Electronic Supplementary Material (ESI) for CrystEngComm.

Supramolecular [Na(15-crown-5)]$^+$ cations anchored to face sharing octahedral lead bromide chains featuring a rotor in a one-dimensional perovskite with a reversible isostructural phase transition near room temperature

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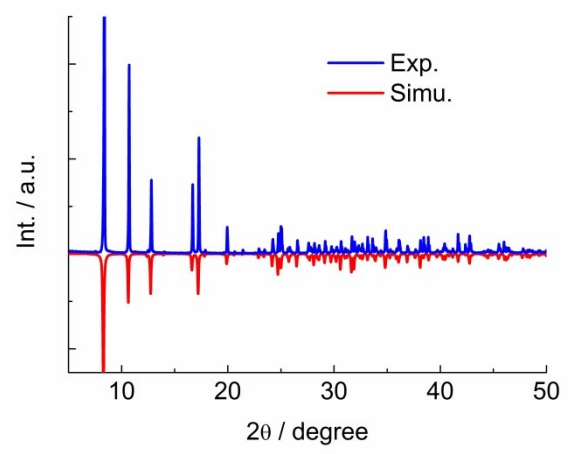

Fig. S1: Simulated and experimental PXRD patterns of **1**.

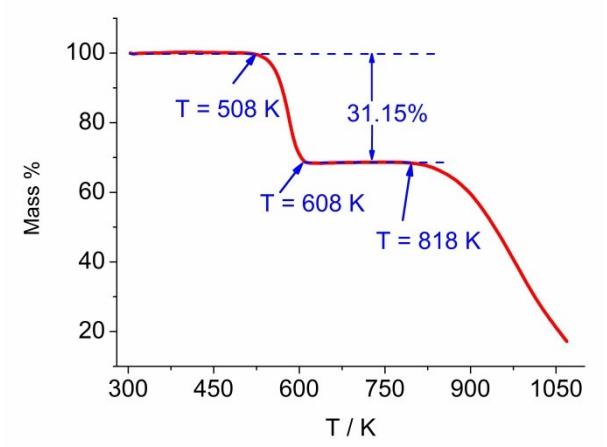

Fig. S2: TG plot of **1** in 303–1068 K.

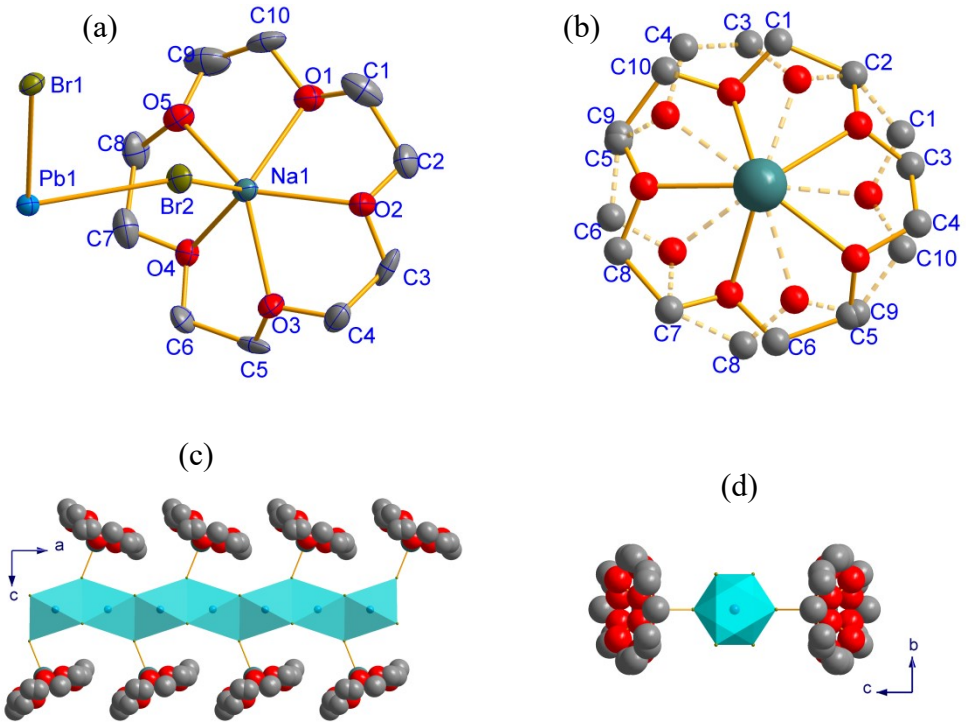

Fig. S3: (a) An asymmetric unit of **1** with non-hydrogen atom labeling (the thermal ellipsoids are drawn at 30% probability level) (b) disordered 15-crown-5 molecule (c, d) A face-sharing octahedral $[PbBr_3]_\infty$ chain linked to supramolecular [Na(15-crown-5)]$^+$ cations viewed along *a*-/*b*-axis, respectively, in HTP at 305 K.

