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Sb- and Bi-based coordination polymers with N-donor ligands with and without lone-pair effects and their photoluminescence properties

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Crystallographic details

Crystallographic details for 1a-c

Table S1 Crystallographic data for **1a-c**.

	1a	**1b**	**1c**
Empirical formula	$C_{12}H_{10}Cl_3N_2Sb$	$C_{12}H_{10}Br_3N_2Sb$	$C_{12}H_{10}I_3N_2Sb$
Formula weight /g·mol^{-1}	410.32	543.70	684.67
Crystal color and shape	colourless block	yellow block	orange plate
Crystal size	0.086 × 0.077 × 0.076	0.284 × 0.113 × 0.104	0.131 × 0.061 × 0.052
Crystal system	triclinic	triclinic	triclinic
Space group	*P*-1	*P*-1	*P*-1
a /Å	885.40(18)	907.36(16)	888.23(7)
b /Å	907.38(18)	909.94(16)	957.02(8)
c /Å	944.45(19)	988.12(17)	1064.66(9)
α /°	77.42(3)	67.632(3)	67.951(3)
β /°	69.22(3)	80.450(4)	85.800(3)
γ /°	75.99(3)	76.867(4)	78.962(3)
V /Å^3	681.0(3)	731.9(2)	823.31(12)
Z	2	2	2
ρ_{calc} /g·cm^{-3}	2.001	2.467	2.762
F(000)	396.0	504.0	612.0
μ(Mo$_{K\alpha}$) /cm^{-1}	2.595	10.058	7.286
Temperature /K	100	100	100
2Θ range /°	4.662 - 56.71	4.476 - 56.794	4.128 – 50.7
No. of measured reflections	10525	31760	6804
No. of independent reflections	3406	3661	3011
R(int)	0.0751	0.0505	0.0357
R_1 ($I > 2\sigma(I)$)	0.0303	0.0173	0.0290
R_1 (all data)	0.0412	0.0184	0.0458
wR_2 (all data)	0.0634	0.0446	0.0607
S (all data)	1.029	1.067	1.039
$\Delta\rho_{max}$, $\Delta\rho_{min}$ /e· Å^{-3}	0.920 / -0.702	1.073 / -0.435	0.99/-0.80

Table S2: Selected interatomic distances (in Å) and angles (in °) in **1a**.
Symmetry operations: I : 1-x, 2-y, 1-z; II: 1+x, 1+y, +z

Sb1 Cl3	2.9663(15)	Cl2 Sb1 Cl3	168.07(3)	N1 Sb1 Cl2	87.15(7)
Sb1 Cl2	2.4077(13)	Cl1 Sb1 Cl3	86.04(4)	N1 Sb1 Cl3^{I}	88.46(7)
Sb1 Cl1	2.4088(11)	Cl1 Sb1 Cl2	92.77(4)	N2^{II} Sb1 Cl3	105.92(7)
Sb1 Cl3^{I}	3.0099(13)	Cl1 Sb1 Cl3^{I}	175.28(3)	N2^{II} Sb1 Cl2	85.83(7)
Sb1 N1	2.348(3)	Cl1 Sb1 N1	88.95(7)	N2^{II} Sb1 Cl1	86.18(7)
Sb1 N2^{II}	2.500(3)	Cl3^{I} Sb1 Cl3	97.44(4)	N2^{II} Sb1 Cl3^{I}	95.88(7)
		Cl3^{I} Sb1 Cl2	83.16(4)	N2^{II} Sb1 N1	171.24(9)
		N1 Sb1 Cl3	80.96(7)		

