	Ca1—(O2, O3,O4)—Ca	3.561(5)	Ca1—(O1, O1′)—Ca1	3.977(1)	Ca1—(O7, O6)—Ca2	3.875(1)	Ca2—(O8, O12, O11)—Ca3	3.641(2)	Ca1—(O1, O2, O2w)—Ca	3.640(1)
	Ca1—(O3, O4)—Ca	4.895(2)	Ca1—(O1, O1′)—Ca	3.633(5)								
	Ca··· Ca (layer)	11.221(2)										

Table S3: Selected angles derived from the crystal structures of **1, 1-H_2O**, **2**, and **3**.

	[Ca(*o*BDC)(H_2O)] (1)		[Ca(*o*BDC)] (1-H_2O)		[Ca(*m*BDC)(H_2O)$_{3.4}$] (2)		[Ca(*p*BDC)(H_2O)$_3$] (3)	
	O1—Ca—O1′	124.750(1)	O1—Ca—O1′	82.476(3)	O1—Ca1—O1‘	69.49	O1—Ca—O1′	126.148(1)
	O1—Ca—O2	**51.001(1)**	O1—Ca—O2	**51.345(3)**	O1—Ca1—O2	**50.28**	O1—Ca—O2	**51.689(1)**
	O1—Ca—O2′	71.487(2)	O1—Ca—O2‘	**154.472(3)**	O1—Ca1—O3	**76.31**	O1—Ca—O2′	71.663(1)
	O1—Ca—O3	142.403(1)	O1—Ca—O3	77.655(3)	O1—Ca1—O4	130.87	O1—Ca—O1w	148.551(1)
	O1—Ca—O4	76.938(1)	O1—Ca—O3‘	128.330(3)	O1—Ca1—O5	133.40	O1—Ca—O2w	101.723(1)
	O1—Ca—O1w	85.320(2)	O1—Ca—O4	76.077(3)	O1—Ca1—O6	155.92	O1—Ca—O2w′	68.188(1)
			O1—Ca—O4**‘**	108.139(3)	O1—Ca1—O7	91.89	O1—Ca—O3w′	93.795(1)
					O2—Ca1—O3	82.04		
	O1′—Ca—O2	73.844(2)	O1′—Ca—O2	125.393(3)	O2—Ca1—O4	83.59	O1′—Ca—O2	78.672(1)
	O1′—Ca—O2′	90.629(2)	O1′—Ca—O2‘	83.476(3)	O2—Ca1—O5	159.07	O1′—Ca—O2′	138.610(1)
	O1′—Ca—O3	90.629(2)	O1′—Ca—O3	80.672(3)	O2—Ca1—O6	136.80	O1′—Ca—O1w	83.542(1)
	O1′—Ca—O4	94.023(2)	O1′—Ca—O3‘	128.473(4)	O2—Ca1—O7	77.89	O1′—Ca—O2w	68.960(1)
	O1′—Ca—O1w	83.329(2)	O1′—Ca—O4	77.073(3)	O3—Ca1—O4	82.13	O1′—Ca—O2w′	147.007(1)
			O1′—Ca—O4**‘**	144.982(4)	O3—Ca1—O5	79.87	O1′—Ca—O3w	72.592(1)
					O3—Ca1—O6	**124.35**		
	O2—Ca—O2′	121.024(2)	O2—Ca—O2′	150.095(3)	O3—Ca1—O7	159.86	O2—Ca—O2′	128.457(1)
O—Ca—O (°)	O2—Ca—O3	**157.254()2**	O2—Ca—O3	110.413(3)	O4—Ca1—O5	83.59	O2—Ca—O1w	**142.664(1)**
	O2—Ca—O4	75.482(2)	O2—Ca—O3′	78.164(3)	O4—Ca1—O6	69.25	O2—Ca—O2w	65.282(1)
	O2—Ca—O1w	81.290(2)	O2—Ca—O4	66.009(3)	O5—Ca1—O6	51.17	O2—Ca—O2w′	96.573(1)
			O2—Ca—O4′	83.565(3)	O5—Ca1—O7	119.49	O2—Ca—O3w	99.133(1)
					O6—Ca1—O7	71.46		
	O2′—Ca—O3	79.198(2)	O2′—Ca—O3	79.139(3)	O6—Ca2—O7	71.09	O2′—Ca—O1w	85.683(1)
	O2′—Ca—O4	106.082(2)	O2′—Ca—O3′	76.832(3)	O6—Ca2—O10	119.96	O2′—Ca—O2w	146.683(1)
	O2′—Ca—O1w	82.342(2)	O2′—Ca—O4	121.023(3)	O6—Ca2—O11	152.18	O2′—Ca—O2w′	68.886(1)
			O2′—Ca—O4′	73.119(3)	O6—Ca2—O12	81.76	O2′—Ca—O3w	72.486(1)
					O6—Ca2—O15	116.79		
	O3—Ca—O4	89.479(2)	O3—Ca—O3′	138.766(3)	O7—Ca2—O8	160.46	O1w—Ca—O2w	77.758(1)
	O3—Ca—O1w	113.936(2)	O3—Ca—O4	147.415(3)	O7—Ca2—O9	122.62	O1w—Ca—O2w	81.010(1)
			O3—Ca—O4′	69.758(3)	O7—Ca2—O10	84.88	O1w—Ca—O3w	106.477(1)
					O7—Ca2—O11	127.58		
	O4—Ca—O1w	156.405(2)	O3′—Ca—O4	73.633(3)	O7—Ca2—O12	96.69	O2w—Ca—O2w′	79.332(1)
			O3′—Ca—O4′	71.430(3)	O7—Ca2—O15	51.93	O2w—Ca—O3w	140.578(1)
					O12—Ca3—O13	48.40		
			O4—Ca—O4′	137.444(3)	O8—Ca2—O11	144.83	O2w′—Ca—O3w	139.945(1)

Table S4. Coordination**,** crystal data, and refinement parameters for compound [Ca(*o*BDC)(H_2O)] (**1**) obtained after milling and the reported crystal structures by Gupta *et al.* (Refcode: CAPHTH), Schuckmann *et al.* (Refcode: CAPHTH01), and Zhang *et al.* (Refcode: CAPHTH02)..

