Supplementary materials

Halogen Bonding Induced Morphotropic Step in a Series of (Lead(II) Halogenide)–3-Halopyridine Complexes

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1. SCXRD data

Table S1. Crystallographic data for compounds $[PbX_2(\mathbf{3Xpy})_2]_n$

Compound	$[PbBr_2(\mathbf{3Clpy})_2]_n$	$[PbCl_2(\mathbf{3Brpy})_2]_n$	$[PbBr_2(\mathbf{3Brpy})_2]_n$
Formula	$PbBr_2C_{10}H_8Cl_2N_2$	$PbCl_2C_{10}H_8Br_2N_2$	$PbBr_2C_{10}H_8Br_2N_2$
M_r	594.09	594.09	683.02
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P\ 2_1/c$	$P\ 2_1/c$	$P\ 2_1/c$
a (Å)	4.2468(2)	4.1496(3)	4.2450(3)
b (Å)	15.3128(6)	15.1987(13)	15.4720(8)
c (Å)	11.4556(5)	11.3724(13)	11.5001(10)
α (°)	90	90	90
β (°)	94.062(4)	92.106(9)	93.198(7)
γ (°)	90	90	90
V (Å^3)	743.09(6)	716.76(11)	754.13(9)
Z	2	2	2
Temperature (K)	170(2)	170(2)	170(2)
D_{calc} (g cm^{-3})	2.655	2.753	3.008
Radiation wavelength λ (Å), μ (mm^{-1})	Mo $K\alpha$ 0.71073, 17.068	Mo $K\alpha$ 0.71073, 17.695	Mo $K\alpha$ 0.71073, 21.762
F (000)	536	536	608
Scan type	Ω	Ω	Ω
h, k, l range	–5 : 5; –19 : 19; –14 : 14	–5 : 5; –19 : 18; –13 : 14	–5 : 5; –16 : 19; –13 : 14
θ range/°	2.22 - 27.00	2.68 – 27.00	2.63 – 27.00
No. measured reflections	11925	5904	5635
No. Independent reflections	1636	1505	1655
No. Observed reflections, $I \geq 2\sigma$	1450	1116	1309
No. refined parameters	79	74	79
R_{int}	0.228	0.178	0.084
R, wR [$I \geq 2\sigma$]	0.0895, 0.2316	0.1123, 0.3048	0.0787,.2030
R, wR [all data]	0.0926, 0.2352	0.1546, 0.3869	0.09620, 0.2138
Goodness of fit on F^2, S	1.077	1.498	1.022
Max, min. El. density (e Å^{-3})	–11.028, 9.973*	–9.924, 5.910*	–4.734, 7.662*
CCDC number	2500574	2500577	2500572

Table S1. Crystallographic data for compounds $[PbX_2(\mathbf{3Xpy})_2]_n$ (continued)

Compound	$[PbCl_2(\mathbf{3Ipy})_2]_n$	$[PbBr_2(\mathbf{3Ipy})_2]_n$	$[PbI_2(\mathbf{3Ipy})_2]_n$
Formula	$PbCl_2C_{10}H_8I_2N_2$	$PbBr_2C_{10}H_8I_2N_2$	$PbI_2C_{10}H_8I_2N_2$
M_r	688.08	777.00	870.98
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\,\bar{1}$	$P\,2_1/c$	$P\,2_1/c$
a (Å)	4.1872(3)	4.31660(10)	4.47850(10)
b (Å)	8.7362(8)	15.7790(4)	16.1466(2)
c (Å)	10.6056(10)	11.5631(4)	11.7633(2)
α (°)	99.179(8)	90	90
β (°)	91.011(7)	92.646(3)	93.924(2)
γ (°)	95.850(7)	90	90
V (Å^3)	380.77(6)	786.74(4)	716.76(11)
Z	1	2	2
Temperature (K)	170(2)	170(2)	170(2)
D_{calc} (g cm^{-3})	3.001	3.280	3.408
Radiation wavelength λ (Å), μ (mm^{-1})	Mo $K\alpha$ 0.71073, 15.462	Mo $K\alpha$ 0.71073, 19.706	Mo $K\alpha$ 0.71073, 17.199
F (000)	304	680	752
Scan type	Ω	Ω	Ω
h, k, l range	–6 : 6; –12 : 12; –15 : 12	–5 : 5; –20 : 19; –14 : 14	–5 : 5; –20 : 20; –14 : 14
θ range/°	2.38 – 33.69	2.19 - 27.00	2.52 – 27.00
No. measured reflections	7256	13053	22622
No. Independent reflections	2620	1719	1862
No. Observed reflections, $I \geq 2\sigma$	1823	1606	1825
No. refined parameters	79	79	79
R_{int}	0.084	0.067	0.039
R, wR [$I \geq 2\sigma$]	0.0948, 0.2520	0.0369, 0.1146	0.0140, 0.0357
R, wR [all data]	0.1274, 0.2720	0.0401, 0.1167	0.0147, 0.0360
Goodness of fit on F^2, S	1.050	1.086	1.089
Max, min. El. density (e Å^{-3})	–3.474, 10.230*	–2.598, 3.755*	-0.612, 1.274
CCDC number	2500575	2500573	2500576

* The large maxima and the minima are located in the immediate vicinity of the heavy atoms (Pb, I. Br) and are artifacts arising from overall low data quality, and possibly anharmonic vibrations.

