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Supplementary Material

Coordination polymers based on aluminum and indium halides together with pyrazine

Thomas C. Schäfer[A], *Jonathan Becker*[A], *Dominik Heuler*[A], *Marcel T. Seuffert*[A], *Alexander E. Sedykh*[A] *and Klaus Müller-Buschbaum*[A,B,*]

[A]Institute of Inorganic and Analytical Chemistry, Justus-Liebig University Giessen, Heinrich-Buff-Ring 17, 35392 Giessen, Germany

[B]Center for Materials Research (LaMa), Justus-Liebig University Giessen, Heinrich-Buff-Ring 16, 35392 Giessen, Germany

*Correspondence to: Email: kmbac@uni-giessen.de

Table S1 Crystallographic data for **1**-**3**. Deviations are given in brackets.

	$^1_\infty$[$AlCl_3$(pyz)] (1)	$^1_\infty$[AlI_3(pyz)] (2)	$^1_\infty$[$InBr_3$(pyz)] (3)
Empirical formula	$C_4H_4AlCl_3N_2$	$C_4H_4AlI_3N_2$	$C_4H_4Br_3InN_2$
Formula weight /g·mol^{-1}	213.42	487.77	434.64
Crystal colour and shape	colourless block	yellow block	colourless needle
Crystal size /mm^3	0.457 × 0.251 × 0.202	0.260 × 0.208 × 0.136	0.588 × 0.151 × 0.092
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*
a /pm	1107.4(2)	1167.06(8)	1172.8(2)
b /pm	634.61(9)	725.85(5)	674.7(1)
c /pm	1159.0(2)	1225.33(9)	1209.3(2)
α /°	90	90	90
β /°	103.419(3)	106.686(2)	102.080(3)
γ /°	90	90	90
V /10^6 pm^3	792.2(2)	994.3(1)	935.8(2)
radiation /pm	71.073	71.073	71.073
ρ_{calc} /g·cm^{-3}	1.789	3.258	3.085
$\mu_{(MoK\alpha)}$ /mm^{-1}	1.187	9.457	15.268
Measurement temp. /K	200.0	100.0	200.0
Absorption correction type	multi-scan	multi-scan	multi-scan
2θ range /°	7.23 to 61.088	6.692 to 61.014	6.892 to 56.674
No. of measured reflections	7300	3787	9350
No. of independent reflections	1208	1507	1158
$R_{(int)}$	0.0376	0.0279	0.0542
No. of parameters	48	47	47
R_1 ($I > 2\sigma(I)$)	0.0222	0.0272	0.0185
ωR_2 (all data)	0.0528	0.0649	0.0423
$R_{(sigma)}$ (all data)	0.0255	0.0340	0.0304
GOF	1.081	1.114	1.093
$\Delta\rho_{max}$, $\Delta\rho_{min}$ /10^{-6} e·pm^{-3}	0.35/-0.25	0.84/-1.74	0.57/-0.83

Table S2 Crystallographic data for **4**-**6**. Deviations are given in brackets.

