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Electronic Supplementary Information(ESI)

Effect of halide solid solution on the structure, phase transition behaviour and dielectric properties of dabcoH$^+$ chains

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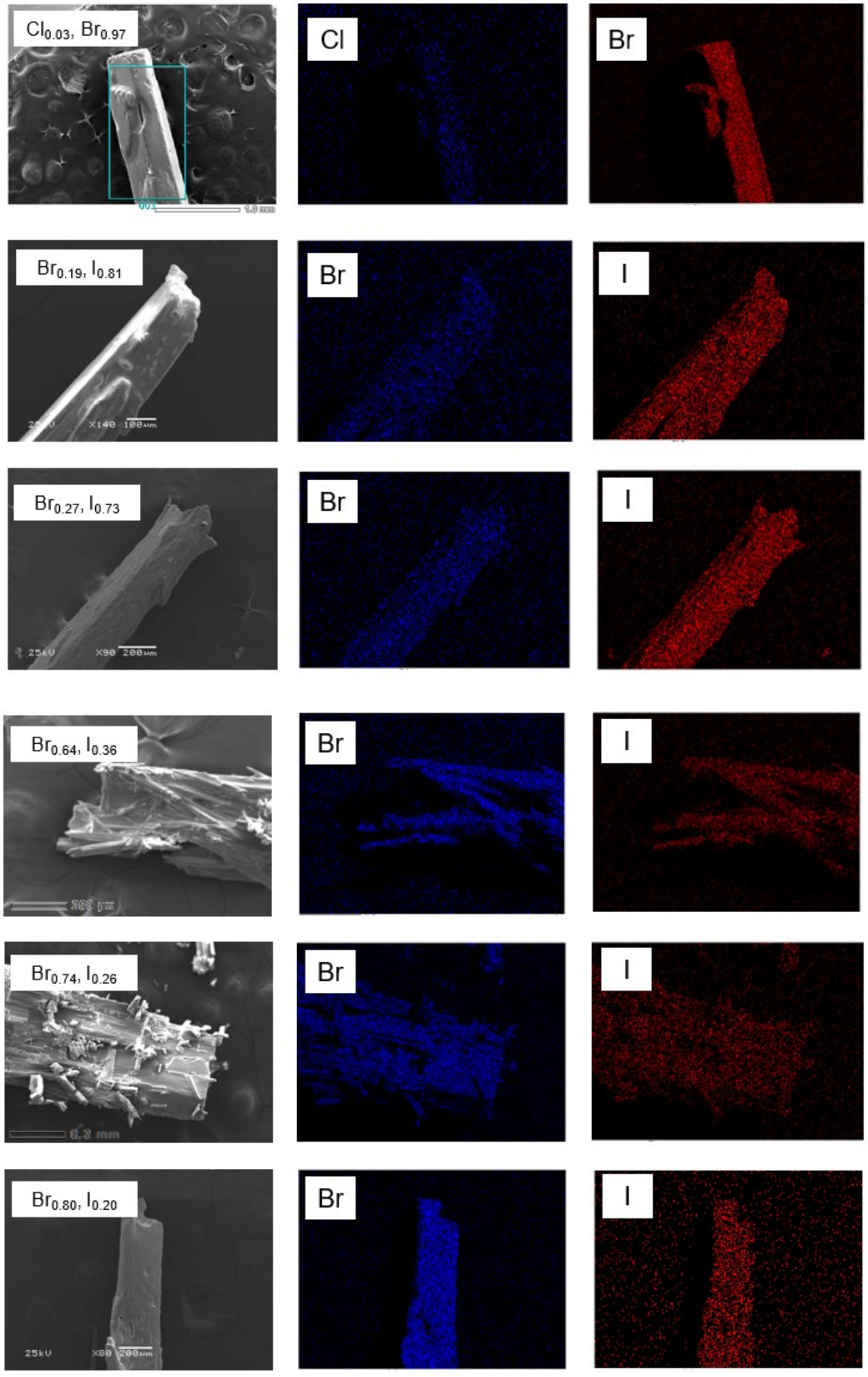
1. SEM-EDS


$Cl_{0.03}$, $Br_{0.97}$
Cl
Br
$Br_{0.19}$, $I_{0.81}$
Br
I
$Br_{0.27}$, $I_{0.73}$
Br
I
$Br_{0.64}$, $I_{0.36}$
Br
I
$Br_{0.74}$, $I_{0.26}$
Br
I
$Br_{0.80}$, $I_{0.20}$
Br
I

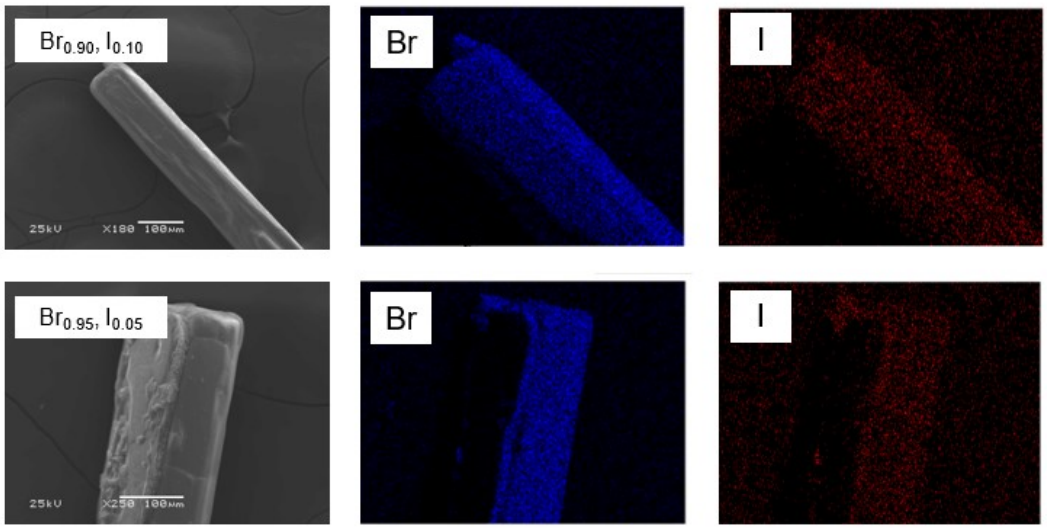


Fig. S1 SEM images and energy-dispersive X-ray spectroscopy (EDS) mapping diagrams were obtained using single crystals. In the solid solution **ClBr**, blue indicates Cl, and red indicates Br. In the solid solution **BrI**, blue indicates Br, and red indicates I.