2. PXRD data

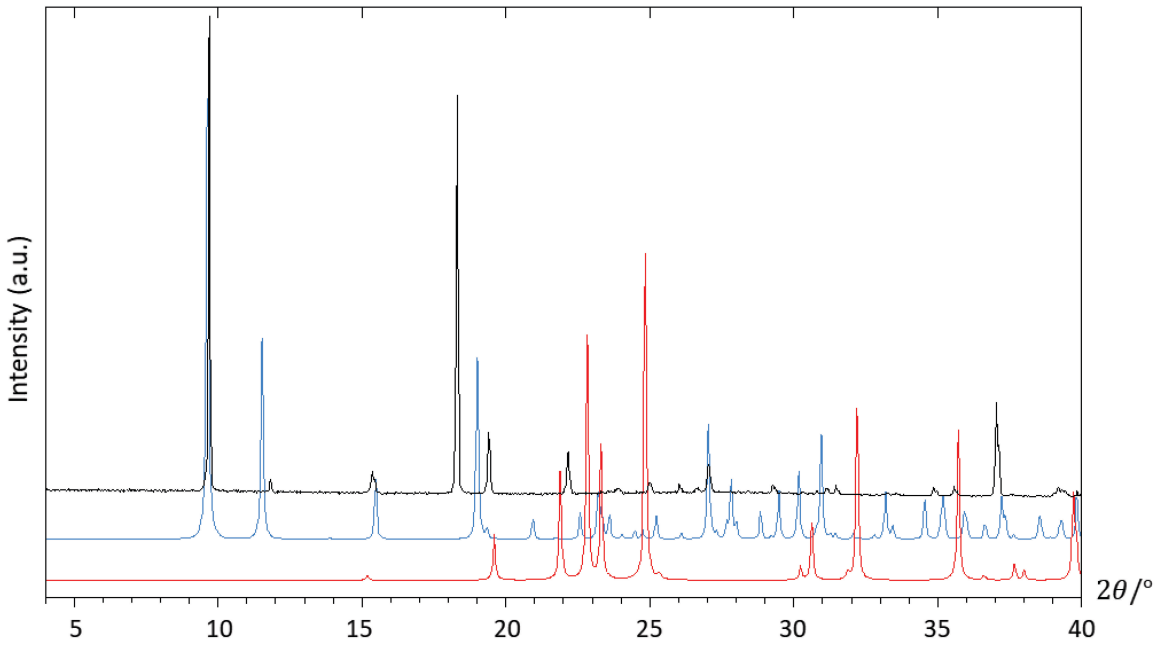

Fig S1. Experimental PXRD pattern of $[PbCl_2(3\text{-}Clpy)_2]_n$ (black); calculated PXRD pattern of $[PbBr_2(3\text{-}Clpy)_2]_n$ (light blue) and $PbCl_2$ (red).

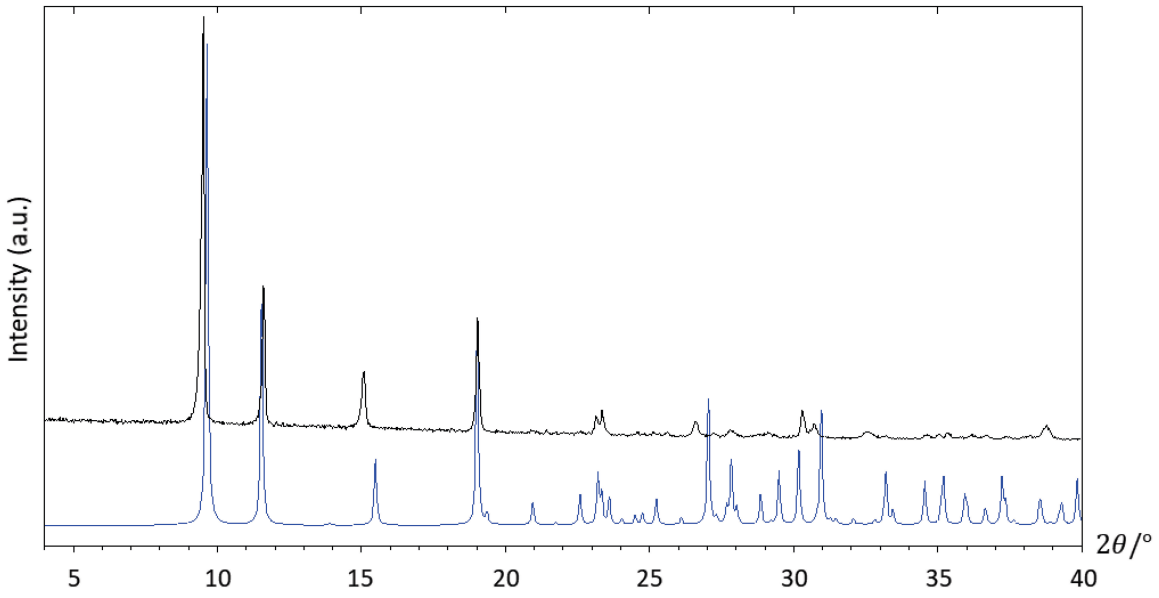

Fig S2. Experimental PXRD pattern of $[PbBr_2(3\text{-}Clpy)_2]_n$ (black); calculated PXRD pattern of $[PbBr_2(3\text{-}Clpy)_2]_n$ (blue).

