Electronic Supplementary Information

Mechanochemical Conversion of Potassium Coordination Polymer Nanostructures to Interpenetrated Sodium Coordination Polymer with Halogen bond, Metal-Carbon and Metal-Metal Interactions

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Table S1. Crystal data and structure refinement for compounds $[Na_2(\mu_4\text{-TBT})(H_2O)_4]_n$ (**1**) and $[K_2(\mu_4\text{-TBT})(H_2O)_4]_n$ (**2**).

Identification code	**1**	**2**
Empirical formula	$C_8H_8Br_4Na_2O_8$	$C_8H_8Br_4K_2O_8$
Formula weight	597.76	629.98
Temperature	130.00(10) K	130.01(10) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Tetragonal	Monoclinic
Space group	*I4₁cd*	*P2₁/c*
Unit cell dimensions	a = 12.3021(4) Å	a = 11.6690(5) Å
	b = 12.3021(4) Å	b = 7.2589(3) Å
	c = 42.415(2) Å	c = 10.7100(5) Å
	α = 90.00°	α = 90.00°
	β = 90.00°	β = 104.479(5)°
	γ = 90.00°	γ = 90.00°
Volume	6419.1(5) Å^3	878.37(7) Å^3
Z	16	2
Density (calculated)	2.474 g/cm^3	2.382 g/cm^3
Absorption coefficient	10.117 mm^{-1}	9.667 mm^{-1}
F(000)	4512	596
Crystal size	0.286×0.250×0.154 mm^3	0.632×0.358×0.072 mm^3
Theta range for data collection	3.449 to 36.41 °	3.336 to 36.486 °
Index ranges	$-19 \le h \le 12$	$-19 \le h \le 19$
	$-20 \le k \le 7$	$-11 \le k \le 12$
	$-70 \le l \le 37$	$-17 \le l \le 17$
Independent reflections	5317	4078
Absorption correction	Gaussian	Gaussian
Data / restraints / parameters	5317 / 273 / 204	4078 / 5 / 116
Goodness-of-fit on F^2	1.033	1.095
Final *R* indices [$I>2\sigma(I)$]	R_1= 0.0498	R_1= 0.0545
	wR_1= 0.1108	wR_1= 0.1023
R Indices (all data)	R_2= 0.0768	R_2= 0.0394
	wR_2= 0.1283	wR_2= 0.0877

Table S2. Selected bond lengths /Å and angles /° for compound $[Na_2(\mu_4\text{-TBT})(H_2O)_4]_n$ (**1**).

O(1)-Na(1)	2.382(10)
O(1)-Na(2)	2.474(10)
O(3)-Na(2)	2.408(10)
O(3)-Na(1)	2.478(11)
O(5)-Na(2)	2.427(5)
O(5)-Na(1)	2.441(5)
O(6)-Na(1)	2.450(9)
O(6)-Na(2)#2	2.530(10)
O(7)-Na(2)	2.433(5)
O(7)-Na(1)#1	2.445(5)
O(8)-Na(2)	2.459(9)
O(8)-Na(1)#3	2.498(9)
Na(1)-Na(2)	3.139(3)
Na(1)-Na(2)#1	3.814(3)
Na(1)-Na(2)#2	3.815(3)
O(1)-Na(1)-O(5)	81.4(4)
O(1)-Na(1)-O(7)#1	99.2(4)
O(5)-Na(1)-O(7)#1	177.6(6)
O(1)-Na(1)-O(6)	165.4(3)
O(5)-Na(1)-O(6)	84.3(3)
O(7)#1-Na(1)-O(6)	95.2(4)
O(1)-Na(1)-O(3)	88.13(17)
O(5)-Na(1)-O(3)	79.0(3)
O(7)#1-Na(1)-O(3)	98.7(4)
O(6)-Na(1)-O(3)	92.4(4)
O(1)-Na(1)-O(8)#2	98.9(4)
O(5)-Na(1)-O(8)#2	99.3(3)
O(7)#1-Na(1)-O(8)#2	82.9(3)
O(6)-Na(1)-O(8)#2	80.1(2)
O(3)-Na(1)-O(8)#2	172.4(4)
O(1)-Na(1)-Na(2)	51.0(2)
O(5)-Na(1)-Na(2)	49.65(13)
O(7)#1-Na(1)-Na(2)	129.07(15)
O(6)-Na(1)-Na(2)	120.1(2)

O(3)-Na(1)-Na(2)	49.1(2)
O(8)#2-Na(1)-Na(2)	134.7(2)
O(1)-Na(1)-Na(2)#1	72.3(2)
O(5)-Na(1)-Na(2)#1	140.23(17)
O(7)#1-Na(1)-Na(2)#1	38.45(11)
O(6)-Na(1)-Na(2)#1	121.6(2)
O(3)-Na(1)-Na(2)#1	71.0(2)
O(8)#2-Na(1)-Na(2)#1	113.6(2)
Na(2)-Na(1)-Na(2)#1	90.63(9)
O(1)-Na(1)-Na(2)#2	136.2(3)
O(5)-Na(1)-Na(2)#2	91.76(14)
O(7)#1-Na(1)-Na(2)#2	89.43(13)
O(6)-Na(1)-Na(2)#2	40.8(2)
O(3)-Na(1)-Na(2)#2	133.2(3)
O(8)#2-Na(1)-Na(2)#2	39.3(2)
Na(2)-Na(1)-Na(2)#2	141.39(8)
Na(2)#1-Na(1)-Na(2)#2	127.83(8)
O(3)-Na(2)-O(5)	80.7(3)
O(3)-Na(2)-O(7)	99.0(4)
O(5)-Na(2)-O(7)	177.6(5)
O(3)-Na(2)-O(8)	165.3(3)
O(5)-Na(2)-O(8)	85.1(3)
O(7)-Na(2)-O(8)	95.4(4)
O(3)-Na(2)-O(1)	87.64(17)
O(5)-Na(2)-O(1)	79.8(4)
O(7)-Na(2)-O(1)	97.7(4)
O(8)-Na(2)-O(1)	93.6(4)
O(3)-Na(2)-O(6)#3	98.8(4)
O(5)-Na(2)-O(6)#3	98.1(3)
O(7)-Na(2)-O(6)#3	84.4(3)
O(8)-Na(2)-O(6)#3	79.30(19)
O(1)-Na(2)-O(6)#3	172.8(4)
O(3)-Na(2)-Na(1)	51.0(2)
O(5)-Na(2)-Na(1)	50.04(13)
O(7)-Na(2)-Na(1)	127.96(15)
O(8)-Na(2)-Na(1)	120.7(2)

O(1)-Na(2)-Na(1)	48.4(2)
O(6)#3-Na(2)-Na(1)	134.6(2)
O(3)-Na(2)-Na(1)#1	71.2(2)
O(5)-Na(2)-Na(1)#1	139.36(16)
O(7)-Na(2)-Na(1)#1	38.67(11)
O(8)-Na(2)-Na(1)#1	123.0(2)
O(1)-Na(2)-Na(1)#1	70.4(2)
O(6)#3-Na(2)-Na(1)#1	114.5(2)
Na(1)-Na(2)-Na(1)#1	89.32(9)
O(3)-Na(2)-Na(1)#3	136.6(3)
O(5)-Na(2)-Na(1)#3	92.89(14)
O(7)-Na(2)-Na(1)#3	89.02(13)
O(8)-Na(2)-Na(1)#3	40.1(2)
O(1)-Na(2)-Na(1)#3	133.7(3)
O(6)#3-Na(2)-Na(1)#3	39.2(2)
Na(1)-Na(2)-Na(1)#3	142.84(8)
Na(1)#1-Na(2)-Na(1)#3	127.69(8)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,z+0 #2 -x+1/2,y-1/2,z #3 -x+1/2,y+1/2,z

Table S3. Hydrogen bond for compound $[Na_2(\mu_4\text{-TBT})(H_2O)_4]_n$ (**1**), [/Å and /°].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(5)-H(5A)...O(2)#4	0.97	1.98	2.843(13)	146.7
O(5)-H(5A)...Br(2)#5	0.97	3.06	3.738(16)	128.5
O(5)-H(5B)...O(4)#6	0.97	2.02	2.884(12)	147.1
O(5)-H(5B)...Br(4)#6	0.97	3.10	3.763(16)	126.4
O(6)-H(6A)...Br(2)#7	0.97	3.05	3.771(8)	132.4
O(6)-H(6A)...Br(3)	0.97	3.05	3.833(7)	138.9
O(6)-H(6B)...O(2)#4	0.97	2.21	3.092(9)	151.2
O(6)-H(6B)...Br(2)#5	0.97	3.12	3.768(9)	125.5
O(6)-H(6B)...Br(3)#8	0.97	2.88	3.524(7)	124.9
O(7)-H(7A)...O(4)#9	0.97	1.90	2.806(13)	153.7
O(7)-H(7A)...Br(1)#1	0.97	2.84	3.521(17)	128.4
O(7)-H(7B)...O(2)#10	0.97	1.93	2.856(13)	158.2
O(7)-H(7B)...Br(3)#1	0.97	2.93	3.596(18)	127.0
O(8)-H(8A)...Br(1)#1	0.97	2.96	3.739(7)	138.5
O(8)-H(8A)...Br(4)#11	0.97	3.10	3.831(8)	133.6
O(8)-H(8B)...O(4)#6	0.97	2.11	3.013(10)	153.4
O(8)-H(8B)...Br(1)#3	0.97	2.97	3.608(7)	124.7
O(8)-H(8B)...Br(4)#6	0.97	3.09	3.703(8)	122.4
O(5)-H(5A)...O(2)#4	0.97	1.98	2.843(13)	146.7
O(5)-H(5A)...Br(2)#5	0.97	3.06	3.738(16)	128.5
O(5)-H(5B)...O(4)#6	0.97	2.02	2.884(12)	147.1
O(5)-H(5B)...Br(4)#6	0.97	3.10	3.763(16)	126.4
O(6)-H(6A)...Br(2)#7	0.97	3.05	3.771(8)	132.4
O(6)-H(6A)...Br(3)	0.97	3.05	3.833(7)	138.9
O(6)-H(6B)...O(2)#4	0.97	2.21	3.092(9)	151.2
O(6)-H(6B)...Br(2)#5	0.97	3.12	3.768(9)	125.5
O(6)-H(6B)...Br(3)#8	0.97	2.88	3.524(7)	124.9
O(7)-H(7A)...O(4)#9	0.97	1.90	2.806(13)	153.7
O(7)-H(7A)...Br(1)#1	0.97	2.84	3.521(17)	128.4
O(7)-H(7B)...O(2)#10	0.97	1.93	2.856(13)	158.2
O(7)-H(7B)...Br(3)#1	0.97	2.93	3.596(18)	127.0
O(8)-H(8A)...Br(1)#1	0.97	2.96	3.739(7)	138.5