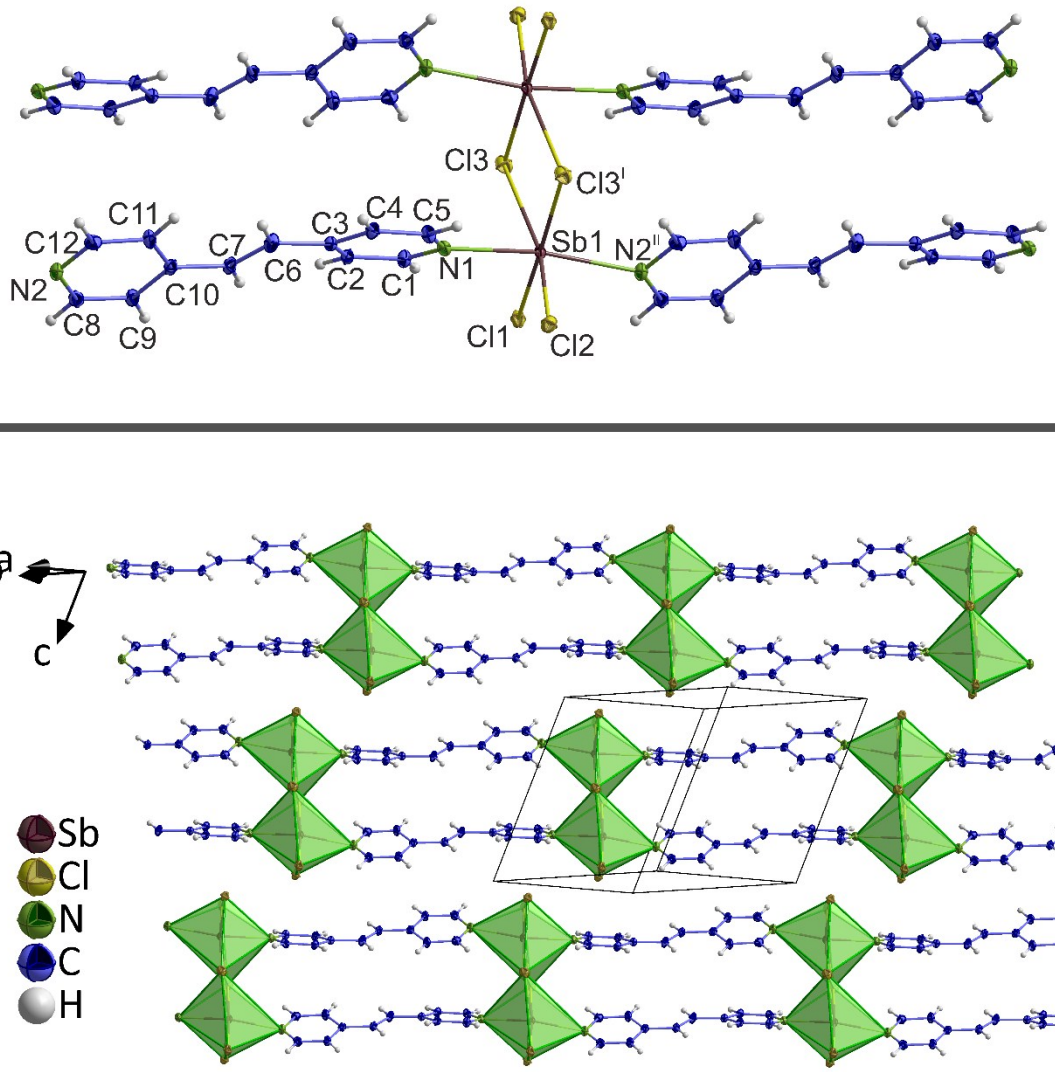

Figure S1. Depiction of the Sb coordination (top) and excerpt of the crystal structure displaying the linear double-strands in $^{1}_{\infty}[Sb_2Cl_6(bpe)_2]$ (**1a**). Symmetry operations: I : 1-x, 2-y, 1-z; II: 1+x, 1+y, +z. Ellipsoids represent a probability level of the atoms of 50 % in this and all following figures.

Table S3: Selected interatomic distances (in Å) and angles (in °) in **1b**.
Symmetry operations: I : -x, 1-y, 1-z; II: 1+x, 1+y, +z