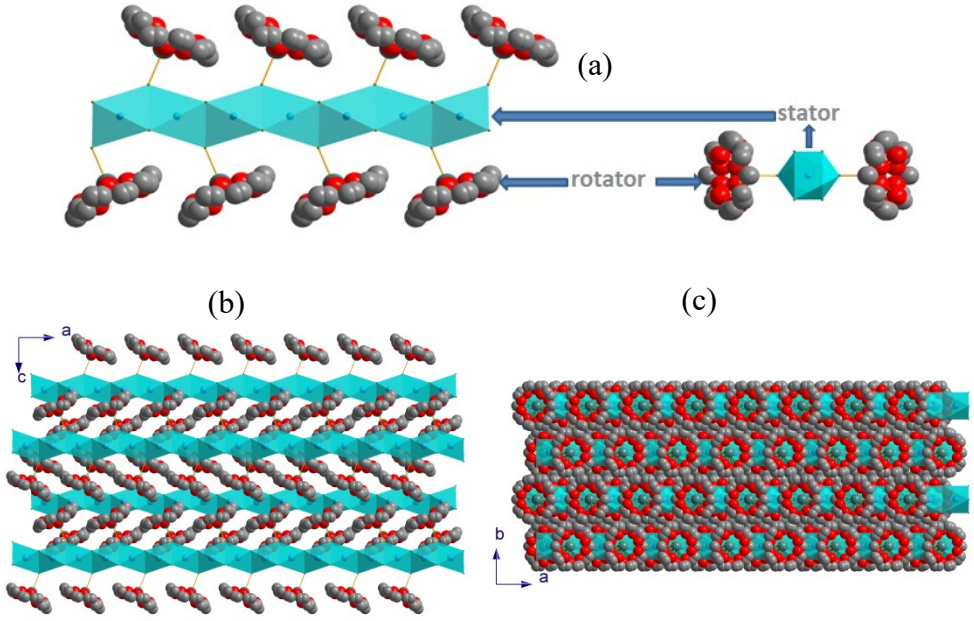

Fig. S4: (a) Illustration for the rotors and stators (b, c) packing diagrams of one-dimensional supramolecular rotors viewed along *b*- and *c*-axes for **1**.

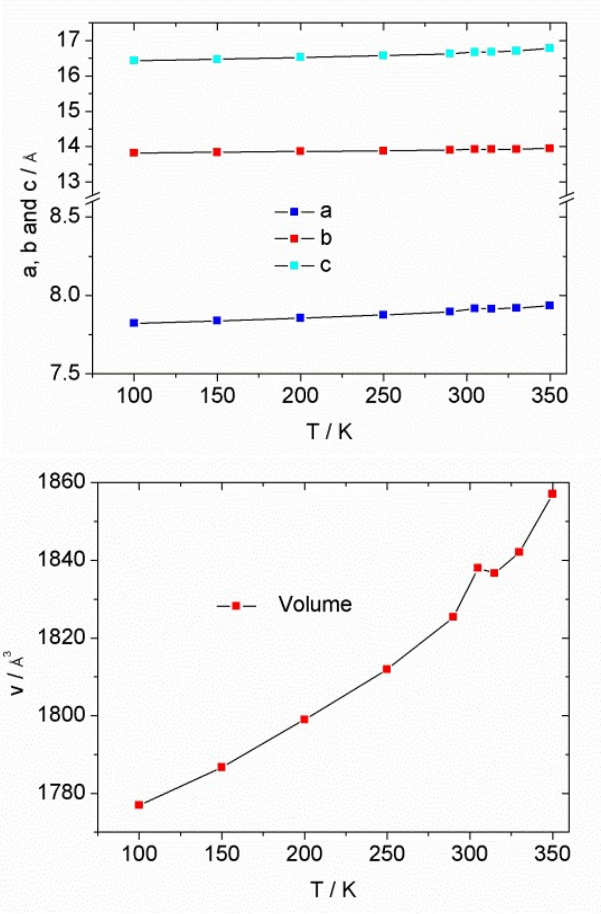

Fig. S5: Variable-temperature cell Parameters in **1** between 100 and 350 K.

