Electronic Supplementary Material for

From isomorphous to "anisomorphous" ionic co-crystals of barbituric acid upon dehydration and return

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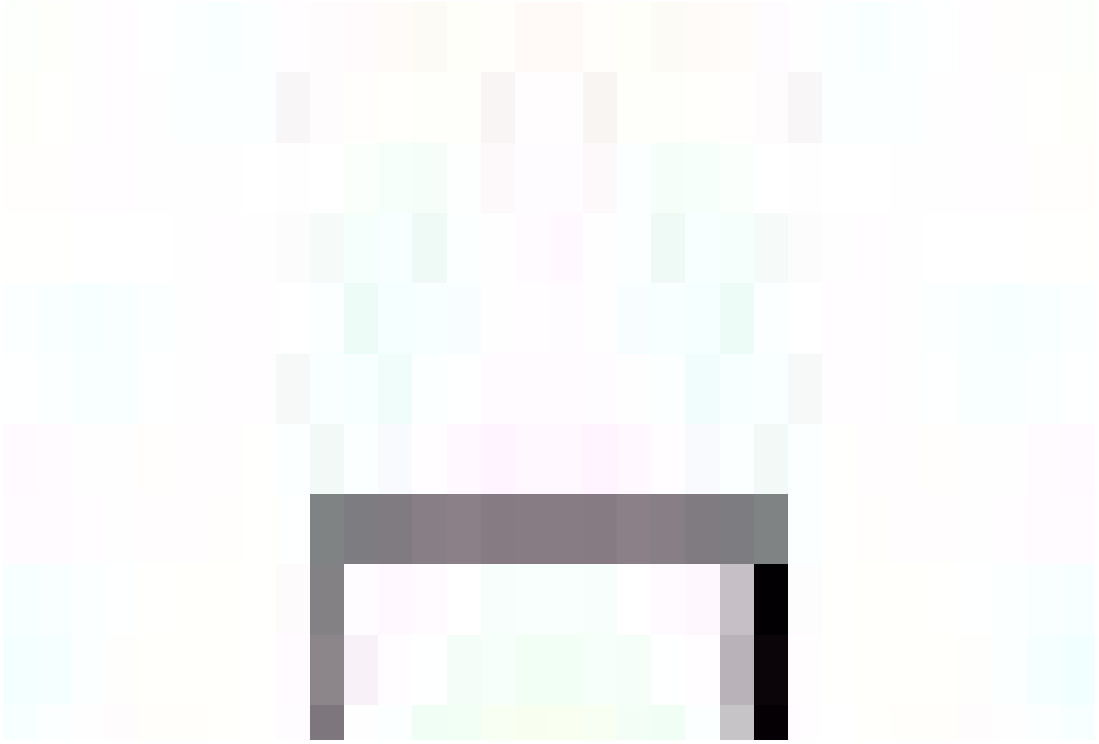

Figure S(1). ^{13}C (100.65 MHz) CPMAS spectra with relevant assignments of BA·RbBr·$2H_2O$, BA·KBr·$2H_2O$, BA·NaBr·$2H_2O$ recorded at 12 kHz.

