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Supplementary Information

A temperature-reduced method for the rapid growth of hybrid perovskite single crystals with primary alcohols

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Experimental Section

Materials and Solvents

1-propanol (>99 %), 1-butanol (>99 %), 1-pentanol (>99 %), 1-hexanol (>99 %), DMF (99.8 %), DMSO (>99.9 %), and FAI (>99 %) were all acquired from Sigma-Aldrich. GBL (>99 %) and $PbBr_2$ (>98 %, trace metals basis) were purchased from Alfa Aesar. PbI_2 (99.99 %, trace metals basis) was bought from TCI. $PbCl_2$ (99.99 % trace metals basis), $PbBr_2$ (99.99 %, trace metals basis), MACl (>99.5 %, recrystallized 4 times), MABr (>99.5 %, recrystallized 4 times), FABr (>99.5 %, recrystallized 4 times), and MAI (>99.5 %, recrystallized 4 times) were all purchased from Lumtec. All chemicals and solvents were used as received without further purification.

Preparation of Solubility Curves

Saturated OLTP solutions were prepared in a nitrogen filled glovebox with water and oxygen contents lower than one parts per million (ppm). First, the precursor salts were weighed into a small bottle with an amount of substance of 0.1 mmol in a ratio of 1:1. The corresponding solvents or solvent mixtures were added stepwise to the precursor salts. The mass concentrations from the literature[1,2] were used as basis for preparing the solubility curves without the admixture of alcohols. In order to indicate the mass concentrations of saturated OLTP solutions as accurately as possible and to avoid diluted solutions, 200 µl less solvent was added to each of the precursor salts than described in the literature. Afterwards, the solutions were stirred for 3 h at the temperatures listed in Fig. 1 and Fig. S1. To finally obtain a saturated OLTP solution, 10 – 15 µl additional solvent was added per hour.
To prepare the solubility curves of the OLTP solutions with the addition of the primary alcohols, 40 µl of propanol, butanol, pentanol or hexanol were first added to each of the weighed precursor salts. At first, the same amounts of solvents or solvent mixtures as for the saturated solutions without alcohol were added, due to the expected poorer solubility of OLTPs with alcohol. The solutions were stirred for 3 h at the temperatures listed in Fig. 1 and Fig. S1. Further solvent was finally added in steps of 10 – 15 µl per hour, until the OLTP solutions were completely dissolved.
For the addition of solvents and solvent mixtures to achieve a saturated OLTP solution, we give an error of ±5 µl.

OLTP Crystal Growth

The precursor solutions $MAPbCl_3$, $MAPbBr_3$, $FAPbBr_3$ and $FAPbI_3$ were stirred for 3 h at RT, until they were completely dissolved. The $MAPbI_3$ solution was stirred at 60 °C for 4 h for complete dissociation of the precursor salts. The OLTP solutions were then filtered via a 0.2 µm pore size polytetrafluoroethylene (PTFE) syringe filter. To start RITC, above 100 µl of a primary alcohol was added before heating the solution to the required growth temperature. The crystal growth took place under ambient conditions at a temperature of 22.5±1 °C and a humidity of 40±20 %.

Hint for crystal growth with RITC

The amount of alcohol added to the precursor solution must be in the range of 90 µl to 120 µl to grow crystals at the temperatures indicated in Fig. 2. However, if much less alcohol is added to the precursor solution, the crystallisation temperature must be increased because the polarity effect of the alcohol is strongly reduced. If large amounts of alcohol (ca. 250 µl) are added to the precursor solution, the polarity effect of the alcohol is much stronger and crystals are formed in a few minutes, which is comparable to Fig. S2. However, it is no longer possible to grow single crystals from these solutions because the nucleation rate is too high.