	[Ca(*o*BDC)(H_2O)] (**1**)	Refcode: CAPHTH	CAPHTH01	CAPHTH02
Method	Mechanochemical synthesis	hydrothermal	hydrothermal	Solvothermal
Reactants	$Ca(OH)_2$ + H_2*o*BDC (1:1) / 130 µL H_2O	CaCO3 + H2oBDC / boiling water	$CaCO_3$ + H_2oBDC / boiling water	$Ca(NO_3)_2$ + H_2*o*BDC (DMF/H_2O)
Structure refinement	From powder X-ray data	Single crystal	Single crystal	Single crystal
C.N.			CaO_7	
O (carboxyl)			6O (from 4 ligand anions)	
Coordinating H_2O molecules			1	
Coordination mode (Ligand)			4 metals (chelate, bridge)	
Ca—O (Å)	2.307(5) — 2.595(5)	2.3137 – 2.3812	2.303 – 2.595	2.379(2) – 2.592(2)
O—Ca—O angle (°)	51.001(1) – 157.254(2)	50.72 -´157.38	51.11 – 157.35	51.00(69) – 157.25(7)
Ca—(chain)—Ca (Å)	Ca– (O1,O2)–Ca = 3.898(3)	3.890	3.896	3.894
Formula sum			$(CaC_8H_6O_5)_4$	
Crystal system			Monoclinic	
Space group			P 1 2_1 /c 1 (14) centrosymmetric	
Cell volume (Å^3)	888.59	884.30	887.1(11)	885.61(10)
Unit cell parameters, a, b, c (Å), α, β, γ (°)	a = 11.2207(3), b = 6.68473(16), c = 11.9906(3), α = γ = 90° , β = 98.8862(8)°	a = 11.280, b = 6.670, c = 11.910, α = γ = 90° , β = 99.30°	a = 11.213(8), b = 6.680(5), c = 11.988(8), α = γ = 90° , β = 98.91(5)°	a = 11.2023(7), b = 6.6774(4), c = 11.9840(8), α = γ = 90° , β = 98.910(7)°
Cell ratio	a/b = 1.6786, b/c = 0.5575, c/a = 1.0686	a/b = 1.6912, b/c = 0.5600, c/a = 1.0559	a/b = 1.6786, b/c = 0.5572, c/a = 1.0691	a/b = 1.6776, b/c = 0.5572, c/a = 1.0698
Z	4	4	4	4
λ (Å)	Cu-$K_{α1}$		Mo-$K_{α1}$	Mo-$K_{α1}$
R_{wp}, R_p,R_{Bragg}, GOF	2.28, 2.62, 1.143, 2.19	R-Factor (%) = 8.2	R-Factor (%) = 2.9	R-Factor (%) = 2.93

Table S5. Synthesis**,** Crystal data, and refinement parameters of compound **(2)** obtained by milling and the reported structures by Elsegood and coworkers (Refcode: EMIDEJ01) and by Li and coworkers (Refcode: EMIDEJ01).

	[Ca(*m*BDC)(H_2O)$_{3.4}$] (**2**)	Refcode: EMIDEJ01	Refcode: EMIDEJ
Synthesis	Mechanochemical synthesis	hydrothermal	hydrothermal
Reactants / solvent	$Ca(OH)_2$ + H_2*m*BDC + 130 µL H_2O	$Ca(OH)_2$ + 1,3-Dicyanobenzene / H_2O	$CaCO_3$ + H_2*m*BDC / H_2O
C.N.		8 (Ca1, Ca2) / 9 (Ca3)	
Oxygen-Carboxylate		6 O (from 4 organic linkers), for each metal	
Coordinating water molecules		Ca1: 2 terminal, Ca2: 1 terminal and 1 bridging, Ca3: 1 terminal and 2 bridging	
Co-crystallized water		4	
Modes (Ligand)		4 metals (chelate, bridge)	
M□O (carboxylate) (Å)	2.3626(1) – 2.6567(1)	2.3297(8) – 2.7643(12)	2.3252(12) – 2.7746(13)
M□O (water) (Å)	2.3446(1) – 2.6373(1)	2.344(2) – 2.5631(9)	2.3568(13) – 2.5800(16)
O—Ca—O angle (°)		50.22(3) – 160.44(3)	51.32(4) – 160.27(4)
Ca—(chain)—Ca (Å)		3.640, 3.870, 3.969	3.659, 3.887, 3.985
Formula sum	$Ca_{20}O_{148}C_{160}H_{80}$	$(Ca_5O_{37}C_{40}H_{54})_4$	$Ca_{20}O_{148}C_{160}H_{80}$
Cell mass (g/mol)	5171.818	5232.34	5376.97
Crystal system		Monoclinic	
Space group		C 1 2/c 1 (15)	
Cell volume (Å^3)	5334.1(5)	5322.1(3)	5290.32(5)
Unit cell parameters,	a=15.5899(7), b=21.4477(12), c=17.1872(8),	a=15.5701(5), b=21.4445(7), c=17.1601(6),	a=15.6289(8), b=21.2640(11), c=17.1852(9),
a, b, c (Å), α, β, γ (°)	α = γ = 90°, β=111.848(3)°	α = γ = 90°, β=111.7400(7)°	α = γ = 90°, β=112.134(2)°
Cell ratio	a/b=0.7269, b/c=1.2479, c/a=1.1025	a/b=0.7261, b/c=1.2497, c/a=1.1021	a/b=0.7350, b/c=1.2373, c/a=1.10996
Z	8	8	4
λ (Å)	Cu-$K_{\alpha1}$	Mo-$K_{\alpha1}$	Mo-$K_{\alpha1}$
R_{wp}, R_p,R_{Bragg}, GOF	2.13, 1.60, 0.571, 1.25	R-Factor (%) = 13.5	R-Factor (%) = 3.3

Table S6. Coordination**,** crystal data, and refinement parameters of compound [Ca(*p*BDC)(H_2O)$_3$] (**3**) obtained by milling and the reported crystal structures by Matsuzaki *et al.* (Refcode: CATPAL), Groeneman *et al.* (Refcode: CATPAL01), Dale *et al.* (Refcode: CATPAL02), and Zhang *et al.* (Refcode: CATPAL03), in addition to the dehydrated compound [Ca(*p*BDC)] (**3-H_2O**) by Mazaj *et al.* (Refcode: DIQGUH).