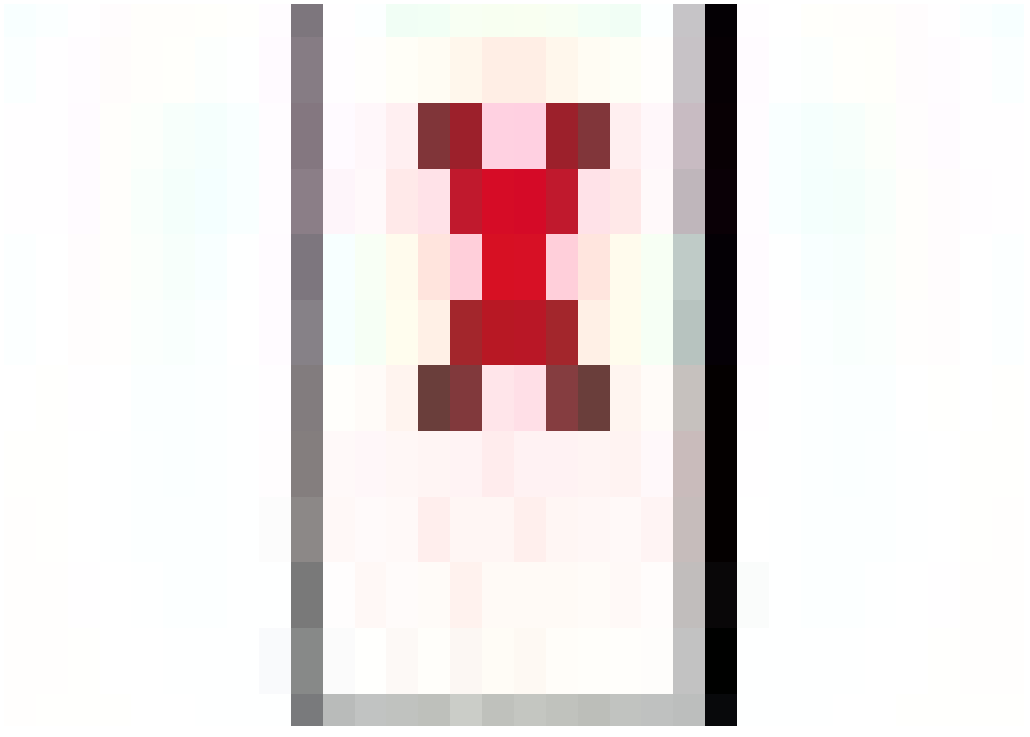

Figure S(2). ^{15}N (40.55 MHz) CPMAS spectra with relevant assignments of BA·RbBr·$2H_2O$, BA·KBr·$2H_2O$, BA·NaBr·$2H_2O$ recorded at 7 kHz.

Figure S(3). ^{1}H (400.23 MHz) spectra with relevant assignments of BA·RbBr·$2H_2O$, BA·KBr·$2H_2O$, BA·NaBr·$2H_2O$ recorded at 32 kHz.

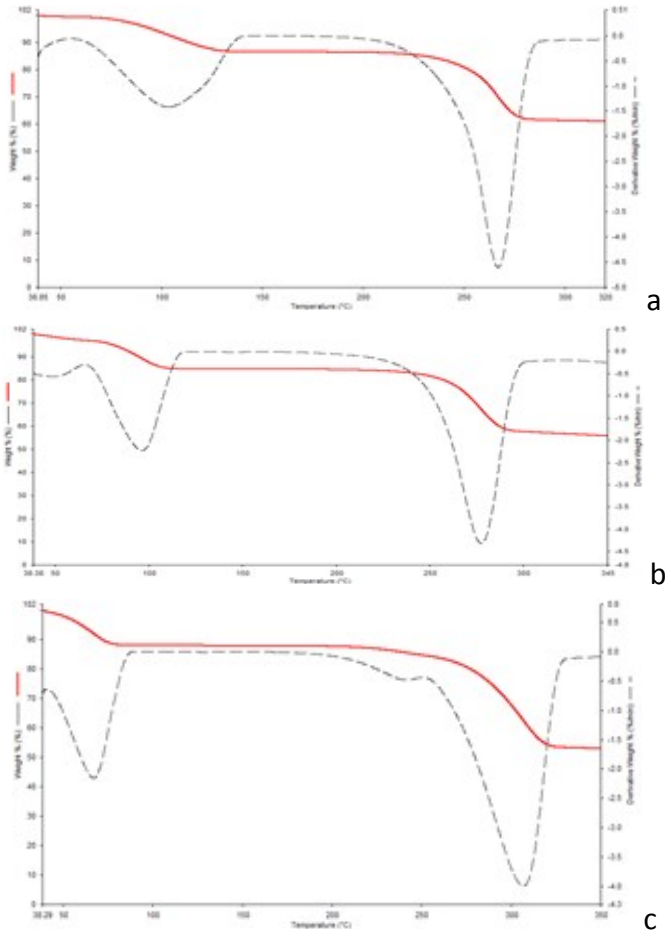

Figure S(4). TGA curves for (a) BA·NaBr·$2H_2O$, (b) BA·KBr·$2H_2O$ and (c) BA·RbBr·$2H_2O$.