O(8)-H(8A)...Br(4)#11	0.97	3.10	3.831(8)	133.6
O(8)-H(8B)...O(4)#6	0.97	2.11	3.013(10)	153.4
O(8)-H(8B)...Br(1)#3	0.97	2.97	3.608(7)	124.7
O(8)-H(8B)...Br(4)#6	0.97	3.09	3.703(8)	122.4

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,z+0 #2 -x+1/2,y-1/2,z #3 -x+1/2,y+1/2,z

#4 y-1/2,-x+1,z-1/4 #5 -y+1/2,x+0,z-1/4 #6 -y+1/2,-x+1,z+1/4

#7 y+0,x-1/2,z-1/4 #8 x-1/2,-y+1/2,z+0 #9 -y+1,x+1/2,z+1/4

#10 -y+1,-x+3/2,z-1/4 #11 y+0,-x+3/2,z+1/4

Table S4. Selected bond lengths /Å and angles /° for compound $[K_2(\mu_4\text{-TBT})(H_2O)_4]_n$ (**2**).

O(1)-K	2.744(2)
O(2)-K	2.772(2)
O(3)-K	2.760(2)
O(4)-K	2.732(2)
O(4)-K#3	2.764(2)
Br(1)-K#2	3.8523(7)
Br(2)-K#1	3.7079(6)
K-K#3	4.3834(11)
O(4)-K-O(1)	99.90(6)
O(4)-K-O(3)	132.80(7)
O(1)-K-O(3)	105.14(6)
O(4)-K-O(4)#3	74.20(7)
O(1)-K-O(4)#3	79.09(7)
O(3)-K-O(4)#3	72.19(6)
O(4)-K-O(2)#4	79.97(6)
O(1)-K-O(2)#4	162.00(6)
O(3)-K-O(2)#4	87.29(6)
O(4)#3-K-O(2)#4	117.67(7)
O(4)-K-Br(2)#1	158.79(5)
O(1)-K-Br(2)#1	63.04(4)
O(3)-K-Br(2)#1	67.01(4)
O(4)#3-K-Br(2)#1	111.98(5)
O(2)#4-K-Br(2)#1	112.15(4)
O(4)-K-Br(1)#4	61.67(5)
O(1)-K-Br(1)#4	103.35(4)
O(3)-K-Br(1)#4	143.76(5)
O(4)#3-K-Br(1)#4	135.66(5)
O(2)#4-K-Br(1)#4	60.52(4)
Br(2)#1-K-Br(1)#4	108.006(16)
O(4)-K-K#3	37.35(5)

O(1)-K-K#3	89.30(4)
O(3)-K-K#3	103.33(5)
O(4)#3-K-K#3	36.85(4)
O(2)#4-K-K#3	100.62(4)
Br(2)#1-K-K#3	144.79(2)
Br(1)#4-K-K#3	98.924(19)
O(4)-K-H(4B)	14.9(4)
O(1)-K-H(4B)	89.5(6)
O(3)-K-H(4B)	147.2(4)
O(4)#3-K-H(4B)	82.4(6)
O(2)#4-K-H(4B)	86.6(7)
Br(2)#1-K-H(4B)	144.1(4)
Br(1)#4-K-H(4B)	53.7(7)
K#3-K-H(4B)	46.7(6)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 x,y+1,z #3 -x+2,-y,-z+1

#4 x,y-1,z

Table S5. Hydrogen bond for compound $[K_2(\mu_4\text{-TBT})(H_2O)_4]_n$ (**2**), [/Å and /°].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(4)-H(4A)...O(3)#5	0.834(10)	2.005(14)	2.828(3)	169(5)
O(3)-H(3B)...O(2)#6	0.829(10)	2.090(15)	2.887(3)	161(4)
O(4)-H(4B)...O(2)#7	0.829(10)	2.12(2)	2.862(3)	149(4)
O(3)-H(3A)...O(1)#8	0.823(10)	1.960(12)	2.776(3)	171(5)
O(3)-H(3A)...Br(2)#1	0.823(10)	3.14(4)	3.657(2)	123(4)

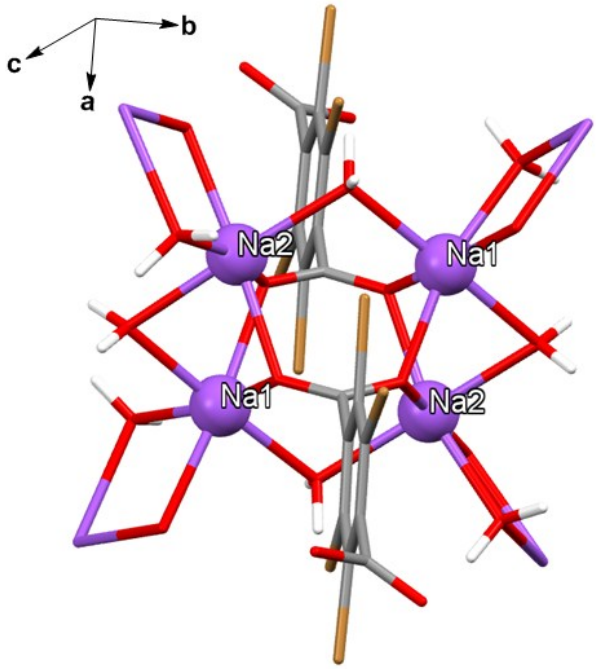
Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 x,y+1,z #3 -x+2,-y,-z+1

#4 x,y-1,z #5 x,-y-1/2,z-1/2 #6 -x+2,y-1/2,-z+3/2

#7 x,-y+1/2,z-1/2 #8 x,-y+1/2,z+1/2

a)



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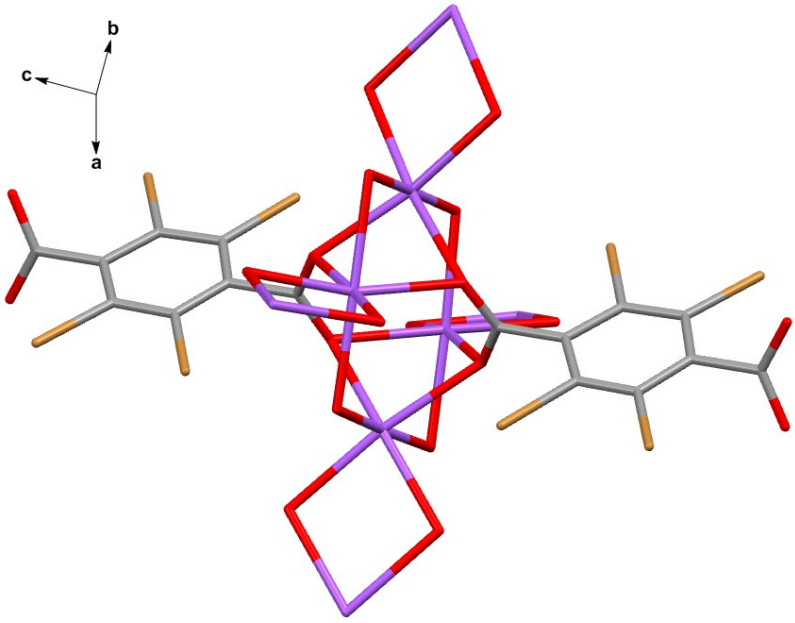


Figure S1. Representation of a) sodium(I) coordination sphere and b) TBT^{2-} coordination mode in $[Na_2(\mu_4\text{-}TBT)(H_2O)_4]_n$ (**1**), (Na = purpule, O = red, Br = brown, C = gray and H = white. In b, H atoms have been removed for clarity).