2. PXRD pattern (solid solution **ClBr**).

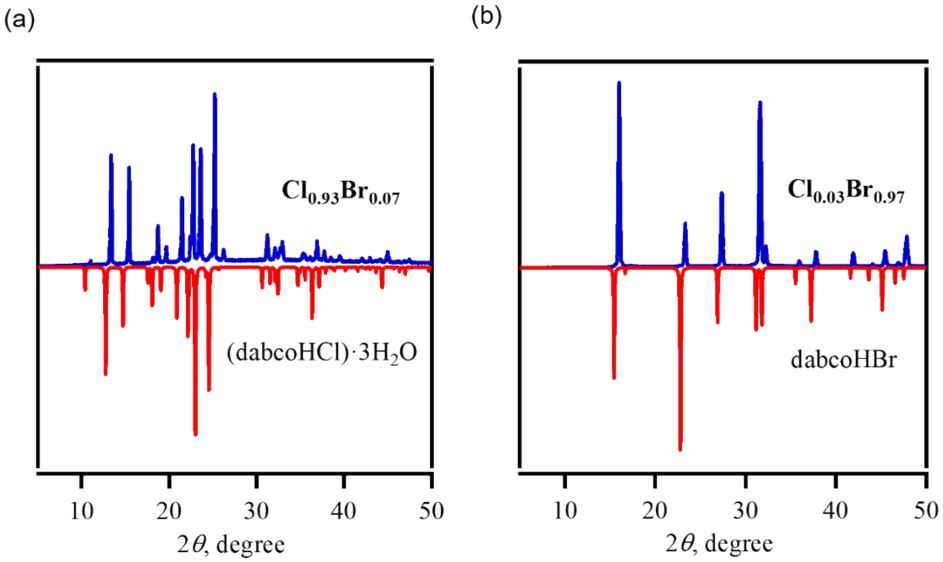
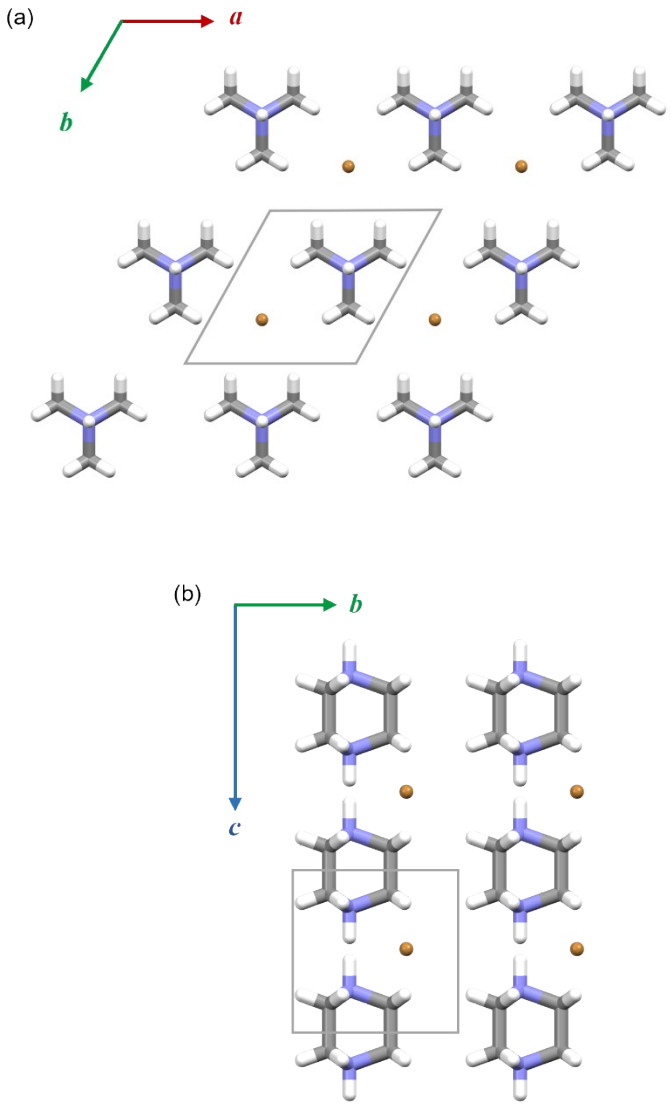


Fig. S2 The simulated and powdered XRD patterns from single-crystal X-ray structural analysis. (a) $\mathbf{Cl_{0.93}Br_{0.07}}$ in solid solution **ClBr** and (dabcoHCl)·$3H_2O$; (b) $\mathbf{Cl_{0.03}Br_{0.97}}$ in solid solution **ClBr** and dabcoHBr.