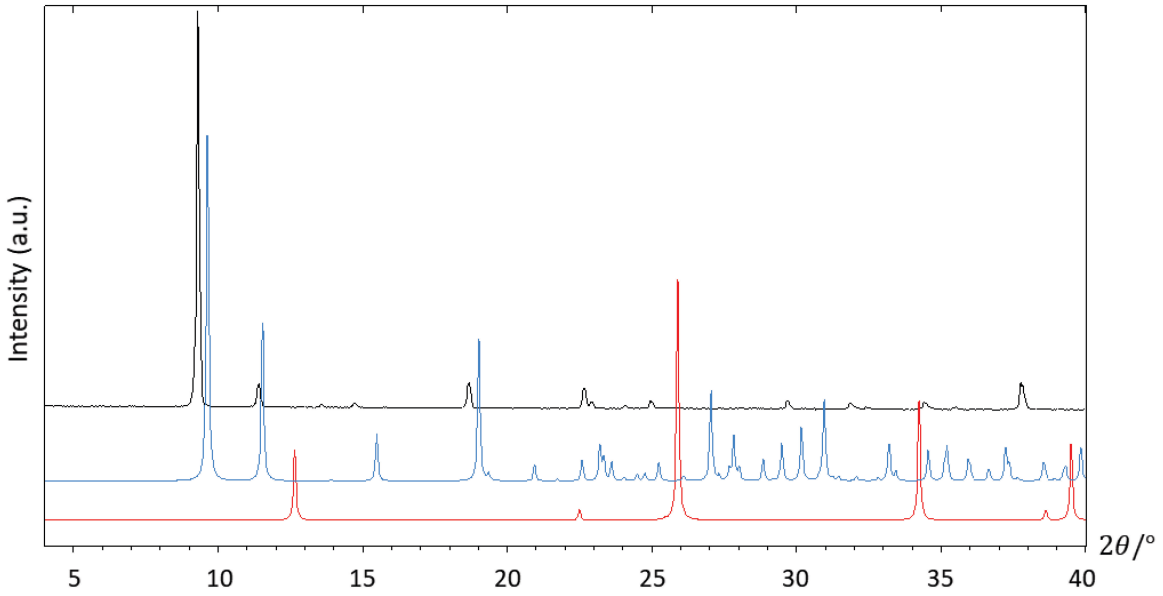

Fig S3. Experimental PXRD pattern of $[PbI_2(3\text{-}Clpy)_2]_n$ (black); calculated PXRD pattern of $[PbBr_2(3\text{-}Clpy)_2]_n$ (light blue) and PbI_2 (red).

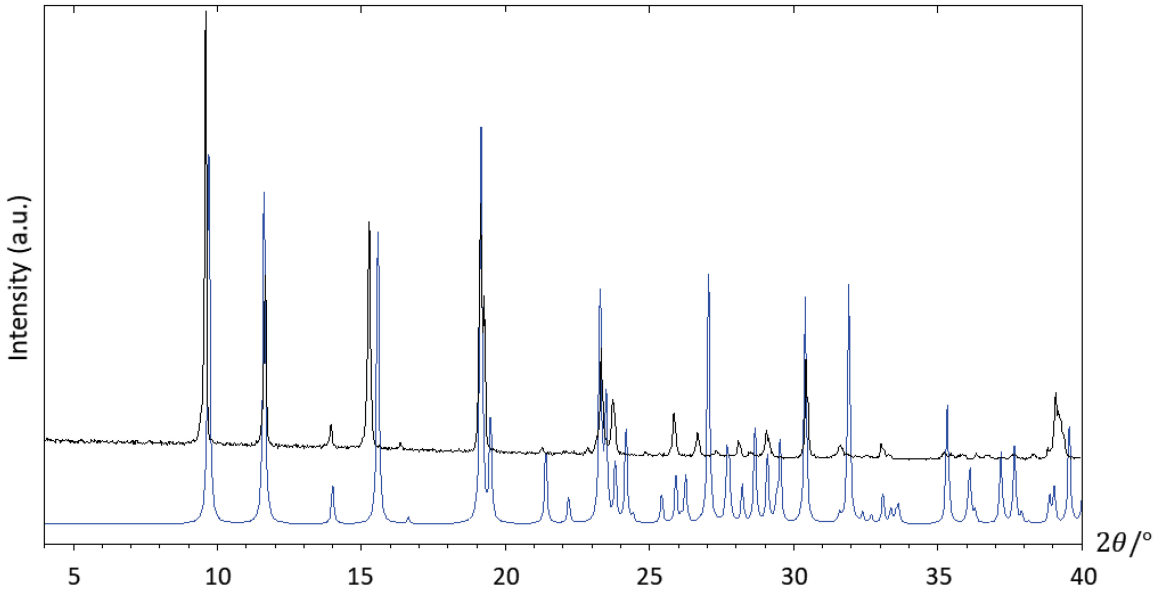

Fig S4. Experimental PXRD pattern of $[PbCl_2(3\text{-}Brpy)_2]_n$ (black); calculated PXRD pattern of $[PbCl_2(3\text{-}Brpy)_2]_n$ (blue).