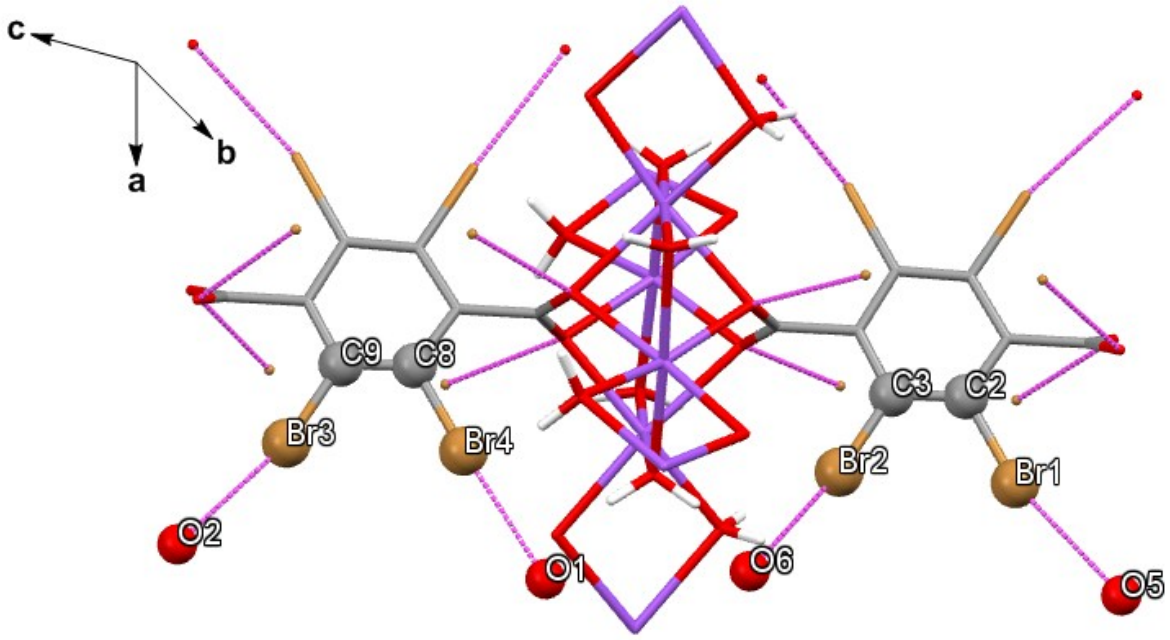
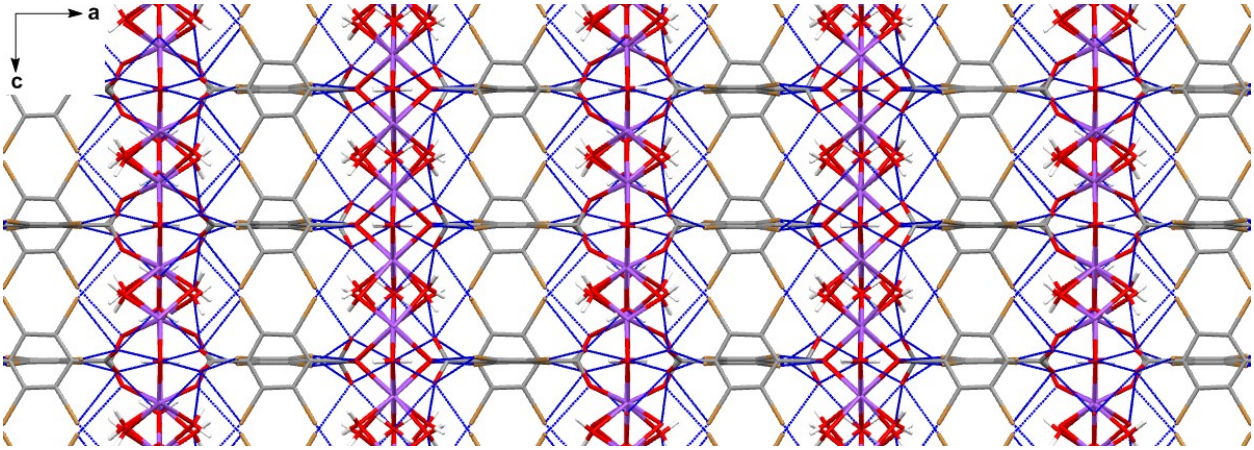


Figure S2. Representation of Br···O interactions in $[Na_2(\mu_4\text{-TBT})(H_2O)_4]_n$ (**1**) with Br(1)-O(4), Br(2)-O(3), Br(3)-O(2), Br(4)-O(1) distances of 2.917, 3.023, 2.881 and 2.994 Å and C(2)-Br(1)…O(5), C(3)-Br(2)…O(6), C(9)-Br(3)…O(2), C(8)-Br(4)…O(1) angles of 165.72, 165.62, 167.10 and 171.49°, (Na = purpule, O = red, Br = brown, C = gray and H = white).

a)



b)

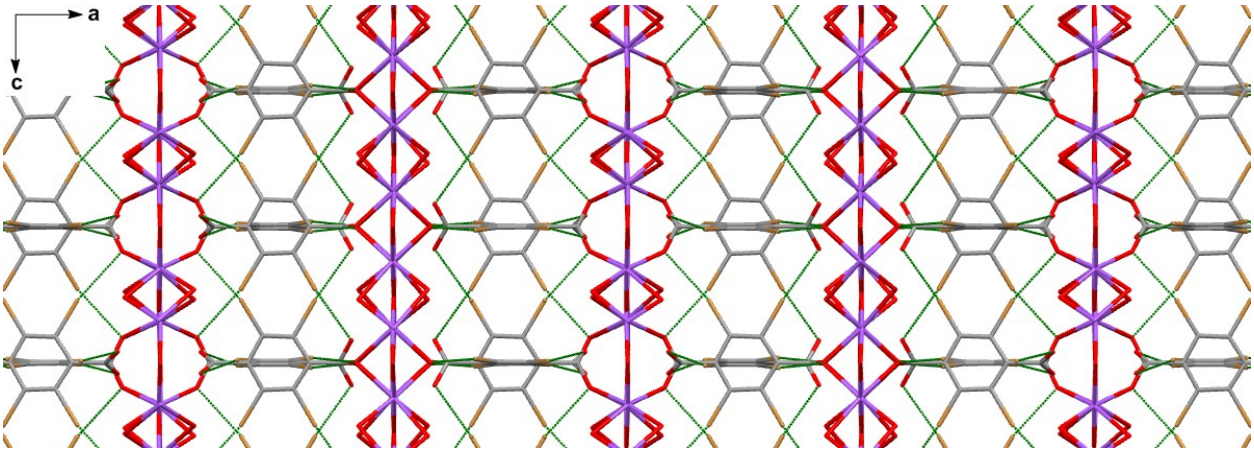
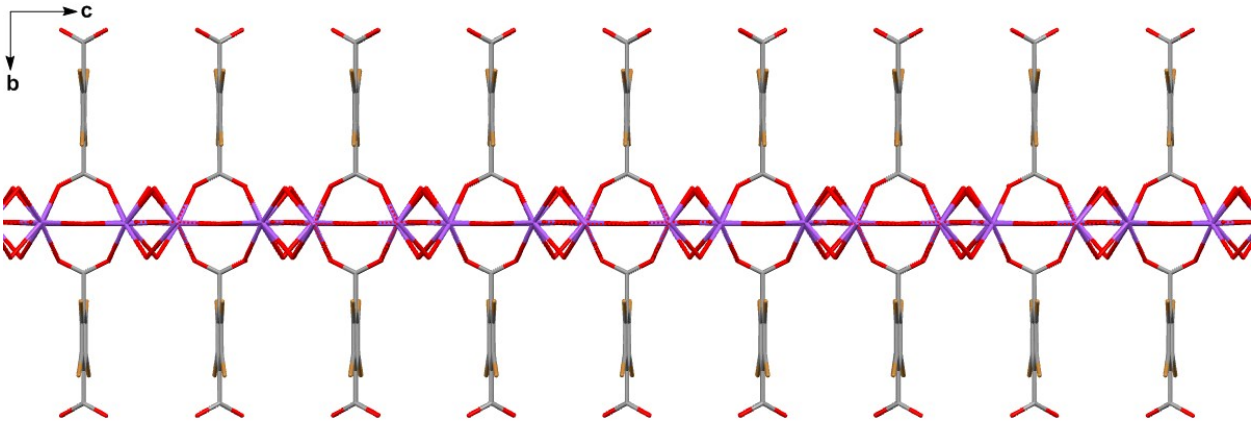


Figure S3. Stabilization of 3D supramolecular polymer which was obtained from perpendicular interpenetration of 2D network in $[Na_2(\mu_4\text{-TBT})(H_2O)_4]_n$ (**1**) with a) secondary hydrogen bonding (blue dashed lines) and b) Br···O interactions (green dashed lines) along the crystallographic *b* axis, (Na = purpule, O = red, Br = brown, C = gray and H = white, in b the H atoms have been removed for clarity).

a)



b)

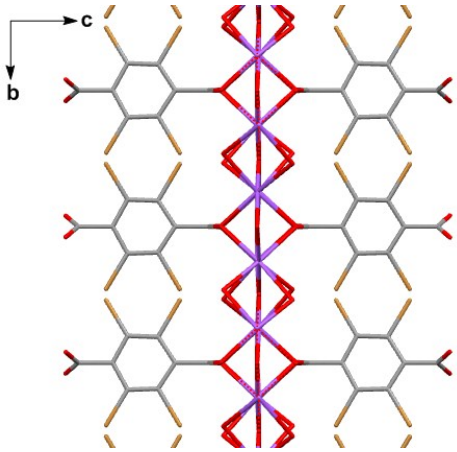
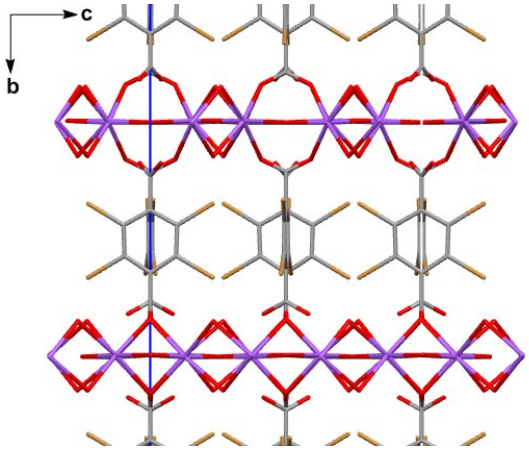


Figure S4. A fragment of 2D coordination network in $[Na_2(\mu_4\text{-TBT})(H_2O)_4]_n$ (**1**) and b) 3D supramolecular polymer from perpendicular interpenetration of 2D network in **1** along the crystallographic *a* axis, (Na = purpule, O = red, Br = brown and C = gray, H atoms have been removed for clarity).