3. SC-XRD (solid solution **ClBr**)



Compound	$Cl_{0.03}Br_{0.97}$
Formula	$C_6H_{13}N_2Cl_{0.03}Br_{0.97}$
T, K	298
C.S.	Hexagonal
S.G.	*P*-6*m*2
a, Å	6.6645(5)
c, Å	5.3238(4)
V, Å^3	204.78(3)
Z	1
ρ_{calc}, g cm^{-3}	1.555
Reflections collected	1438
Independent reflections	236
Data/restraints/parameters	236/0/12
Goodness of fit on F_2	1.161
Final R indices [I ≥ 2σ(I)]	R_1 = 0.0333 wR_2 = 0.0842
Final R indices [all data]	R_1 = 0.351 wR_2 = 0.0846

Fig. S3 Single-crystal X-ray structure of solid solution **$Cl_{0.03}Br_{0.97}$**. (a) *ab*-plane, (b) *bc*-plane and crystallographic data.

4. PXRD before and after heating (**$Cl_{0.03}Br_{0.97}$**)

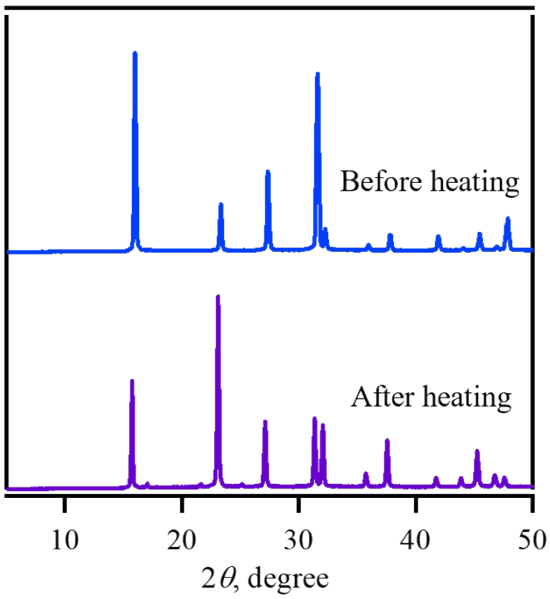
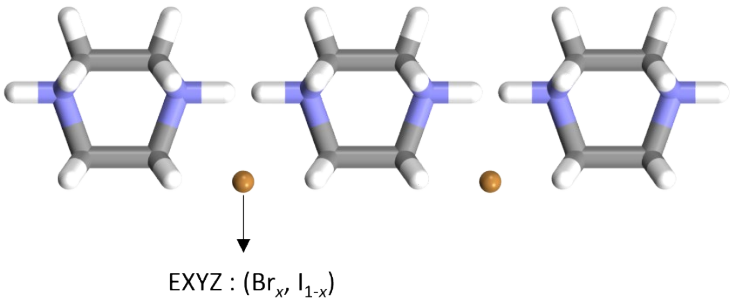


Fig. S4 XRD patterns at 298 K before and after heating of the $\mathbf{Cl_{0.03}Br_{0.97}}$.

5. SC-XRD (solid solution **BrI**). About the anion site.

Table S1 Occupancy optimisation (lower panel) and elemental analysis values (upper panel) at anion sites in single-crystal X-ray structural analysis.

E. A.	19 : 81	27 : 73	64 : 36	74 : 26	80 : 20	90 : 10	95 : 05
SC-XRD	17 : 83	27 : 73	62 : 38	73 : 27	81 : 19	93 : 07	98 : 02



Optimisation was performed by setting the solid solution anions at the same site and the Br-to-I ratio to 1.

<u>Composition dependence of C(-H)···X distance.</u>

Fig. S5 shows the composition dependence of the C···X distance. The C···X distances show a linear variation with composition. The typical C(-H)···Br distance is shown in purple and the C(-H)···I distance is in green dotted lines.[1] All solid solution C···X distances are longer than typical C(-H)···Br distances, indicating that C-H···Br interactions are weak in solid solutions. On the other hand, for $x \geq 0.64$ the C···X distances are shorter than typical C(-H)···I distances, which indicates CH···I interactions are strong.

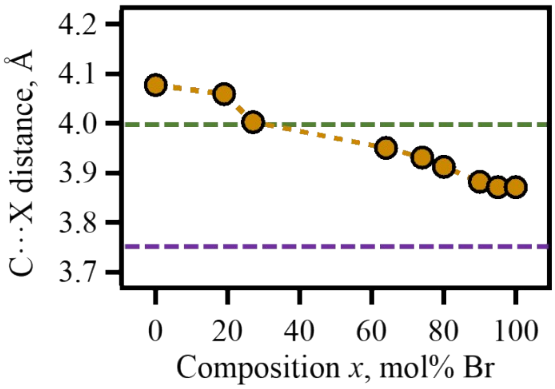


Fig. S5 Plot of C···X distance with *x*. Purple and green dotted lines represent typical C···Br^- and C···I^- distances.[1]

6. SC-XRD (dabcoHBr and solid solution $\mathbf{Br_{0.80}I_{0.20}}$). Uniformity of the structure of each crystal.

Table S2 Mean and standard deviation of dabcoHBr and the solid solution $\mathbf{Br_{0.80}I_{0.20}}$.

	Mean	σ
a (Br)	6.6649	0.0163
c (Br)	5.3150	0.0569
a ($\mathbf{Br_{0.80}I_{0.20}}$)	6.7323	0.0172
c ($\mathbf{Br_{0.80}I_{0.20}}$)	5.3246	0.00615

7. SC-XRD (solid solution $Br_{0.80}I_{0.20}$). Temperature dependence.

Table S3 Crystallographic data for $Br_{0.80}I_{0.20}$. Temperature dependence.