Sb1 Br3	3.0609(4)	Br2 Sb1 Br3	171.287(8)	N1 Sb1 Br2	88.65(4)
Sb1 Br2	2.5849(4)	Br1 Sb1 Br3	86.010(14)	N1 Sb1 $Br3^{I}$	88.99(4)
Sb1 Br1	2.5701(4)	Br1 Sb1 Br2	93.675(15)	$N2^{II}$ Sb1 Br3	101.65(4)
Sb1 $Br3^{I}$	3.1562(4)	Br1 Sb1 $Br3^{I}$	178.568(8)	$N2^{II}$ Sb1 Br2	87.03(4)
Sb1 N1	2.3772(17)	Br1 Sb1 N1	89.79(4)	$N2^{II}$ Sb1 Br1	87.44(4)
Sb1 $N2^{II}$	2.5299(17)	$Br3^{I}$ Sb1 Br3	94.569(13)	$N2^{II}$ Sb1 $Br3^{I}$	93.72(4)
		$Br3^{I}$ Sb1 Br2	85.553(14)	$N2^{II}$ Sb1 N1	174.70(6)
		N1 Sb1 Br3	82.64(4)		

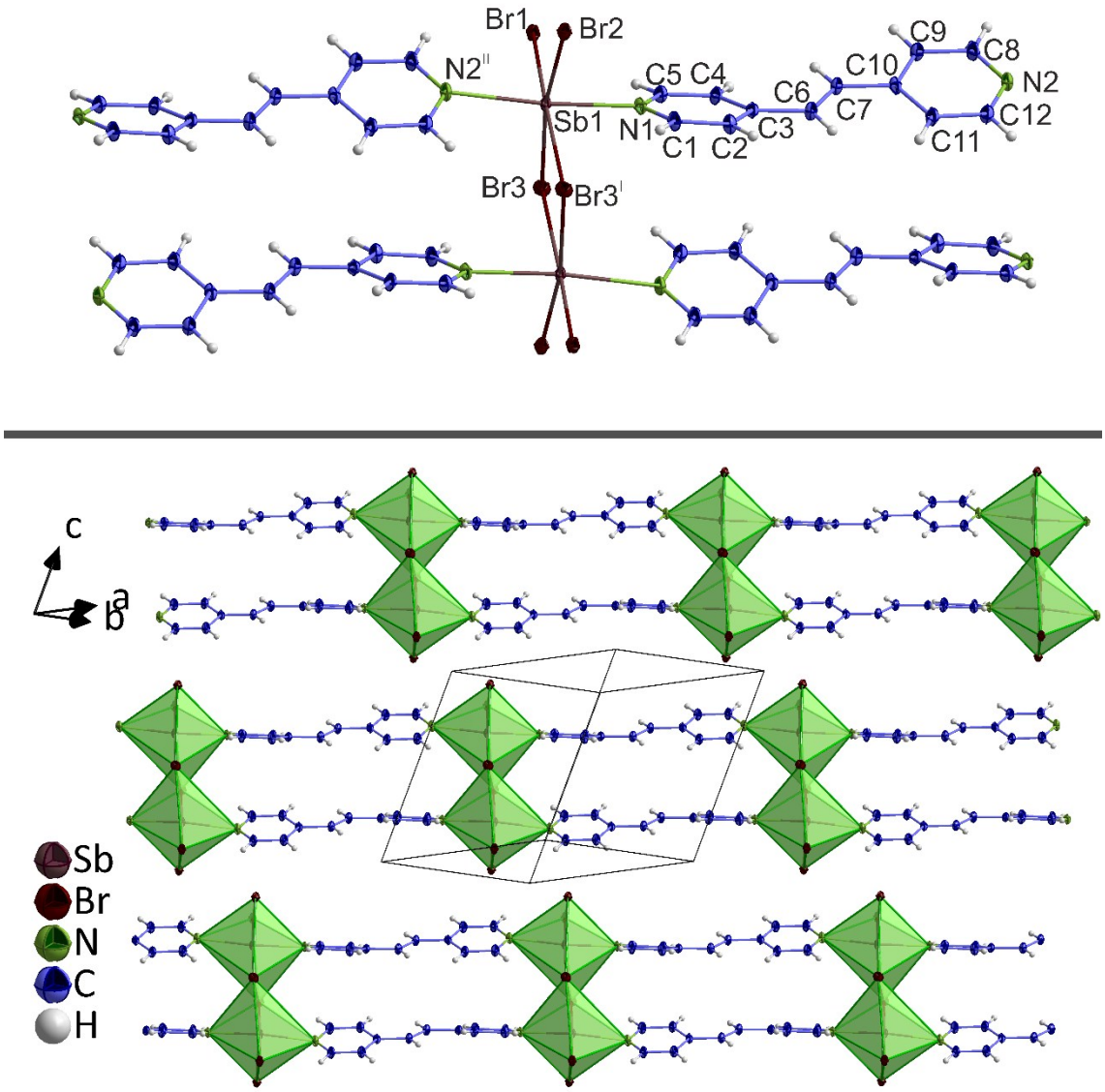

Figure S2. Depiction of the Sb coordination (top) and excerpt of the crystal structure displaying the linear double-strands in $^{1}_{\infty}[Sb_2Br_6(bpe)_2]$ (**1b**). Symmetry operations: I : -x, 1-y, 1-z; II: 1+x, 1+y, +z.