Crystal Characterisation

The mass fractions of the elements hydrogen, carbon, and nitrogen were determined with a micro elemental analyzer of the model vario MICRO cube. EDX measurements were performed in high vacuum with a scanning electron microscope (SEM) Carl Zeiss Ultra 55+ and an INCAPentaFET-x3 Si(Li) detector to determine the mass fractions of chlorine, bromine, iodine and lead on the crystal surfaces. Powder, single crystal XRD spectra and rocking scans were carried out by an X-ray diffraction system General Electric XRD 3003 TT using a Cu(Copper)-$K_{\alpha 1}$ radiation source with a wavelength λ of 1.5406 Å (V = 40 kV, I = 40 mA) at ambient conditions.

[1] M. I. Saidaminov, A. L. Abdelhady, G. Maculan and O. M. Bakr, *Chemical Communications*, 2015, **51**, 17658-17661.

[2] G. Maculan, A. D. Sheikh, A. L. Abdelhady, M. I. Saidaminov, M. A. Haque, B. Murali, E. Alarousu, O. F. Mohammed, T. Wu and O. M. Bakr, *The Journal of Physical Chemistry Letters*, 2015, **6**, 3781-3786.

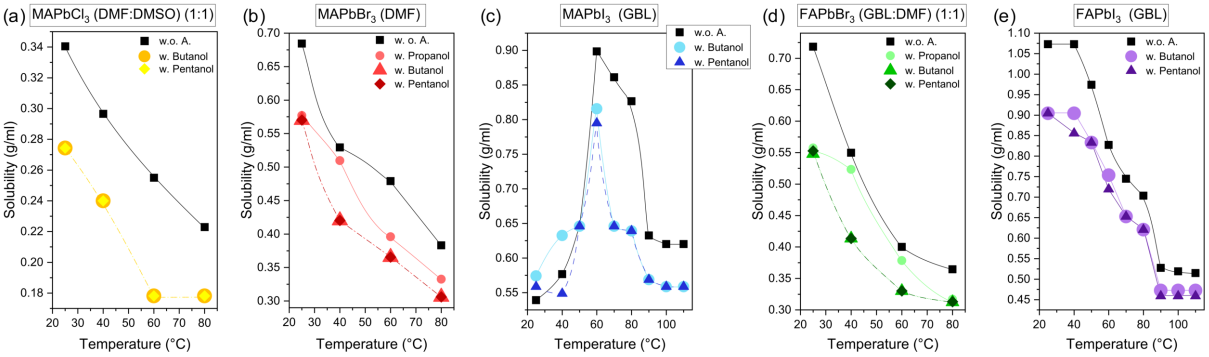

Figure S1. (a) – (e) Solubility curves of the OLTP solutions with propanol, butanol and pentanol. The black-labelled curves represent the retrograde solubility of the OLTP solutions without additives.

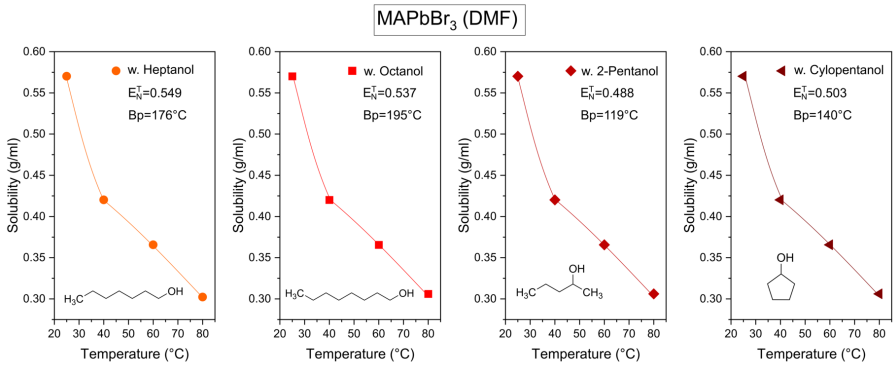

Figure S2. Solubility curves of $MAPbBr_3$ solutions with the long-chained primary alcohols 1-heptanol, 1-octanol, the secondary alcohol 2-pentanol and the cyclic alcohol cyclopentanol, in addition with their polarity values E_N^T[3] and their boiling points Bp[4]. The presented solubility curves show an almost identical course as the solubility curve of the ($MAPbBr_3$/ 1-hexanol) mixture in Fig. 1 and suggests that the solubility cannot be further reduced with strongly nonpolar alcohols.