	[Ca(*p*BDC)(H_2O)$_3$] (**3**)	Refcode: CATPAL	Refcode: CATPAL01	Refcode: CATPAL02	Refcode: CATPAL03	Refcode: DIQGUH
Method	Mechanochemical synthesis	Hydrothermal	Hydrothermal	Solvothermal	Autoclave	Thermal annealing of **3**
Reactants / solvent	$Ca(OH)_2$ + H_2*p*BDC + 130 µL H_2O	$CaCO_3$ + H_2*p*BDC / boiling H_2O	$CaCl_2$ + Na_2(*p*BDC) / H_2O	$CaCO_3$ + H2pBDC (H_2O, reflux)	$Ca(NO_3)_2 \cdot 4H_2O$+ H_2*p*BDC / (DMF/H_2O)	
Structure Refinement	Powder data	Single crystal	Single crystal	Single crystal	Single crystal	Powder data
Ca—O (carboxylate/water) (Å)		2.350 – 2.642	2.351(6) – 2.642(6)	2.339(2) – 2.633(2)	2.362(3) – 2.633(3)	2.287 – 2.401
O—Ca—O angle (°)	51.001(1) – 157.254(2)	51.83 – 148.91	52.1(2) – 149.4	51.83(7) – 149.48(7)	51.68(9) – 148.57(9)	73.7 – 176.1
Ca—(distance)—Ca (Å)	Ca– (O1,O2)–Ca = 3.898(3)	3.644	3.637(2)	3.621	3.636	3.832
Formula sum	$(CaC_8H_{10}O_7)_4$	$(CaC_8H_{10}O_7)_4$	$(CaC_8H_{10}O_7)_4$	$(CaC_8H_{10}O_7)_4$	$(CaC_8H_{10}O_7)_4$	$(CaC_8H_4O_4)_4$
Crystal system	Monoclinic, $P2_1/c$ (14)	Monoclinic, $P2_1/c$ (14)	Monoclinic, $P2_1/c$ (14)	Monoclinic, $P2_1/c$ (14)	Monoclinic, $P2_1/c$ (14)	Monoclinic, C2/c (15)
Cell volume (Å^3)	1014.53(7)	1014.53(230)	1008.76(15)	998.50(34)	1010.82(13)	698.34(5)
Unit cell parameters, a, b, c (Å), α, β, γ (°)	a = 7.1114(2), b = 21.6561(9), c = 6.5925(3), α = γ = 90° , β = 92.208(5)°	a = 7.11(1), b = 21.67(2), c = 6.59(1), α = γ = 90° , β = 92.3(2)°	a = 7.0688(6), b = 21.680(2), c = 6.5903(5), α = γ = 90° , β = 92.812(2)°	a = 7.0455(15), b = 21.623(4), c = 6.5622(13), α = γ = 90° , β = 92.831(3)°	a = 7.0982(5), b = 21.6400(15), c = 6.5856(5), α = γ = 90°, β = 92.217(7)°	a = 18.843(6), b = 5.332(3), c = 6.960(3), α = γ = 90°, β = 87.005(5)°
Cell ratio		a/b=0.3281 b/c=3.2883 c/a=0.9269	a/b = 0.3261, b/c = 3.2897, c/a = 0.9323	a/b = 0.3258, b/c = 3.2951, c/a=0.9314	a/b = 0.3280, b/c = 3.2860, c/a = 0.9278	a/b = 3.5337, b/c = 0.7662, c/a = 0.3693
Z	4	4	4	4	4	4
λ (Å)	Cu-$K_{\alpha1}$	Cu-$K_{\alpha1}$	Mo-$K_{\alpha1}$	Mo-$K_{\alpha1}$	Mo-$K_{\alpha1}$	Cu-$K_{\alpha1}$
R_{wp}, R_p,R_{Bragg}, GOF	3.14, 2.00, 1.747, 3.00	R-Factor (%) = 13.5	R-Factor (%) = 11	R-Factor (%) = 5.44	R-Factor (%) = 4.85	5.60

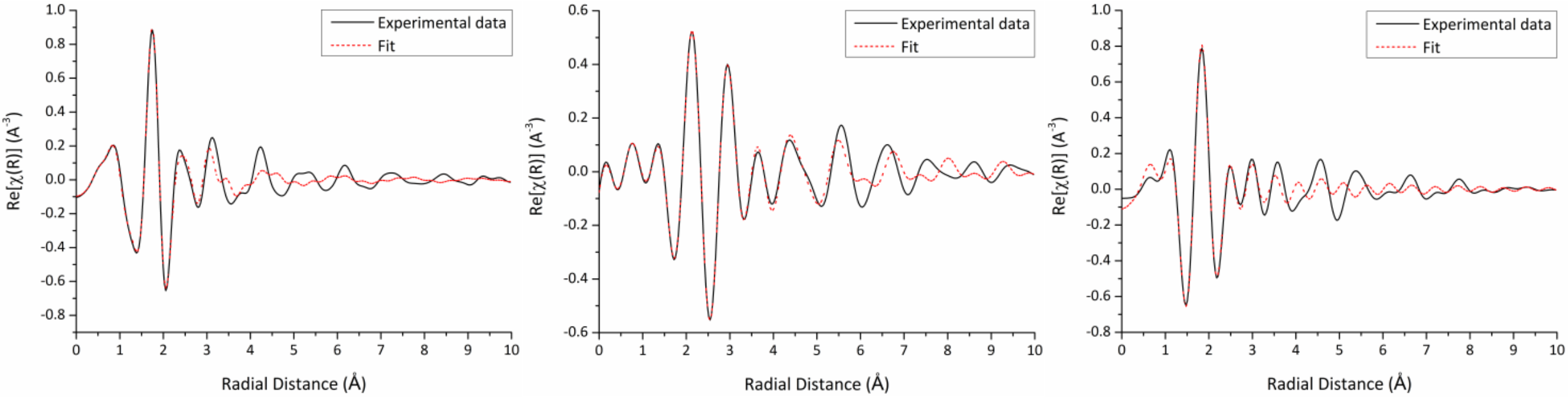


Figure S5. Ca *K*-edge EXAFS spectra shown in real space for compounds [Ca(*o*BDC)(H_2O)] **1 (a),** [Ca(*m*BDC)(H_2O)] **2 (b),** and [Ca(*p*BDC)(H_2O)$_3$] **3 (c).** The experimental data (black line) are presented along with the best fit model of the FT magnitude (red dotted line). Fit values and scattering paths are given in Table S7.

Table S7. EXAFS fit parameters and scattering paths for the compounds **1**, **2,** and **3**.

[Ca(*o*BDC)(H_2O)] (**1**)				[Ca(*m*BDC)(H_2O)$_{3.4}$] (**2**)				[Ca(*p*BDC)(H_2O)$_3$] (**3**)			
Scattering path	R_{model} (Å)	R_{fit} (Å)	R_{diff}^2 (Å)	Selected scattering path	R_{model} (Å)	R_{fit} (Å)	R_{diff}^2 (Å)	scattering path	R_{model} (Å)	R_{fit} (Å)	R_{diff}^2 (Å)
Ca1—O1	**2.59**	2.62	0.0009	$M1^{II}$–O1.1 (bridge)	2.37	2.48	0.0121	Ca1—O1	2.530	2.503	0.000729
Ca1—O1’	**2.31**	2.35	0.0016	$M1^{II}$–O1.2 (chelate)	2.66	2.77	0.0121	Ca1—O1’	2.351	2.339	0.000144
Ca1—O2	2.49	2.52	0.0009	$M1^{II}$–O2.1 (chelate)	2.53	2.64	0.0121	Ca1—O2	2.492	2.467	0.000625
Ca1—O2’	2.33	2.35	0.0004	$M1^{II}$–O3 (water)	2.37	2.48	0.0121	Ca1—O2’	2.350	2.339	0.00121
Ca1—O3	2.39	2.42	0.0009	$M1^{II}$–O4.1 (water)	2.43	2.54	0.0121	Ca1—O1w	2.375	2.339	0.001296
Ca1—O4	2.33	2.35	0.0004	$M1^{II}$–O5 (chelate)	2.53	2.64	0.0121	Ca1—O2w	2.637	2.613	0.000576
Ca1—O1w	2.38	2.42	0.0016	$M1^{II}$–O6 (chelate)	2.56	2.68	0.0144	Ca1—O2w’	2.525	2.503	0.000484
				$M1^{II}$–O7 (bridge)	2.37	2.48	0.0121	Ca1—O3w	2.398	2.374	0.000576
Average (Å)	2.40	2.48		Average (Å)	2.48	2.59			2.457	2.435	
RMSE			0.0067	RMSE			0.012				0.0007
R-factor			0.03				0.04				0.02
Reduced chi-square			662.61				374.64				576.822