a)



b)

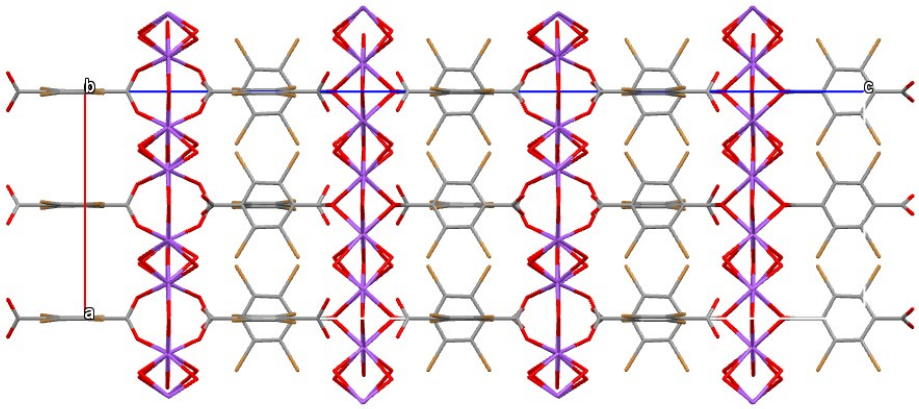
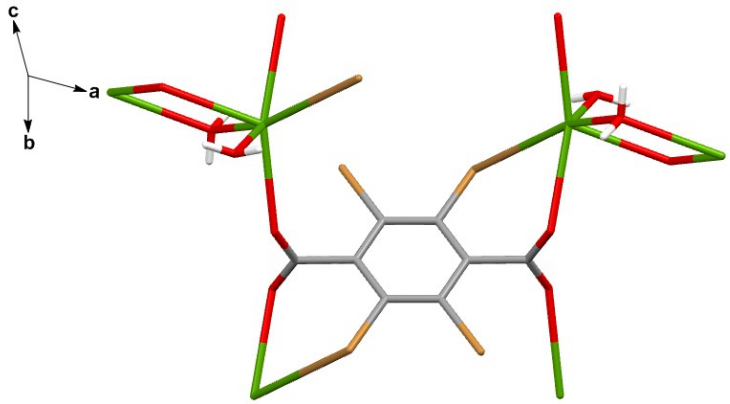
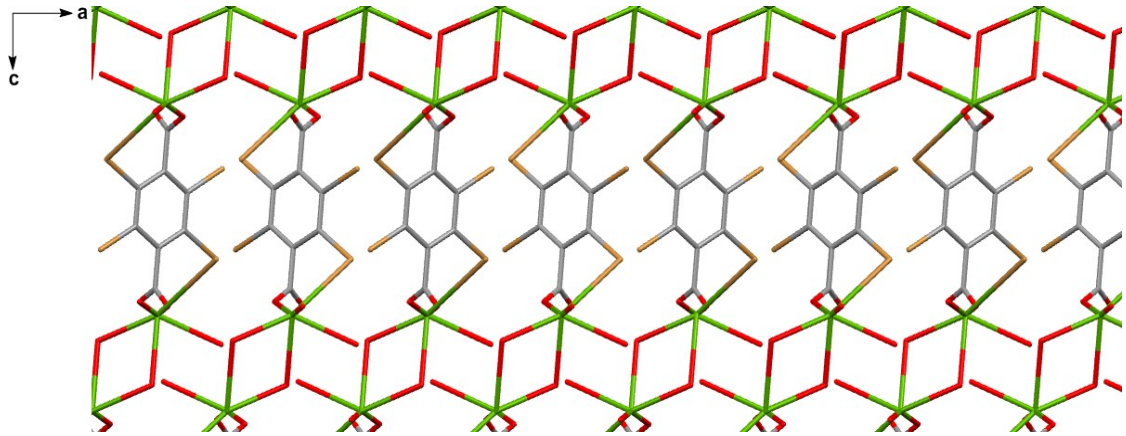


Figure S5. A fragment of 2D coordination network in $[Na_2(\mu_4\text{-TBT})(H_2O)_4]_n$ (**1**) and b) 3D supramolecular polymer from perpendicular interpenetration of 2D network in **1** along the crystallographic *b* axis, (Na = purpule, O = red, Br = brown and C = gray, H atoms have been removed for clarity).

a)



b)



c)

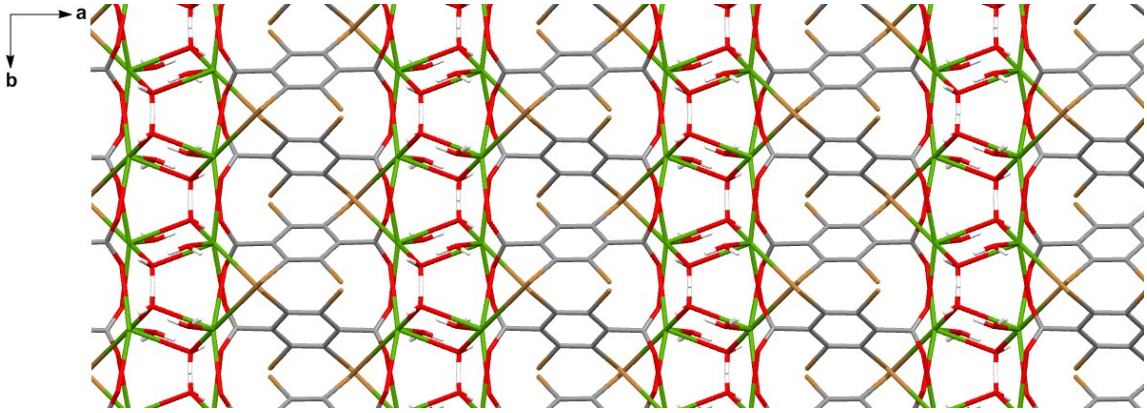
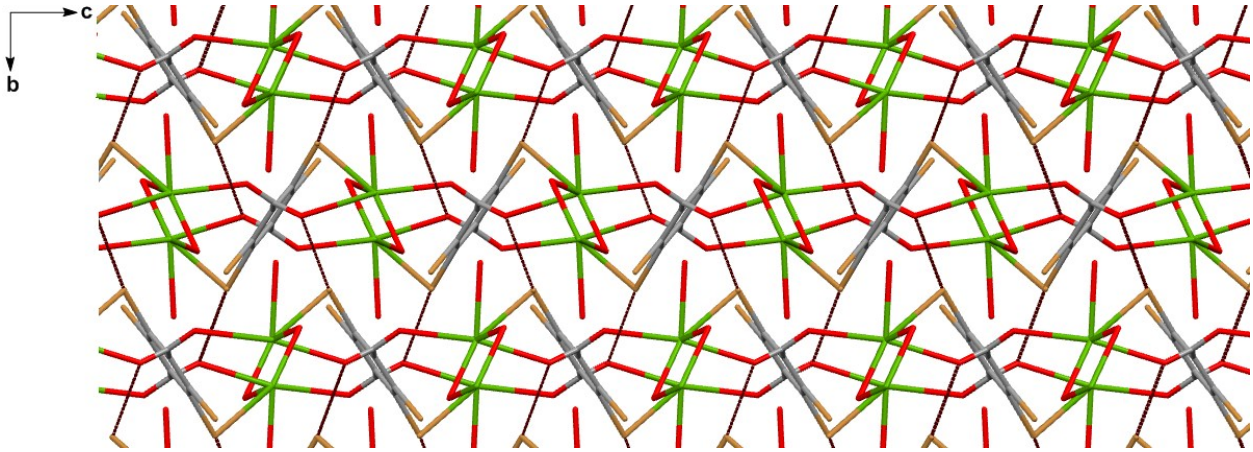


Figure S6. Representation of a) potassium(I) coordination sphere and TBT^{2-} coordination mode in $[K_2(\mu_4\text{-TBT})(H_2O)_4]_n$ (**2**) and 2D coordination polymer in **2** along the crystallographic b) *b* axis and c) *c* axis (K = green, O = red, Br = brown, C = gray and H = white. In b, H atoms have been removed for clarity).

a)



b)

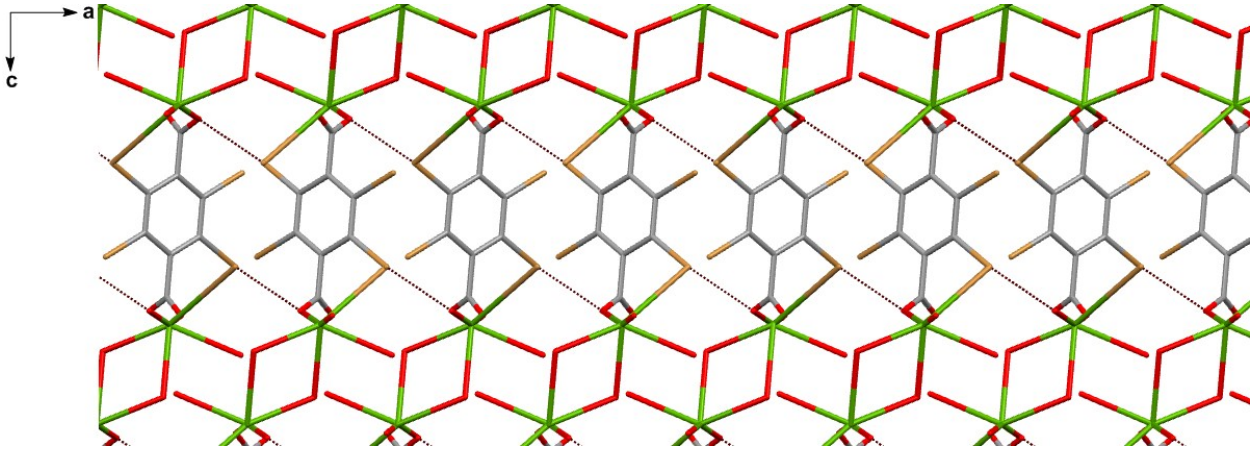


Figure S7. Representation of Br···O interactions in $[K_2(\mu_4\text{-TBT})(H_2O)_4]_n$ (**2**) along the crystallographic a) *a* axis and b) *b* axis, (K = green, O = red, Br = brown and C = gray, H atoms have been removed for clarity).