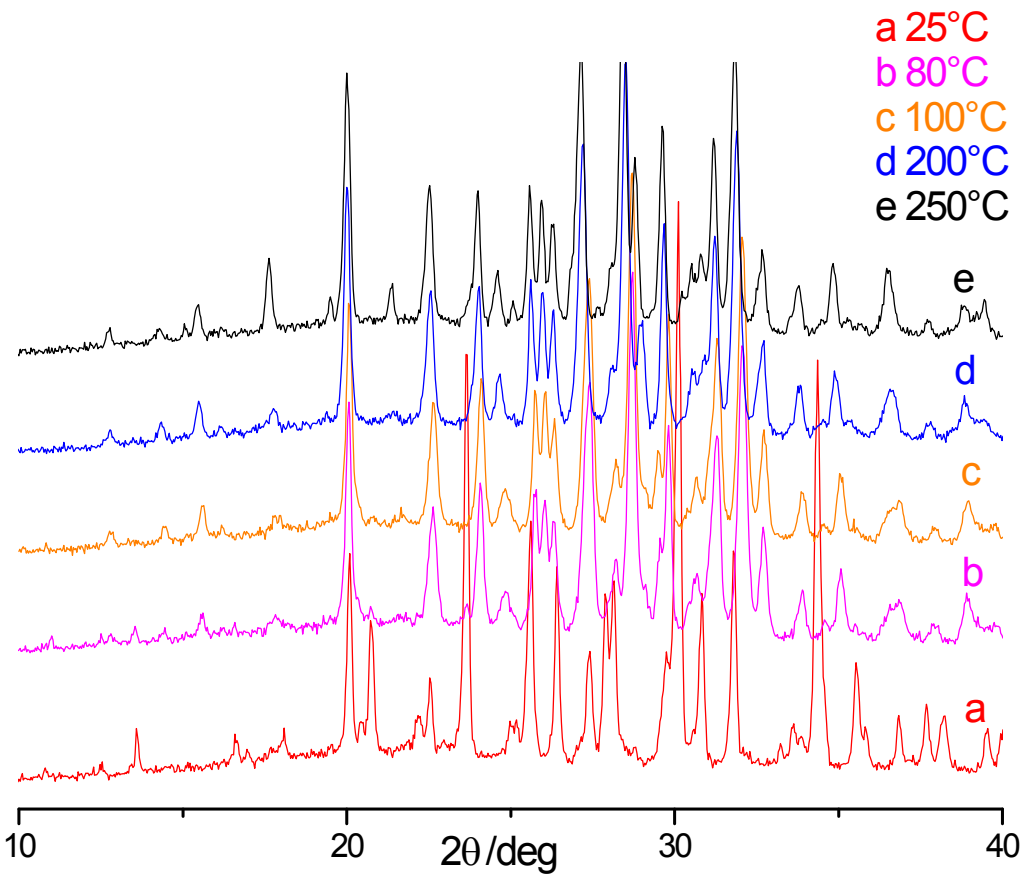

Figure S(5). Variable Temperature XRPD measurements for BA·NaBr·2H_2O.

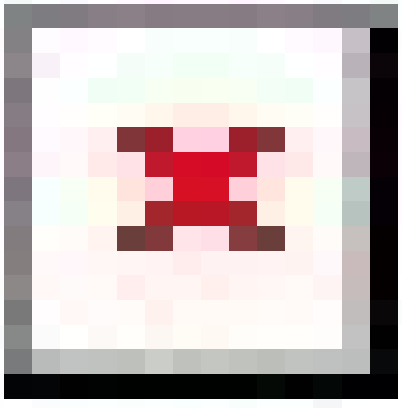

Figure S(6). ^{15}N (40.55 MHz) CPMAS spectra with relevant assignments of BA·CsBr, BA·RbBr, BA·KBr, BA·NaBr recorded at 7 kHz.