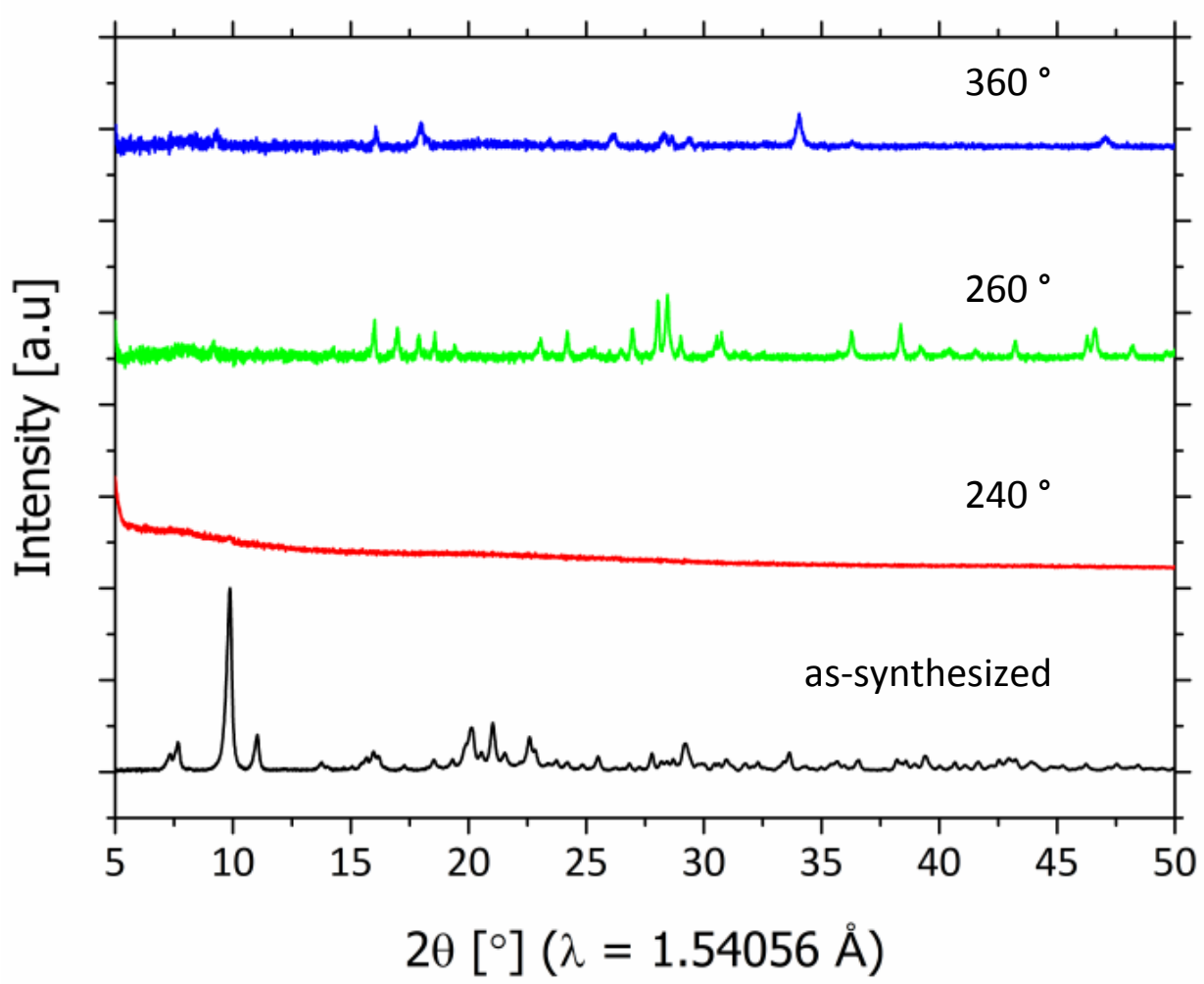


Figure S6. PXRD patterns of the compound [Ca(*m*BDC)(H_2O)$_{3.4}$] (**2**) as-synthesized (black PXRD patterns) and after the thermal post-treatments at different temperatures (red, green, and blue PXRD patterns)