Compound	$Br_{0.80}I_{0.20}$						
Formula	$C_6H_{13}N_2Br_{0.80}I_{0.20}$						
T, K	112	158	205	250	275	298	317
C.S.	Hexagonal						
S.G.	*P*-6*m*2						
a, Å	6.7014(5)	6.7111(5)	6.7200(5)	6.7378(5)	6.7561(6)	6.7541(6)	6.7627(6)
c, Å	5.3164(3)	5.3194(3)	5.3205(3)	5.3315(4)	5.3430(4)	5.333(4)	5.3437(4)
V, Å^3	206.77(3)	207.48(3)	208.08(3)	209.61(3)	211.21(4)	210.90(4)	211.65(4)
Z	1						
ρ_{calc}, g cm^{-3}	1.626	1.621	1.616	1.604	1.592	1.594	1.589
Reflections collected	1173	1047	1061	994	981	941	911
Independent reflections	229	230	230	231	231	231	231
Data/restraints/parameters	229/0/13	230/0/12	230/0/12	231/0/12	231/0/12	231/0/12	231/0/12
Goodness of fit on F_2	1.141	1.102	1.157	1.126	1.122	1.114	1.110
Final R indices [$I \geq 2\sigma(I)$]	R_1 = 0.0313	R_1 = 0.0348	R_1 = 0.0333	R_1 = 0.0221	R_1 = 0.0379	R_1 = 0.0389	R_1 = 0.0345
	wR_2 = 0.0715	wR_2 = 0.0845	wR_2 = 0.0780	wR_2 = 0.0460	wR_2 = 0.0898	wR_2 = 0.0930	wR_2 = 0.0800
Final R indices [all data]	R_1 = 0.313	R_1 = 0.0348	R_1 = 0.0333	R_1 = 0.0221	R_1 = 0.0379	R_1 = 0.0394	R_1 = 0.0352
	wR_2 = 0.0715	wR_2 = 0.0845	wR_2 = 0.0780	wR_2 = 0.0460	wR_2 = 0.0898	wR_2 = 0.0933	wR_2 = 0.0803

Compound	$Br_{0.80}I_{0.20}$							
Formula	$C_6H_{13}N_2Br_{0.80}I_{0.20}$							
T, K	326	336	340	345	350	354	364	373
C.S.	Hexagonal							
S.G.	*P*-6*m*2							
a, Å	6.7647(7)	6.7667(7)	6.7670(8)	6.7670(8)	6.7705(8)	6.7733(8)	6.7773(8)	6.7800(8)
c, Å	5.3453(5)	5.3437(5)	5.3435(5)	5.3435(5)	5.3460(5)	5.3446(5)	5.3488(5)	5.3483(6)
V, Å^3	212.84(5)	211.90(5)	211.91(5)	211.91(5)	212.23(5)	212.35(5)	212.77(5)	212.91(6)
Z	1							
ρ_{calc}, g cm^{-3}	1.587	1.587	1.587	1.587	1.584	1.583	1.580	1.579
Reflections collected	1261	1264	1259	1259	1264	1250	1254	1254
Independent reflections	231	231	231	231	233	232	233	232
Data/restraints/parameters	231/0/12	231/0/12	231/0/12	231/0/12	233/0/12	232/0/12	233/0/12	232/0/12
Goodness of fit on F_2	1.126	1.104	1.110	1.111	1.137	1.133	1.118	1.098
Final R indices [I ≥ 2σ(I)]	R_1 =0.0357 wR_2 = 0.0833	R_1 = 0.0341 wR_2 = 0.0831	R_1 = 0.0378 wR_2 = 0.0906	R_1 = 0.0378 wR_2 = 0.0907	R_1 = 0.0361 wR_2 = 0.0911	R_1 = 0.0379 wR_2 = 0.0941	R_1 = 0.0362 wR_2 = 0.0886	R_1 = 0.0329 wR_2 = 0.0793
Final R indices [all data]	R_1 = 0.0362 wR_2 = 0.0836	R_1 = 0.0362 wR_2 = 0.0837	R_1 = 0.0392 wR_2 = 0.0912	R_1 = 0.0392 wR_2 = 0.0913	R_1 = 0.0386 wR_2 = 0.0925	R_1 = 0.0422 wR_2 =0.0979	R_1 = 0.0403 wR_2 = 0.0907	R_1 = 0.0374 wR_2 = 0.0811