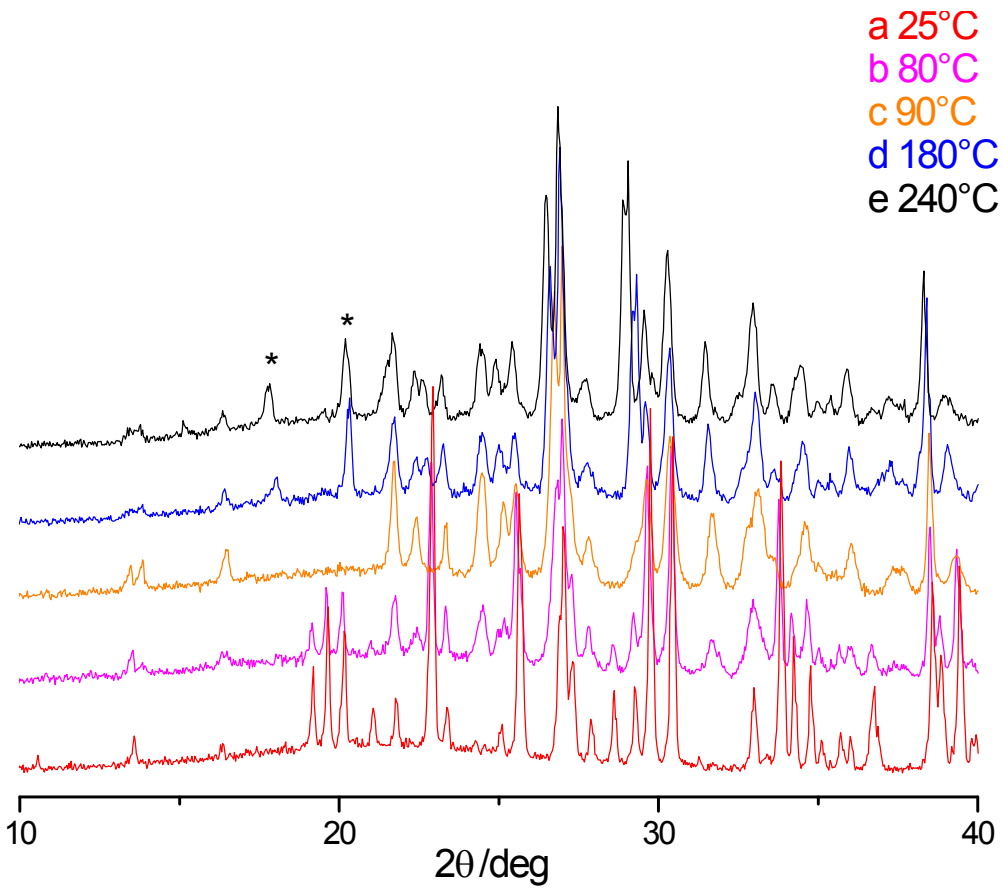

Figure S(7). Variable Temperature XRPD measurements for BA·KBr·2H_2O.

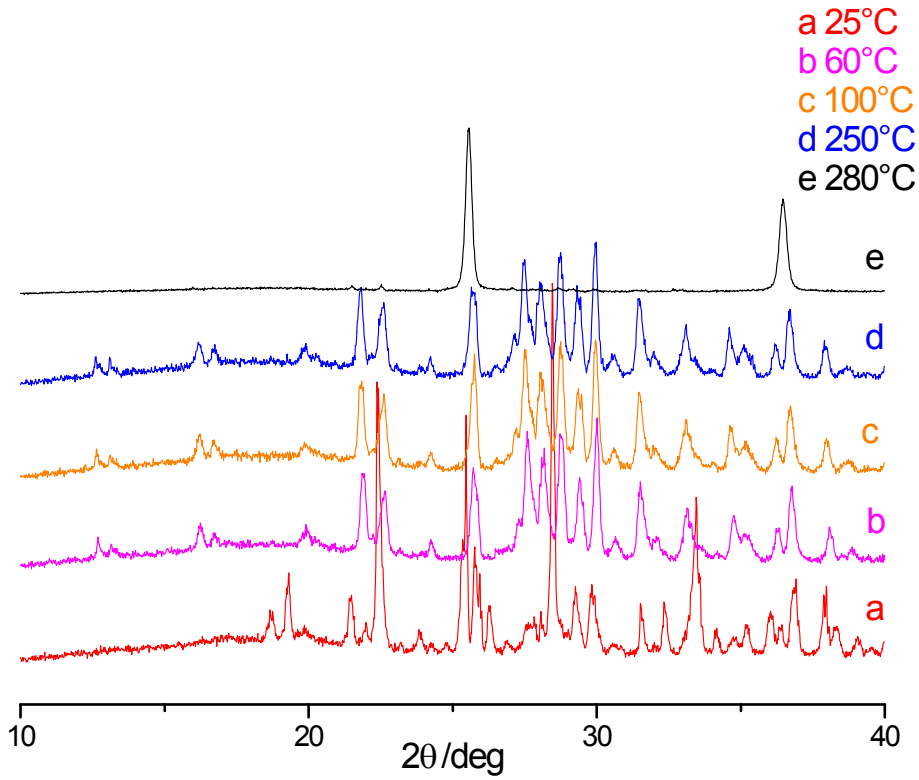

Figure S(8). Variable Temperature XRPD measurements for BA·RbBr·2H_2O.

