Electronic Supplementary Material (ESI) for Dalton Transactions.

Two-step thermotropic phase transition and dielectric relaxation in 1D supramolecular lead iodide perovskite [NH_4@18-crown ether]PbI_3

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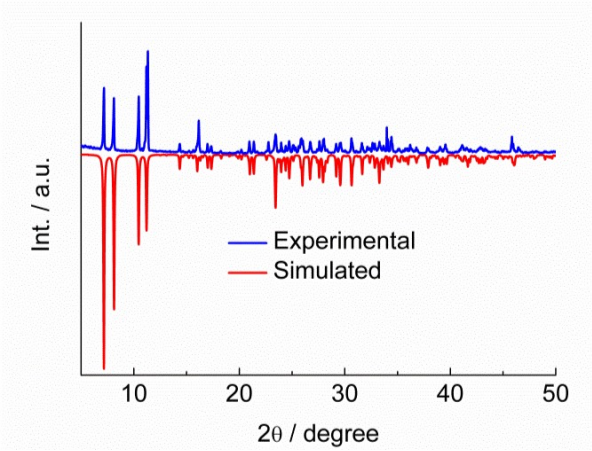

Fig. S1: Comparison of simulated and experimental Powder X-ray diffraction profiles for **1**.

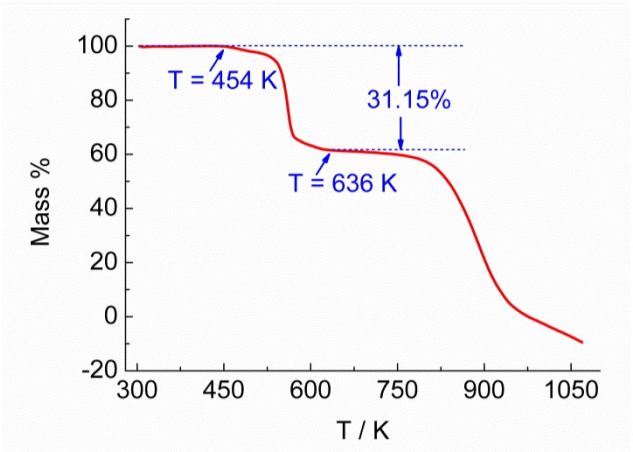

Fig. S2: TG plot for **1** in the temperature range of 303-1068 K.

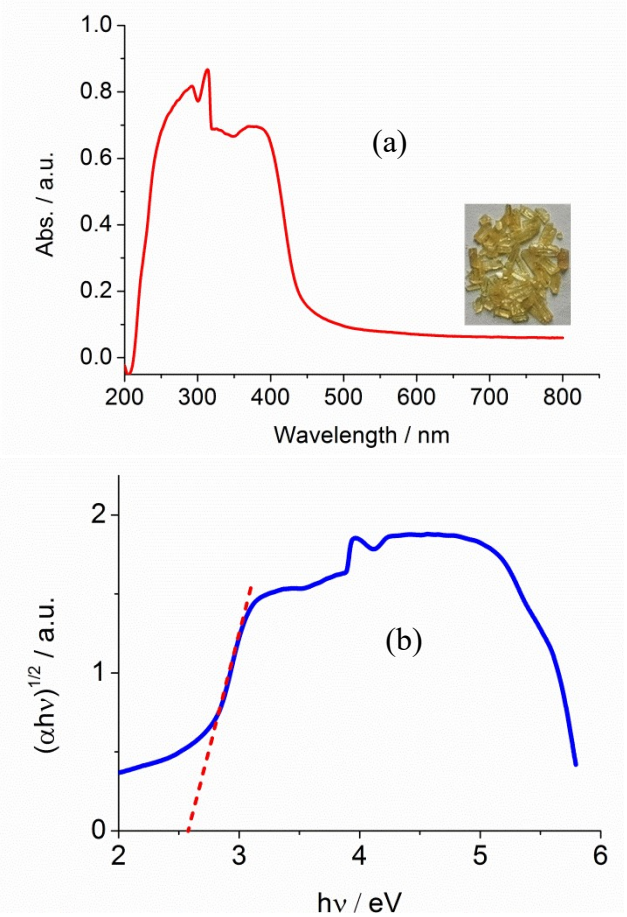

Fig S3: (a) Solid state UV-visible spectrum at ambient condition (Inset: photo of crystal **1**) and (b) Tauc plot obtained by the Kubelka-Munk function transformation for **1**, and the optical bandgap is estimated to be 2.57 eV.