	$^{1}_{\infty}$[InI$_3$(pyz)] (4)	[(AlCl$_3$)$_2$(pyz)$_5$] (5)	[(InI$_3$)$_2$(pyz)] (6)
Empirical formula	$C_4H_4I_3InN_2$	$C_{10}H_{10}AlCl_3N_5$	$C_4H_4I_6In_2N_2$
Formula weight /g·mol^{-1}	575.61	333.56	1071.13
Crystal colour and shape	colourless block	colourless block	yellow block
Crystal size /mm^3	0.425 × 0.195 × 0.131	0.261 × 0.213 × 0.163	0.131 × 0.126 × 0.126
Crystal system	monoclinic	monoclinic	triclinic
Space group	*C*2/*c*	*P*2$_1$/*c*	$P\bar{1}$
a /pm	2027.9(1)	659.4(1)	654.6(1)
b /pm	977.07(7)	2566.9(4)	755.7(1)
c /pm	1451.5(1)	826.6(1)	980.7(1)
α /°	90	90	81.874(7)
β /°	130.792(1)	99.160(5)	85.163(7)
γ /°	90	90	69.183(6)
V /10^6 pm^3	2177.4(3)	1381.4(4)	448.6(1)
radiation /pm	71.073	71.073	71.073
ρ_{calc} /g·cm^{-3}	3.512	1.604	3.965
$\mu_{(MoK\alpha)}$ /mm^{-1}	10.621	0.719	12.869
Measurement temp. /K	200.0	100.0	100.0
Absorption correction type	multi-scan	multi-scan	multi-scan
2θ range /°	4.942 to 56.556	5.238 to 54.962	4.198 to 56.52
No. of measured reflections	17430	29699	19532
No. of independent reflections	2695	3180	2223
$R_{(int)}$	0.0574	0.0702	0.0526
No. of parameters	92	172	64
R_1 ($I > 2\sigma(I)$)	0.0230	0.0275	0.0171
ωR_2 (all data)	0.0564	0.0613	0.0397
$R_{(sigma)}$ (all data)	0.0345	0.0352	0.0243
GOF	1.062	0.951	1.112
$\Delta\rho_{max}$, $\Delta\rho_{min}$ /10^{-6} e·pm^{-3}	0.96/-1.06	0.34/-0.26	0.70/-1.16

Table S3 Pawley refinements for **1**, **2** and **4**. Deviations are given in brackets.

	$^1_\infty$[AlCl$_3$(pyz)] (1)	$^1_\infty$[AlI$_3$(pyz)] (2)	$^1_\infty$[InI$_3$(pyz)] (4)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*
a /pm	1113.27(4)	1180.29(7)	2043.8(3)
b /pm	638.40(3)	731.88(5)	985.9(1)
c /pm	1163.48(4)	1239.26(7)	1460.9(2)
α /°	90	90	90
β /°	103.65(1)	107.42(1)	131.01(1)
γ /°	90	90	90
Rwp /%	7.86	6.96	4.67
GOF	2.07	1.02	1.30

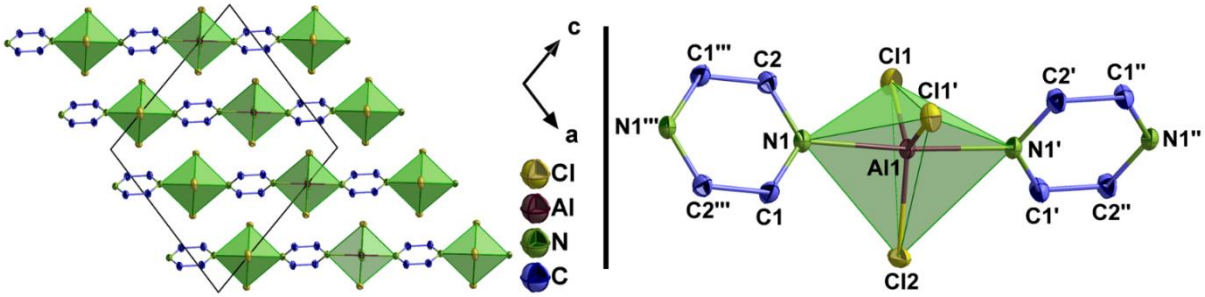

Figure S1: Crystal structure of $^1_\infty$[AlCl$_3$(pyz)] (**1**) with a view along [010] (Left) and extended coordination of Al^{3+} in **1** (Right). The polyhedra of the one-dimensional coordination polymer are highlighted in green and thermal ellipsoids shown at 50 % probability level. For better clarity, all hydrogen-atoms are omitted. Symmetry operations: I = 1-x, y, 1.5-z, 0.5-z; II = 0.5+x, 0.5-y, 0.5+z; III = 0.5-x, 0.5-y, 1-z.

Table S4 Interatomic distances and angles of **1**. Deviations are given in brackets. Symmetry operations: I = 1-x, y, 1.5-z, 0.5-z.