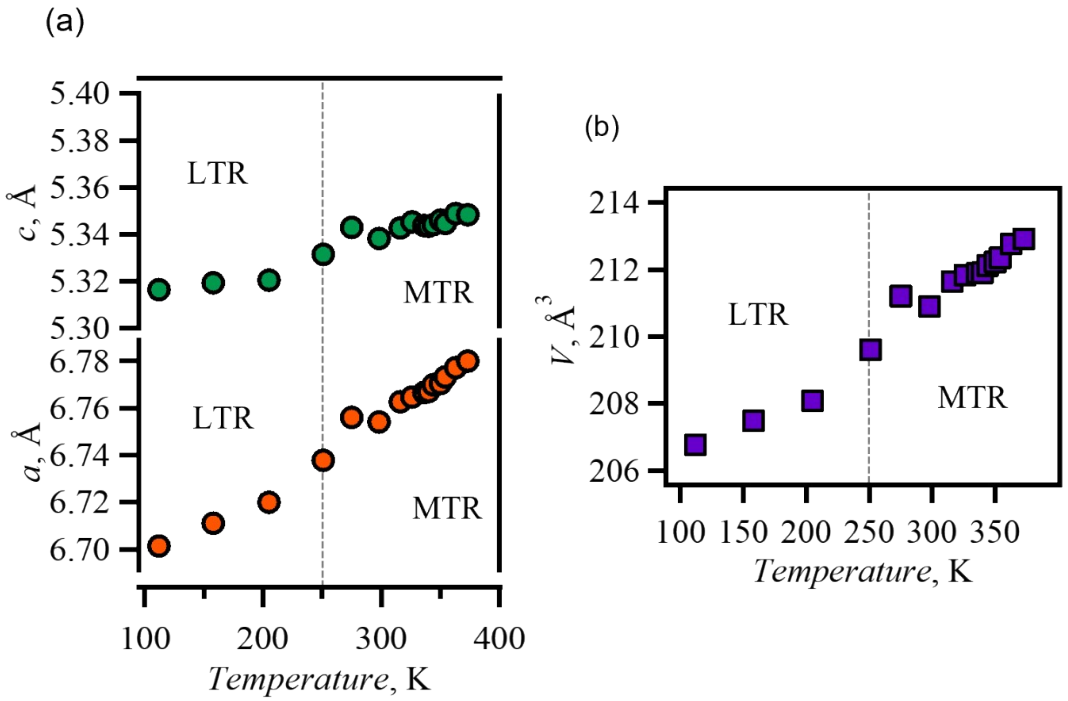


Fig. S6 Temperature dependence of the lattice length (a) and lattice volume (b) in solid solution $\mathbf{Br_{0.80}I_{0.20}}$.

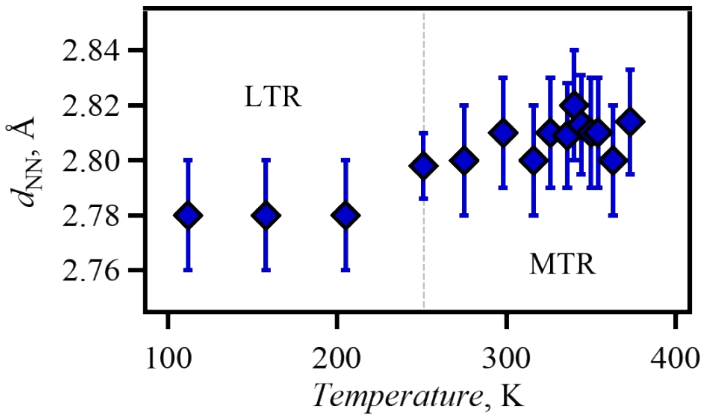


Fig. S7 Temperature dependence of N…N distance in solid solution $\mathbf{Br_{0.80}I_{0.20}}$

8. DFT

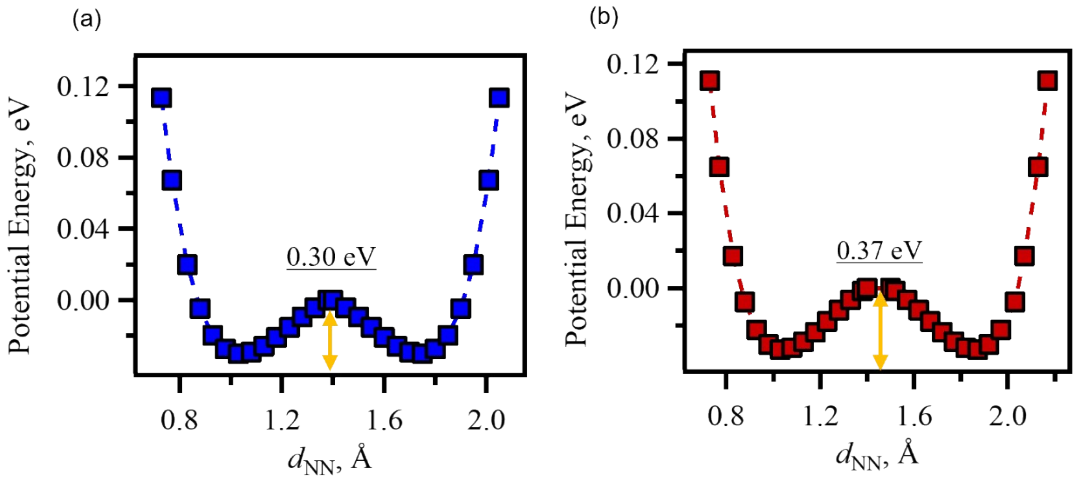


Fig. S8 The activation barriers for proton motility were calculated using DFT. (a) LTR (b) MTR.

9. *P-E* hysteresis

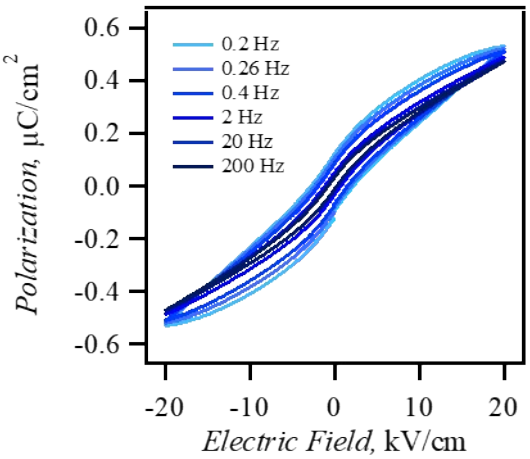


Fig. S9 Temperature dependence of *P-E* hysteresis at 0.4 Hz.