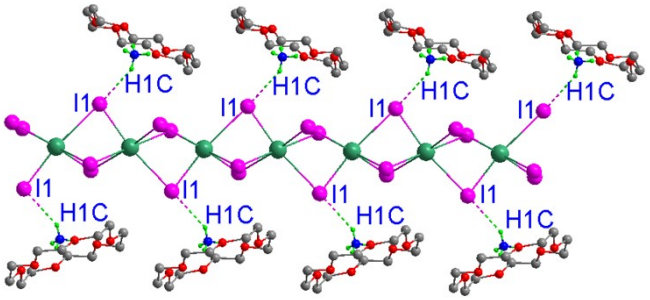

Fig. S4: Straight face-sharing $\{PbI_3\}_\infty$ chain linked to $[NH_4(18\text{-crown-6})]^+$ through charge-assisted H…I for **1** at 293 K.

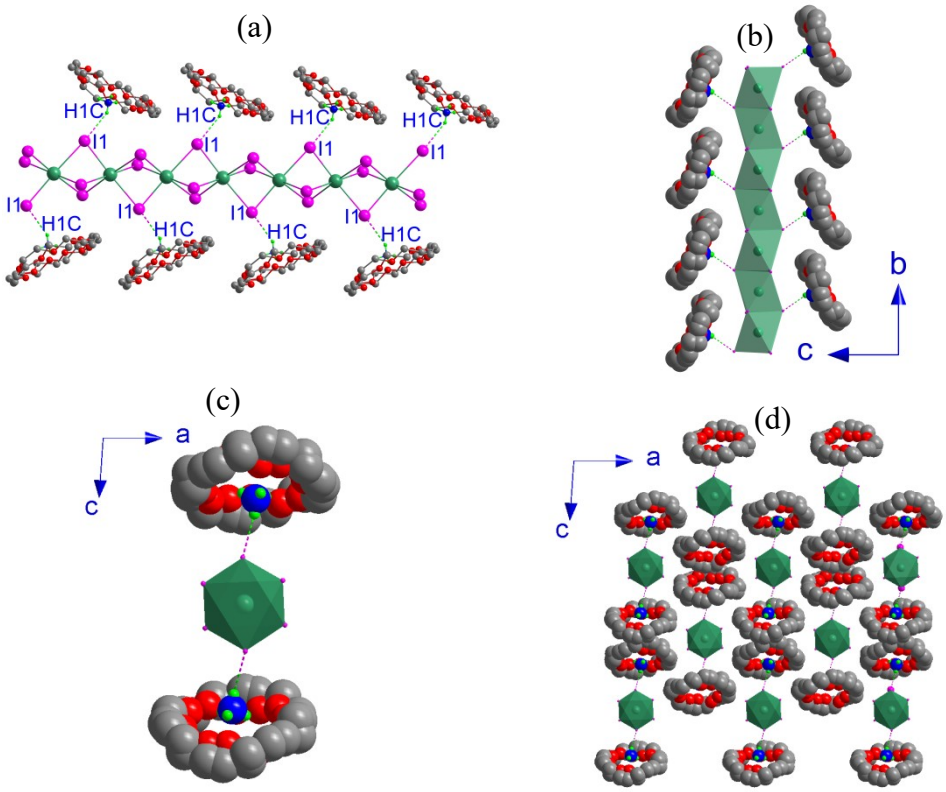

Fig. S5: (a, b and c) Straight face-sharing $\{PbI_3\}_\infty$ chain linked to $[NH_4(18\text{-crown-6})]^+$ through charge-assisted H…I; (d) Packing diagram viewed along the b-axes for **1** at 363 K.