Atoms	**distances /pm**	**atoms**	**angles /°**
Al1-N1	212.54(9)	N1-Al-N1’	175.08(4)
Al1-N1’	212.54(9)	N1-Al1-Cl1	90.625(3)
Al1-Cl1	215.60(5)	N1-Al1-Cl1’	87.144(3)
Al1-Cl1’	215.60(5)	N1-Al1-Cl2	92.459(3)
Al1-Cl2	214.51(7)	N1’-Al1-Cl1	87.144(3)
C1-C2	138.2(2)	N1’-Al1-Cl1’	90.625(3)
C1-N1	133.8(2)	N1’-Al1-Cl2	92.459(3)
C2-N2	133.6(2)	Cl1-Al1-Cl2	116.97(1)
		Cl2-Al1-Cl1’	116.97(1)
		Cl1’-Al-Cl1	126.07(1)

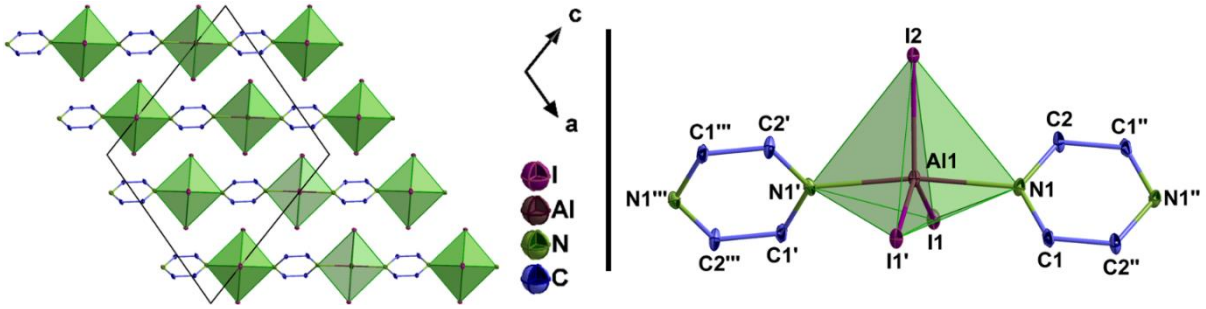

Figure S2: Crystal structure of $^{1}_{\infty}[AlI_3(pyz)]$ (**2**) with a view along [010] (Left) and extended coordination of Al^{3+} in **2** (Right). The polyhedra of the one-dimensional coordination polymer are highlighted in green and thermal ellipsoids shown at 50 % probability level. For better clarity, all hydrogen-atoms are omitted. Symmetry operations: I = 1-x, y, 0.5-z; II = 1.5-x, 1.5-y, 1-z; III = 0.5+x, 1.5-y, -0.5+z.

Table S5 Interatomic distances and angles of **2**. Deviations are given in brackets. Symmetry operations: I = 1-x, y, 0.5-z.

Atoms	**distances /pm**	**atoms**	**angles /°**
Al1-N1	218.3(3)	N1-Al-N1^{I}	170.7(1)
Al1-N1^{I}	218.3(3)	N1-Al1-I1	85.69(9)
Al1-I1	256.41(7)	N1-Al1-I1^{I}	90.52(9)
Al1-I1^{I}	256.41(7)	N1-Al1-I2	94.65(8)
Al1-I2	254.9(2)	N1^{I}-Al1-I1	90.52(9)
C1-C2	138.7(5)	N1^{I}-Al1-I1^{I}	85.69(9)
C1-N1	133.7(5)	N1^{I}-Al1-I2	94.65(8)
C2-N1	134.5(6)	I1-Al1-I2	114.078(5)
		I2-Al1-I1^{I}	114.078(5)
		I1^{I}-Al-I1	131.844(8)