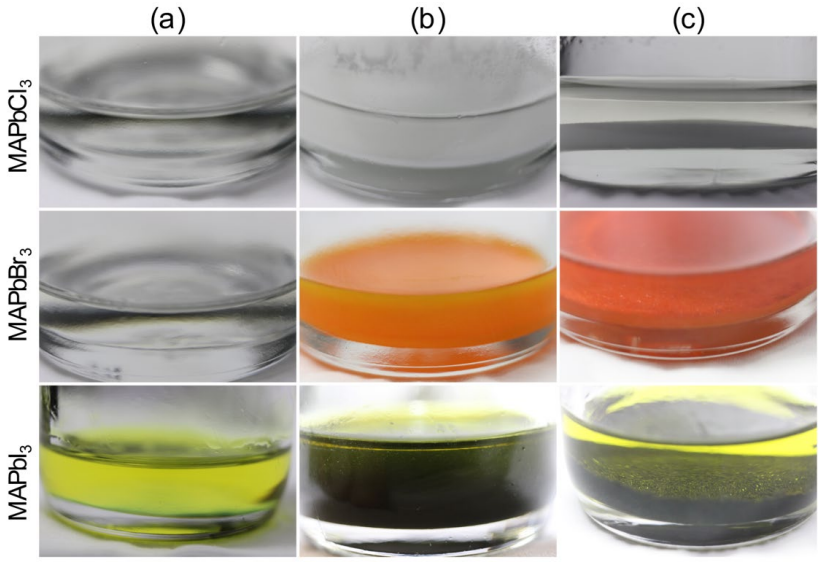

Figure S3. (a) Preliminary precipitation tests with saturated $MAPbCl_3$, $MAPbBr_3$ and $MAPbI_3$ solutions based on the insights from the solubility curves, to grow OLTP crystals with RITC. For this, the $MAPbCl_3$, $MAPbBr_3$ and $MAPbI_3$ precursor solutions were heated up to temperatures of 45 °C, 50 °C and 95 °C, respectively. (b) Perovskite particles precipitated directly in solution by adding an excess of butanol (250 µl). The transparent $MAPbCl_3$ and $MAPbBr_3$ solutions and the clear yellow solution of $MAPbI_3$ suddenly became white, red and black. As a result, the admixture of the alcohol directly disturbed the chemical equilibrium of the perovskites. (c) In the supersaturated solutions, the finely dispersed perovskite sediments were deposited on the vessel bottoms and grew into polycrystalline carpets within 15 min.

[3] C. Reichardt, *Chemical Reviews*, 1994, **94**, 2319-2358.

[4] B. Spingler, S. Schnidrig, T. Todorova and F. Wild, *CrystEngComm*, 2012, **14**, 751-757.