10. Temperature-variable PXRD (solid solution $Br_{0.80}I_{0.20}$)

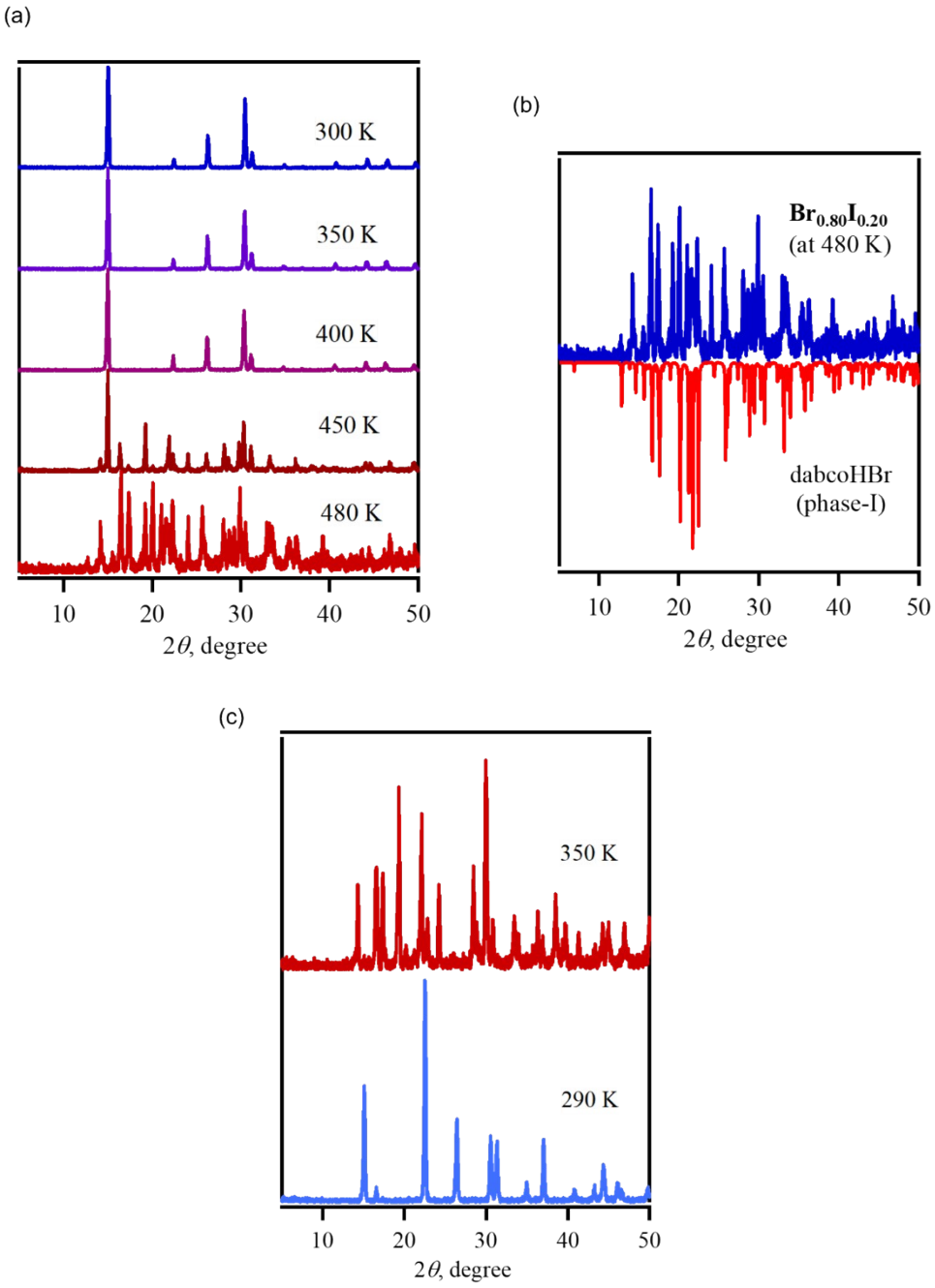


Fig. S10 (a) Variation in the powder diffraction patterns at temperatures ranging between 300-480 K in solid solution $Br_{0.80}I_{0.20}$ (heating process). (b) The diffraction patterns at 480 K in $Br_{0.80}I_{0.20}$ and phase I in dabcoHBr. (c) Changes in diffraction patterns from 350 K to 290 K (cooling process).

11. DSC and temperature-variable PXRD (solid solution $Br_{0.19}I_{0.81}$)

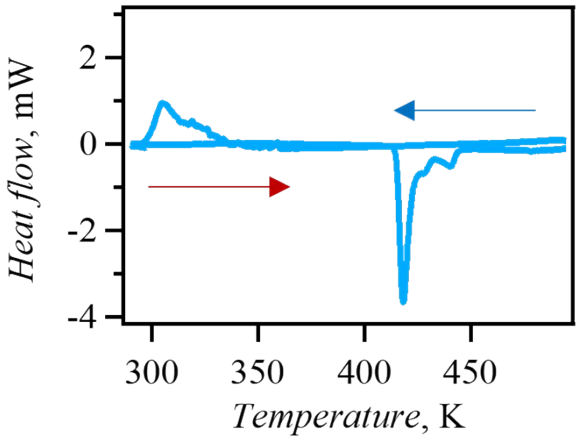


Fig. S11 DSC of solid solution $B_{r0.19}I_{0.81}$. Measurements were conducted between 273–500 K, at a sweep rate of 10 K min^{-1} and under N_2 atmosphere.