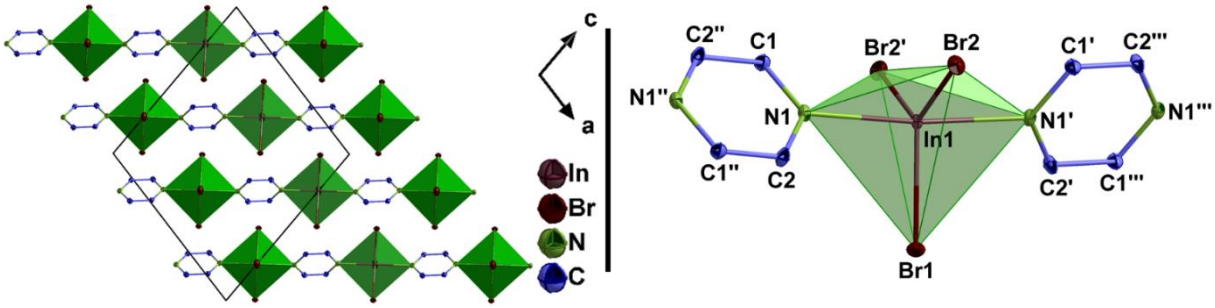

Figure S3: Crystal structure of $^{1}_{\infty}[InBr_3(pyz)]$ (**3**) with a view along [010] (Left) and extended coordination of In^{3+} in **3** (Right). The polyhedra of the one-dimensional coordination polymer are highlighted in green and thermal ellipsoids are shown at 50 % probability level. For better clarity, all hydrogen-atoms are omitted. Symmetry operations: I = 1-x, y, 1.5-z; II = 0.5-x, 0.5-y, 1-z; III = 0.5+x, 0.5-y, 0.5+z.

Table S6 Interatomic distances and angles of **3**. Deviations are given in brackets. Symmetry operations: I = 1-x, y, 1.5-z.

Atoms	**distances /pm**	**atoms**	**angles /°**
In1-N1	236.7(2)	N1-In1-N1^{I}	173.79(7)
In1-N1^{I}	236.7(2)	N1-In1-Br1	93.10(5)
In1-Br1	249.19(6)	N1-In1-Br2^{I}	89.99(5)
In1-Br2^{I}	249.71(4)	N1-In1-Br2	87.40(5)
N1-Br2	249.71(4)	N1^{I}-In1-Br1	93.10(5)
C1-C2	139.0(3)	N1^{I}-In1-Br2^{I}	87.40(5)
C1-N1	134.0(3)	N1^{I}-In1-Br2	89.99(5)
C2-N1	133.5(3)	Br1-In1-Br2^{I}	114.907(8)
		Br1-In1-Br2	114.907(8)
		Br2^{I}-In1-Br2	130.185(8)

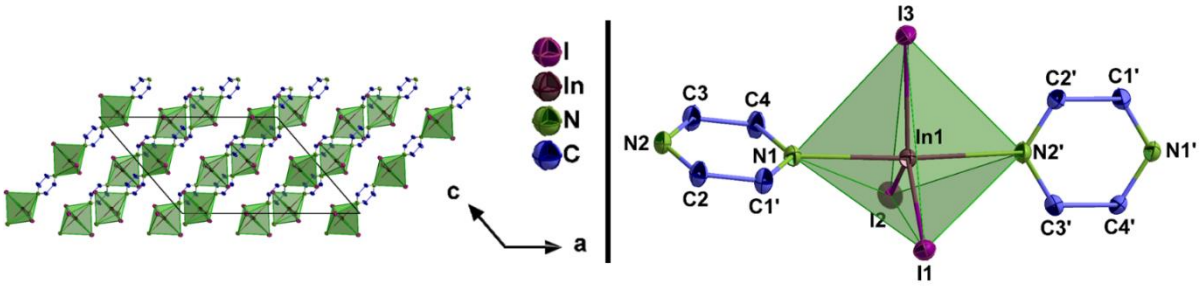

Figure S4: Crystal structure of $^{1}_{\infty}[InI_3(pyz)]$ (**4**) with a view along [010] (Left) and extended coordination of In^{3+} in **4** (Right). The polyhedra of the one-dimensional coordination polymer are highlighted in green and thermal ellipsoids are shown at 50 % probability level. For better clarity, all hydrogen-atoms are omitted. Symmetry operations: I = -0.5+x, 0.5-y, -0.5+z.

Table S7 Interatomic distances and angles of **4**. Deviations are given in brackets. Symmetry operations: I = -0.5+x, 0.5-y, -0.5+z.