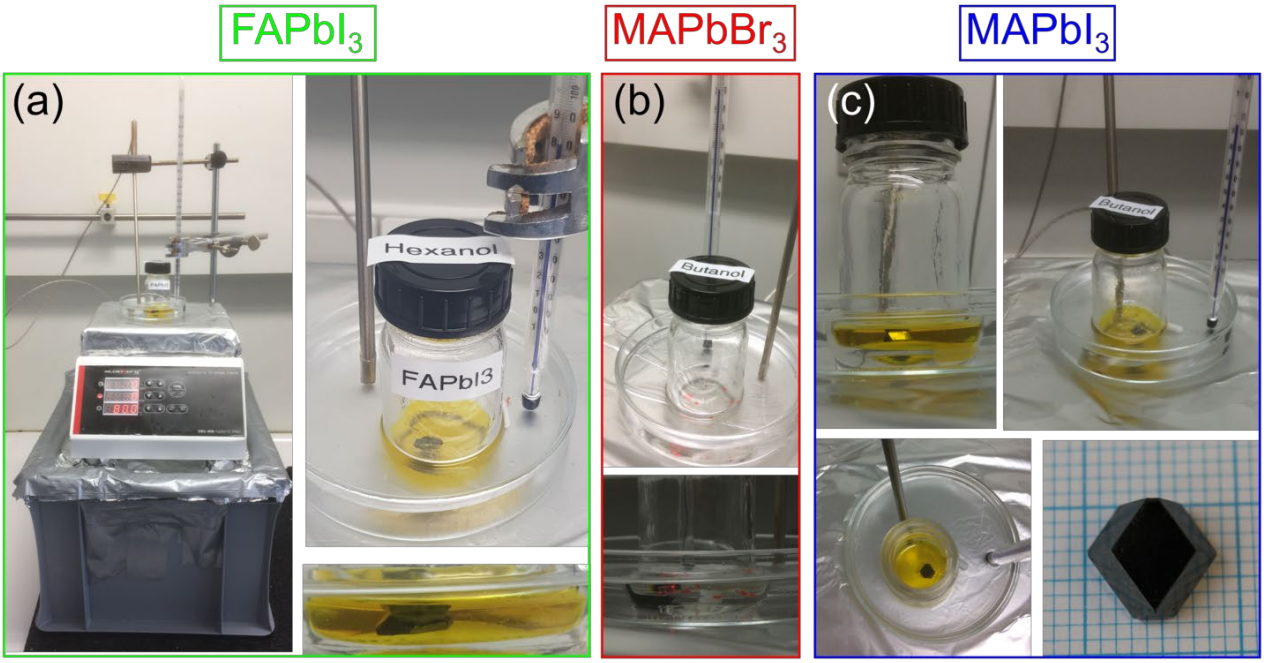

Figure S4. (a) Setup to grow OLTP crystals with RITC. Evidence for growing a $FAPbI_3$ crystal at 80 °C with the reagent hexanol. $FAPbI_3$ crystal in a hexanol containing solution (3 ml) at 80 °C, with a size of above 0.81 cm^2, obtained after 7 h. (b) $MAPbBr_3$ crystals in a butanol containing solution (3 ml) at 50 °C. (c) $MAPbI_3$ crystals in butanol containing solutions (4 ml) at 95°C. The $MAPbI_3$ crystal reached a maximum size of above 0.69 cm^2 after a growth period of 8 h.

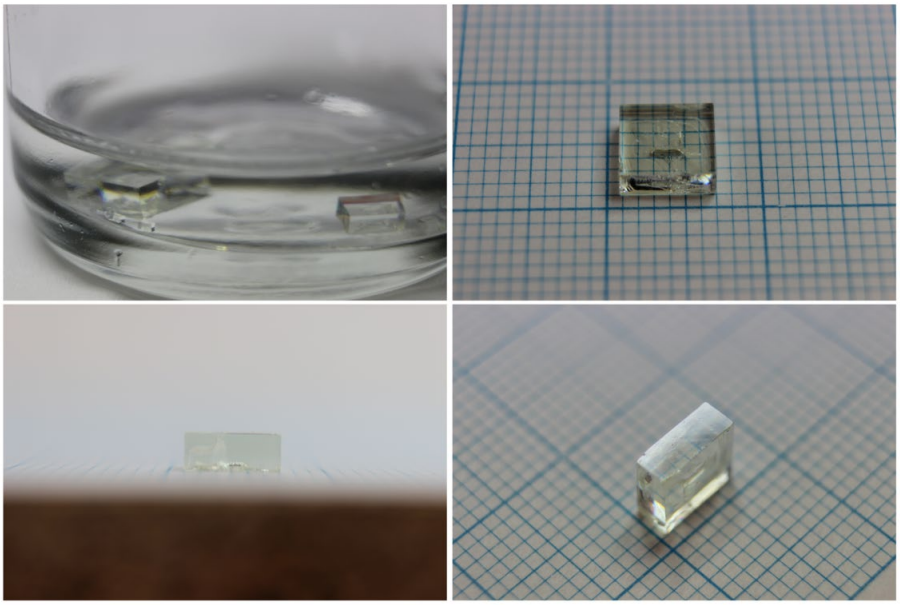

Figure S5. $MAPbCl_3$ crystals grown at RT by adding 100 µl of propanol to the precursor solution. The crystals reached a maximum size of 0.36 cm^2 after one month. Since $MAPbCl_3$ crystals have merely grown by adding propanol to the perovskite solution without further heating, we assign the crystal growth process to the reactive crystallisation (RC)[5].