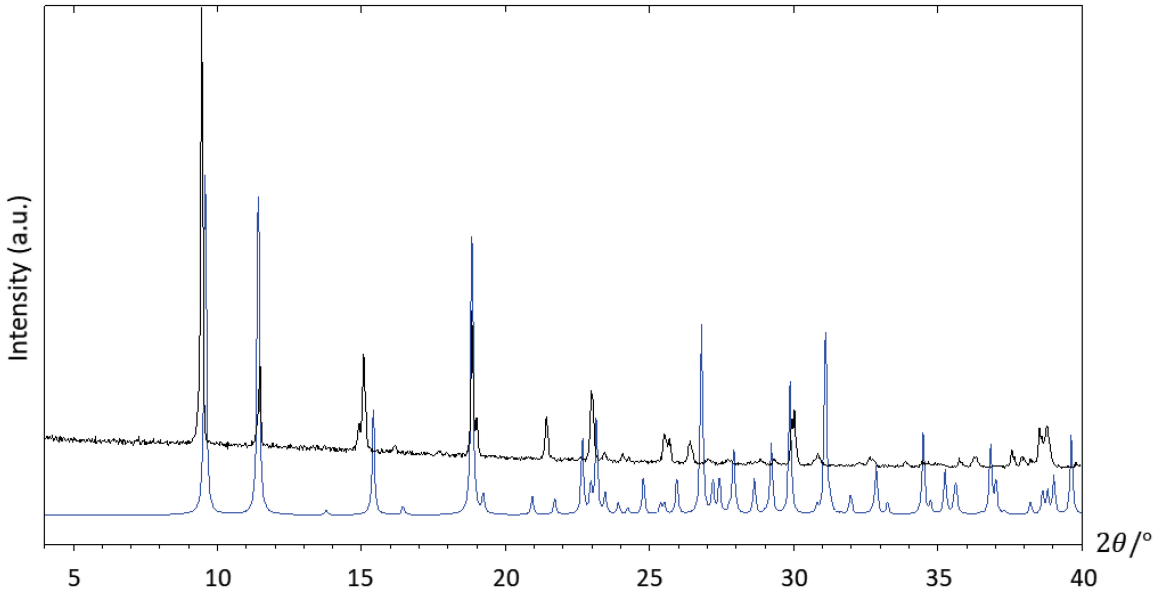

Fig S5. Experimental PXRD pattern of $[PbBr_2(3\text{-}Brpy)_2]_n$ (black); calculated PXRD pattern of $[PbBr_2(3\text{-}Brpy)_2]_n$ (blue).

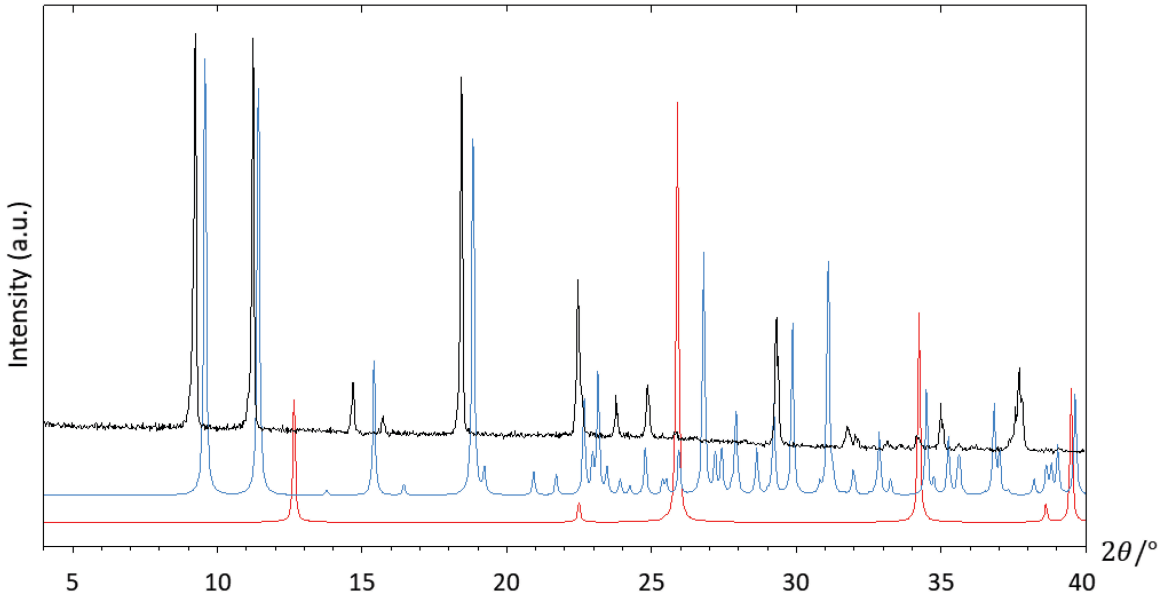

Fig S6. Experimental PXRD pattern of $[PbI_2(3\text{-}Brpy)_2]_n$ (black); calculated PXRD pattern of $[PbBr_2(3\text{-}Brpy)_2]_n$ (light blue) and PbI_2 (red).