Atoms	**distances /pm**	**atoms**	**angles /°**
In1-N1	246.5(3)	N1-In1-$N2^{I}$	175.7(1)
In1-$N2^{I}$	247.2(3)	N1-In1-I1	92.62(7)
In1-I1	269.02(5)	N1-In1-I2	90.59(9)
In1-I2	269.23(7)	N1-In1-I3	85.88(7)
In1-I3	269.26(5)	$N2^{I}$-In1-I1	91.34(7)
C-C/C=C (range)	137.5(5)-139.7(4)	$N2^{I}$-In1-I2	89.13(9)
C-N (range)	132.5(5)-134.0(6)	$N2^{I}$-In1-I3	90.59(7)
		I1-In1-I2	117.12(1)
		I1-In1-I3	121.43(1)
		I2-In1-I3	121.43(1)

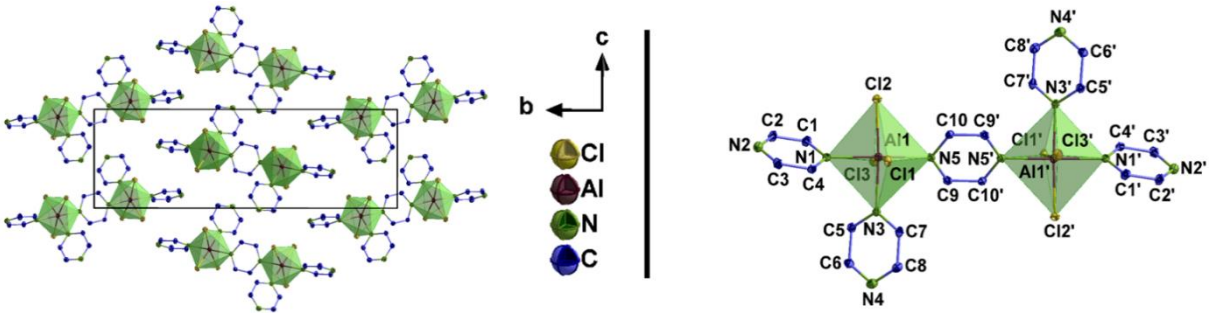

Figure S5: Crystal structure of $[(AlCl_3)_2(pyz)_5]$ (**5**) with a view along [100] (Left) and extended coordination of Al^{3+} in **5** (Right). The polyhedra of the monomeric complexes are highlighted in green and thermal ellipsoids shown at 50 % probability level. For better clarity, all hydrogen-atoms are omitted. Symmetry operations: I = -x, 1-y, 1-z.

Table S8 Interatomic distances and angles of **5**. Deviations are given in brackets.

Atoms	**distances /pm**	**atoms**	**angles /°**
Al1-N1	207.9(1)	N1-Al1-N5	178.20(6)
Al1-N5	210.7(1)	N1-Al1-N3	87.73(6)
Al1-N3	212.1(1)	N1-Al1-Cl2	88.91(4)
Al1-Cl12	224.97(7)	N1-Al1-Cl3	93.41(4)
Al1-Cl2	226.87(8)	N1-Al1-Cl1	92.30(4)
Al1-Cl3	228.67(8)	N5-Al1-N3	91.39(6)
C-C/C=C (range)	138.3(3)-139.2(3)	N5-Al1-Cl2	91.98(4)
C-N (range)	133.0(2)-135.1(2)	N5-Al1-Cl3	88.09(4)
		N5-Al1-Cl1	86.08(4)
		N3-Al1-Cl2	176.63(5)
		N3-Al1-Cl3	86.00(4)
		N3-Al1-Cl1	86.30(4)
		Cl2-Al1-Cl3	94.22(2)
		Cl2-Al1-Cl1	93.82(3)
		Cl3-Al1-Cl1	170.22(3)