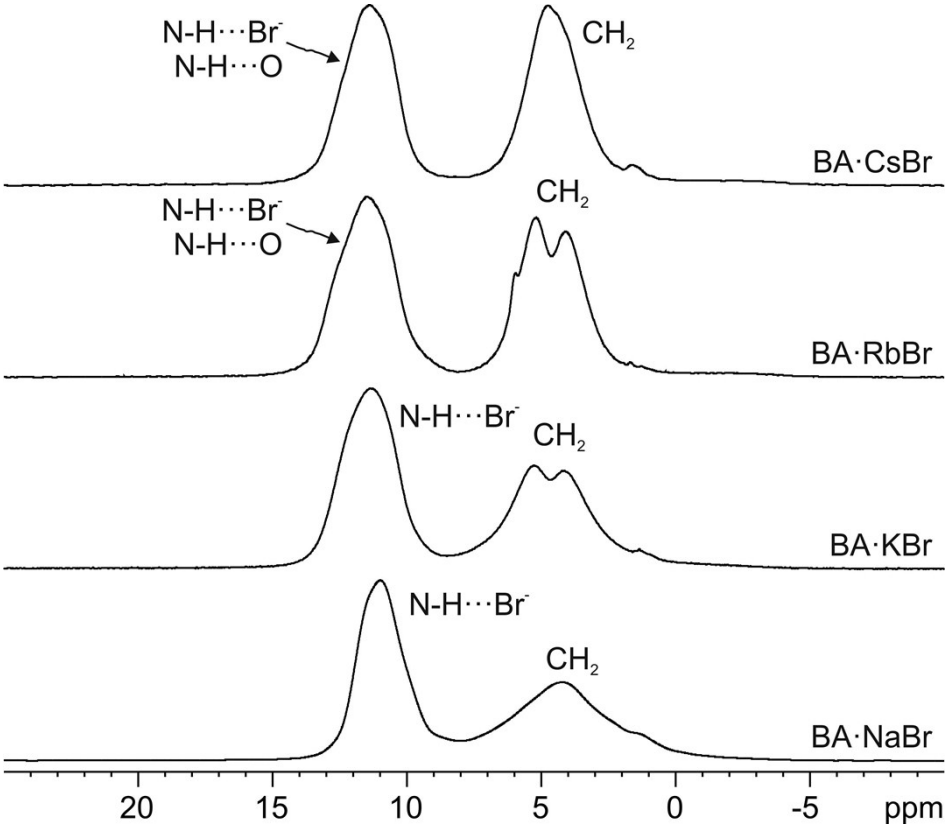

Figure S(9). ^{13}H (400.23 MHz) spectra with relevant assignments of BA·CsBr, BA·RbBr, BA·KBr, BA·NaBr.