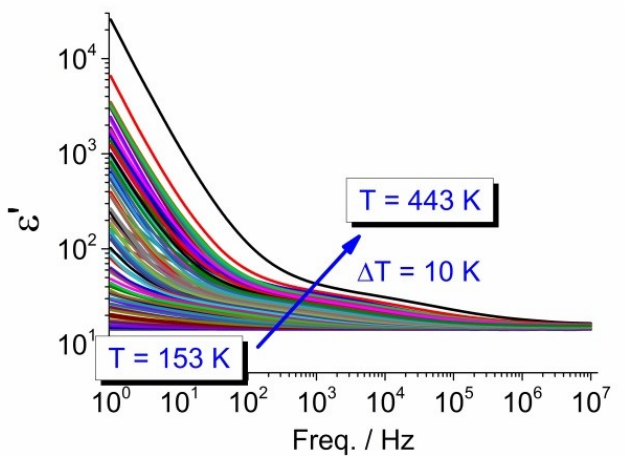

Fig. S6: Plots of dielectric permittivity real part versus frequency in 153–443 K for **1**.

Table S1: Crystal data and structure refinements for **1** at 100, 150, 200, 250, 315, 330 and 350 K

Temp./K	100	150	200	250
Wavelength/Å	0.71073	0.71073	0.71073	0.71073
Formula	$C_{10}H_{20}Br_3NaO_5Pb$	$C_{10}H_{20}Br_3NaO_5Pb$	$C_{10}H_{20}Br_3NaO_5Pb$	$C_{10}H_{20}Br_3NaO_5Pb$
Formula WG	690.17	690.17	690.17	690.17
SG	Pnma	Pnma	Pnma	Pnma
CCDC no.	1951851	1951853	1951870	2098317
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
a (Å)	7.8228(3)	7.8377(3)	7.8558(3)	7.8755(3）
b (Å)	13.8222(6)	13.8396(6)	13.8616(5)	13.8822(5)
c (Å)	16.4334(8)	16.4718(8)	16.5205(7)	16.5729(7)
V(Å^3)/Z	1776.92(13)/4	1786.71(13)/4	1798.98(12)/4	1811.90(12)
ρ (g·cm^{-1})	2.580	2.566	2.548	2.530
F(000)	1272	1272	1272	1272
Abs. coeff. (mm^{-1})	16.277	16.188	16.077	15.962
θ Ranges/°	2.48-27.55	2.473-28.335	2.47-28.24	2.46-28.33
Index ranges	-10≤ h ≤ 10	-10≤ h ≤ 10	-10≤ h ≤ 10	-10≤ h ≤ 10
	-17≤ k ≤ 17	-17≤k≤ 17	-17≤ k ≤ 17	-17≤ k ≤ 17
	-21 ≤ l ≤ 20	-21 ≤ l ≤ 21	-21 ≤ l ≤ 22	-21 ≤ l ≤ 22
R_{int}	0.0474	0.0500	0.0523	0.0537
Indep. refl/	2122/	2297/	2313/	2321/
restr.	158/	153/	158/	158/
/para.	60	0	0	6
Refinement method	The least square refinement on F^2			
Goodness of fit on F^2	1.042	1.036	0.992	1.031
R_1, wR_2 [I>2σ(I)]	0.0226	0.0258	0.0262	0.0272
	0.0467	0.0492	0.0507	0.0496
R_1, wR_2 [all data]	0.0296	0.0363	0.0403	0.0474
	0.0487	0.0521	0.0546	0.0543
Residual (e·Å^{-3})	2.623/	2.355/	1.760/	1.527/
	-1.158	-1.602	-1.308	-1.635

$R_1 = \sum||F_o| - |F_c||/|F_o|$, $wR_2 = [\sum w(\sum F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