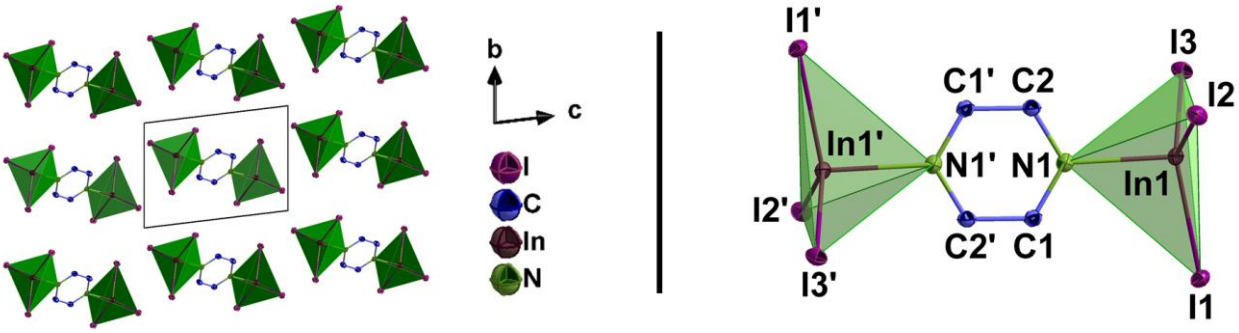

Figure S6: Crystal structure of $[(InI_3)_2(pyz)]$ (**6**) with a view along [100] (Left) and extended coordination of In^{3+} in **6** (Right). The polyhedra of the monomeric complexes are highlighted in green and thermal ellipsoids shown at 50 % probability level. For better clarity, all hydrogen-atoms are omitted. Symmetry operations: I = -x, 1-y, 1-z

Table S9 Interatomic distances and angles of **6**. Deviations are given in brackets.

Atoms	**distances /pm**	**atoms**	**angles /°**
In1-N1	231.2(3)	N1-In1-I2	96.91(7)
In1-I2	265.23(4)	N1-In1-I3	97.99(7)
In1-I3	267.34(5)	N1-In1-I1	99.11(7)
In1-I1	268.91(4)	I2-In1-I3	117.70(1)
$C1^{I}$-C2	138.4(4)	I2-In1-I1	121.72(1)
C1-N1	133.6(4)	I3-In1-I1	114.85(1)
C2-N1	133.8(4)		

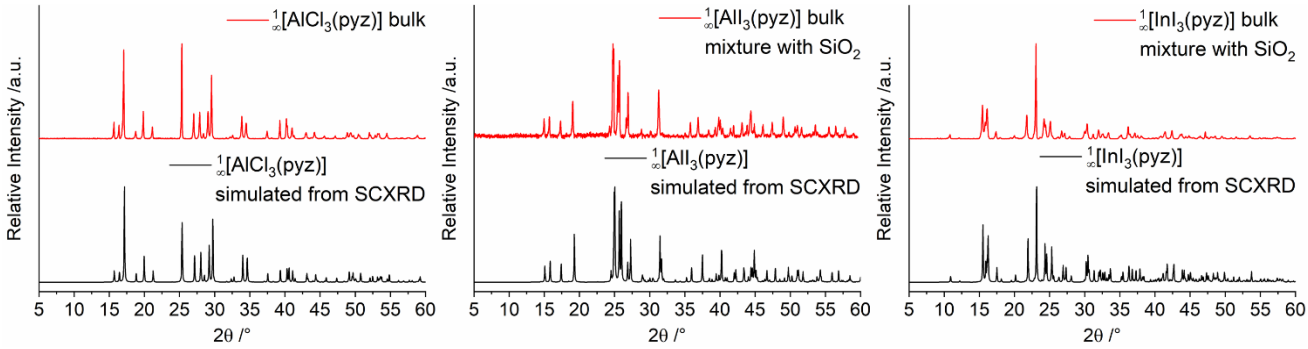

Figure S7: Comparison of the experimental (Red, Top) and simulated (Black, Bottom) diffraction pattern of **1** (Left), **2** (Center) and **4** (Right). (Cu-Kα_1 = 154.1 pm).