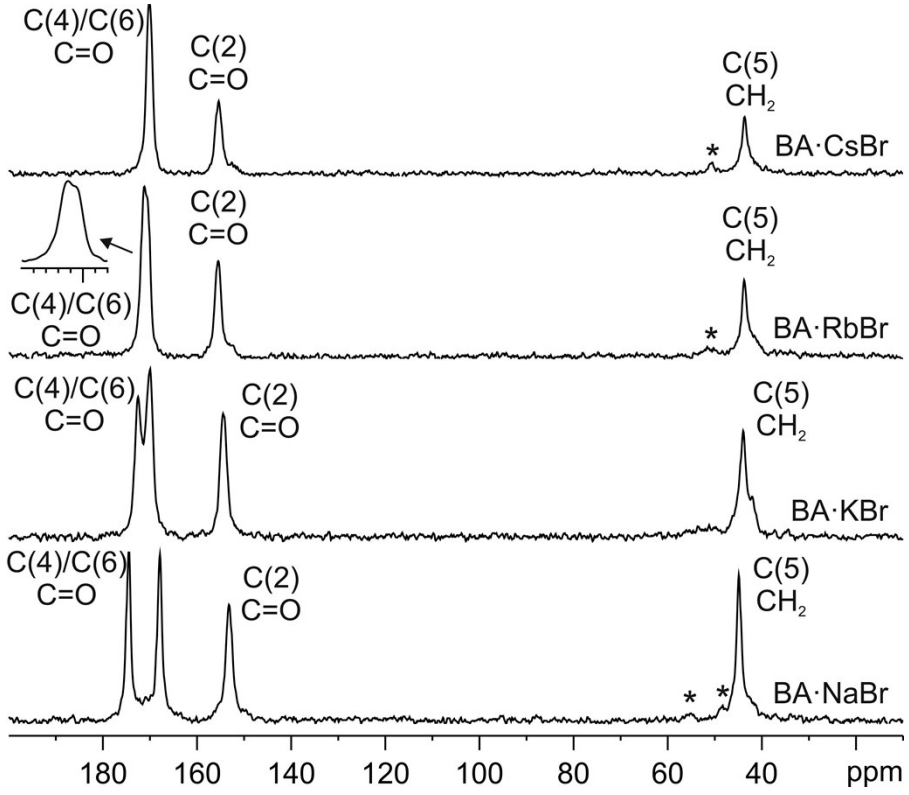

Figure S(10). ^{13}C (100.65 MHz) CPMAS spectra with relevant assignments of BA·CsBr, BA·RbBr, BA·KBr, BA·NaBr recorded at 12 kHz.

Structure solution from powder for BA·NaBr

Powder diffraction data were analysed with the software EXPO2009. Peaks were automatically chosen in the 2ϑ range 5-40°. A peak at 29.9° was assigned to unreacted NaBr and excluded in the indexing process.

A few peaks at low angle (e.g. at 14°) had a strong asymmetry and a broad left shoulder: these shoulder features were indeed peaks of BA·NaBr·$2H_2O$ phase, present as small impurity. A monoclinic cell with volume of 1429 Å^3 was finally found using the N-TREOR algorythm. Such volume can contain 8 formula units (Z = 8). Le Bail refinement was automatically performed to extract weighted intensities for space group determination, although some low angle peaks were badly fitted because of BA·NaBr·$2H_2O$ peaks overlap. EXPO found space group $P2_1/c$. Since multiplicity of $P2_1/c$ is 4, Z' was likely to be 2 (two independent molecules, cations and anions per asymmetric unit). We performed both direct methods and simulated annealing trials (using two independent BA molecules, two Na cations, and two Br anions). In all trials, R_{wp} value was relatively high, because of the small amount of impurities, and the badly modelled peak shape. However the best solution of simulated annealing trials could reasonably fit intensities and had good chemical sense.

Rietveld refinement was performed in space group $C2/c$ with software Topas. A shifted Chebyshev function with 6 parameters and a Pseudo-Voigt function were used to fit respectively background and peak shape. A spherical harmonic model was used to describe preferred orientation. BA molecules were refined as rigid bodies. An overall thermal parameter for each atom species was adopted. NaBr and BA·NaBr·$2H_2O$ phase parameters were kept fixed but cell parameters and scale factors. Refinement converged with χ^2 = 8.73, R_{wp} = 0.105 R_{F2}= 0.065, Figure 4 shows experimental, calculated and difference curves.