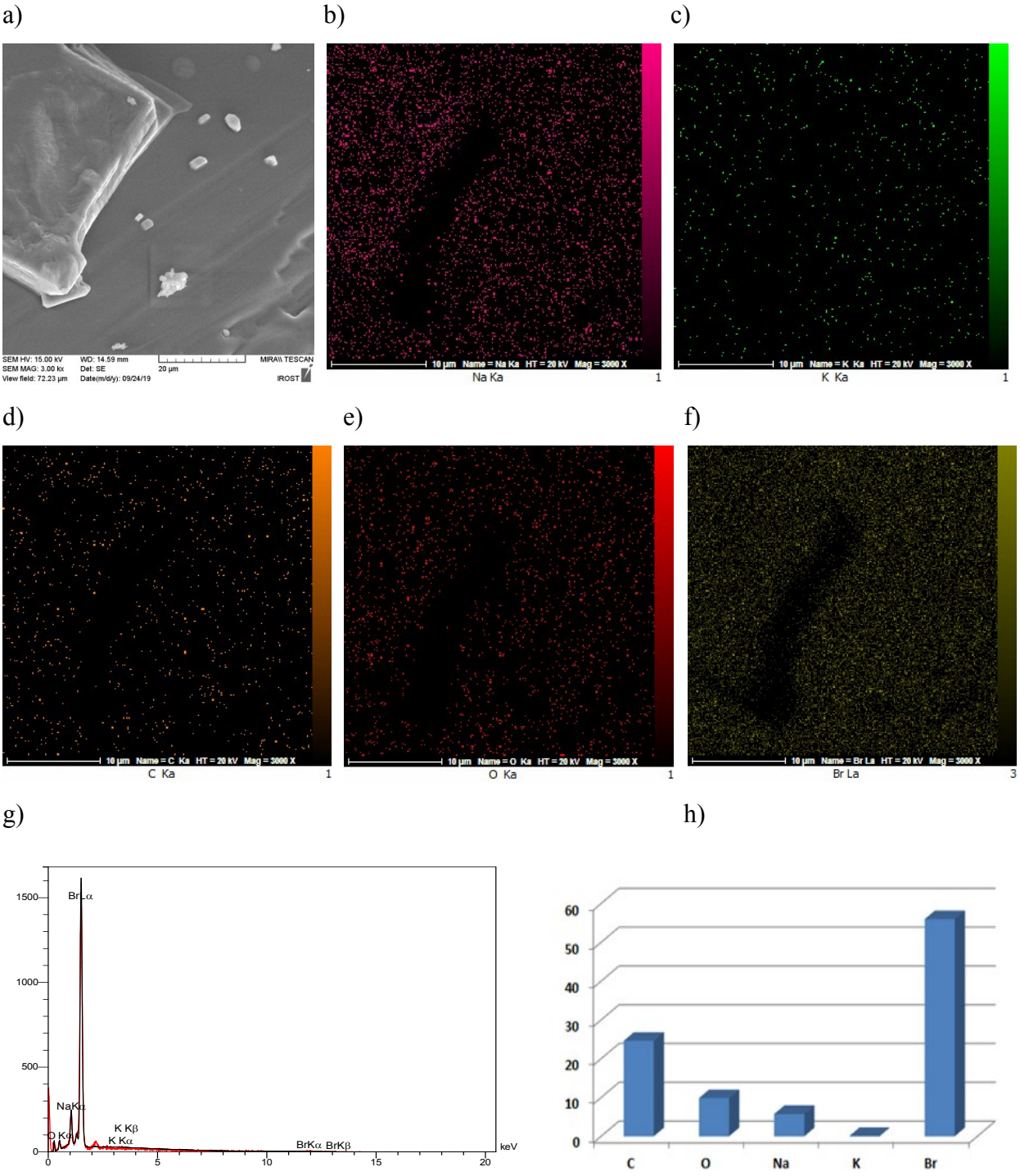
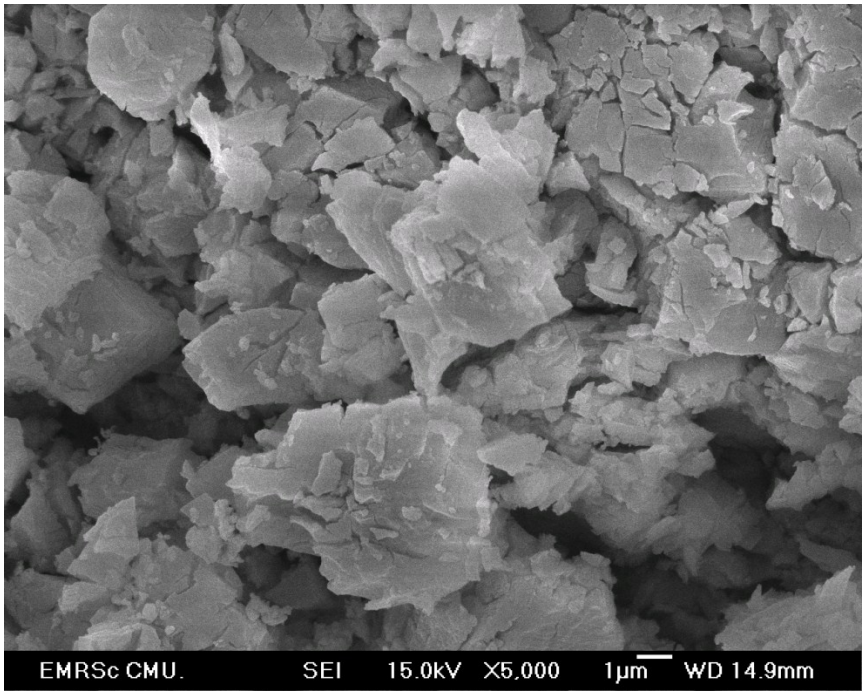
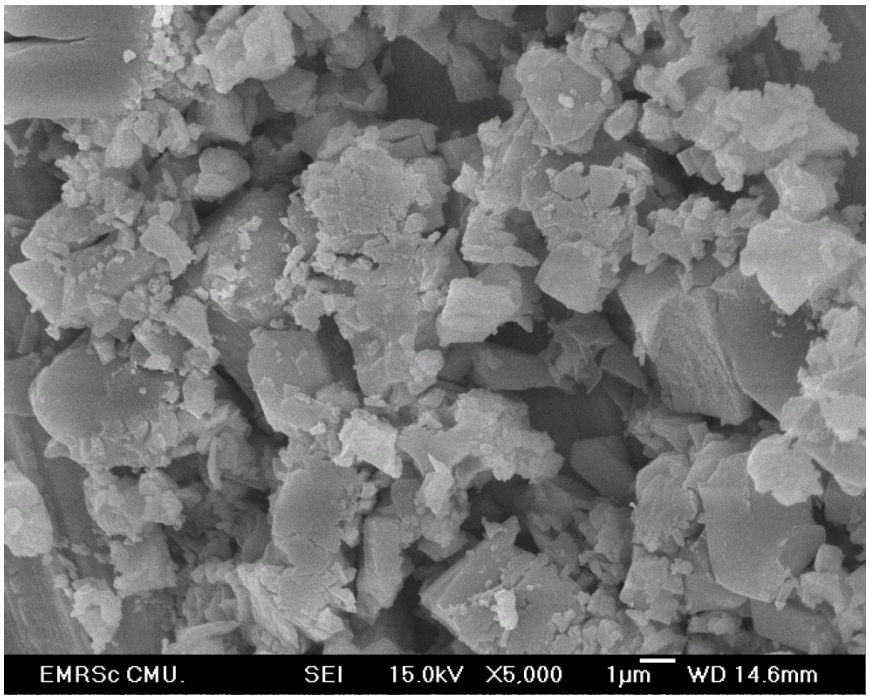


Figure S8. a) Area of the EDAX measurement, b-f) elemental mapping of Na, K, C, O and Br, respectively, g) EDAX spectrum and h) distribution of chemical composition respective for Na, K, C, O and Br in $[Na_2(\mu_4\text{-TBT})(H_2O)_4]_n$ (**1**) synthesized under ultrasonic irradiations.