To continue Table S1

Temp./K	315	330	350
Wavelength/Å	0.71073	0.71073	0.71073
Formula	$C_{10}H_{20}Br_3NaO_5Pb$	$C_{10}H_{20}Br_3NaO_5Pb$	$C_{10}H_{20}Br_3NaO_5Pb$
Formula WG	690.17	690.17	690.17
SG	Pnma	Pnma	Pnma
CCDC no.	2098325	2098430	2098327
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
a (Å)	7.9139(3)	7.9192(3)	7.9357(3)
b (Å)	13.9195(6)	13.9256(6)	13.9514(6)
c (Å)	16.6734(8)	16.7036(8)	16.7733(8)
V(Å^3)/Z	1836.70(14)	1842.07(14)	1857.04(14)/4
ρ (g·cm^{-1})	2.496	2.489	2.469
F(000)	1272	1272	1272
Abs. coeff. (mm^{-1})	15.747	15.701	15.574
θ Ranges/°	2.44-27.45	2.43-27.36	2.43-27.36
Index ranges	-10≤ h ≤ 10	-10≤ h ≤ 10	-10≤ h ≤10
	-17≤ k ≤ 17	-17≤ k ≤17	-17≤k≤17
	-21 ≤ l ≤ 21	-21 ≤ l ≤ 21	-21≤l≤ 21
R_{int}	0.0592	0.0608	0.0604
Indep. refl/	2184/	2186/	2214/
restr.	158/	158/	158/
/para.	12	120	120
Refinement method	The least square refinement on F^2		
Goodness of fit on F^2	1.027	1.038	1.027
R_1, wR_2 [I>2σ(I)]	0.0282	0.0314	0.0340
	0.0444	0.0518	0.0543
R_1, wR_2 [all data]	0.0536	0.0589	0.0676
	0.0494	0.0577	0.0619
Residual (e·Å^{-3})	1.151/	1.003/	1.074/
	-0.966	-0.932	-0.832

$R_1 = \sum||F_o| - |F_c||/|F_o|$, $wR_2 = [\sum w(\sum F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

Table S2: Selected bond lengths (Å) for **1** in LTP at 100 K

Bond	Bond lengths / Å	Bond	Bond lengths / Å
Na(1)-Br(2)	2.9254(18)	Na(1)-O(1)	2.3853(47)
Pb(1)-Br(1)	2.9662(3)	Na(1)-O(1)’	2.3853(47)
Pb(1)-Br(1)#1	3.0568(3)	Na(1)-O(2)	2.4120(46)
Pb(1)-Br(1)#2	2.9662(3)	Na(1)-O(2)’	2.4120(46)
Pb(1)-Br(1)#3	3.0568(3)	Na(1)-O(3)	2.4202(42)
Pb(1)-Br(2)	3.0921(5)	Na(1)-O(3)’	2.4202(42)
Pb(1)-Br(2)#4	3.0644(5)	Na(1)-O(4)	2.4438(42)
		Na(1)-O(4)’	2.4438(42)
		Na(1)-O(5)	2.3270(45)
		Na(1)-O(5)’	2.3270(45)

Symmetry transformations used to generate equivalent atoms:

#1 = x+1/2, -y+3/2, -z+3/2; #2 = x, -y+3/2, z; #3 = x+1/2, y, -z+3/2; #4 = x+1/2, -y+3/2, -z+3/2

Table S3: Selected bond lengths (Å) for **1** in LTP at 150 K

Bond	Bond lengths / Å	Bond	Bond lengths / Å
Na(1)-Br(2)	2.9251(20)	Na(1)-O(1)	2.3887(48)
Pb(1)-Br(1)	2.9689(3)	Na(1)-O(1)’	2.3887(48)
Pb(1)-Br(1)#1	3.0577(3)	Na(1)-O(2)	2.4149(58)
Pb(1)-Br(1)#2	3.0577(3)	Na(1)-O(2)’	2.4149(58)
Pb(1)-Br(1)#3	2.9689(3)	Na(1)-O(3)	2.4140(42)
Pb(1)-Br(2)	3.0950(6)	Na(1)-O(3)’	2.4140(42)
Pb(1)-Br(2)#4	3.0681(6)	Na(1)-O(4)	2.4389(50)
		Na(1)-O(4)’	2.4389(50)
		Na(1)-O(5)	2.3298(48)
		Na(1)-O(5)’	2.3298(48)

Symmetry transformations used to generate equivalent atoms:

#1 = x+1/2, -y+3/2, -z+3/2; #2 = x, -y+3/2, z; #3 = x+1/2, y, -z+3/2; #4 = x+1/2, -y+3/2, -z+3/2

Table S4: Selected bond lengths (Å) for **1** in LTP at 200 K

Bond	Bond lengths / Å	Bond	Bond lengths / Å
Na(1)-Br(2)	2.9311(20)	Na(1)-O(1)	2.3992(55)
Pb(1)-Br(1)	2.9718(3)	Na(1)-O(1)’	2.3992(55)
Pb(1)-Br(1)#1	3.0587(3)	Na(1)-O(2)	2.4099(62)
Pb(1)-Br(1)#2	2.9718(3)	Na(1)-O(2)’	2.4099(62)
Pb(1)-Br(1)#3	3.0587(3)	Na(1)-O(3)	2.4080(42)
Pb(1)-Br(2)	3.0961(6)	Na(1)-O(3)’	2.4080(42)
Pb(1)-Br(2)#4	3.0743(6)	Na(1)-O(4)	2.4477(57)
		Na(1)-O(4)’	2.4477(57)
		Na(1)-O(5)	2.3331(48)
		Na(1)-O(5)’	2.3331(48)

Symmetry transformations used to generate equivalent atoms:

#1 = x+1/2, -y+3/2, -z+3/2; #2 = x, -y+3/2, z; #3 = x+1/2, y, -z+3/2; #4 = x+1/2, -y+3/2, -z+3/2

Table S5: Selected bond lengths (Å) for **1** in LTP at 250 K

Bond	Bond lengths / Å	Bond	Bond lengths / Å
Na(1)-Br(2)	2.9322(21)	Na(1)-O(1)	2.3953(63)
Pb(1)-Br(1)	2.9750(4)	Na(1)-O(1)’	2.3953(63)
Pb(1)-Br(1)#1	3.0594(4)	Na(1)-O(2)	2.4132(67)
Pb(1)-Br(1)#2	2.9750(4)	Na(1)-O(2)’	2.4132(67)
Pb(1)-Br(1)#3	3.0594(4)	Na(1)-O(3)	2.3924(56)
Pb(1)-Br(2)	3.0937(6)	Na(1)-O(3)’	2.3924(56)
Pb(1)-Br(2)#4	3.0838(6)	Na(1)-O(4)	2.4331(57)
		Na(1)-O(4)’	2.4331(57)
		Na(1)-O(5)	2.3452(59)
		Na(1)-O(5)’	2.3452(59)

Symmetry transformations used to generate equivalent atoms:

#1 = x+1/2, -y+3/2, -z+3/2; #2 = x, -y+3/2, z; #3 = x+1/2, y, -z+3/2; #4 = x+1/2, -y+3/2, -z+3/2

Table S6: Selected bond lengths (Å) for **1** in LTP at 290 K

Bond	Bond lengths / Å	Bond	Bond lengths / Å
Na(1)-Br(2)	2.9356(24)	Na(1)-O(1)	2.3982(78)
Pb(1)-Br(1)	2.9794(5)	Na(1)-O(1)’	2.3982(78)
Pb(1)-Br(1)#1	3.0595(5)	Na(1)-O(2)	2.4132(79)
Pb(1)-Br(1)#2	2.9794(5)	Na(1)-O(2)’	2.4132(79)
Pb(1)-Br(1)#3	3.0595(5)	Na(1)-O(3)	2.4029(70)
Pb(1)-Br(2)	3.0865(7)	Na(1)-O(3)’	2.4029(70)
Pb(1)-Br(2)#4	3.1001(7)	Na(1)-O(4)	2.4317(68)
		Na(1)-O(4)’	2.4317(68)
		Na(1)-O(5)	2.3514(67)
		Na(1)-O(5)’	2.3514(67)

Symmetry transformations used to generate equivalent atoms:

#1 = x+1/2, -y+3/2, -z+3/2; #2 = x, -y+3/2, z; #3 = x+1/2, y, -z+3/2; #4 = x+1/2, -y+3/2, -z+3/2