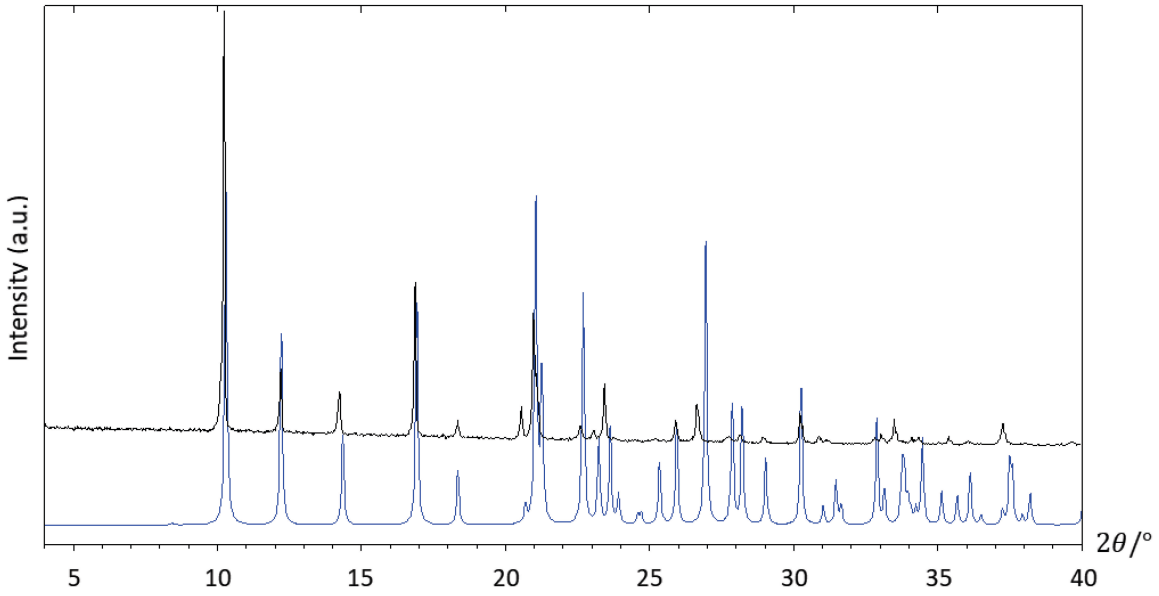

Fig S7. Experimental PXRD pattern of $[PbCl_2(3\text{-}Ipy)_2]_n$ (black); calculated PXRD pattern of $[PbCl_2(3\text{-}Ipy)_2]_n$ (blue).

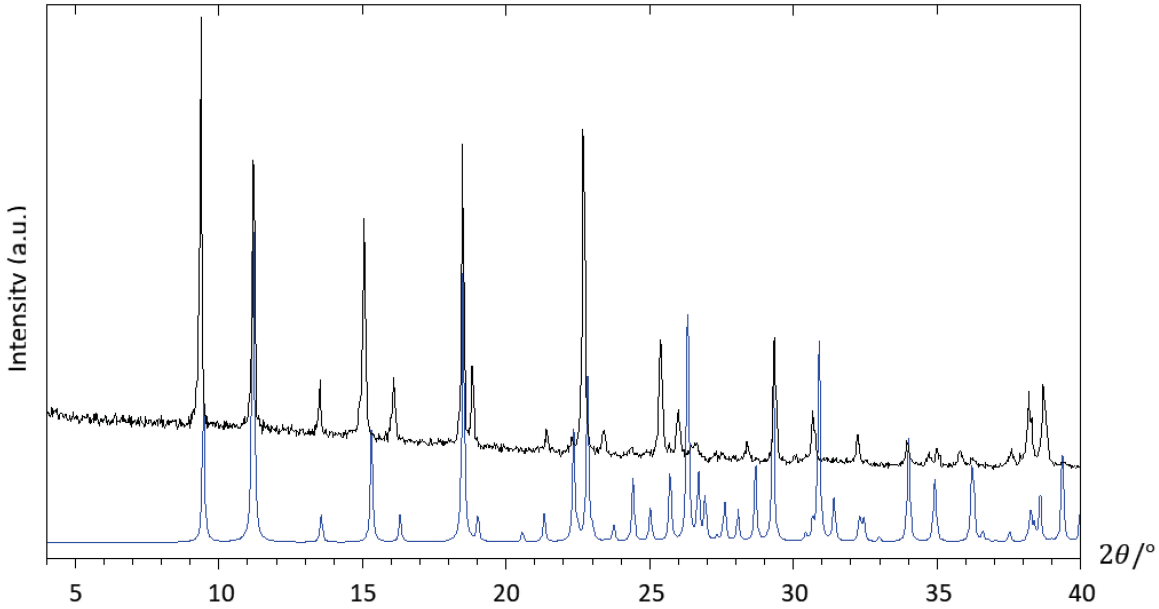

Fig S8. Experimental PXRD pattern of $[PbBr_2(3\text{-}Ipy)_2]_n$ (black); calculated PXRD pattern of $[PbBr_2(3\text{-}Ipy)_2]_n$ (blue).