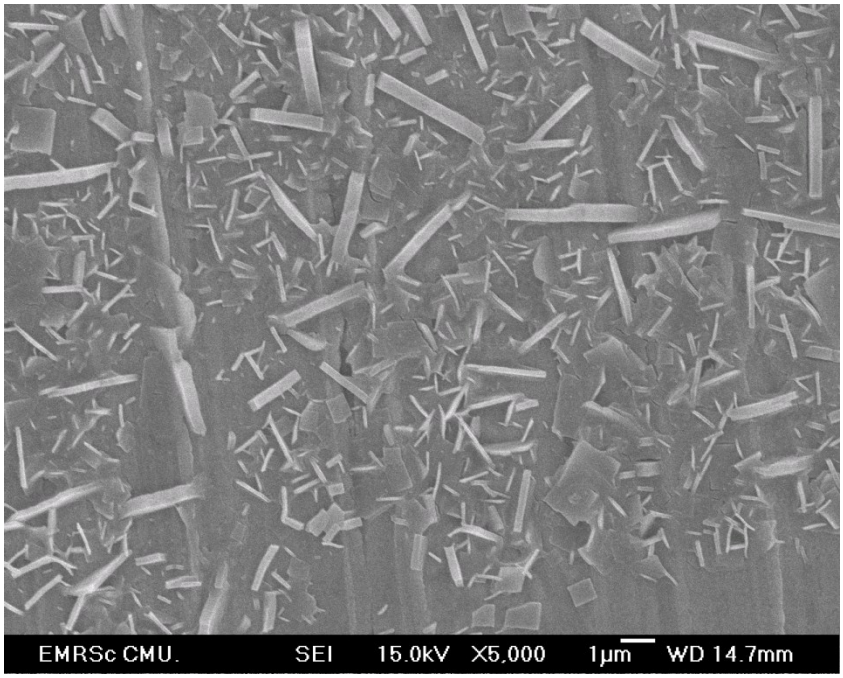
a)


EMRSc CMU. SEI 15.0kV X5,000 1µm WD 14.9mm

b)


EMRSc CMU. SEI 15.0kV X5,000 1µm WD 14.6mm

c)



d)

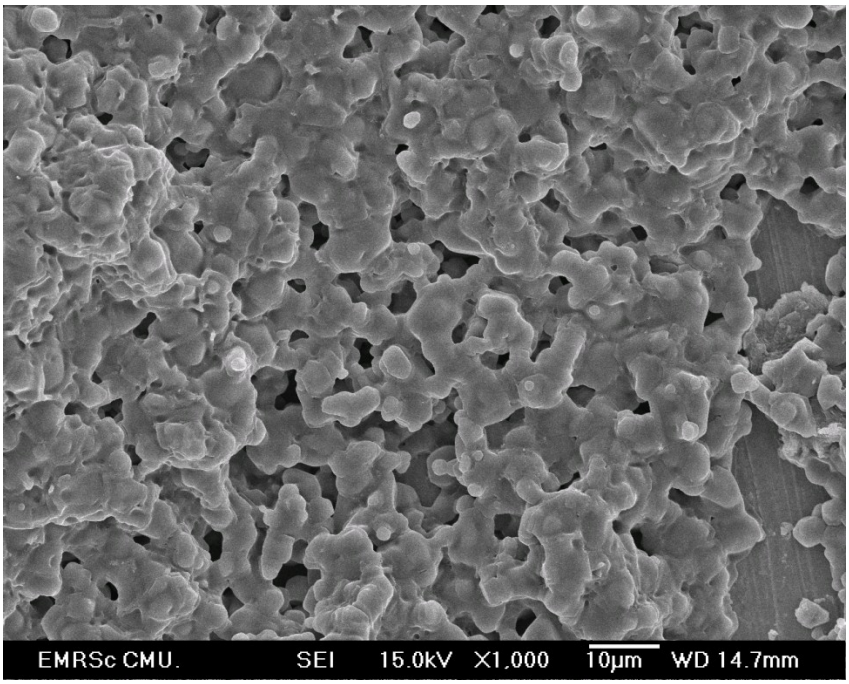


Figure S9. Other SEM images of a) $[Na_2(\mu_4\text{-TBT})(H_2O)_4]_n$ (**1**) synthesized under ultrasonic irradiations, d) compound **1** after a LAG reaction with excess KNO_3, c) $[K_2(\mu_4\text{-TBT})(H_2O)_4]_n$ (**2**) synthesized under ultrasonic irradiations, d) compound **2** after a LAG reaction with excess $NaNO_3$.

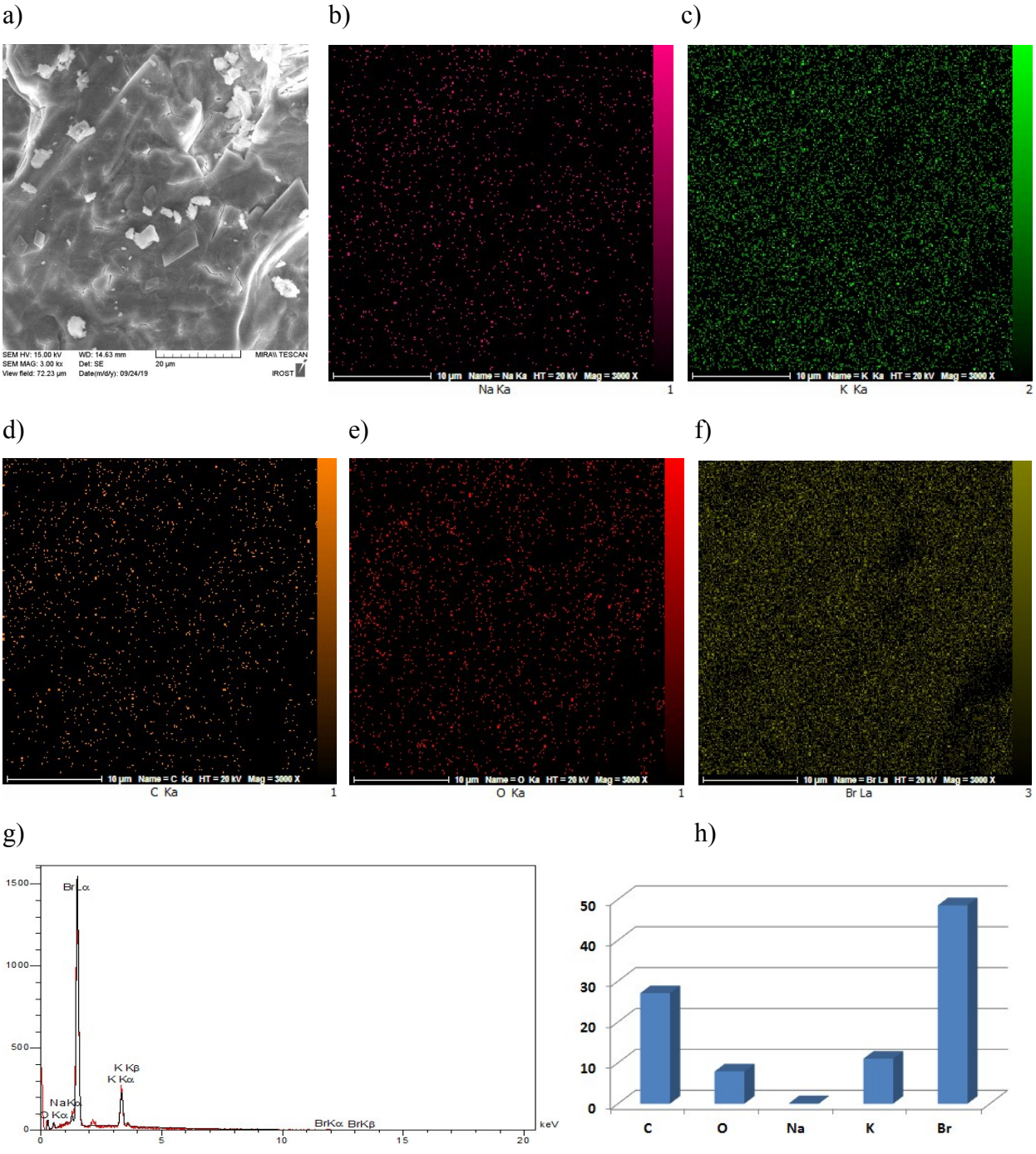


Figure S10. a) Area of the EDAX measurement, b-f) elemental mapping of Na, K, C, O and Br, respectively, g) EDAX spectrum and h) distribution of chemical composition respective for Na, K, C, O and Br in $[K_2(\mu_4\text{-TBT})(H_2O)_4]_n$ (**2**) synthesized under ultrasonic irradiations.