Table S4: Selected interatomic distances (in Å) and angles (in °) in **1c**.
Symmetry operations: I : 2-x, 1-y, 1-z; II: 1+x, 1+y, +z

Sb1 I3	3.1529(6)	I2 Sb1 I3	175.18(2)	N1 Sb1 I2	90.27(12)
Sb1 I2	2.8549(6)	I1 Sb1 I3	89.080(18)	N1 Sb1 $I3^{I}$	87.66(13)
Sb1 I1	2.7829(6)	I1 Sb1 I2	93.552(18)	$N2^{II}$ Sb1 I3	91.89(12)
Sb1 $I3^{I}$	3.4145(6)	I1 Sb1 $I3^{I}$	177.093(18)	$N2^{II}$ Sb1 I2	92.24(12)
Sb1 N1	2.384(5)	I1 Sb1 N1	89.41(13)	$N2^{II}$ Sb1 I1	88.24(13)
Sb1 $N2^{II}$	2.517(5)	$I3^{I}$ Sb1 I3	90.686(16)	$N2^{II}$ Sb1 $I3^{I}$	94.73(12)
		$I3^{I}$ Sb1 I2	86.481(16)	$N2^{II}$ Sb1 N1	176.66(17)
		N1 Sb1 I3	85.71(12)		