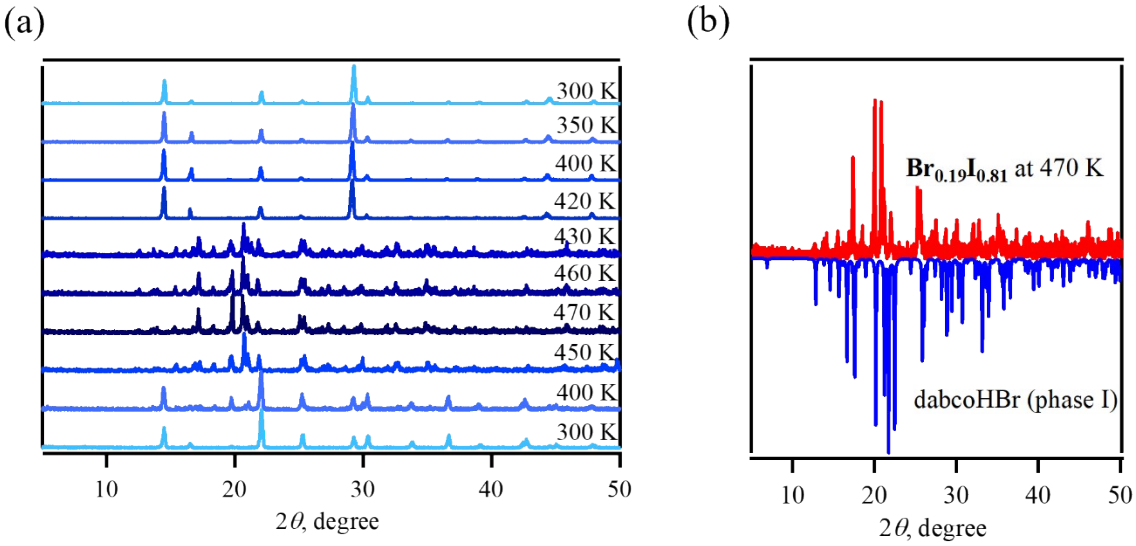


Fig. S12 (a) Variation in the powder diffraction patterns at temperatures ranging between 300-470 K in solid solution $Br_{0.19}I_{0.81}$.
(b) The diffraction patterns at 470 K in $Br_{0.19}I_{0.81}$ and phase I in dabcoHBr.

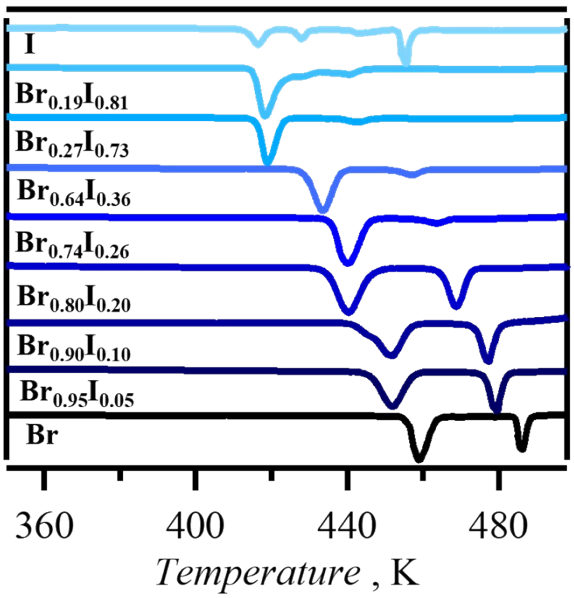


Fig. 13 DSC of solid solution **BrI**. Measurements were conducted between 273–500 K, at a sweep rate of 10 K min^{-1} and under N_2 atmosphere.

12. Solid solution preparation and crystal images

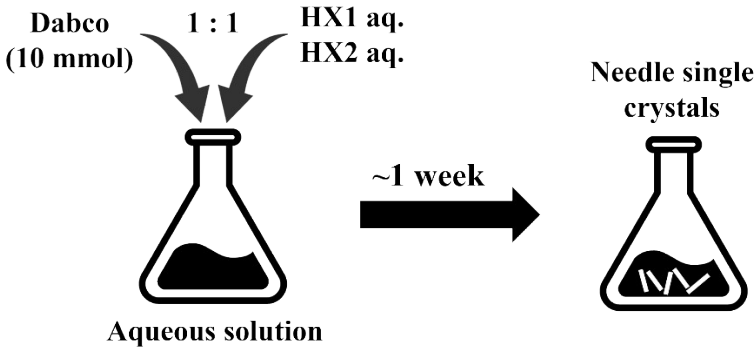


Fig. S14 Schematic of sample preparation.

Crystallization detail (**$Cl_{0.03}Br_{0.97}$**)

A 10 mmol of dabco was dissolved in 2 ml of water. And then, 0.20 ml of HCl_{aq} (35.0-37.0 %) and 0.83 ml of HBr_{aq} (47.0-49.0 %) were slowly dropped. This solution was followed to slow evaporation in dark conditions at 313 K. After a few days, colourless crystals were precipitated (yield; 44.6 %).

Crystallization detail (**$Cl_{0.93}Br_{0.07}$**)

A 10 mmol of dabco was dissolved in 2 ml of water. And then, 0.60 ml of HCl_{aq} (35.0-37.0 %) and 0.28 ml of HBr_{aq} (47.0-49.0 %) were slowly dropped. This solution was followed to slow evaporation in dark conditions at 313 K. After a few days, colourless crystals were precipitated (yield; 35.5 %).

Crystallization detail (**$Br_{0.19}I_{0.81}$**)

A 10 mmol of dabco was dissolved in 2 ml of water. And then, 0.28 ml of HBr_{aq} (47.0-49.0 %) and 1.05 ml of HI_{aq} (55.0-58.0 %) were slowly dropped. This solution was followed to slow evaporation in dark conditions at 313 K. After a few days, colourless crystals were precipitated (yield; 45.8 %).

Crystallization detail (**$Br_{0.27}I_{0.73}$**)

A 10 mmol of dabco was dissolved in 2 ml of water. And then, 0.55 ml of HBr_{aq} (47.0-49.0 %) and 0.70 ml of HI_{aq} (55.0-58.0 %) were slowly dropped. This solution was followed to slow evaporation in dark conditions at 313 K. After a few days, colourless crystals were precipitated (yield; 35.2 %).

Crystallization detail (**$Br_{0.64}I_{0.36}$**)

A 10 mmol of dabco was dissolved in 2 ml of water. And then, 0.72 ml of HBr_{aq} (47.0-49.0 %) and 0.49 ml of HI_{aq} (55.0-58.0 %) were slowly dropped. This solution was followed to slow evaporation in dark conditions at 313 K. After a few days, colourless crystals were precipitated (yield; 32.2 %).