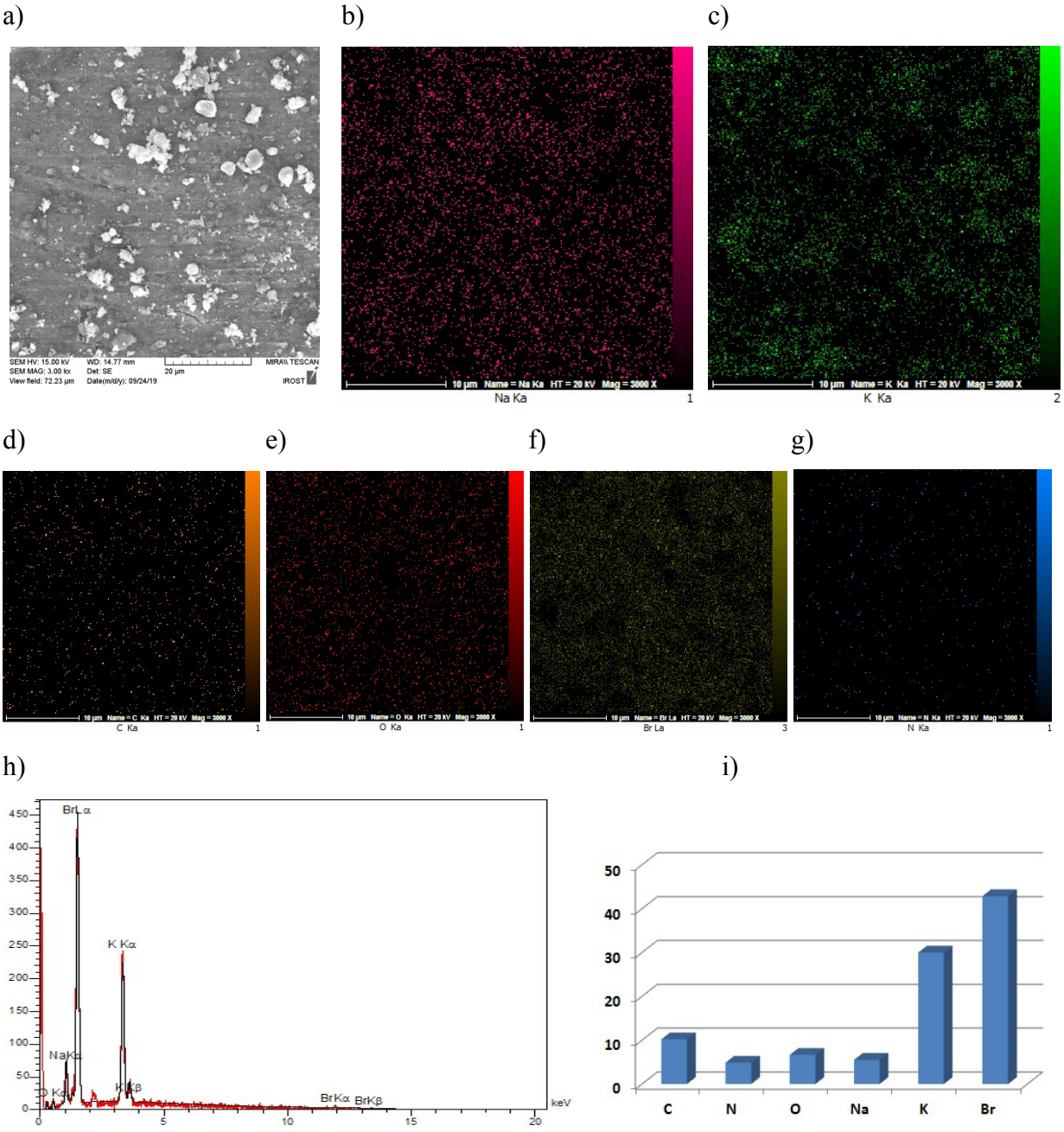


Figure S11. a) Area of the EDAX measurement, b-g) elemental mapping of Na, K, C, O, Br and N, respectively, h) EDAX spectrum and i) distribution of chemical composition respective for Na, K, C, O, Br and N in compound **1** after a LAG reaction with excess KNO_3.

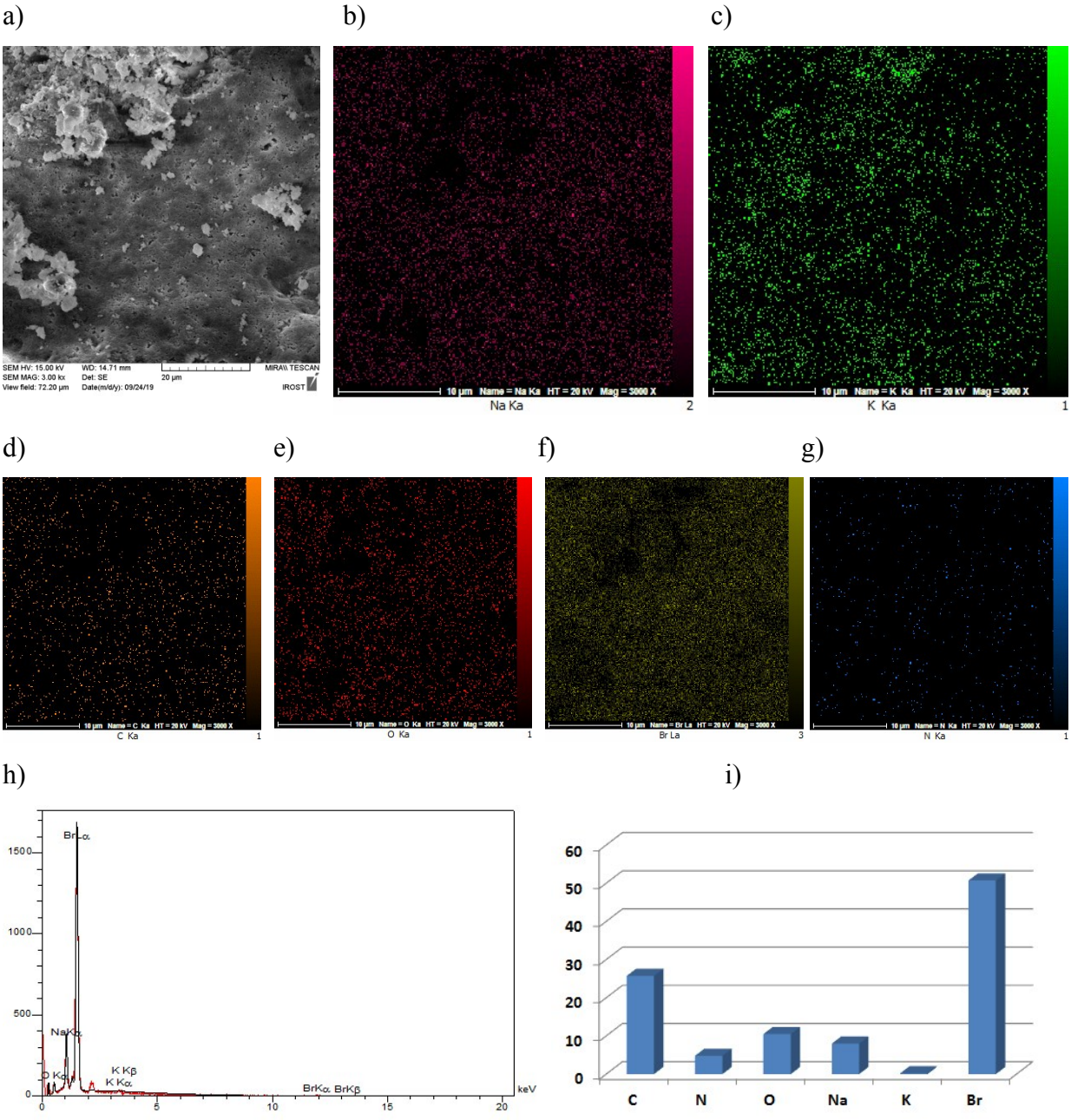


Figure S12. a) Area of the EDAX measurement, b-g) elemental mapping of Na, K, C, O, Br and N, respectively, h) EDAX spectrum and i) distribution of chemical composition respective for Na, K, C, O, Br and N in compound **2** after a LAG reaction with excess $NaNO_3$.