[5] E. L. Paul, H.-H. Tung and M. Midler, *Powder Technology*, 2005, **150**, 133-143.

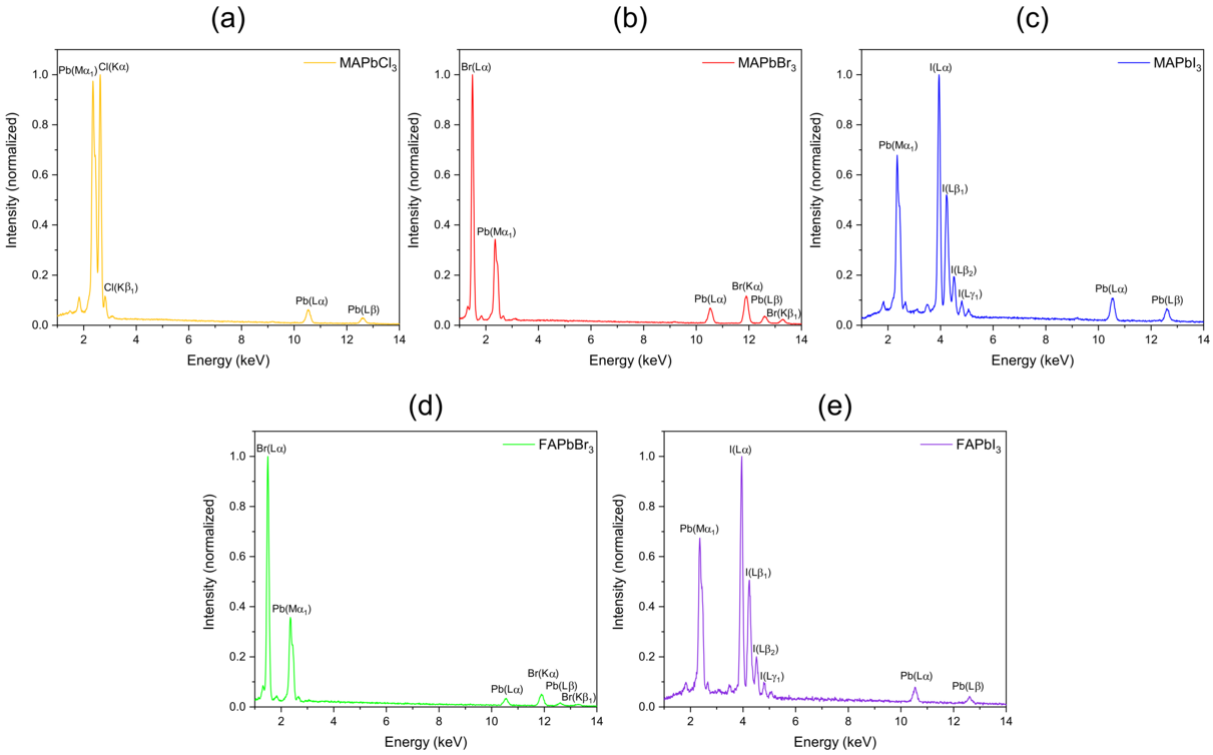

Figure S6. EDX spectra of the (a) $MAPbCl_3$, (b) $MAPbBr_3$, (c) $MAPbI_3$, (d) $FAPbBr_3$ and (e) $FAPbI_3$ crystal surfaces to identify the elements chlorine, bromine, iodine and lead. Based on their characteristic emission lines, the elements could be precisely assigned.