Crystallization detail (**$Br_{0.74}I_{0.26}$**)

A 10 mmol of dabco was dissolved in 2 ml of water. And then, 0.77 ml of HBr_{aq} (47.0-49.0 %) and 0.42 ml of HI_{aq} (55.0-58.0 %) were slowly dropped. This solution was followed to slow evaporation in dark conditions at 313 K. After a few days, colourless crystals were precipitated (yield; 31.4 %).

Crystallization detail (**$Br_{0.80}I_{0.20}$**)

A 10 mmol of dabco was dissolved in 2 ml of water. And then, 0.83 ml of HBr_{aq} (47.0-49.0 %) and 0.35 ml of HI_{aq} (55.0-58.0 %) were slowly dropped. This solution was followed to slow evaporation in dark conditions at 313 K. After a few days, colourless crystals were precipitated (yield; 43.8 %).

Crystallization detail (**$Br_{0.90}I_{0.10}$**)

A 10 mmol of dabco was dissolved in 2 ml of water. And then, 0.94 ml of HBr_{aq} (47.0-49.0 %) and 0.21 ml of HI_{aq} (55.0-58.0 %) were slowly dropped. This solution was followed to slow evaporation in dark conditions at 313 K. After a few days, colourless crystals were precipitated (yield; 37.5 %).

Crystallization detail (**$Br_{0.95}I_{0.05}$**)

A 10 mmol of dabco was dissolved in 2 ml of water. And then, 0.99 ml of HBr_{aq} (47.0-49.0 %) and 0.14 ml of HI_{aq} (55.0-58.0 %) were slowly dropped. This solution was followed to slow evaporation in dark conditions at 313 K. After a few days, colourless crystals were precipitated (yield; 41.5 %).

Elemental Anal (%) in **ClBr**: C 37.407, H 6.790, and N 14.492 for the **$Cl_{0.03}Br_{0.97}$**. C 34.974, H 8.009, N 13.493 for **$Cl_{0.93}Br_{0.07}$**. **ClBr** was also investigated using halogen analysis (%) owing to its low miscibility. Cl 0.97 Br 42.30 for **$Cl_{0.03}Br_{0.97}$**. Cl 13.18 Br 8.57 for **$Cl_{0.93}Br_{0.07}$**.

Elemental Anal (%) in **BrI**: C 31.123, H 5.790, N 12.111 for **$Br_{0.19}I_{0.81}$**. C 31.687, H 5.790, N 12.308 for **$Br_{0.27}I_{0.73}$**. C 33.802, H 6.464, N 13.153 for **$Br_{0.64}I_{0.36}$**. C 34.913, H 6.423, N 13.525 for **$Br_{0.74}I_{0.26}$**. C 35.573, H 6.512, N 13.781 for **$Br_{0.80}I_{0.20}$**. C 36.239, H 6.288, N 14.200 for **$Br_{0.90}I_{0.10}$**. C 36.551, H 6.705, N 14.170 for **$Br_{0.95}I_{0.05}$**.

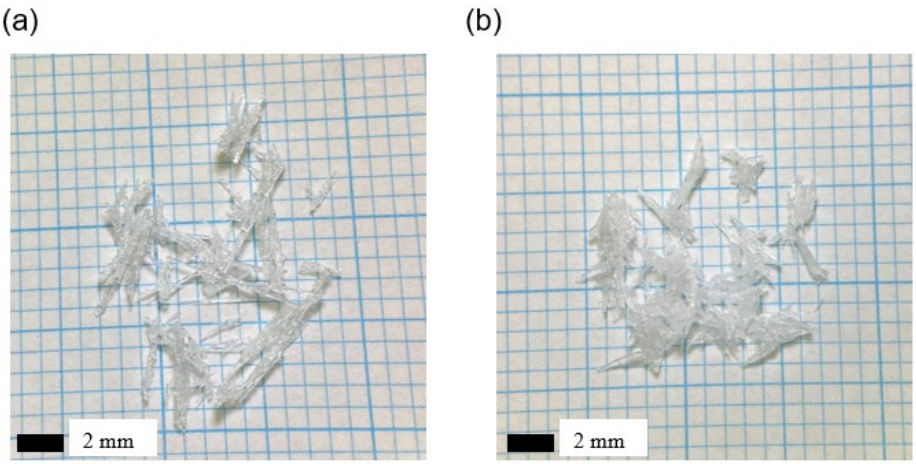


Fig. S15 Image of solid solution crystals. (a) Solid solution **$Cl_{0.03}Br_{0.97}$**, and (b) solid **$Br_{0.80}I_{0.20}$**; the squares in the images are 1 mm^2.

Single-crystal X-ray diffraction analysis

Single-crystal analysis of $\mathbf{Cl_{0.03}Br_{0.97}}$; 298 K, 2340574

$\mathbf{Br_{0.19}I_{0.81}}$; 298 K, 2340566

$\mathbf{Br_{0.27}I_{0.73}}$; 298 K, 2340567

$\mathbf{Br_{0.64}I_{0.36}}$; 298 K, 2340568

$\mathbf{Br_{0.74}I_{0.26}}$; 298 K, 2340569

$\mathbf{Br_{0.80}I_{0.20}}$; 298 K, 2340570

; 112 K, 2340571

$\mathbf{Br_{0.90}I_{0.10}}$; 298 K, 2340572

$\mathbf{Br_{0.95}I_{0.05}}$; 298 K, 2340573

Details of the crystallographic analysis are summarised in the CIF file deposited at the CCDC.

Reference

[1] T. Steiner, *Acta Cryst*., 1998, **B54**, 456-463.