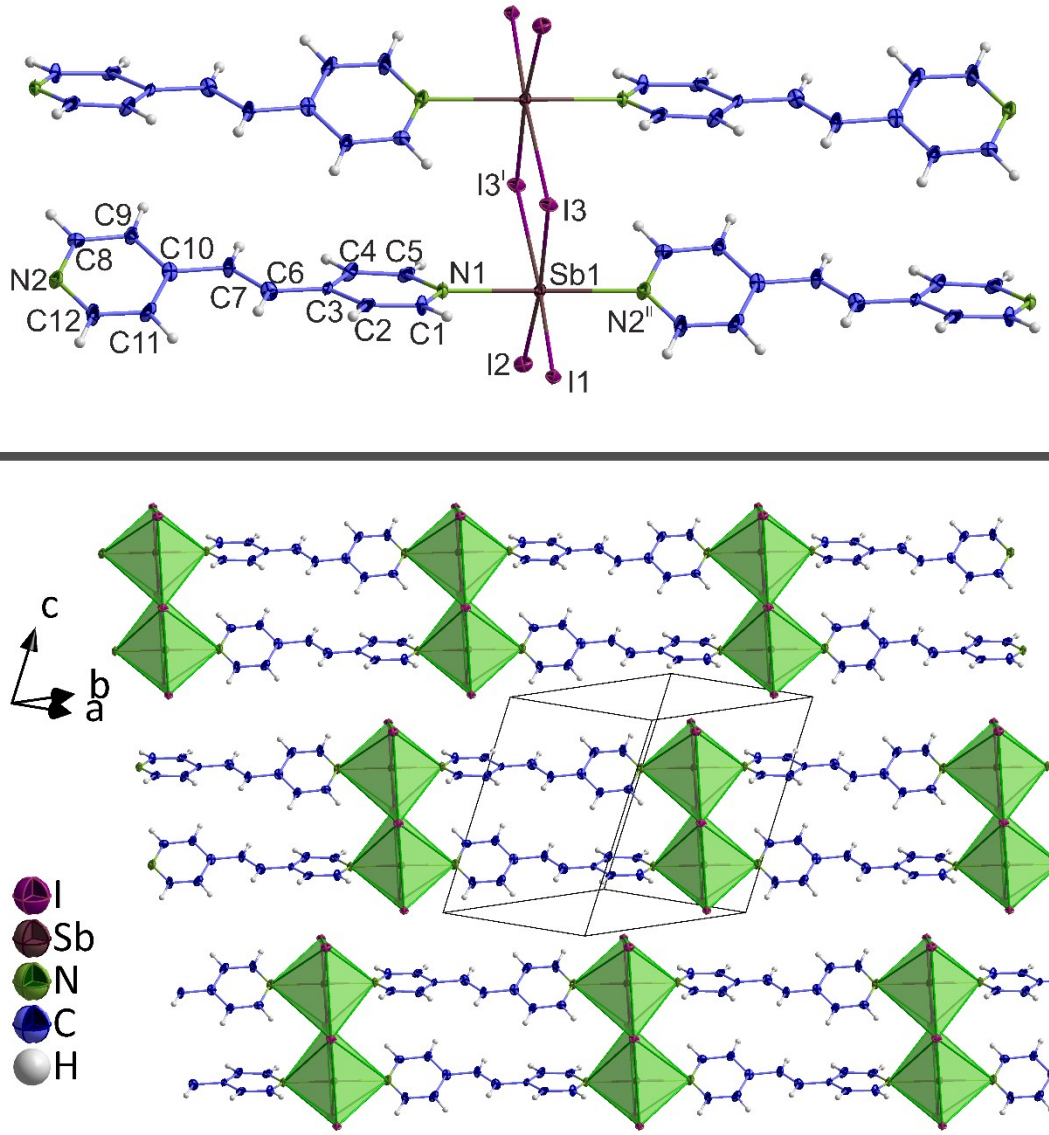

Figure S3. Depiction of the Sb coordination (top) and excerpt of the crystal structure displaying the linear double-strands in $^{1}_{\infty}[Sb_2I_6(bpe)_2]$ (**1c**). Symmetry operations: I : 2-x, 1-y, 1-z; II: 1+x, 1+y, +z.

Crystallographic details for 2a-c

Table S5 Crystallographic data for **2a-c**.

	2a	**2a'**	**2b**	**2c**
Empirical formula	$C_{12}H_{12}Cl_3N_2Sb$	$C_{12}H_{12}Cl_3N_2Sb$	$C_{12}H_{12}Br_3N_2Sb$	$C_{12}H_{12}I_3N_2Sb$
Formula weight /g·mol^{-1}	412.34	412.34	545.72	686.69
Crystal color and shape	colourless plate	colourless plate	colourless block	yellow block
Crystal size	0.302 × 0.243 × 0.098	0.367 × 0.22 × 0.176	0.753 × 0.383 × 0.288	0.197 × 0.13 × 0.103
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1
a /Å	892.01(19)	897.15(11)	891.20(7)	910.35(10)
b /Å	903.85(18)	909.39(13)	945.83(8)	981.91(11)
c /Å	989.6(2)	1018.97(15)	1055.49(9)	1097.15(13)
α /°	73.326(7)	70.894(4)	68.216(2)	66.414(3)
β /°	72.259(7)	73.050(3)	71.675(2)	73.361(3)
γ /°	76.842(7)	77.176(3)	80.174(2)	84.398(3)
V /Å^3	719.3(3)	744.02(18)	782.80(11)	861.00(17)
Z	2	2	2	2
ρ_{calc} /g·cm^{-3}	1.904	1.841	2.315	2.649
F(000)	400.0	400.0	508.0	616.0
μ(Mo$_{K\alpha}$) /cm^{-1}	2.458	2.376	9.403	6.967
Temperature/K	100	300	200	100
2Θ range /°	4.446 - 53.602	4.356 - 50.036	4.322 - 61.324	4.208 - 56.678
No. of measured reflections	13412	13861	19689	35032
No. of independent reflections	3054	2632	4810	4292
R(int)	0.0974	0.1160	0.0548	0.0650
R_1 ($I > 2\sigma(I)$)	0.0526	0.0411	0.0401	0.0240
R_1 (all data)	0.0842	0.0583	0.0583	0.0318
wR_2 (all data)	0.1275	0.1019	0.0902	0.0510
S (all data)	1.004	1.034	1.038	1.032
$\Delta\rho_{max}$, $\Delta\rho_{min}$ /e· Å^{-3}	1.38 / -2.43	0.77 / -1.06	1.533 / -1.729	0.943 / -0.918