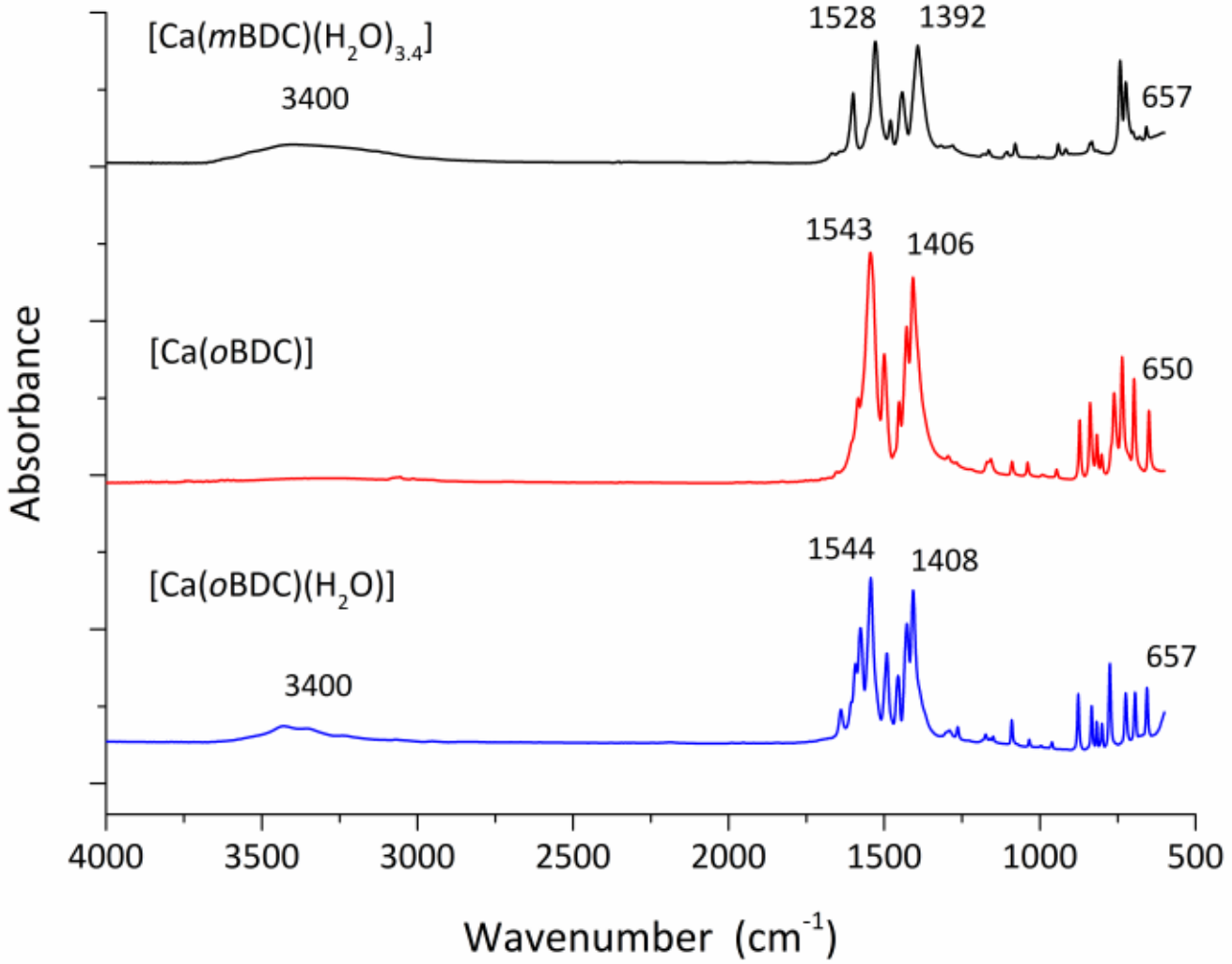


Figure S7. The ATR-IR spectra of compound **1** (blue spectrum), compound (**1-H_2O)** (red spectrum), and compound **2** (black spectrum).

Figure S8. Isotherm curves of the compound [Ca(*o*BDC)(H_2O)] (1). Adsorption (crosses) and desorption pore volume (circles) isotherm for nitrogen at room temperature