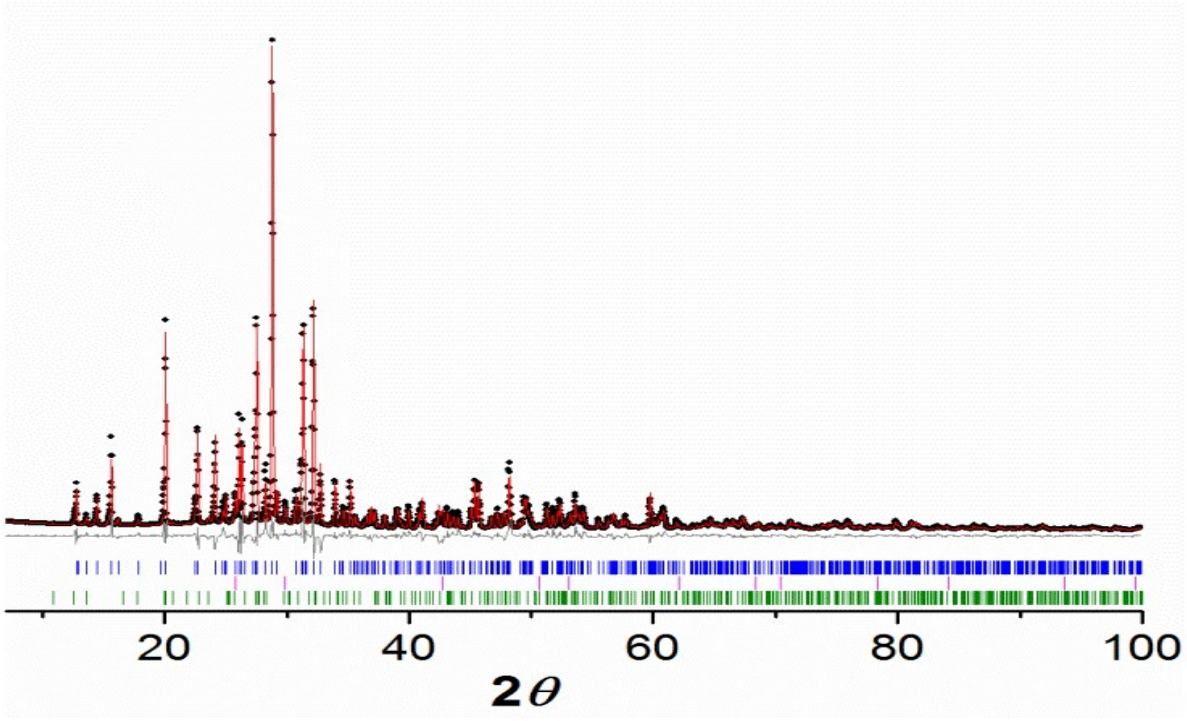

Figure S(11). Rietveld refinement of BA·NaBr: experimental (black dots), calculated (red line) and difference (grey line) curves. Peak positions for BA·NaBr, NaBr and BA·NaBr·$2H_2O$ are shown with blue, pink and green marks, respectively.

Structure solution from powder for BA·KBr

The crystal structure was determined with the software DASH using powder diffraction data collected on a sample heated in a capillary and sealed. 18 Peaks were chosen in the 2θ range 5-30°, and a monoclinic cell with volume of 874 Å3 was finally found using the algorythm DICVOL. Space group statistics performed on peak intensities extracted with a Pawley refinement suggested space group $P2_1/c$ and Z'=1. The best solution from the simulated annealing runs was used for Rietveld refinement with software Topas. A shifted Chebyshev function with 6 parameters and a Pseudo-Voigt function were used to fit respectively background and peak shape. A spherical harmonic model was used to describe preferred orientation. BA molecules were refined as rigid bodies. An overall thermal parameter for each atom species was adopted. KBr was found to be present in the powder as a minor impurity and was thus inserted in the refinement, allowing the cell parameter and scale factor only to be refined. Refinement converged with χ^2 = 2.09, R_{wp} = 0.029 R_{F2}= 0.012. Figure 5 shows experimental, calculated and difference curves.