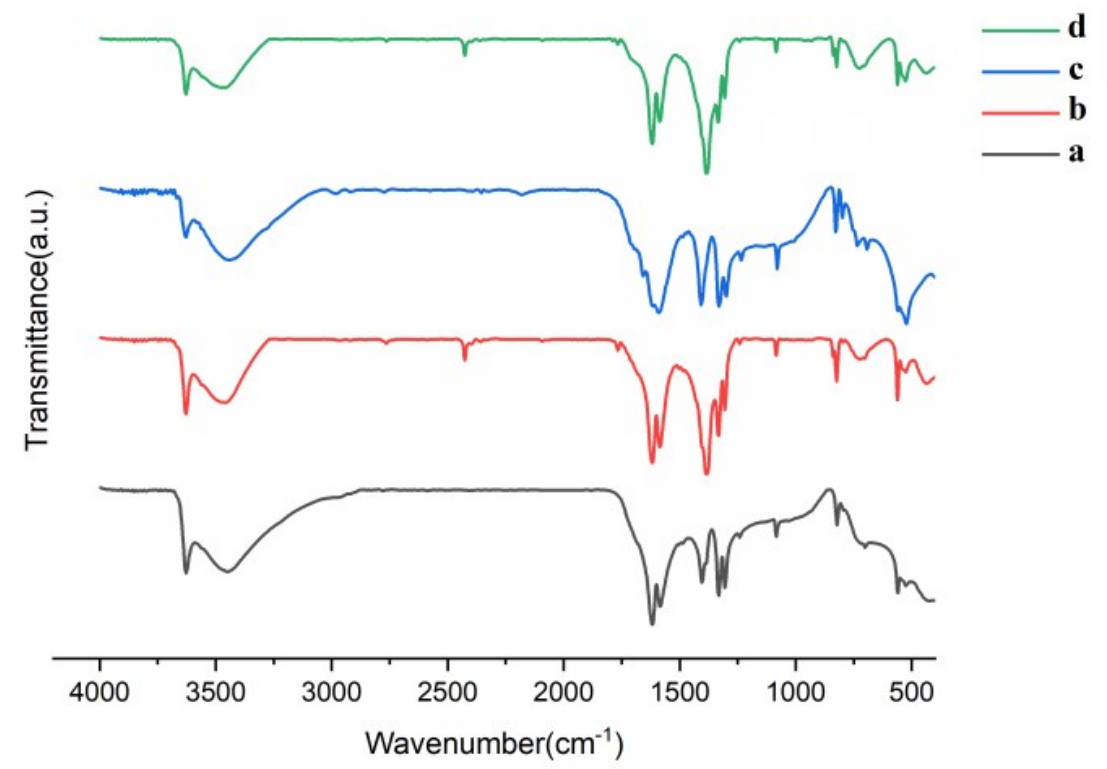
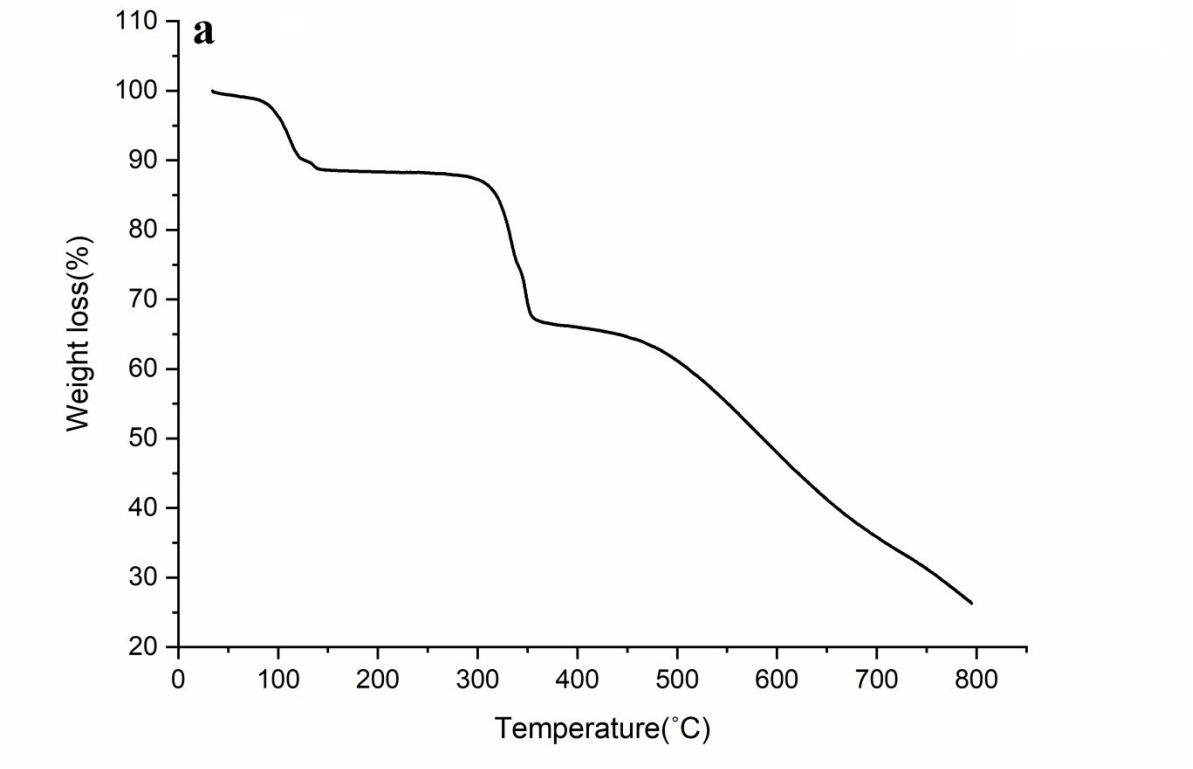
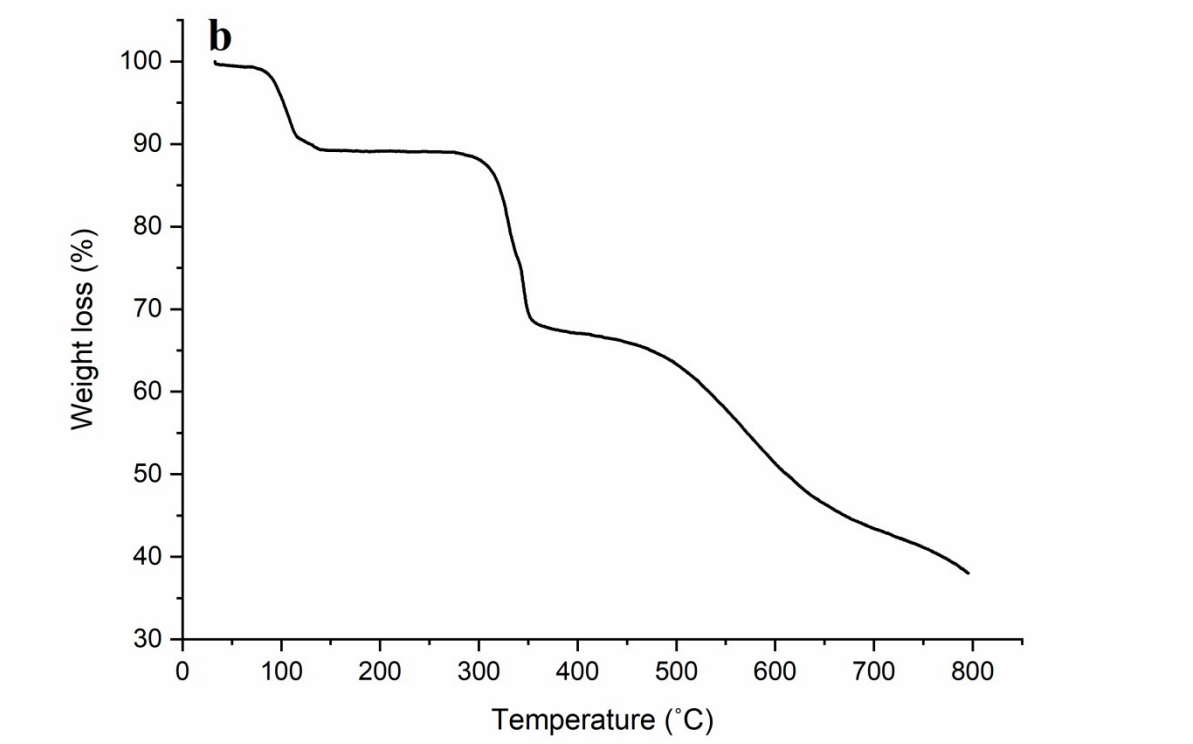


Figure S13. IR spectra of a) $[Na_2(\mu_4\text{-TBT})(H_2O)_4]_n$ (**1**) synthesized under ultrasonic irradiations, d) compound **1** after a LAG reaction with excess KNO_3, c) $[K_2(\mu_4\text{-TBT})(H_2O)_4]_n$ (**2**) synthesized under ultrasonic irradiations, d) compound **2** after a LAG reaction with excess $NaNO_3$.


a
Weight loss(%)
Temperature(˚C)
110
100
90
80
70
60
50
40
30
20
0
100
200
300
400
500
600
700
800


b
Weight loss (%)
Temperature (˚C)
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90
80
70
60
50
40
30
0
100
200
300
400
500
600
700
800

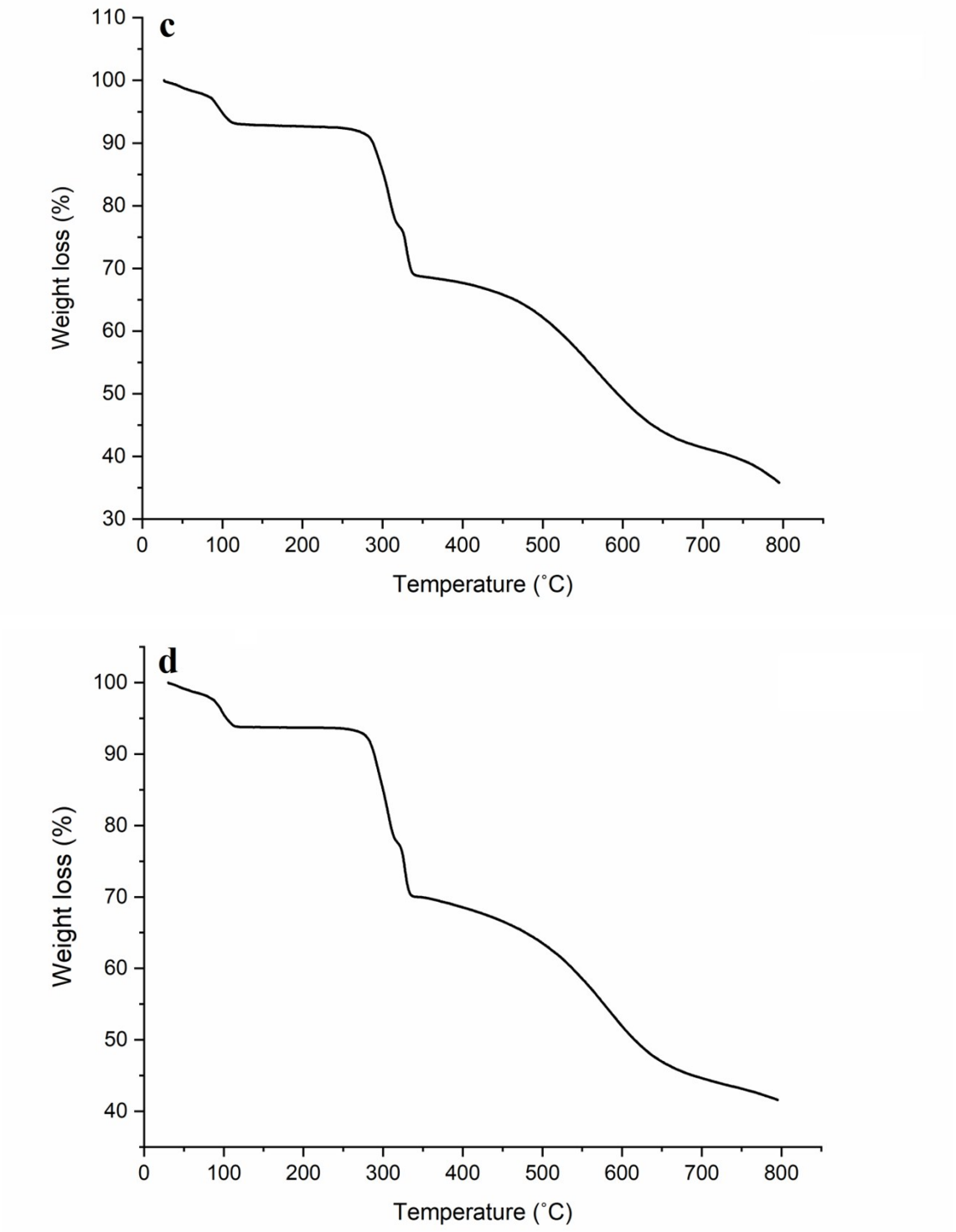

Figure S14. Thermal behavior of a) $[Na_2(\mu_4\text{-TBT})(H_2O)_4]_n$ (**1**) synthesized under ultrasonic irradiations, d) compound **1** after a LAG reaction with excess KNO_3, c) $[K_2(\mu_4\text{-TBT})(H_2O)_4]_n$ (**2**) synthesized under ultrasonic irradiations, d) compound **2** after a LAG reaction with excess $NaNO_3$.