Table S6: Selected interatomic distances (in Å) and angles (in °) in **2a**.
Symmetry operations: I : 1-x, 1-y, 1-z; II: -1+x, -1+y, +z

Sb1 Cl3	2.865(2)	Cl2 Sb1 Cl3	173.04(5)	N1 Sb1 Cl2	89.01(15)
Sb1 Cl2	2.4285(18)	Cl1 Sb1 Cl3	88.35(6)	N1 Sb1 Cl3^{I}	86.19(15)
Sb1 Cl1	2.3992(18)	Cl1 Sb1 Cl2	91.38(7)	N2^{II} Sb1 Cl3	99.69(14)
Sb1 Cl3^{I}	3.125(2)	Cl1 Sb1 Cl3^{I}	171.92(5)	N2^{II} Sb1 Cl2	87.19(14)
Sb1 N1	2.332(5)	Cl1 Sb1 N1	86.38(15)	N2^{II} Sb1 Cl1	83.87(13)
Sb1 N2^{II}	2.501(5)	Cl3^{I} Sb1 Cl3	94.02(5)	N2^{II} Sb1 Cl3^{I}	103.31(13)
		Cl3^{I} Sb1 Cl2	85.33(6)	N2^{II} Sb1 N1	169.4(2)
		N1 Sb1 Cl3	84.03(15)		