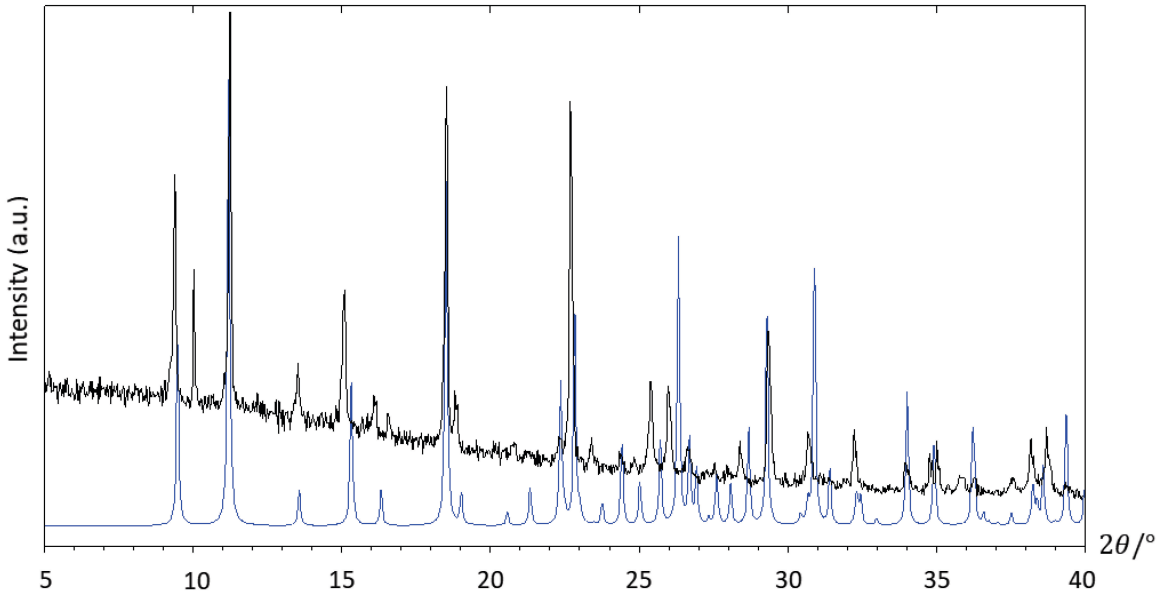

Fig S9. Experimental PXRD pattern of $[PbBr_2(3\text{-}Ipy)_2]_n$ (black); calculated PXRD pattern of $[PbBr_2(3\text{-}Ipy)_2]_n$ (blue).

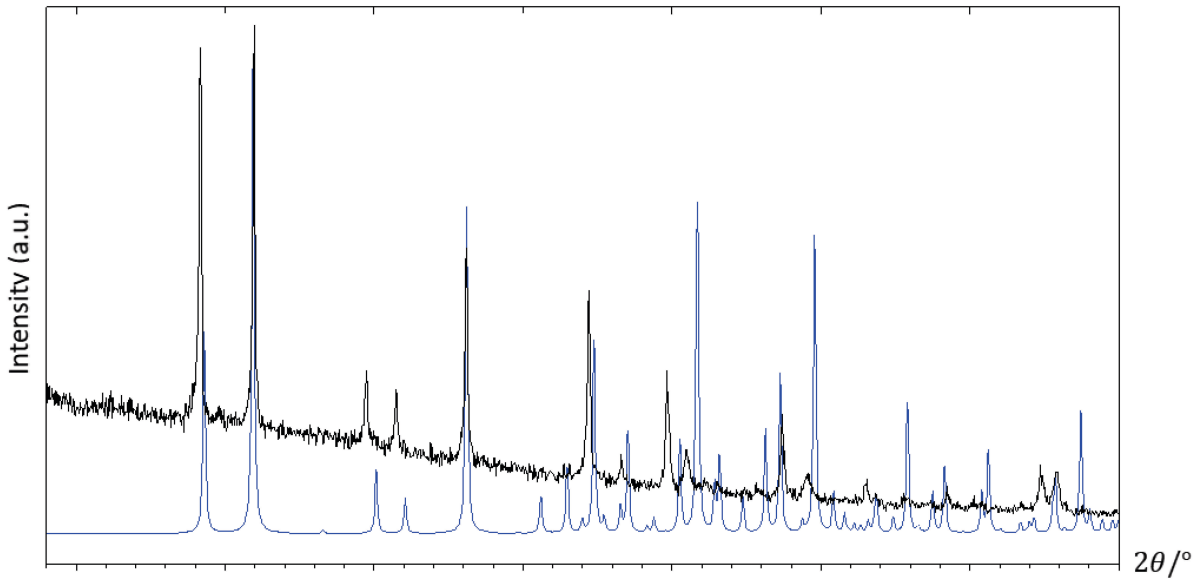

Fig S10. Experimental PXRD pattern of $[PbI_2(3\text{-}Ipy)_2]_n$ (black); calculated PXRD pattern of $[PbI_2(3\text{-}Ipy)_2]_n$ (blue).