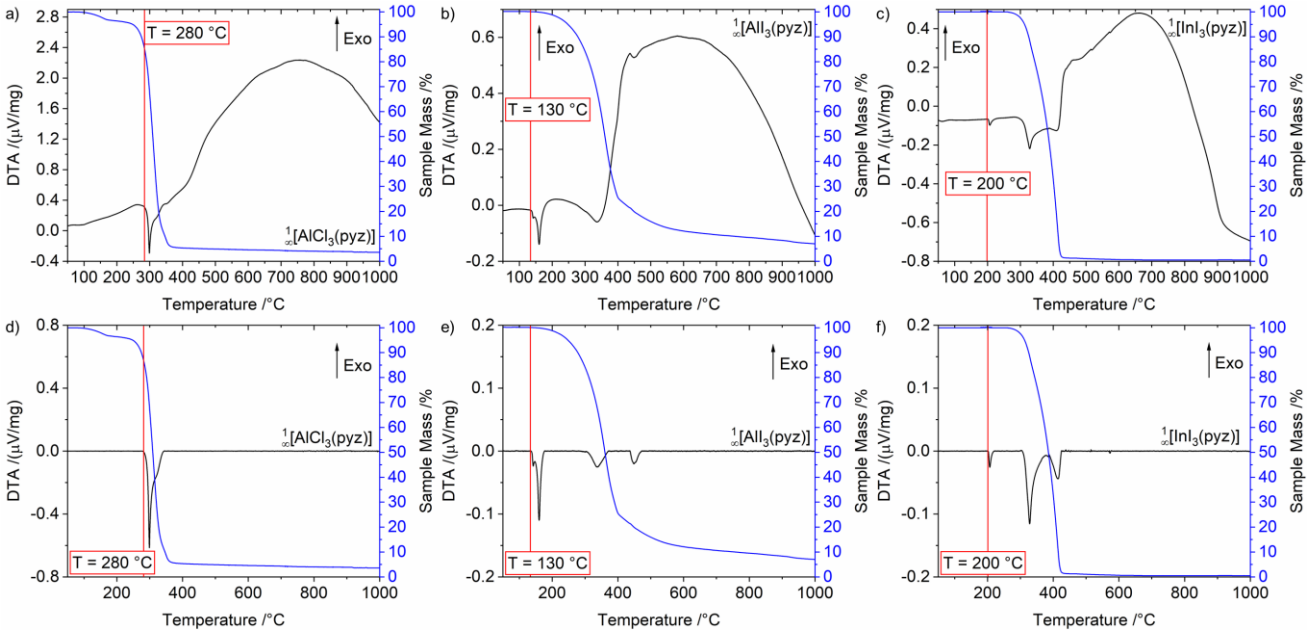

Figure S8: Simultaneous DTA/TG with (Bottom) and without (Top) baseline corrected data of **1** (Left), **2** (Center) and **4** (Right). All measurements were performed in a constant argon flow of 50 mL·min^{-1} with a heating rate of 5 K·min^{-1} from room temperature to 1000 °C.

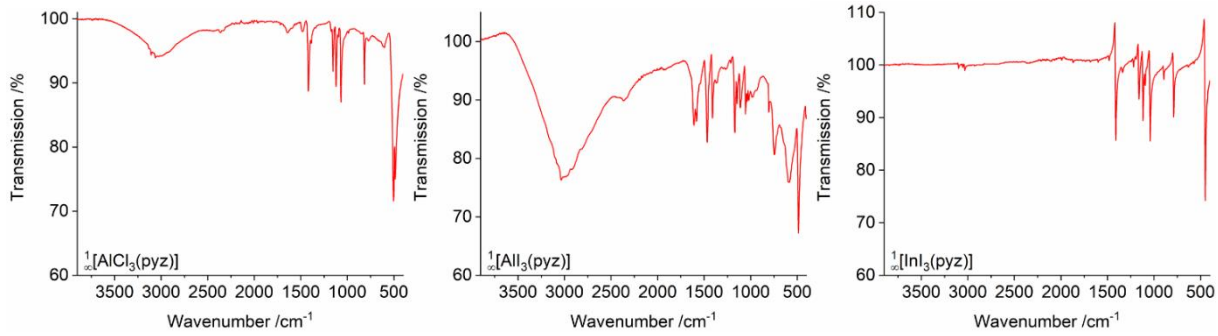

Figure S9: Infrared spectra (ATR) of **1** (Left), **2** (Center) and **4** (Right).