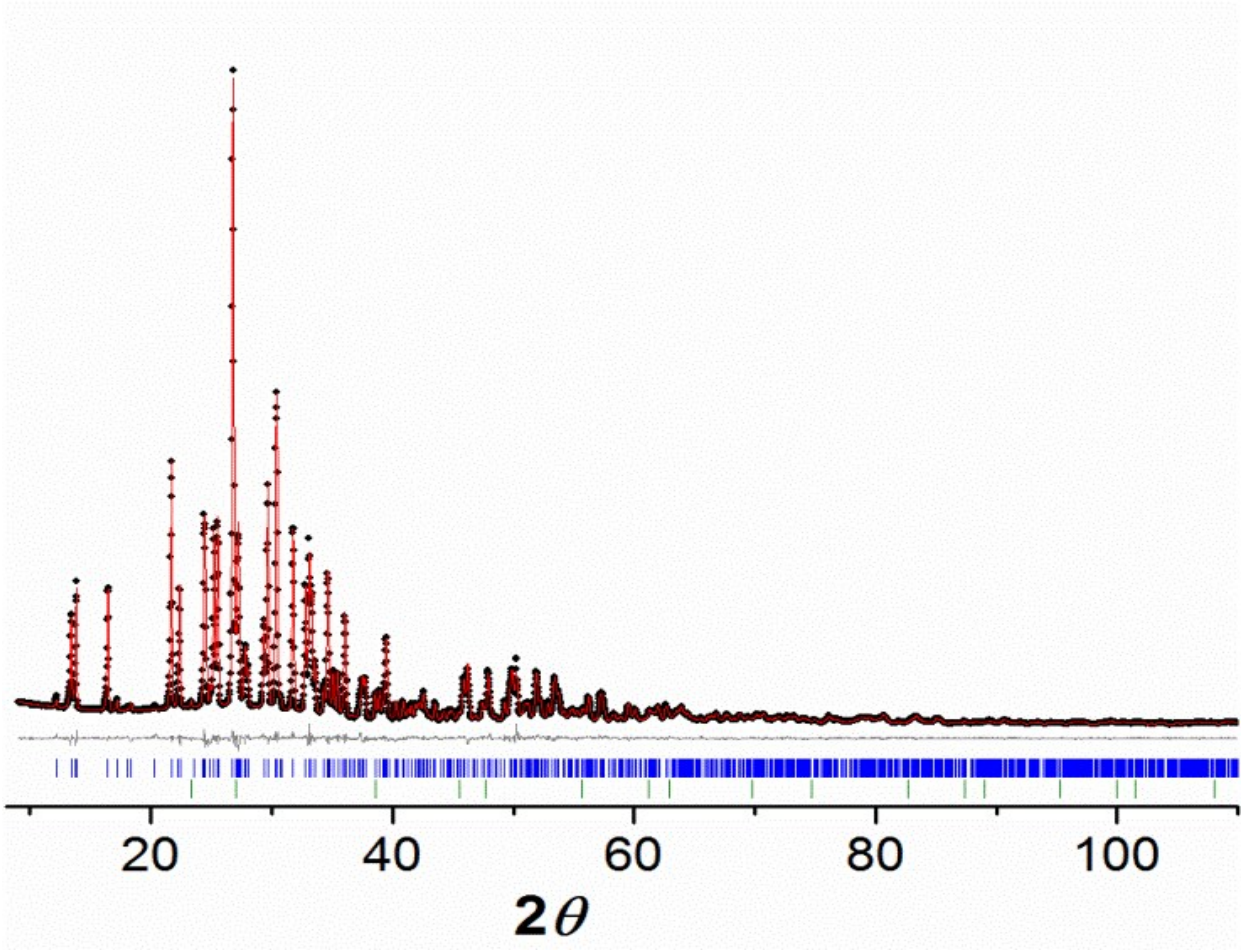

Figure S(12): Rietveld refinement of BA·KBr - experimental (black dots), calculated (red line) and difference (grey line) curves. Peak positions for BA·KBr and KBr are shown with blue and green marks respectively.

Table 1. Summary of the crystallographic data.

Form	BA·NaBr	BA·KBr	BA·RbBr	BA_2·RbBr
Formula	$C_4H_4O_3N_2Na_1Br_1$	$C_4H_4O_3N_2K_1Br_1$	$C_4H_4O_3N_2Rb_1Br_1$	$C_4H_4O_3N_2Rb_{0.5}Br_{0.5}$
Mol wt	230.98	247.09	293.47	210.78
System	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	Pnma
a (Å)	14.1387(6)	13.3229(5)	8.984(5)	8.2776(4)
b (Å)	7.3735(3)	7.3225(3)	8.756(5)	21.885(3)
c (Å)	3.9819(6)	8.0131(3)	10.296(5)	7.1600(6)
β (°)	102.141(2)	97.8649(9)	92.949(5)	90
V ($Å^3$)	1425.03(10)	774.39(5)	808.9(8)	1297.10(19)
Z/Z’	8/1	4/1	4/1	8/1
Density (g cm^{-3})	2.153	2.119	2.410	2.159
F(000)			552	816
μ(MoKα)(mm^{-1})	-	-	11.021	6.929
Measured reflns	-	-	3512	7626
Unique reflns	-	-	1843	1608
Refined parameters	-	-	108	102
GOF on F^2	8.85	2.09	0.933	0.934
R_1(onF, I >2σ(I)/R_{exp}	0.012	0.014	0.0524	0.0246
WR_2 (F^2, all data) R_{wp}	0.10	0.0290	0.1159	0.0501