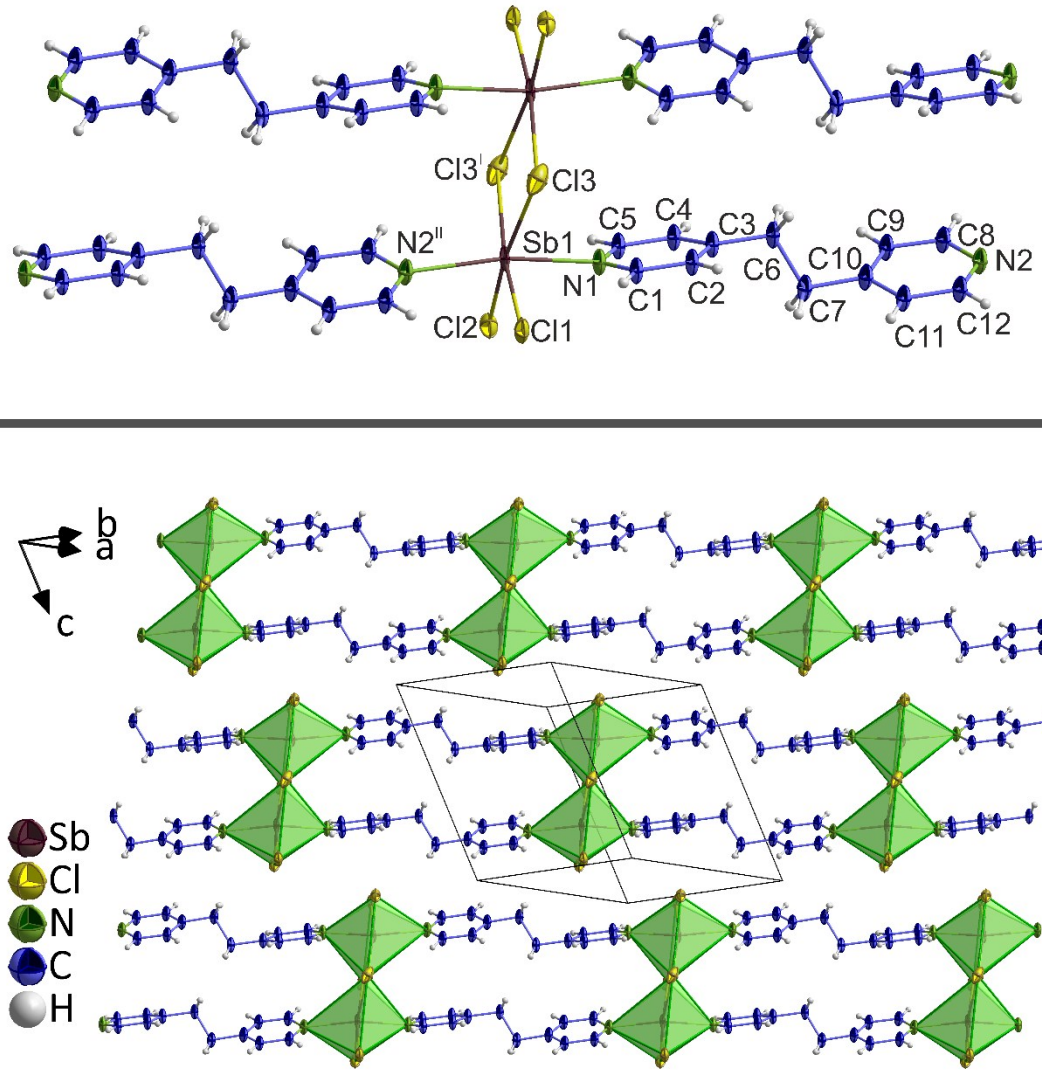

Figure S4. Depiction of the Sb coordination (top) and excerpt of the crystal structure displaying the linear double-strands in □-$^{1}_{\infty}[Sb_2Cl_6(bpa)_2]$ (**2a**). Symmetry operations: I : 1-x, 1-y, 1-z; II: -1+x, -1+y, +z.

Table S7: Selected interatomic distances (in Å) and angles (in °) in **2a'**.
Symmetry operations: I : 1-x, 1-y, 1-z; II: -1+x, -1+y, +z

Sb1 Cl3	2.9816(18)	Cl2 Sb1 Cl3	174.80(6)	N1 Sb1 Cl2	87.18(11)
Sb1 Cl2	2.4223(13)	Cl1 Sb1 Cl3	85.79(6)	N1 Sb1 $Cl3^{I}$	83.27(13)
Sb1 Cl1	2.4072(17)	Cl1 Sb1 Cl2	91.58(6)	$N2^{II}$ Sb1 Cl3	98.50(11)
Sb1 $Cl3^{I}$	3.004(2)	Cl1 Sb1 $Cl3^{I}$	170.98(6)	$N2^{II}$ Sb1 Cl2	85.80(11)
Sb1 N1	2.345(5)	Cl1 Sb1 N1	88.04(13)	$N2^{II}$ Sb1 Cl1	86.52(12)
Sb1 $N2^{II}$	2.518(5)	$Cl3^{I}$ Sb1 Cl3	91.54(5)	$N2^{II}$ Sb1 $Cl3^{I}$	102.41(12)
		$Cl3^{I}$ Sb1 Cl2	90.38(6)	$N2^{II}$ Sb1 N1	170.98(15)
		N1 Sb1 Cl3	88.25(11)		