Table S7: Selected bond lengths (Å) for **1** in HTP at 305 K

Bond	Bond lengths / Å	Bond	Bond lengths / Å
Na(1)-Br(2)	2.9434(26)	Na(1)-O(1)	2.4093(78)
Pb(1)-Br(1)	2.9848(5)	Na(1)-O(1)’	2.4093(78)
Pb(1)-Br(1)#1	3.0635(5)	Na(1)-O(2)	2.3977(95)
Pb(1)-Br(1)#2	2.9848(5)	Na(1)-O(2)’	2.3977(95)
Pb(1)-Br(1)#3	3.0635(5)	Na(1)-O(3)	2.3805(70)
Pb(1)-Br(2)	3.0830(7)	Na(1)-O(3)’	2.3805(70)
Pb(1)-Br(2)#4	3.1145(7)	Na(1)-O(4)	2.4270(75)
		Na(1)-O(4)’	2.4270(75)
		Na(1)-O(5)	2.3726(78)
		Na(1)-O(5)’	2.3726(78)

Symmetry transformations used to generate equivalent atoms:

#1 = x+1/2, -y+3/2, -z+3/2; #2 = x, -y+3/2, z; #3 = x+1/2, y, -z+3/2; #4 = x+1/2, -y+3/2, -z+3/2

Table S8: Selected bond lengths (Å) for **1** in HTP at 315 K

Bond	Bond lengths / Å	Bond	Bond lengths / Å
Na(1)-Br(2)	2.9372(26)	Na(1)-O(1)	2.4290(79)
Pb(1)-Br(1)	2.9836(5)	Na(1)-O(1)’	2.4290(79)
Pb(1)-Br(1)#1	3.0601(5)	Na(1)-O(2)	2.4175(99)
Pb(1)-Br(1)#2	2.9836(5)	Na(1)-O(2)’	2.4175(99)
Pb(1)-Br(1)#3	3.0601(5)	Na(1)-O(3)	2.3766(70)
Pb(1)-Br(2)	3.0774(7)	Na(1)-O(3)’	2.3766(70)
Pb(1)-Br(2)#4	3.1162(7)	Na(1)-O(4)	2.4306(75)
		Na(1)-O(4)’	2.4306(75)
		Na(1)-O(5)	2.3668(78)
		Na(1)-O(5)’	2.3668(78)

Symmetry transformations used to generate equivalent atoms:

#1 = x+1/2, -y+3/2, -z+3/2; #2 = x, -y+3/2, z; #3 = x+1/2, y, -z+3/2; #4 = x+1/2, -y+3/2, -z+3/2

Table S9: Selected bond lengths (Å) for **1** in HTP at 330 K

Bond	Bond lengths / Å	Bond	Bond lengths / Å
Na(1)-Br(2)	2.9366(29)	Na(1)-O(1)	2.4126(94)
Pb(1)-Br(1)	2.9837(5)	Na(1)-O(1)’	2.4126(94)
Pb(1)-Br(1)#1	3.0603(5)	Na(1)-O(2)	2.3720(99)
Pb(1)-Br(1)#2	2.9837(5)	Na(1)-O(2)’	2.3720(99)
Pb(1)-Br(1)#3	3.0603(5)	Na(1)-O(3)	2.3746(84)
Pb(1)-Br(2)	3.0755(9)	Na(1)-O(3)’	2.3746(84)
Pb(1)-Br(2)#4	3.1197(9)	Na(1)-O(4)	2.4183(75)
		Na(1)-O(4)’	2.4183(75)
		Na(1)-O(5)	2.3677(78)
		Na(1)-O(5)’	2.3677(78)

Symmetry transformations used to generate equivalent atoms:

#1 = x+1/2, -y+3/2, -z+3/2; #2 = x, -y+3/2, z; #3 = x+1/2, y, -z+3/2; #4 = x+1/2, -y+3/2, -z+3/2

Table S10: Selected bond lengths (Å) for **1** in HTP at 350 K

Bond	Bond lengths / Å	Bond	Bond lengths / Å
Na(1)-Br(2)	2.9402(33)	Na(1)-O(1)	2.4156(117)
Pb(1)-Br(1)	2.9886(6)	Na(1)-O(1)’	2.4156(117)
Pb(1)-Br(1)#1	3.0651(6)	Na(1)-O(2)	2.3669(116)
Pb(1)-Br(1)#2	2.9886(6)	Na(1)-O(2)’	2.3669(116)
Pb(1)-Br(1)#3	3.0651(6)	Na(1)-O(3)	2.3722(98)
Pb(1)-Br(2)	3.0793(9)	Na(1)-O(3)’	2.3722(98)
Pb(1)-Br(2)#4	3.1275(9)	Na(1)-O(4)	2.4287(92)
		Na(1)-O(4)’	2.4287(92)
		Na(1)-O(5)	2.3862(102)
		Na(1)-O(5)’	2.3862(102)