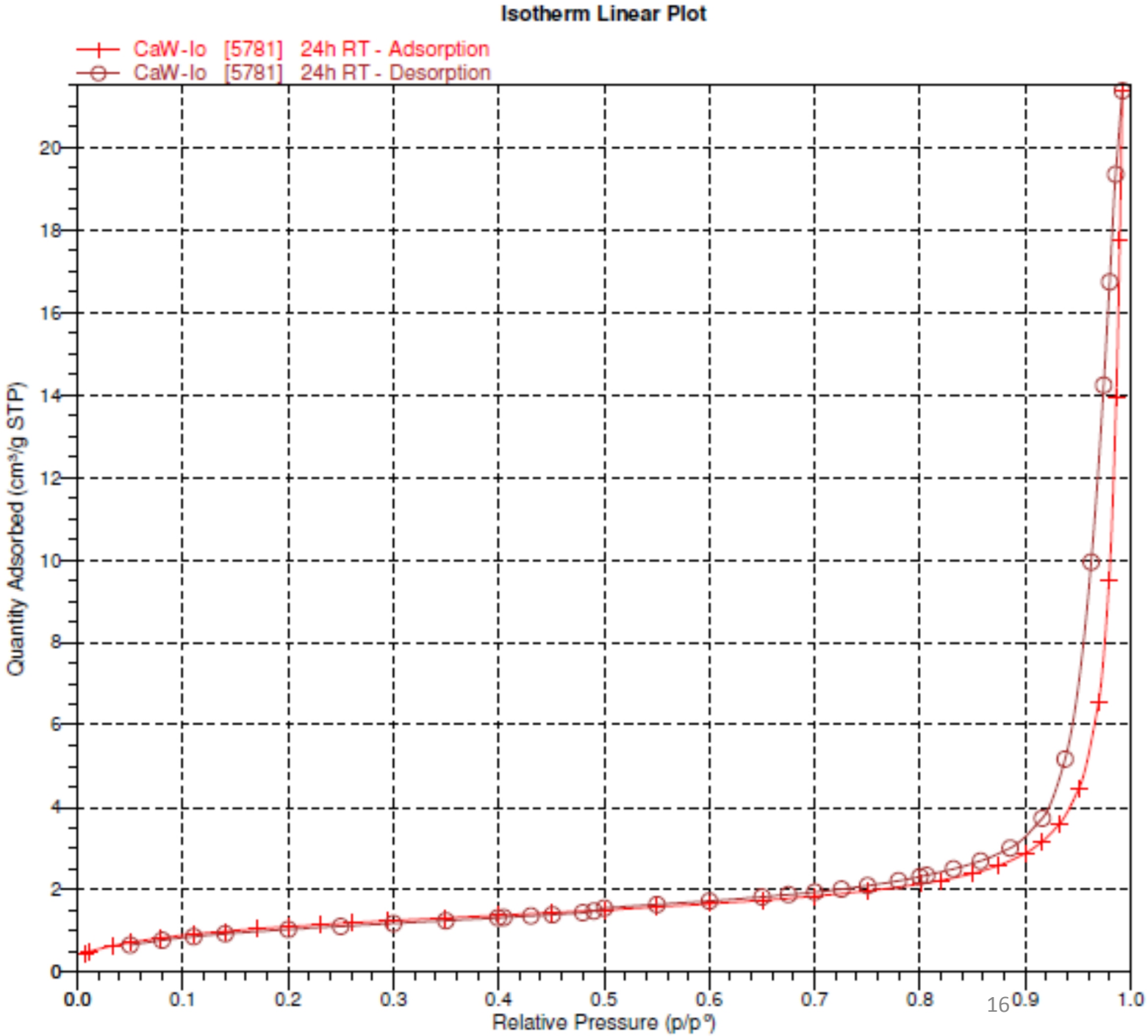
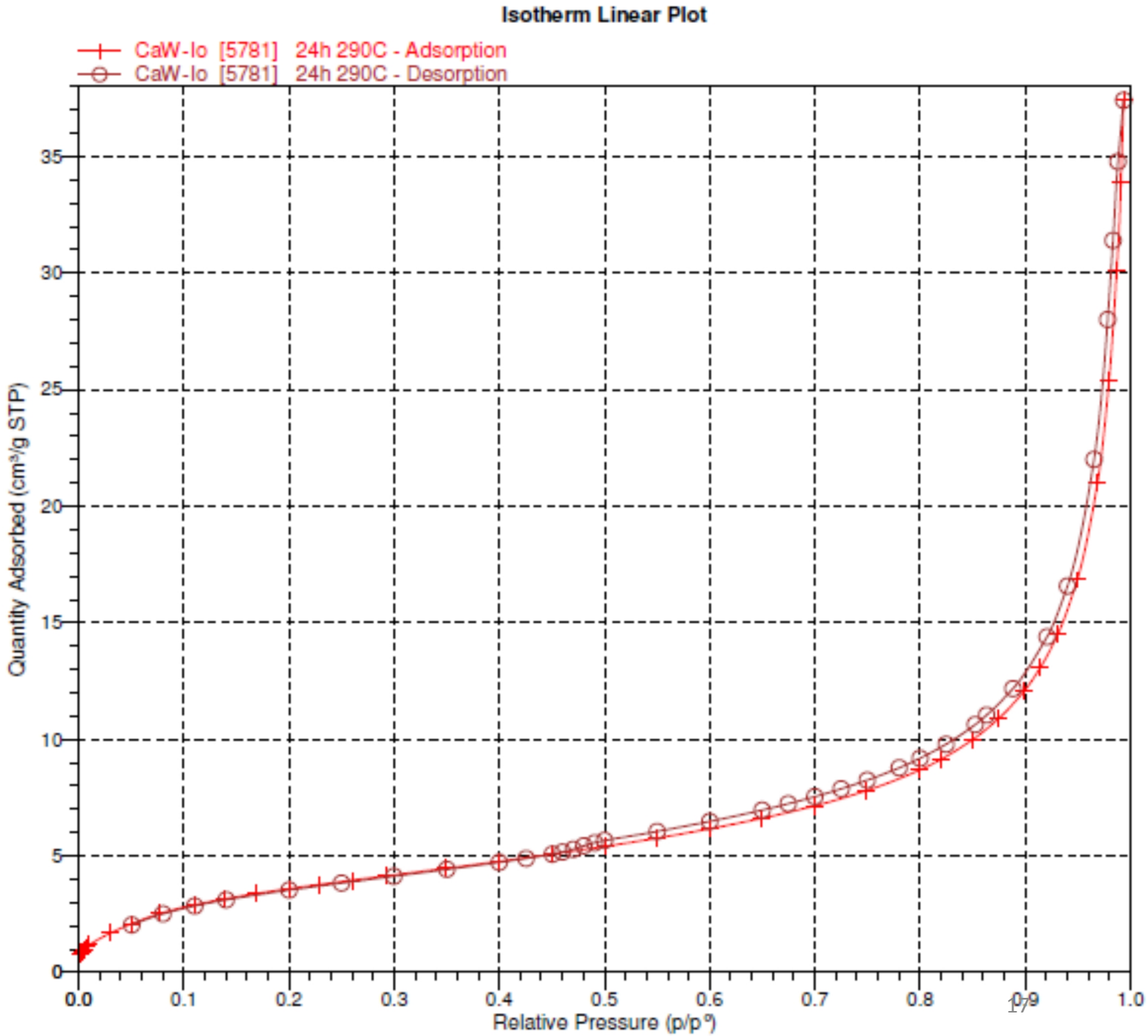
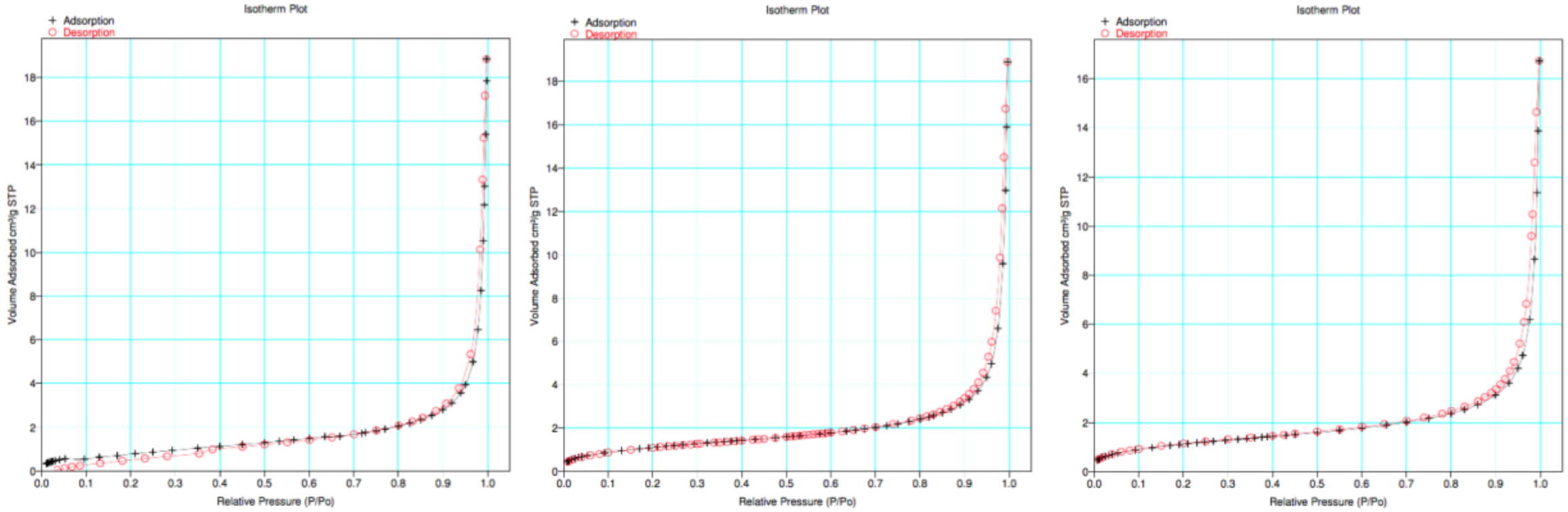