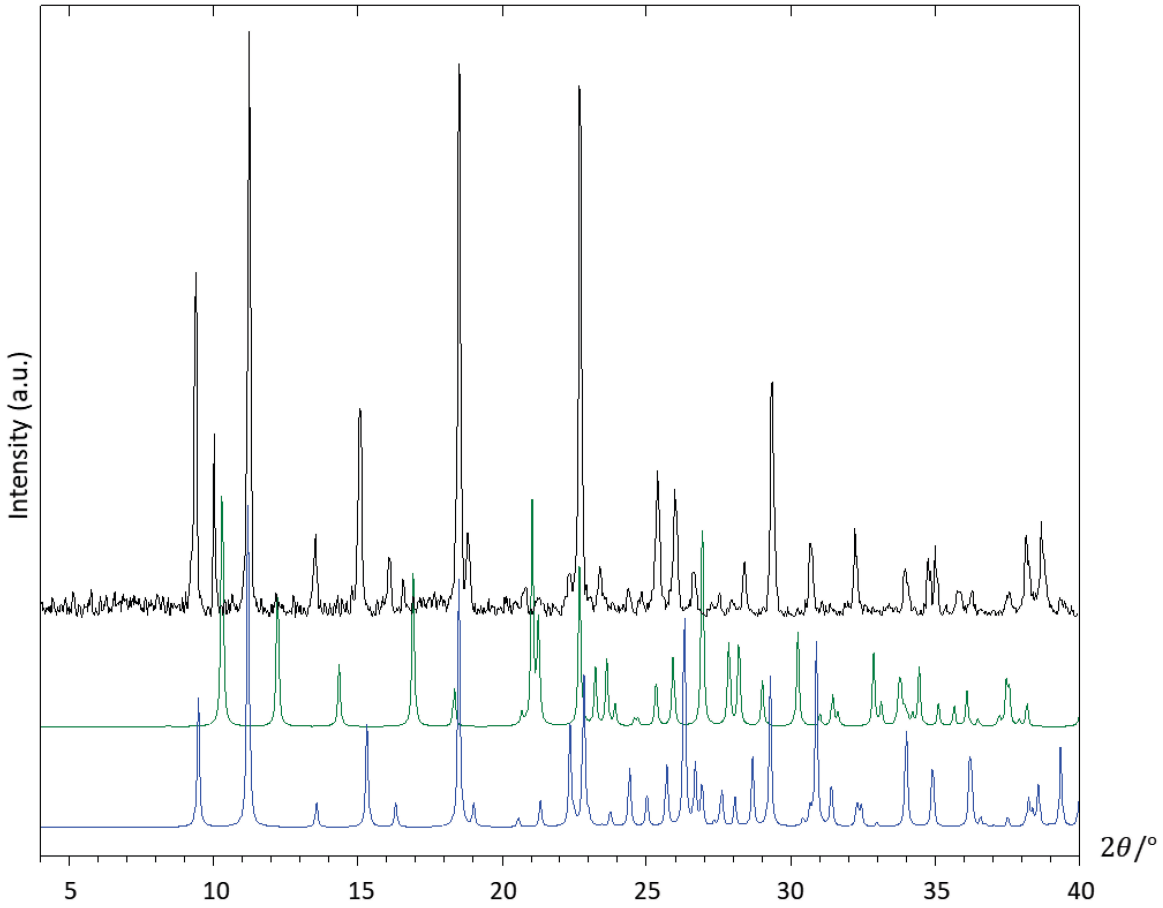

Fig S11. Experimental PXRD pattern of $[PbBr_2(3\text{-Ipy})_2]_n$ (black); calculated PXRD pattern of $[PbBr_2(3\text{-Ipy})_2]_n$ (blue); calculated PXRD pattern of $[PbCl_2(3\text{-Ipy})_2]_n$ (green).