Symmetry transformations used to generate equivalent atoms:

#1 = x+1/2, -y+3/2, -z+3/2; #2 = x, -y+3/2, z; #3 = x+1/2, y, -z+3/2; #4 = x+1/2, -y+3/2, -z+3/2

Table S11: The parameters of U_{eq} in **1** at 100, 150, 200, 250, 290, 305, 315, 330 and 350 K

Temp. / K	100	150	200	250	290
Pb1	0.00985(8)	0.01465(8)	0.02015(8)	0.02640(9)	0.03232(9)
Na1	0.0132(4)	0.0183(4)	0.0243(4)	0.0317(5)	0.0399(6)
Br1	0.01526(10)	0.02132(10)	0.02824(11)	0.03615(12)	0.04353(13)
Br2	0.01506(12)	0.02226(13)	0.03029(14)	0.03947(16)	0.04769(17)
O1	0.0170(10)	0.0227(11)	0.0289(12)	0.0453(15)	0.0615(19)
O2	0.0129(11)	0.0204(12)	0.0308(14)	0.0407(16)	0.055(2)
O3	0.0133(10)	0.0173(10)	0.0260(12)	0.0372(14)	0.0459(16)
O4	0.0141(10)	0.0193(10)	0.0290(12)	0.0363(13)	0.0468(16)
O5	0.0145(10)	0.0214(11)	0.0310(12)	0.0437(15)	0.0527(17)
C1	0.0166(16)	0.0227(18)	0.033(2)	0.046(3)	0.067(5)
C2	0.0214(11)	0.0287(12)	0.0413(15)	0.0529(17)	0.066(2)
C3	0.0136(14)	0.0206(16)	0.0309(19)	0.045(3)	0.061(4)
C4	0.0144(18)	0.022(2)	0.031(2)	0.043(3)	0.063(6)
C5	0.013(3)	0.013(2)	0.021(4)	0.038(5)	0.046(6)
C6	0.0124(15)	0.023(2)	0.030(2)	0.039(3)	0.050(4)
C7	0.0247(12)	0.0339(14)	0.0410(15)	0.0548(18)	0.070(2)
C8	0.0177(17)	0.029(2)	0.037(2)	0.050(3)	0.069(5)
C9	0.021(4)	0.022(4)	0.036(6)	0.043(5)	0.049(5)
C10	0.0186(19)	0.024(2)	0.041(3)	0.056(5)	0.073(7)

To Continue Table S11

Temp. / K	305	315	330	350
Pb1	0.03511(10)	0.03693(10)	0.03961(11)	0.04339(13)
Na1	0.0431(6)	0.0461(6)	0.0503(7)	0.0550(8)
Br1	0.04702(14)	0.04933(14)	0.05283(17)	0.05791(19)
Br2	0.05152(18)	0.05392(18)	0.0574(2)	0.0629(3)
O1	0.068(2)	0.072(2)	0.086(3)	0.100(4)
O2	0.067(2)	0.074(3)	0.079(3)	0.093(4)
O3	0.0558(19)	0.0605(19)	0.066(2)	0.072(3)
O4	0.0517(17)	0.0548(17)	0.061(2)	0.071(3)
O5	0.0571(19)	0.0596(19)	0.068(2)	0.077(3)
C1	0.087(6)	0.134(11)	0.093(6)	0.113(8)
C2	0.074(2)	0.079(2)	0.086(3)	0.097(4)
C3	0.061(4)	0.079(7)	0.077(4)	0.087(5)
C4	0.069(6)	0.069(4)	0.074(4)	0.089(6)
C5	0.049(7)	0.080(11)	0.088(8)	0.087(9)
C6	0.058(4)	0.056(4)	0.063(4)	0.068(4)
C7	0.083(3)	0.088(3)	0.092(3)	0.104(4)
C8	0.072(5)	0.077(6)	0.087(5)	0.091(6)
C9	0.108(13)	0.085(13)	0.061(5)	0.081(8)
C10	0.076(8)	0.074(6)	0.086(6)	0.095(7)