Table S1. Mass fractions of the elements carbon (C), hydrogen (H), nitrogen (N), chlorine (Cl), bromine (Br), iodine (I) and lead (Pb). The mass fractions of methylammonium (CH_3NH_3) and formamidinium (CH_5N_2) were experimentally determined by elemental analysis for each OLTP crystals. The experimental data of EDX together with the crystal powder results of the elemental analysis are in good agreement with the theoretical predictions, which are written in cursive letters.

M [%]	**$CH_3NH_3PbCl_3$**		**$CH_3NH_3PbBr_3$**		**$CH_3NH_3PbI_3$**		**$CH_5N_2PbBr_3$**		**$CH_5N_2PbI_3$**	
C	*3.48*	3.62	*2.51*	2.51	*1.94*	1.94	*2.44*	2.53	*1.90*	2.04
H	*1.75*	1.77	*1.26*	1.22	*0.98*	0.98	*1.02*	1.03	*0.80*	0.84
N	*4.05*	4.32	*2.92*	2.79	*2.26*	2.26	*5.69*	5.54	*4.43*	4.31
Pb	*59.95*	58.09	*43.26*	41.12	*33.42*	29.67	*42.12*	40.03	*32.73*	31.85
Cl, Br or I	*30.77*	35.70	*50.05*	55.48	*61.41*	61.89	*48.72*	52.78	*60.15*	61.79

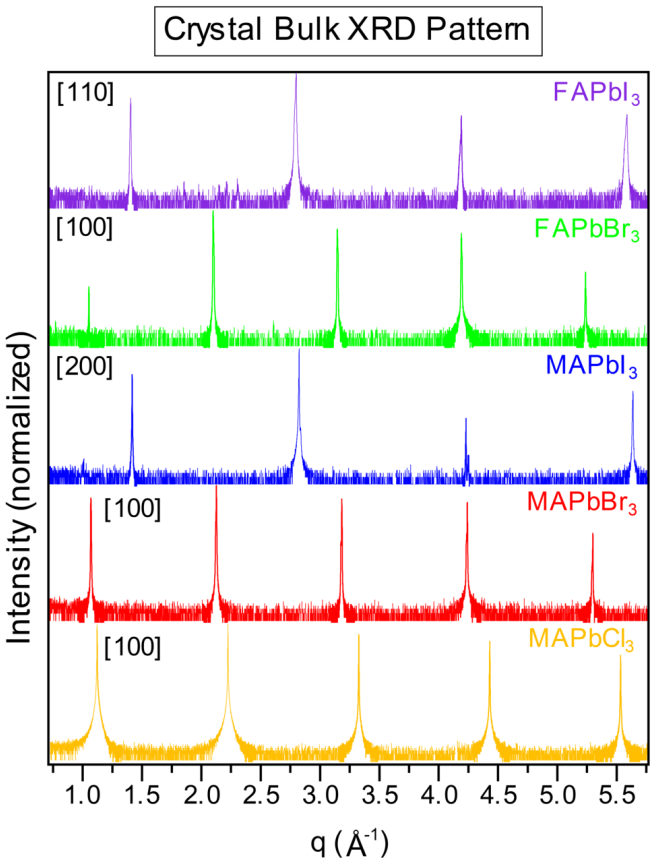

Figure S7. Out-of-plane XRD bulk measurements to confirm OLTP single crystal growth with RITC. To perform the bulk measurements, the crystals were halved with a scalpel along their crystallographic directions: [100] direction for $MAPbCl_3$, $MAPbBr_3$ and $FAPbBr_3$; [200] direction for $MAPbI_3$ and [110] direction for $FAPbI_3$.