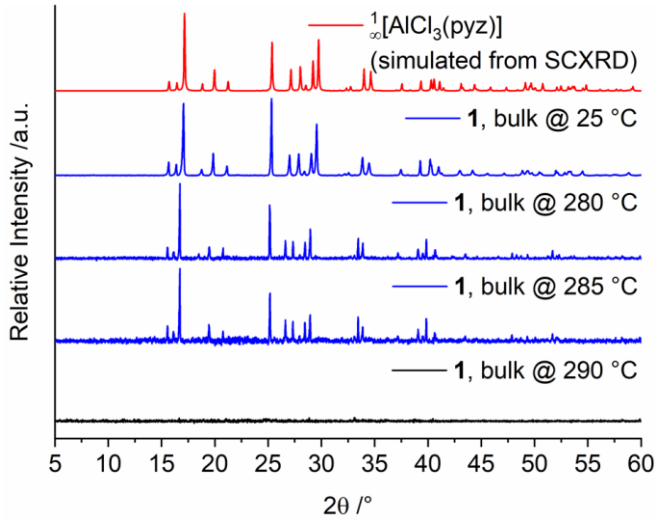

Figure S10 HT-PXRD measurement of bulk **1**, showing the diffraction patterns at different temperatures of 25 °C, 280 °C, 285 °C and 295 °C together with the pattern simulated from SCXRD data of **1**. (Cu-Kα_1 = 154.1 pm).

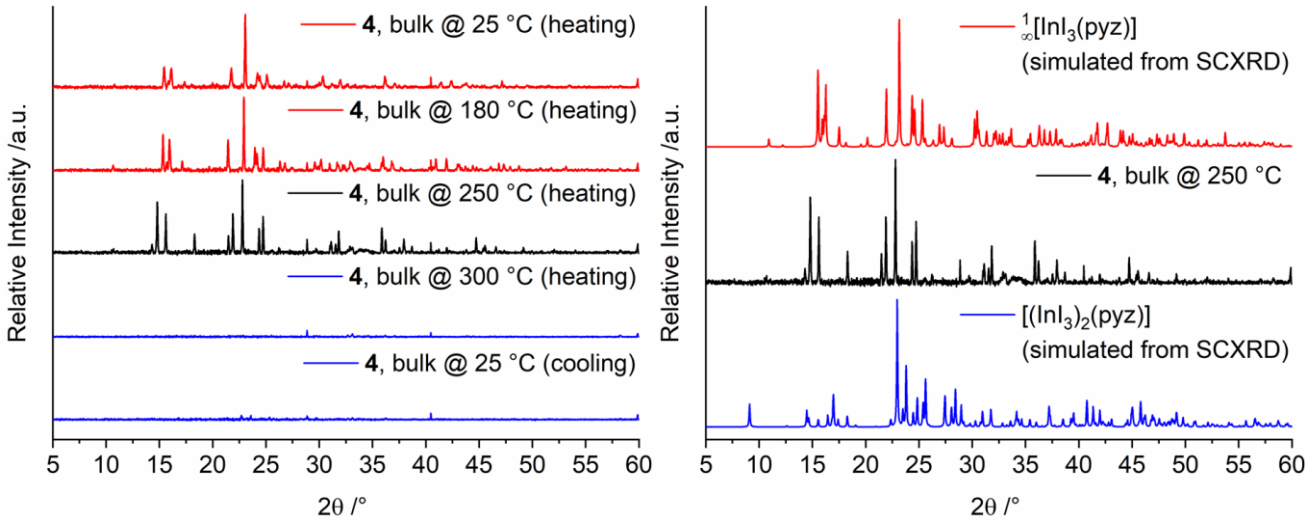

Figure S11 HT-PXRD measurement, showing the diffraction patterns of bulk **4** at different temperatures of 25 °C, 180 °C, 250 °C, 300 °C and after the measurement at 25 °C (Left). Comparison of the formed, unknown phase at 250 °C (Black) with the patterns simulated from SCXRD data of **4** (Red) and **6** (Blue) (Right). (Cu-Kα_1 = 154.1 pm).