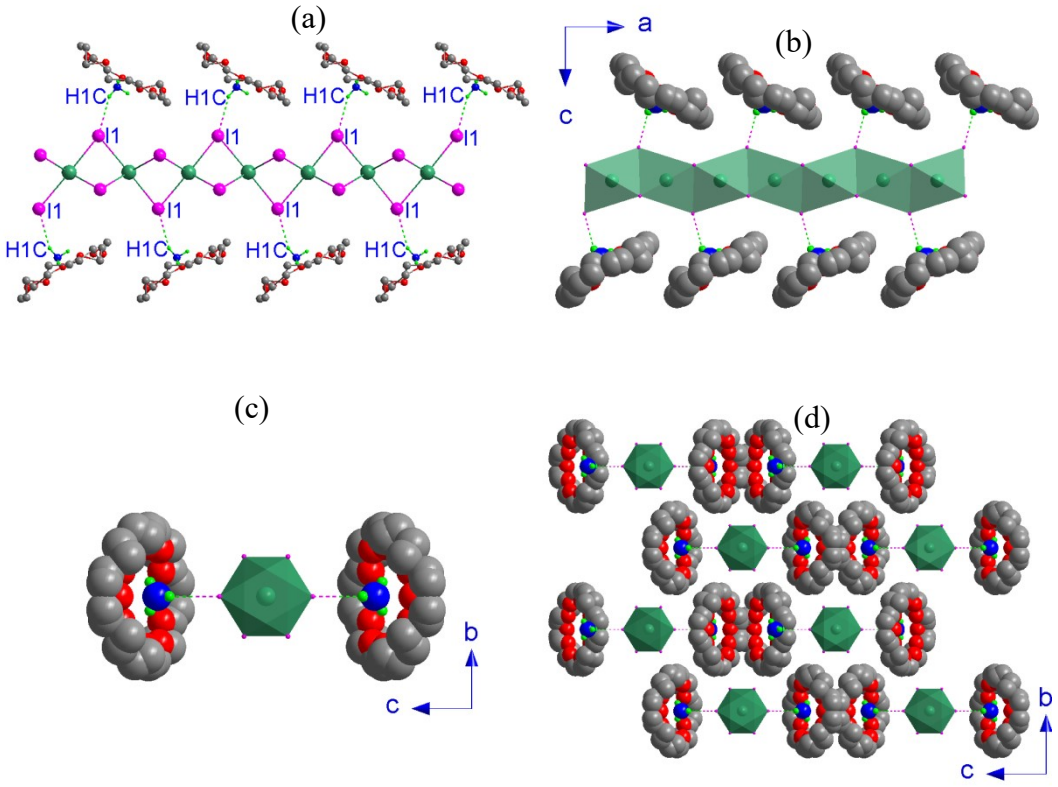

Fig. S6: (a, b and c) Straight face-sharing $\{PbI_3\}_\infty$ chain linked to $[NH_4(18\text{-crown-6})]^+$ through charge-assisted H…I; (d) Packing diagram viewed along the b-axes for **1** at 403 K.

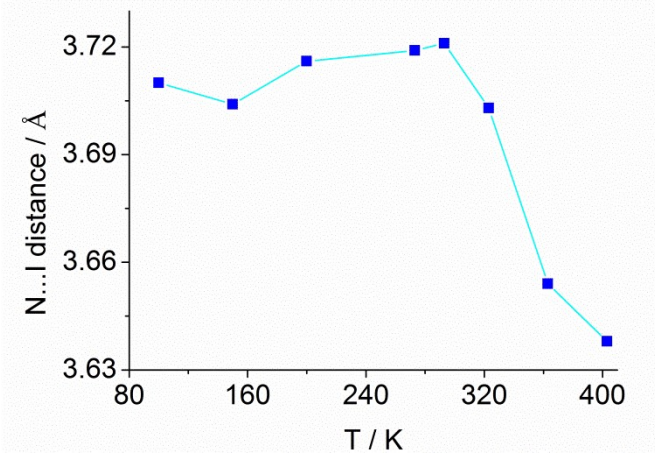

Fig. S7: The shortest N…I distances in **1** between 100 and 403 K.

Table S1: Crystal data and structure refinements for **1** at 100, 150, 200, 273 and 323 K

Temp./K	100	150	200	273	323
SG	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
CCDC no.	2111959	2111960	2111962	2111963	2111965
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a (Å)	15.9602(7)	15.9485(6)	15.9465(6)	15.9434(6)	15.9339(7)
b (Å)	8.6135(3)	8.6219(3)	8.6266(3)	8.6315(3)	8.5831(3)
c (Å)	16.5827(7)	16.6746(7)	16.7569(7)	16.9273(7)	17.2046(8)
α (°)	90	90	90	90	90
β (°)	98.3610(10)	98.1810(10)	97.9190(10)	97.4200(10)	96.483(2)
γ (°)	90	90	90	90	90
V(Å^3)/Z	2255.45(16) /4	2269.53(15)/4	2283.17(15)/4	2309.95(15)/4	2337.89(17)/4
ρ (g·cm^{-1})	2.563	2.547	2.532	2.502	2.472
F(000)	1584	1584	1584	1584	1584
Abs. coeff. (mm^{-1})	11.609	11.537	11.468	11.335	11.200
θ Ranges/°	2.58-24.999	2.692-25.01	2.454-25.004	2.427-25.002	2.38-25.01
Index ranges	-18≤ h ≤17	-18≤ h ≤18	-18≤ h ≤18	-18≤ h ≤18	-17≤ h ≤18
	-9≤ k ≤10	-9≤ k ≤10	-9≤ k ≤10	-9≤ k ≤10	-9≤ k ≤10
	-19≤ l ≤17	-19≤ l ≤18	-19≤ l ≤18	-20≤ l ≤18	-20≤ l ≤19
R_{int}	0.0434	0.0419	0.0444	0.0443	0.0607
Indep. refl/	3913/	3958/	3982/	4022/	4086/
restr.	217/	217/	217/	217/	217/
/para.	209	209	209	209	209
Goodness of fit on F^2	1.123	1.108	1.125	1.099	1.042
R_1, wR_2 [I>2σ(I)]	0.0305	0.0280	0.0316	0.0322	0.0404
	0.0749	0.0686	0.0740	0.0707	0.1039
R_1, wR_2 [all data]	0.0335	0.0320	0.0367	0.0408	0.0565
	0.0765	0.0707	0.0760	0.0739	0.1115
Residual (e·Å^{-3})	1.066/	1.141/	1.152/	1.021/	0.856/
	-2.519	-2.265	-1.628	-0.919	-0.945