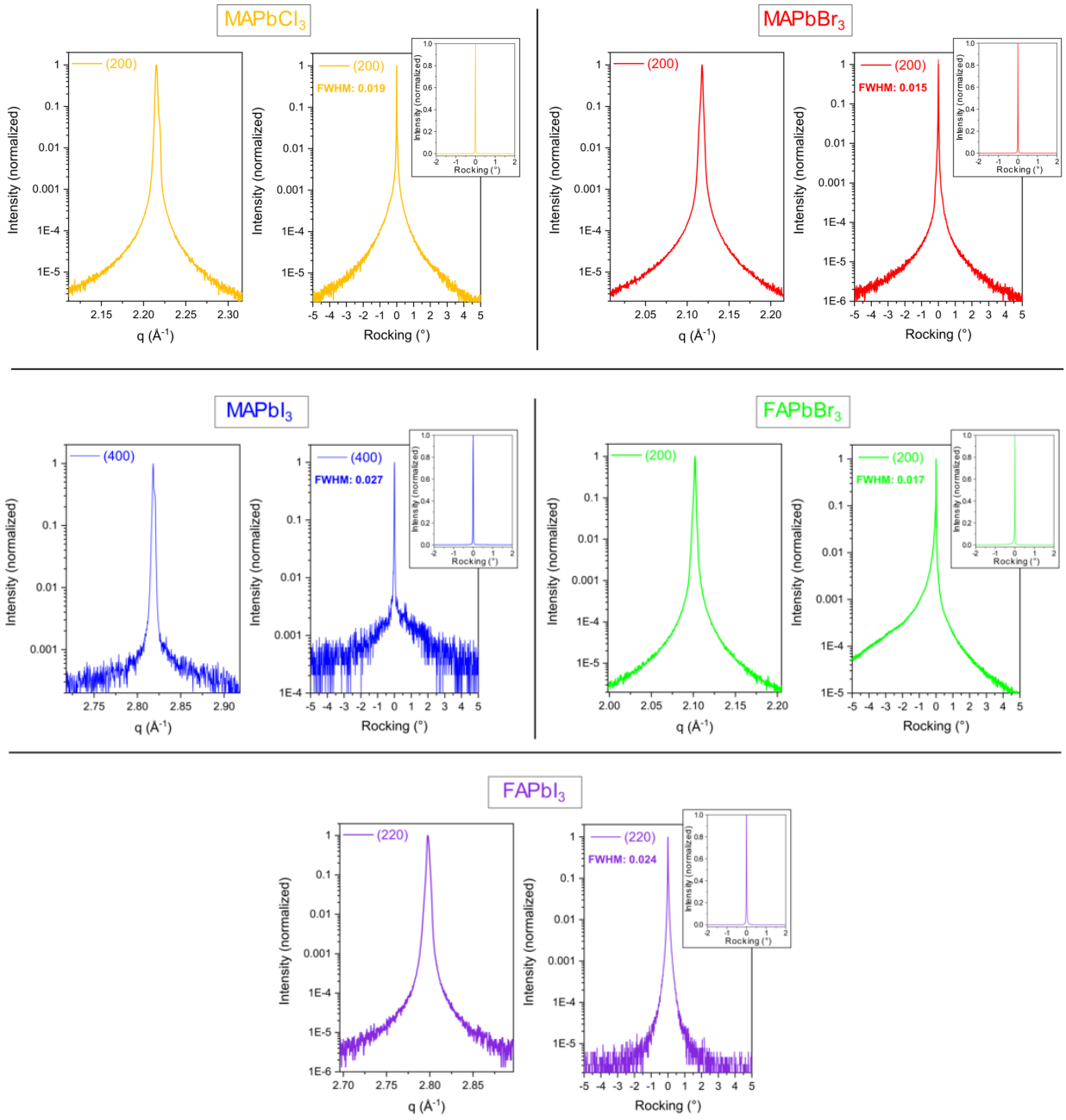

Figure S8. The presented radiographic investigations are used to determine the real structure[6] of the RITC crystals. First, the reflexes of the different OLTP crystal surfaces were determined to record rocking curves in the following, which can reveal possible disturbances in the lattice structure[6]. The shown rocking curves (diffraction curves) show in each case a sharp peak. The full width at half maxima (FWHM) are in the range of 0.015 to 0.027. The narrow rocking peaks and the fact that no further peaks are present in the linear as well as in the logarithmic plots suggest a good crystal quality.

[6]. W. Kleber, H.-J. Bautsch, J. Bohm and I. Kleber, in *Einführung in die Kristallographie (sixteenth edition)*, Verlag Technik, Berlin, 1977, pp. 360-361.