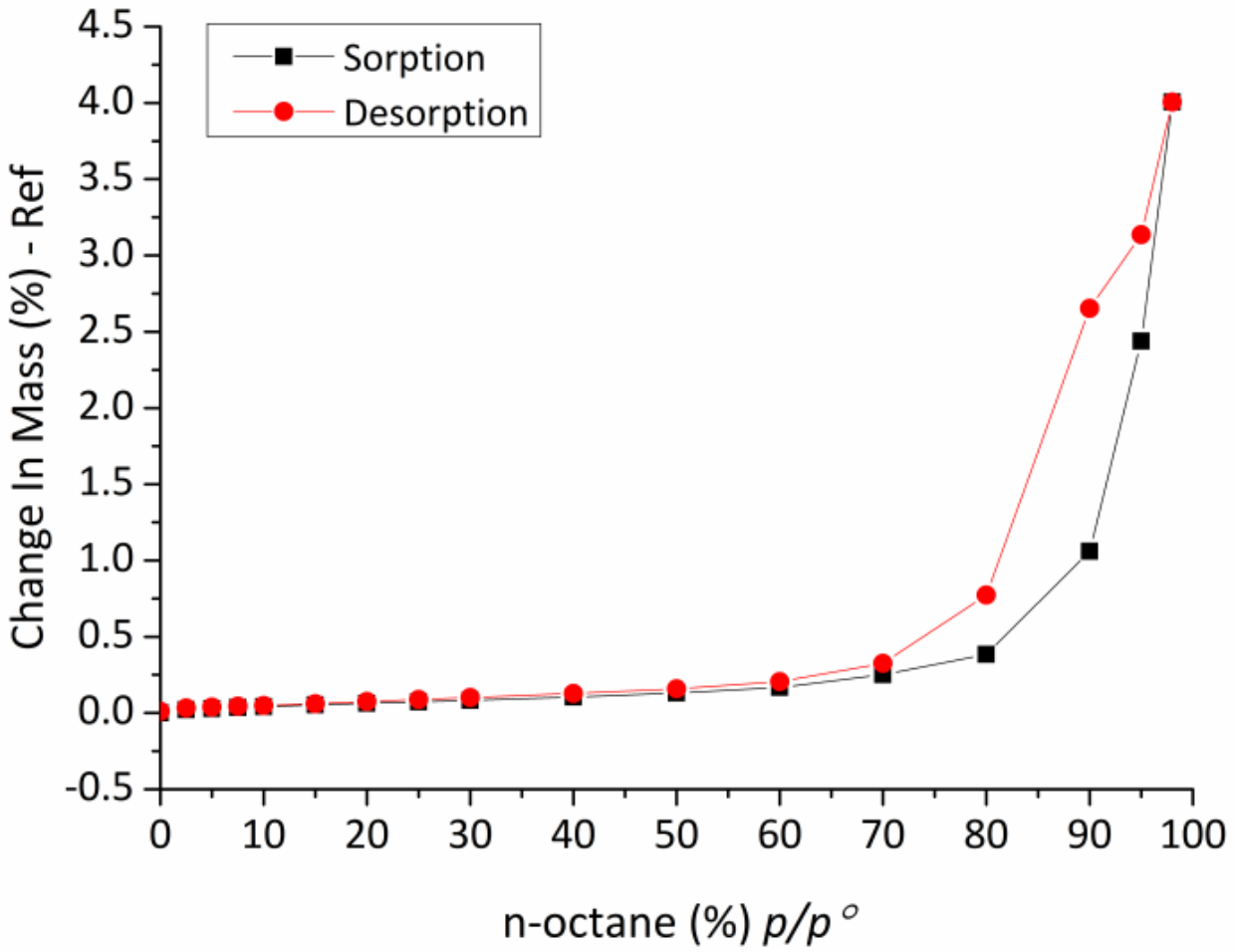
Figure S9. Isotherm curves of the compound [Ca(*o*BDC)] (1-H_2O). Adsorption (crosses) and desorption pore volume (circles) isotherm for nitrogen at room temperature



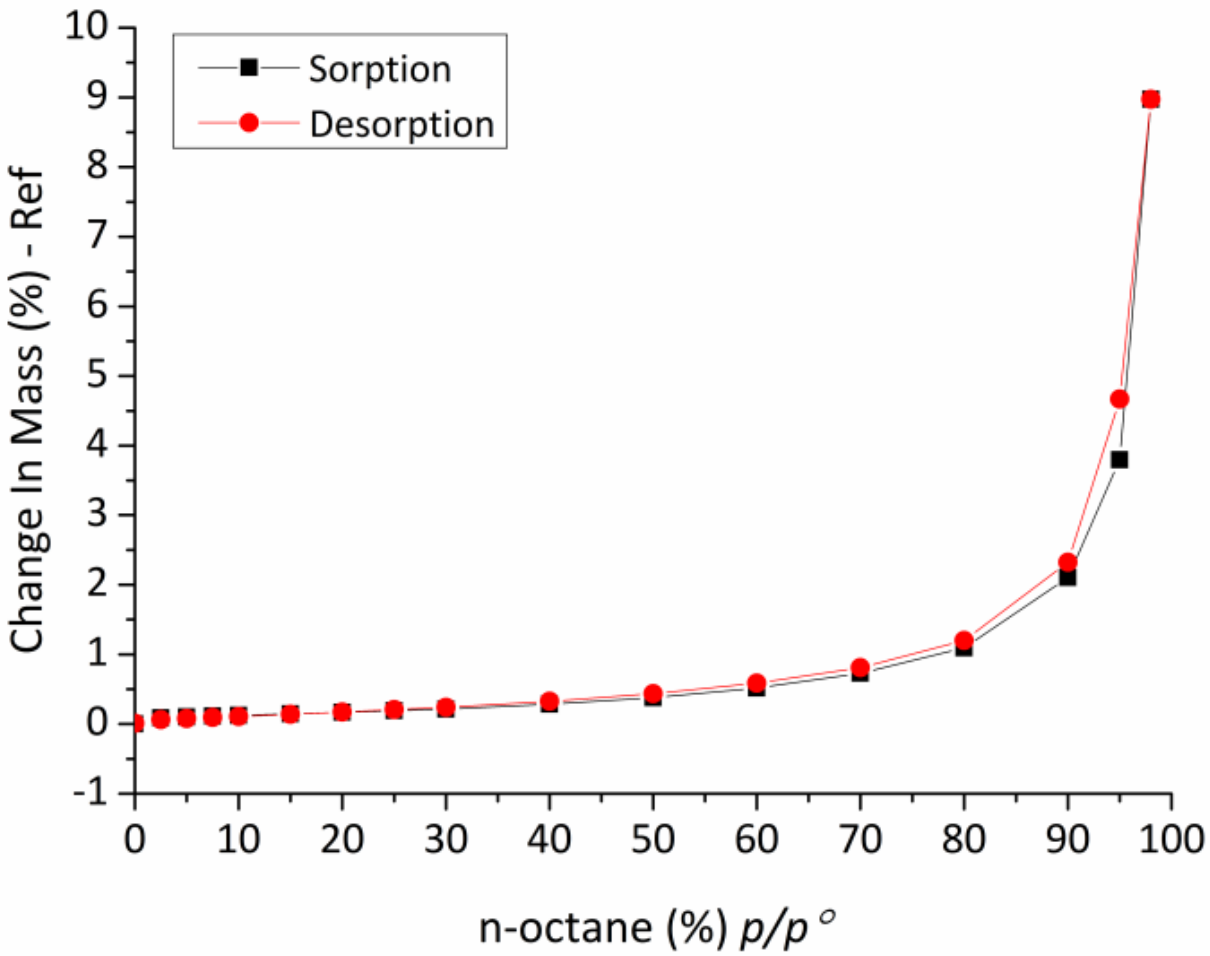


a b c

Figure S10. Isotherm curves of the compound **2**. Adsorption (crosses) and desorption pore volume (circles) isotherm for nitrogen at room temperature (a) at 240 °C (b), and at 260 °C (c)