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

Table S2: Distortion parameters for each PbI_6 octahedron at the selected temperatures

	100K	150K	200K	273K	293K	323K	363K	403K
d_m [Å]	3.2724	3.2746	3.2765	3.2792	3.2781	3.2738	3.2553	3.2474
$\triangle_{oct}\times10^{-3}$	3.258	3.195	3.137	2.966	2.731	2.269	0.551	0.145
σ^2_{oct}	98.849	97.419	95.578	92.324	88.959	82.718	59.302	48.380

Table S3: Selected bond lengths / Å for **1** at LTP at 100 K

Bond	Bond lengths	Bond	Bond lengths	Bond	Bond lengths
Pb(1)-I(1)	3.0626(6)	N(1)-I(1)	8.1594(65)	N(1)-O(1)	2.9206(82)
Pb(1)-I(1)#1	3.5176(6)	N(1)-I(1)#1	10.6847(68)	N(1)-O(2)	2.9878(86)
Pb(1)-I(2)	3.2855(5)	N(1)-I(2)	7.0775(70)	N(1)-O(3)	2.9204(81)
Pb(1)-I(2)#2	3.2117(5)	N(1)-I(2)#2	11.2312(66)	N(1)-O(4)	3.0753(79)
Pb(1)-I(3)	3.0534(6)	N(1)-I(3)	7.3661(65)	N(1)-O(5)	2.814(8)
Pb(1)-I(3)#3	3.5035(6)	N(1)-I(3)#3	10.9356(68)	N(1)-O(6)	3.1122(76)
Mean bond	3.2724	Mean bond	9.2424	Mean bond	

Symmetry transformations used to generate equivalent atoms:

#1 = -x+1/2, y-1/2, -z+1/2

#2 = -x+1/2, y-1/2, -z+1/2

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

Table S4: Selected bond lengths / Å for **1** at LTP at 150 K

Bond	Bond lengths	Bond	Bond lengths	Bond	Bond lengths
Pb(1)-I(1)	3.0670(5)	N(1)-I(1)	8.1378(49)	N(1)-O(1)	2.9258(69)
Pb(1)-I(1)#1	3.5251 (5)	N(1)-I(1)#1	10.6994(52)	N(1)-O(2)	2.9879(73)
Pb(1)-I(2)	3.2805(5)	N(1)-I(2)	7.0941(52)	N(1)-O(3)	2.9242(68)
Pb(1)-I(2)#2	3.2206(5)	N(1)-I(2)#2	11.2246(50)	N(1)-O(4)	3.0715 (67)
Pb(1)-I(3)	3.0573(6)	N(1)-I(3)	7.3675(51)	N(1)-O(5)	2.8147(68)
Pb(1)-I(3)#3	3.4972(6)	N(1)-I(3)#3	10.9394(52)	N(1)-O(6)	3.1091(65)
Mean bond	3.2746	Mean bond	9.2438		

Symmetry transformations used to generate equivalent atoms:

#1 = -x+1/2, y-1/2, -z+1/2

#2 = -x+1/2, y-1/2, -z+1/2

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

Table S5: Selected bond lengths / Å for **1** at LTP at 200 K

Bond	Bond lengths	Bond	Bond lengths	Bond	Bond lengths
Pb(1)-I(1)	3.0686(6)	N(1)-I(1)	8.1220(65)	N(1)-O(1)	2.9378(82)
Pb(1)-I(1)#1	3.5331(6)	N(1)-I(1)#1	10.7110(68)	N(1)-O(2)	2.9902(86)
Pb(1)-I(2)	3.2771(6)	N(1)-I(2)	7.0982(70)	N(1)-O(3)	2.9164(81)
Pb(1)-I(2)#2	3.2311(6)	N(1)-I(2)#2	11.2275(66)	N(1)-O(4)	3.0483 (80)
Pb(1)-I(3)	3.0612(6)	N(1)-I(3)	7.3773(65)	N(1)-O(5)	2.8079(80)
Pb(1)-I(3)#3	3.4876(6)	N(1)-I(3)#3	10.9373(68)	N(1)-O(6)	3.1000(76)
Mean bond	3.2765	Mean bond	9.2456		

Symmetry transformations used to generate equivalent atoms:

#1 = -x+1/2, y-1/2, -z+1/2

#2 = -x+1/2, y-1/2, -z+1/2

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

Table S6: Selected bond lengths / Å for **1** at LTP at 273 K

Bond	Bond lengths	Bond	Bond lengths	Bond	Bond lengths
Pb(1)-I(1)	3.0752(6)	N(1)-I(1)	8.0891(65)	N(1)-O(1)	2.9289(79)
Pb(1)-I(1)#1	3.5426(6)	N(1)-I(1)#1	10.7178(67)	N(1)-O(2)	2.9795 (97)
Pb(1)-I(2)	3.2662(6)	N(1)-I(2)	7.1098(70)	N(1)-O(3)	2.9226(84)
Pb(1)-I(2)#2	3.2510(6)	N(1)-I(2)#2	11.2173(64)	N(1)-O(4)	3.0326 (74)
Pb(1)-I(3)	3.0710(6)	N(1)-I(3)	7.3758(63)	N(1)-O(5)	2.8082(79)
Pb(1)-I(3)#3	3.4692(6)	N(1)-I(3)#3	10.9358(68)	N(1)-O(6)	3.0820(82)
Mean bond	3.2792	Mean bond	9.2409		