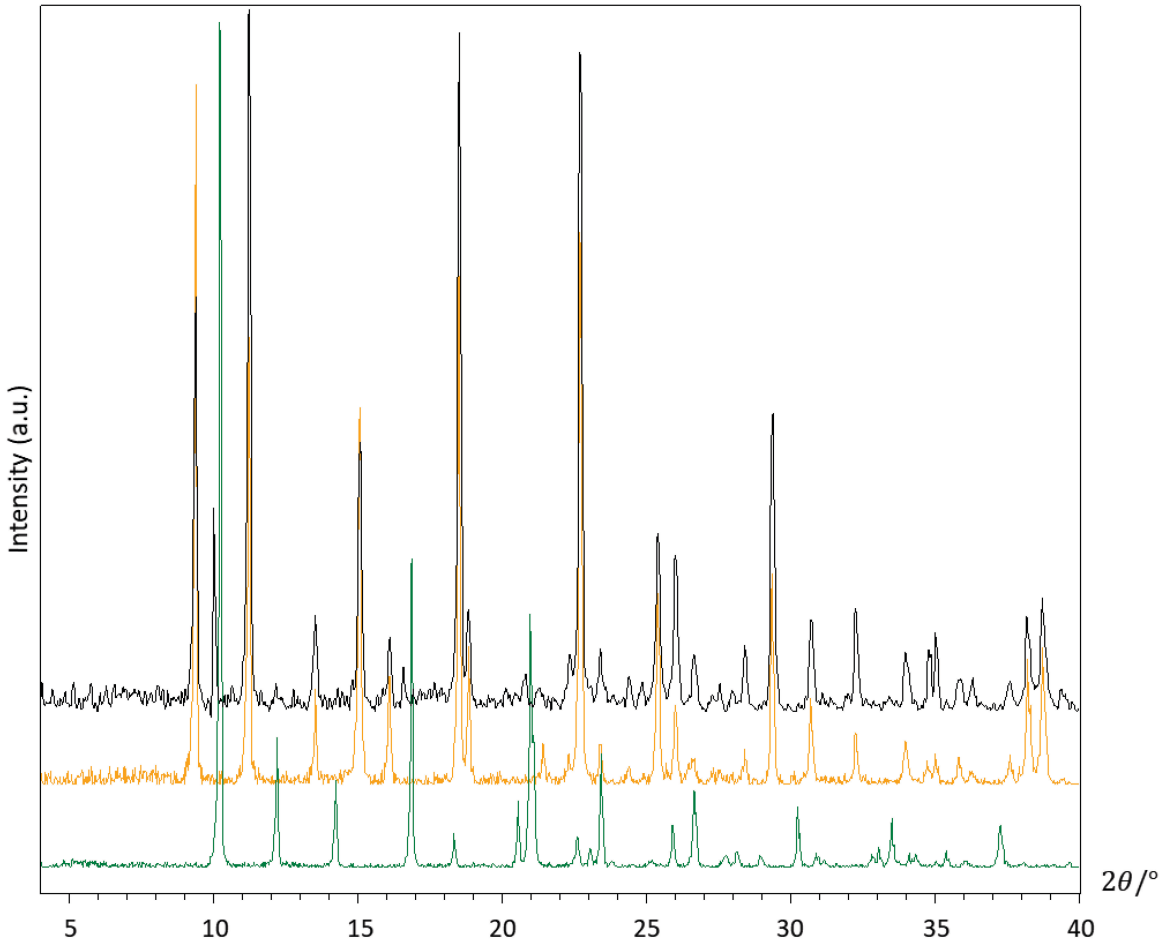

Fig S12. Experimental PXRD patterns of M+T $[PbBr_2(3\text{-Ipy})_2]_n$ (black), M $[PbBr_2(3\text{-Ipy})_2]_n$ (orange); of T $[PbCl_2(3\text{-Ipy})_2]_n$ (green).

3. Synthetic procedure

The lead(II) halogenide salt is added to water and the mixture is heated under reflux conditions until the salt dissolves. In case trace amounts of the starting salt remain undissolved they are removed via filtration and 1 mL of water is added to the filtrate which is heated again until a clear solution is obtained. The lead salt solution is removed from the heater and an ethanol solution of 3-halopyridine is added to it. Crystals of products form upon cooling of the reaction mixture.

Synthesis of $[PbCl_2(3\text{-}Clpy)_2]_n$

$PbCl_2$ (180 mg, 0.65 mmol) was dissolved in water (7,5 mL), 3-chloropyridine (3-Clpy, 500 µL, 5.26 mmol) was dissolved in 2 mL of ethanol and the solutions were mixed. Colourless crystals formed upon cooling of the solution.

Synthesis of $[PbBr_2(3\text{-}Clpy)_2]_n$

$PbBr_2$ (71.4 mg, 0.19 mmol) was dissolved in water (14 mL), 3-chloropyridine (3-Clpy, 500 µL, 5.26 mmol) was dissolved in 3 mL of ethanol and the solutions were mixed. Colourless crystals formed upon cooling of the solution.

Synthesis of $[PbI_2(3\text{-}Clpy)_2]_n$

PbI_2 (35.8 mg, 0.08 mmol) was dissolved in water (14 mL), trace amounts of undissolved PbI_2 were removed via filtration and 1 mL of water was added to the filtrate. 3-chloropyridine (3-Clpy, 500 µL, 5.26 mmol) was dissolved in 3 mL of ethanol and the solutions were mixed. Colourless crystals formed upon cooling of the solution.

Synthesis of $[PbCl_2(3\text{-}Brpy)_2]_n$

$PbCl_2$ (66.5 mg, 0.24 mmol) was dissolved in water (14 mL), 3-bromopyridine (3-Brpy, 500 µL, 5.19 mmol) was dissolved in 3 mL of ethanol and the solutions were mixed. Colourless crystals formed upon cooling of the solution.

Synthesis of $[PbBr_2(3\text{-Brpy})_2]_n$

$PbBr_2$ (75.4 mg, 0.21 mmol) was dissolved in water (14 mL), 3-bromopyridine (3-Brpy, 500 µL, 5.19 mmol) was dissolved in 3 mL of ethanol and the solutions were mixed. Colourless crystals formed upon cooling of the solution.

Synthesis of $[PbI_2(3\text{-Brpy})_2]_n$

PbI_2 (35.2 mg, 0.08 mmol) was dissolved in water (14 mL), trace amounts of undissolved PbI_2 were removed via filtration and 1 mL of water was added to the filtrate. 3-bromopyridine (3-Brpy, 500 µL, 5.19 mmol) was dissolved in 3 mL of ethanol and the solutions were mixed. Colourless crystals formed upon cooling of the solution.

Synthesis of $[PbCl_2(3\text{-Ipy})_2]_n$

$PbCl_2$ (76.7 mg, 0.28 mmol) was dissolved in water (14 mL), 3-iodopyridine (3-Ipy, 158 mg, 0.77 mmol) was dissolved in 3 mL of ethanol and the solutions were mixed. Colourless crystals formed upon cooling of the solution.

Synthesis of $[PbBr_2(3\text{-Ipy})_2]_n$

$PbBr_2$ (62.0 mg, 0.17 mmol) was dissolved in water (14 mL), 3-iodopyridine (3-Ipy, 101 mg, 0.49 mmol) was dissolved in 3 mL of ethanol and the solutions were mixed. Colourless crystals formed upon cooling of the solution.

Synthesis of $[PbI_2(3\text{-Ipy})_2]_n$

PbI_2 (40.1 mg, 0.09 mmol) was dissolved in water (14 mL), trace amounts of undissolved PbI_2 were removed via filtration and 1 mL of water was added to the filtrate. 3-iodopyridine (3-Ipy, 98 mg, 0.48 mmol) was dissolved in 3 mL of ethanol and the solutions were mixed. Colourless crystals formed upon cooling of the solution.