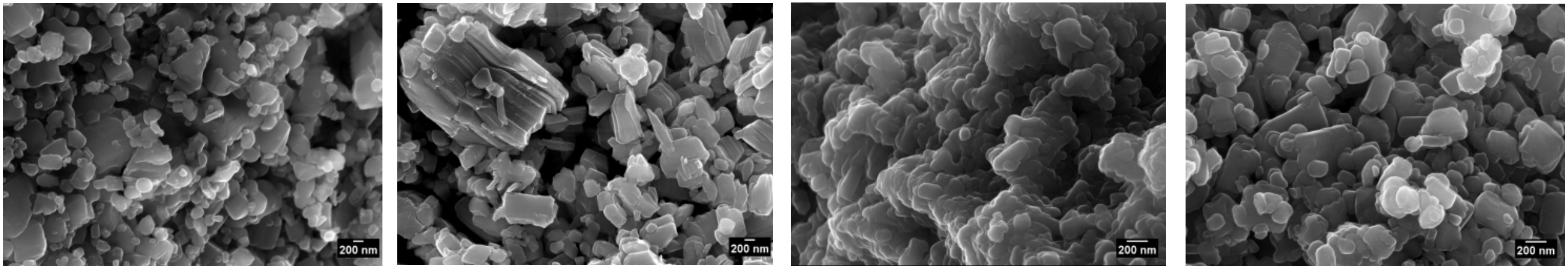


a



b

Figure S11. (a) Isotherm curves for the dynamic vapor sorption of *n*-octane on a sample of compound [Ca(*o*BDC)(H_2O)] (**1**). (**b**) Isotherm curves for the dynamic vapor sorption of *n*-octane on a sample of compound [Ca(*o*BDC)] (**1-H_2O**).



a **b** **c** **d**

Figure S12. SEM images of (a) [Ca(*o*BDC)(H_2O)] (**1**), (b) [Ca(*o*BDC)] (**1-H_2O**), (c) [Ca(*m*BDC)(H_2O)$_{3.4}$] (**2**) , (d) [Ca(*p*BDC)(H_2O)$_3$] (**3**)

[Ca(*o*BDC)(H_2O)] (**1**)	[Ca(*o*BDC)] (**1-H_2O**)	[Ca(*m*BDC)(H_2O)$_{3.4}$] (**2**)	[Ca(*p*BDC)(H_2O)$_3$] (**3**)	[Ca(*p*BDC)] (**3-H_2O**)

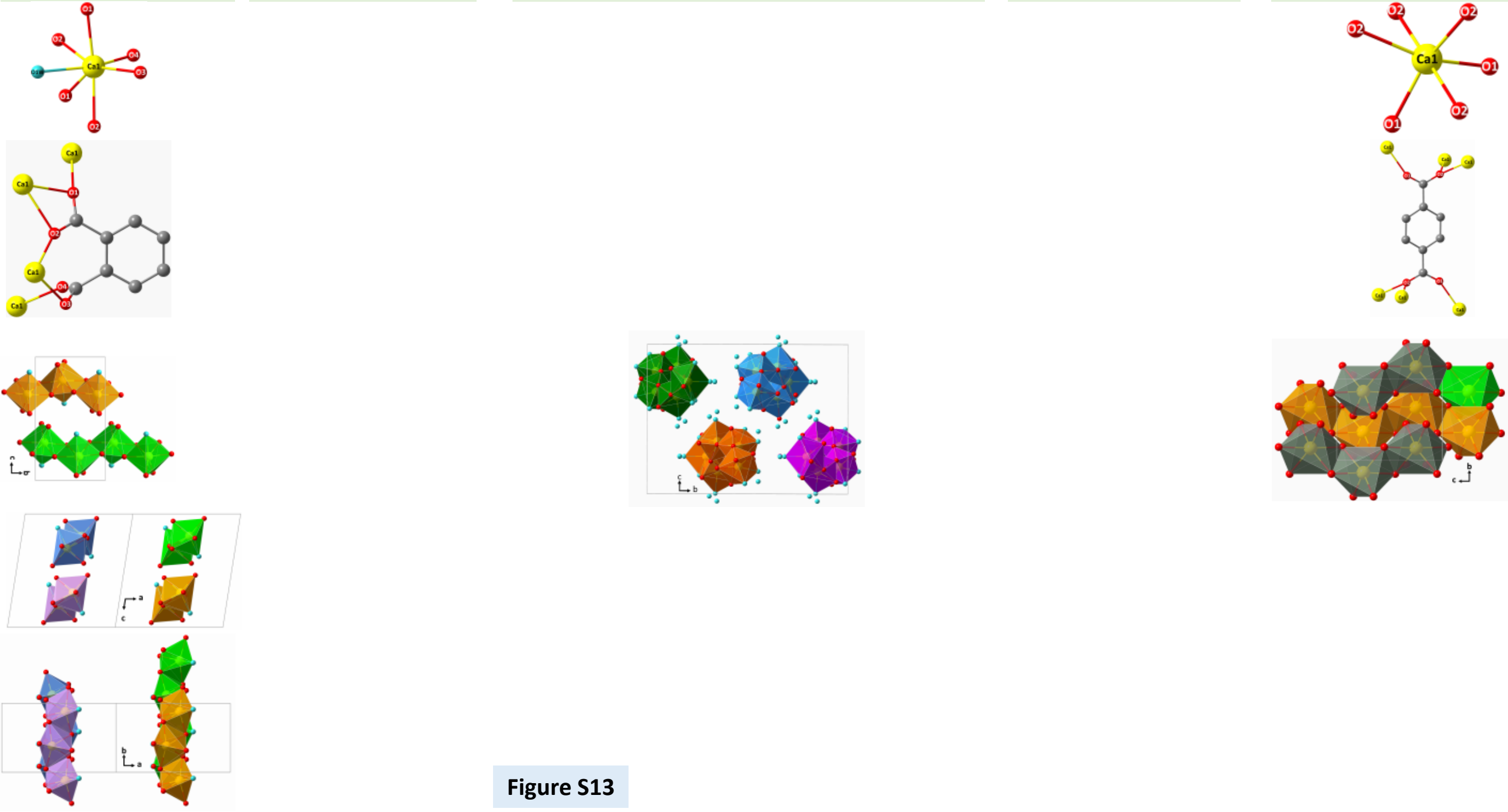


Figure S13