Symmetry transformations used to generate equivalent atoms:

#1 = -x+1/2, y-1/2, -z+1/2

#2 = -x+1/2, y-1/2, -z+1/2

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

Table S7: Selected bond lengths / Å for **1** at LTP at 293 K

Bond	Bond lengths	Bond	Bond lengths	Bond	Bond lengths
Pb(1)-I(1)	3.0825(6)	N(1)-I(1)	8.0649(65)	N(1)-O(1)	2.9247(84)
Pb(1)-I(1)#1	3.5391(6)	N(1)-I(1)#1	10.7023(67)	N(1)-O(2)	2.9662(97)
Pb(1)-I(2)	3.2530(6)	N(1)-I(2)	7.107(7)	N(1)-O(3)	2.9281(86)
Pb(1)-I(2)#2	3.2637(6)	N(1)-I(2)#2	11.2012(64)	N(1)-O(4)	3.0312(74)
Pb(1)-I(3)	3.0800(6)	N(1)-I(3)	7.3648(63)	N(1)-O(5)	2.8099(89)
Pb(1)-I(3)#3	3.4503(6)	N(1)-I(3)#3	10.9263(68)	N(1)-O(6)	3.0617(85)
Mean bond	3.2781	Mean bond	9.2278		

Symmetry transformations used to generate equivalent atoms:

#1 = -x+1/2, y-1/2, -z+1/2

#2 = -x+1/2, y-1/2, -z+1/2

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

Table S8: Selected bond lengths / Å for **1** at LTP at 323 K

Bond	Bond lengths	Bond	Bond lengths	Bond	Bond lengths
Pb(1)-I(1)	3.0959(7)	N(1)-I(1)	8.0498(66)	N(1)-O(1)	2.9249(106)
Pb(1)-I(1)#1	3.5198(7)	N(1)-I(1)#1	10.6962(75)	N(1)-O(2)	2.9709(115)
Pb(1)-I(2)	3.2319(6)	N(1)-I(2)	7.1280(78)	N(1)-O(3)	2.9492 (109)
Pb(1)-I(2)#2	3.2784(6)	N(1)-I(2)#2	11.1975(67)	N(1)-O(4)	3.0268(92)
Pb(1)-I(3)	3.0979(8)	N(1)-I(3)	7.3643(68)	N(1)-O(5)	2.8099(93)
Pb(1)-I(3)#3	3.4188(8)	N(1)-I(3)#3	10.9414(73)	N(1)-O(6)	3.0424(101)
Mean bond	3.2738	Mean bond	9.2295		

Symmetry transformations used to generate equivalent atoms:

#1 = -x+1/2, y-1/2, -z+1/2

#2 = -x+1/2, y-1/2, -z+1/2

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

Table S9: Selected bond lengths / Å for **1** at LTP at 363 K

Bond	Bond lengths	Bond	Bond lengths	Bond	Bond lengths
Pb(1)-I(1)	3.1903(8)	N(1)-I(1)	3.6550(85)	N(1)-O(1)	2.9936(176)
Pb(1)-I(1)#1	3.3860(8)	N(1)-I(1)#1	8.5892(88)	N(1)-O(1)A	2.9037(201)
Pb(1)-I(2)	3.1769(8)	N(1)-I(2)	5.1698(83)	N(1)-O(2)	3.0098(174)
Pb(1)-I(2)#2	3.2913(8)	N(1)-I(2)#2	7.7135(89)	N(1)-O(2)A	2.7584(178)
Pb(1)-I(3)	3.1890(7)	N(1)-I(3)	7.1849(86)	N(1)-O(3)	3.0581(158)
Pb(1)-I(3)#3	3.2988(7)	N(1)-I(3)#3	5.9078(86)	N(1)-O(3)A	2.9302(184)
				N(1)-O(4)	2.7932(163)
				N(1)-O(4)A	2.905(22)
				N(1)-O(5)	2.9493(173)
				N(1)-O(5)A	3.0778(196)
				N(1)-O(6)	2.8505(170)
				N(1)-O(6)A	2.9726(189)
Mean bond	3.2553	Mean bond	6.3700		

Symmetry transformations used to generate equivalent atoms:

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

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

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

Table S10: Selected bond lengths / Å for **1** at LTP at 403 K

Bond	Bond lengths	Bond	Bond lengths	Bond	Bond lengths
Pb(1)-I(1)	3.2652(12)	N(1)-I(1)	3.6384(128)	N(1)-O(1)	2.8531(270)
Pb(1)-I(1)#1	3.2914(12)	N(1)-I(1)#1	10.0741(128)	N(1)-O(1)#5	2.8531(270)
Pb(1)-I(2)	3.1933(9)	N(1)-I(2)	7.4679(121)	N(1)-O(1)A	3.1810(434)
Pb(1)-I(2)#2	3.2706(9)	N(1)-I(2)#2	7.5434(123)	N(1)-O(2)	2.8568(243)
Pb(1)-I(2)#3	3.1933(9)	N(1)-I(2)#3	7.4679(121)	N(1)-O(2)#6	2.8568(243)
Pb(1)-I(2)#4	3.2706(9)	N(1)-I(2)#4	7.5434(123)	N(1)-O(2)A	3.0183(273)
				N(1)-O(2)A#7	3.0183(273)
				N(1)-O(3)	2.8740(263)
				N(1)-O(3)#8	2.8740(273)
				N(1)-O(3)A	3.1094(311)
				N(1)-O(3)A#9	3.1094(311)
				N(1)-O(4)A	2.9430(389)
Mean bond	3.2474	Mean bond	7.2892		

Symmetry transformations used to generate equivalent atoms:

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

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

#3 = x, -y+3/2, z

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

#5 = x, -y+3/2, z

#6 = x, -y+3/2, z

#7 = x, -y+3/2, z

#8 = x, -y+3/2, z

#9 = x, -y+3/2, z

Table S11: Selected bond Angle / ° for **1** at LTP at 100 K

Bond	Angle/°	Bond	Angle/°
∠I(1)-Pb(1)-I(2)	84.286(14)	∠I(2)-Pb(1)-I(3)	94.225(14)
∠I(1)-Pb(1)-I(3) #3	81.344(15)	∠I(3)#3-Pb(1)-I(1)#1	106.776(14)
∠I(1)-Pb(1)-I(2) #2	94.253(14)	∠I(3)#3-Pb(1)-I(2)#2	101.230(14)
∠I(1)-Pb(1)-I(3)	91.394(15)	∠I(1)#1-Pb(1)-I(2)#2	78.464(13)
∠I(2)-Pb(1)-I(3)#3	78.159(13)	∠I(1)#1-Pb(1)-I(3)	81.236(15)
∠I(2)-Pb(1)-I(1)#1	103.036(13)	∠I(2)#2-Pb(1)-I(3)	86.219(14)

Symmetry transformations used to generate equivalent atoms:

#1 = -x+1/2, y-1/2, -z+1/2

#2 = -x+1/2, y-1/2, -z+1/2

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

Table S12: Selected bond Angle / ° for **1** at LTP at 150 K

Bond	Angle/°	Bond	Angle/°
∠I(1)-Pb(1)-I(2)	84.344(13)	∠I(2)-Pb(1)-I(3)	94.478(12)
∠I(1)-Pb(1)-I(3) #3	81.528(13)	∠I(3)#3-Pb(1)-I(1)#1	106.279(12)
∠I(1)-Pb(1)-I(2) #2	94.598(13)	∠I(3)#3-Pb(1)-I(2)#2	101.202(13)
∠I(1)-Pb(1)-I(3)	91.695(13)	∠I(1)#1-Pb(1)-I(2)#2	78.278(13)
∠I(2)-Pb(1)-I(3)#3	78.265(13)	∠I(1)#1-Pb(1)-I(3)	81.202(13)
∠I(2)-Pb(1)-I(1)#1	102.818(13)	∠I(2)#2-Pb(1)-I(3)	85.942(12)

Symmetry transformations used to generate equivalent atoms:

#1 = -x+1/2, y-1/2, -z+1/2

#2 = -x+1/2, y-1/2, -z+1/2

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

Table S13: Selected bond Angle / ° for **1** at LTP at 200 K

Bond	Angle/°	Bond	Angle/°
∠I(1)-Pb(1)-I(2)	84.453(15)	∠I(2)-Pb(1)-I(3)	94.675(14)
∠I(1)-Pb(1)-I(3) #3	81.734(15)	∠I(3)#3-Pb(1)-I(1)#1	105.767(14)
∠I(1)-Pb(1)-I(2) #2	94.951(15)	∠I(3)#3-Pb(1)-I(2)#2	101.096(14)
∠I(1)-Pb(1)-I(3)	92.066(16)	∠I(1)#1-Pb(1)-I(2)#2	78.093(15)
∠I(2)-Pb(1)-I(3)#3	78.464(14)	∠I(1)#1-Pb(1)-I(3)	81.088(15)
∠I(2)-Pb(1)-I(1)#1	102.539(15)	∠I(2)#2-Pb(1)-I(3)	85.710(14)

Symmetry transformations used to generate equivalent atoms:

#1 = -x+1/2, y-1/2, -z+1/2

#2 = -x+1/2, y-1/2, -z+1/2

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

Table S14: Selected bond Angle / ° for **1** at LTP at 273 K

Bond	Angle/°	Bond	Angle/°
∠I(1)-Pb(1)-I(2)	84.643(16)	∠I(2)-Pb(1)-I(3)	95.000(15)
∠I(1)-Pb(1)-I(3) #3	82.086(15)	∠I(3)#3-Pb(1)-I(1)#1	104.835(14)
∠I(1)-Pb(1)-I(2) #2	95.563(16)	∠I(3)#3-Pb(1)-I(2)#2	100.910(14)
∠I(1)-Pb(1)-I(3)	92.703(17)	∠I(1)#1-Pb(1)-I(2)#2	77.796(15)
∠I(2)-Pb(1)-I(3)#3	78.888(14)	∠I(1)#1-Pb(1)-I(3)	80.940(15)
∠I(2)-Pb(1)-I(1)#1	102.021(15)	∠I(2)#2-Pb(1)-I(3)	85.217(15)

Symmetry transformations used to generate equivalent atoms:

#1 = -x+1/2, y-1/2, -z+1/2

#2 = -x+1/2, y-1/2, -z+1/2

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

Table S15: Selected bond Angle / ° for **1** at LTP at 293 K

Bond	Angle/°	Bond	Angle/°
∠I(1)-Pb(1)-I(2)	84.803(16)	∠I(2)-Pb(1)-I(3)	95.145(15)
∠I(1)-Pb(1)-I(3) #3	82.337(16)	∠I(3)#3-Pb(1)-I(1)#1	104.121(15)
∠I(1)-Pb(1)-I(2) #2	95.931(17)	∠I(3)#3-Pb(1)-I(2)#2	100.742(14)
∠I(1)-Pb(1)-I(3)	93.116(18)	∠I(1)#1-Pb(1)-I(2)#2	77.731(15)
∠I(2)-Pb(1)-I(3)#3	79.328(14)	∠I(1)#1-Pb(1)-I(3)	80.917(16)
∠I(2)-Pb(1)-I(1)#1	101.536(15)	∠I(2)#2-Pb(1)-I(3)	84.836(15)

Symmetry transformations used to generate equivalent atoms:

#1 = -x+1/2, y-1/2, -z+1/2

#2 = -x+1/2, y-1/2, -z+1/2

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

Table S16: Selected bond Angle / ° for **1** at LTP at 323 K

Bond	Angle/°	Bond	Angle/°
∠I(1)-Pb(1)-I(2)	84.917(19)	∠I(2)-Pb(1)-I(3)	95.157(17)
∠I(1)-Pb(1)-I(3) #3	82.717(18)	∠I(3)#3-Pb(1)-I(1)#1	102.948(17)
∠I(1)-Pb(1)-I(2) #2	96.533(19)	∠I(3)#3-Pb(1)-I(2)#2	100.379(17)
∠I(1)-Pb(1)-I(3)	93.67(2)	∠I(1)#1-Pb(1)-I(2)#2	77.791(16)
∠I(2)-Pb(1)-I(3)#3	80.160(17)	∠I(1)#1-Pb(1)-I(3)	81.041(18)
∠I(2)-Pb(1)-I(1)#1	100.733(16)	∠I(2)#2-Pb(1)-I(3)	84.383(17)

Symmetry transformations used to generate equivalent atoms:

#1 = -x+1/2, y-1/2, -z+1/2

#2 = -x+1/2, y-1/2, -z+1/2

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

Table S17: Selected bond Angle / ° for **1** at LTP at 363 K

Bond	Angle/°	Bond	Angle/°
∠I(1)-Pb(1)-I(2)	95.93(2)	∠I(2)-Pb(1)-I(3)	95.22(2)
∠I(1)-Pb(1)-I(3) #3	98.11(2)	∠I(3)#3-Pb(1)-I(1)#1	79.89(2)
∠I(1)-Pb(1)-I(2) #2	83.52(2)	∠I(3)#3-Pb(1)-I(2)#2	98.46(2)
∠I(1)-Pb(1)-I(3)	84.58(2)	∠I(1)#1-Pb(1)-I(2)#2	98.39(2)
∠I(2)-Pb(1)-I(3)#3	83.20(2)	∠I(1)#1-Pb(1)-I(3)	97.39(2)
∠I(2)-Pb(1)-I(1)#1	82.21(2)	∠I(2)#2-Pb(1)-I(3)	83.14(2)

Symmetry transformations used to generate equivalent atoms:

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

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

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

Table S18: Selected bond Angle / ° for **1** at LTP at 403 K

Bond	Angle/°	Bond	Angle/°
∠I(1)-Pb(1)-I(2)	95.57(3)	∠I(2)-Pb(1)-I(2)#4	95.64(2)
∠I(1)-Pb(1)-I(2)#2	82.61(2)	∠I(2)#1-Pb(1)-I(2)#2	98.442(14)
∠I(1)-Pb(1)-I(2)#3	95.57(3)	∠I(2)#1-Pb(1)-I(2)#3	83.390(15)
∠I(1)-Pb(1)-I(2)#4	82.61(2)	∠I(2)#1-Pb(1)-I(2)#4	98.442(14)
∠I(2)-Pb(1)-I(2)#1	83.390(15)	∠I(2)#2-Pb(1)-I(2)#3	95.64(2)
∠I(2)-Pb(1)-I(2)#3	85.57(3)	∠I(2)#2-Pb(1)-I(2)#4	83.09(3)

Symmetry transformations used to generate equivalent atoms:

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

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

#3 = x, -y+3/2, z

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

Table S19: The parameters U_{eq} of non-H atoms in **1** at 100, 150, 200, 273, 293, 323, 363 and 403 K

Non-H atom	100K	150K	200K	273K	293K	323K	363K	403K
Pb1	0.0113(1)	0.0149(1)	0.0208(1)	0.0311(1)	0.0362(1)	0.0438(2)	0.0561(2)	0.0675(3)
N1	0.015(1)	0.019(1)	0.024(1)	0.038(2)	0.043(2)	0.053(2)	0.077(2)	0.089(4)
I1	0.0163(1)	0.0227(1)	0.0315(2)	0.0467(2)	0.054(2)	0.064(2)	0.0807(3)	0.0984(4)
I2	0.0141(1)	0.0193(1)	0.027(1)	0.0403(2)	0.0466(2)	0.0557(2)	0.0821(3)	0.0893(3)
I3	0.0156(1)	0.0215(1)	0.0298(2)	0.045(2)	0.0531(2)	0.0645(2)	0.0696(2)	
O1	0.015(1)	0.02(1)	0.030(1)	0.049(1)	0.061(2)	0.086(2)	0.091(4)	0.147(6)
O1A							0.094(5)	0.172(9)
O2	0.016(1)	0.022(1)	0.032(1)	0.052(1)	0.067(2)	0.091(2)	0.095(5)	0.149(6)
O2A							0.092(5)	0.175(6)
O3	0.016(1)	0.022(1)	0.031(1)	0.051(1)	0.066(2)	0.093(2)	0.089(4)	0.135(6)
O3A							0.100(5)	0.175(7)
O4	0.014(1)	0.0198(9)	0.029(1)	0.048(1)	0.060(2)	0.083(2)	0.097(4)	
O4A							0.116(6)	0.162(9)
O5	0.016(1)	0.0217(9)	0.03(1)	0.049(1)	0.061(2)	0.089(2)	0.103(5)	
O5A							0.100(5)	
O6	0.016(1)	0.0210(9)	0.0309(12)	0.052(1)	0.066(2)	0.092(2)	0.093(4)	
O6A							0.082(5)	
C1	0.019(2)	0.024(1)	0.0346(18)	0.054(2)	0.068(2)	0.088(3)	0.107(6)	0.151(8)
C1A							0.097(6)	0.171(8)
C2	0.02(2)	0.026(1)	0.038(2)	0.056(2)	0.071(2)	0.084(3)	0.098(6)	0.158(7)
C2A							0.096(6)	0.164(7)
C3	0.018(2)	0.024(1)	0.037(2)	0.059(2)	0.075(2)	0.105(3)	0.103(6)	0.154(7)
C3A							0.103(7)	0.178(7)
C4	0.019(2)	0.024(1)	0.035(2)	0.057(2)	0.071(2)	0.097(3)	0.104(6)	0.145(7)
C4A							0.110(7)	0.177(8)
C5	0.018(2)	0.024(1)	0.034(2)	0.057(2)	0.072(2)	0.096(3)	0.099(6)	0.143(7)
C5A							0.108(7)	0.26(3)
C6	0.018(2)	0.024(1)	0.034(2)	0.054(2)	0.067(2)	0.082(3)	0.091(6)	0.146(8)
C6A							0.108(6)	0.166(9)
C7	0.017(2)	0.024(1)	0.032(2)	0.052(2)	0.070(2)	0.093(3)	0.106(6)	
C7A							0.105(6)	
C8	0.017(2)	0.022(1)	0.033(2)	0.052(2)	0.066(2)	0.088(3)	0.107(6)	
C8A							0.112(6)	
C9	0.019(2)	0.025(1)	0.036(2)	0.060(2)	0.074(2)	0.098(3)	0.117(6)	
C9A							0.093(7)	
C10	0.019(2)	0.026(1)	0.038(2)	0.061(2)	0.075(2)	0.094(3)	0.101(6)	
C10A							0.096(6)	
C11	0.016(2)	0.022(1)	0.033(2)	0.053(2)	0.070(2)	0.094(3)	0.100(6)	
C11A							0.094(7)	
C12	0.017(2)	0.024(1)	0.037(2)	0.057(2)	0.068(2)	0.084(3)	0.092(6)	
C12A							0.091(6)	