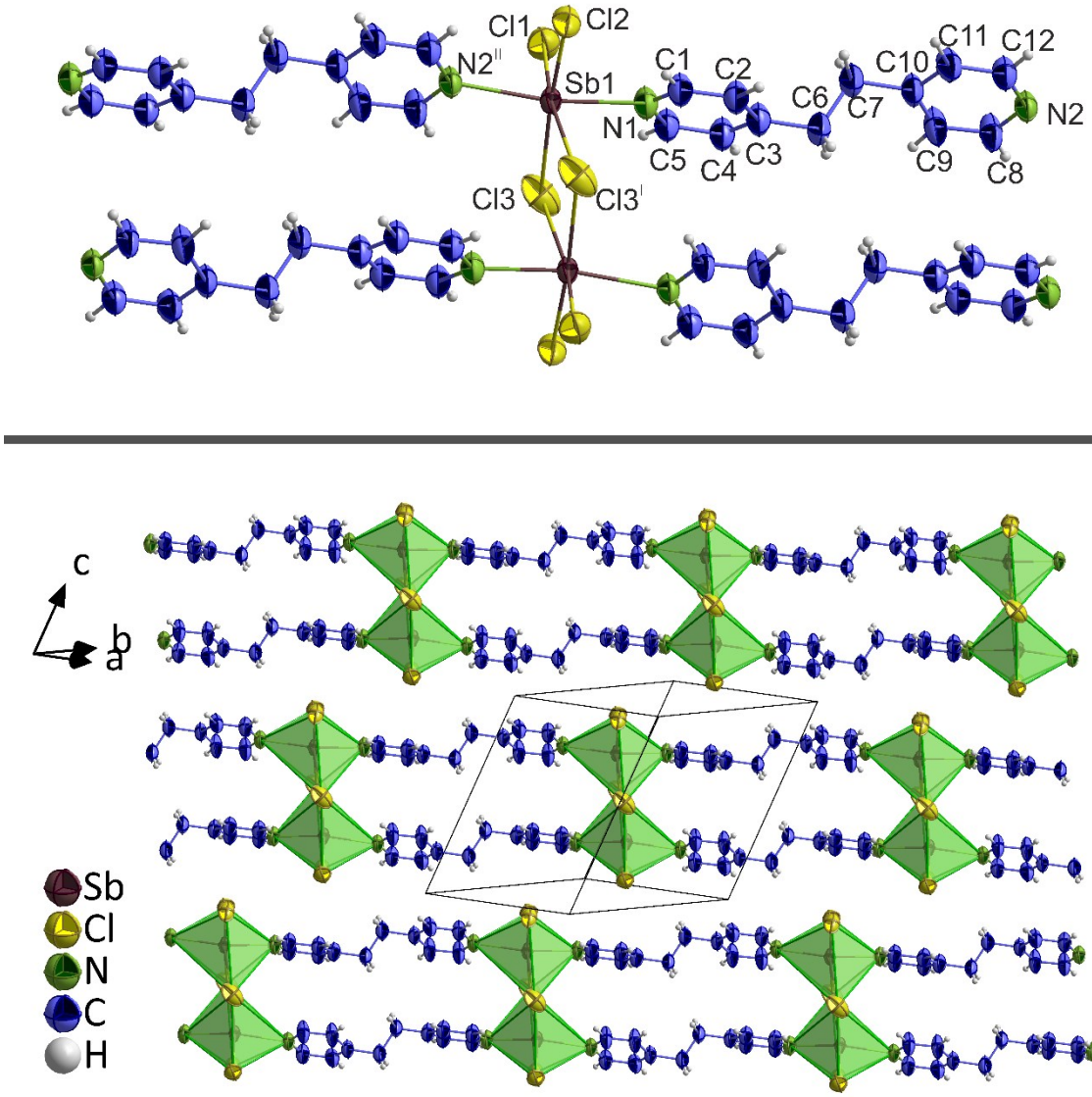

Figure S5. Depiction of the Sb coordination (top) and excerpt of the crystal structure displaying the linear double-strands in □-$^1_\infty[Sb_2Cl_6(bpa)_2]$ (**2a'**). Symmetry operations: I : 1-x, 1-y, 1-z; II: -1+x, -1+y, +z.

Table S8: Selected interatomic distances (in Å) and angles (in °) in **2b**.
Symmetry operations: I : 1-x, -y, 1-z; II: 1+x, 1+y, +z

Sb1 Br3	3.0719(6)	Br2 Sb1 Br3	178.17(2)	N1 Sb1 Br2	88.39(10)
Sb1 Br2	2.5803(6)	Br1 Sb1 Br3	89.349(19)	N1 Sb1 Br3^{I}	91.28(10)
Sb1 Br1	2.5802(6)	Br1 Sb1 Br2	92.24(2)	N2^{II} Sb1 Br3	92.45(10)
Sb1 Br3^{I}	3.1364(6)	Br1 Sb1 Br3^{I}	178.13(2)	N2^{II} Sb1 Br2	88.55(10)
Sb1 N1	2.397(3)	Br1 Sb1 N1	88.24(10)	N2^{II} Sb1 Br1	86.80(10)
Sb1 N2^{II}	2.474(4)	Br3^{I} Sb1 Br3	92.463(16)	N2^{II} Sb1 Br3^{I}	93.58(10)
		Br3^{I} Sb1 Br2	85.942(19)	N2^{II} Sb1 N1	174.06(14)
		N1 Sb1 Br3	90.76(10)		

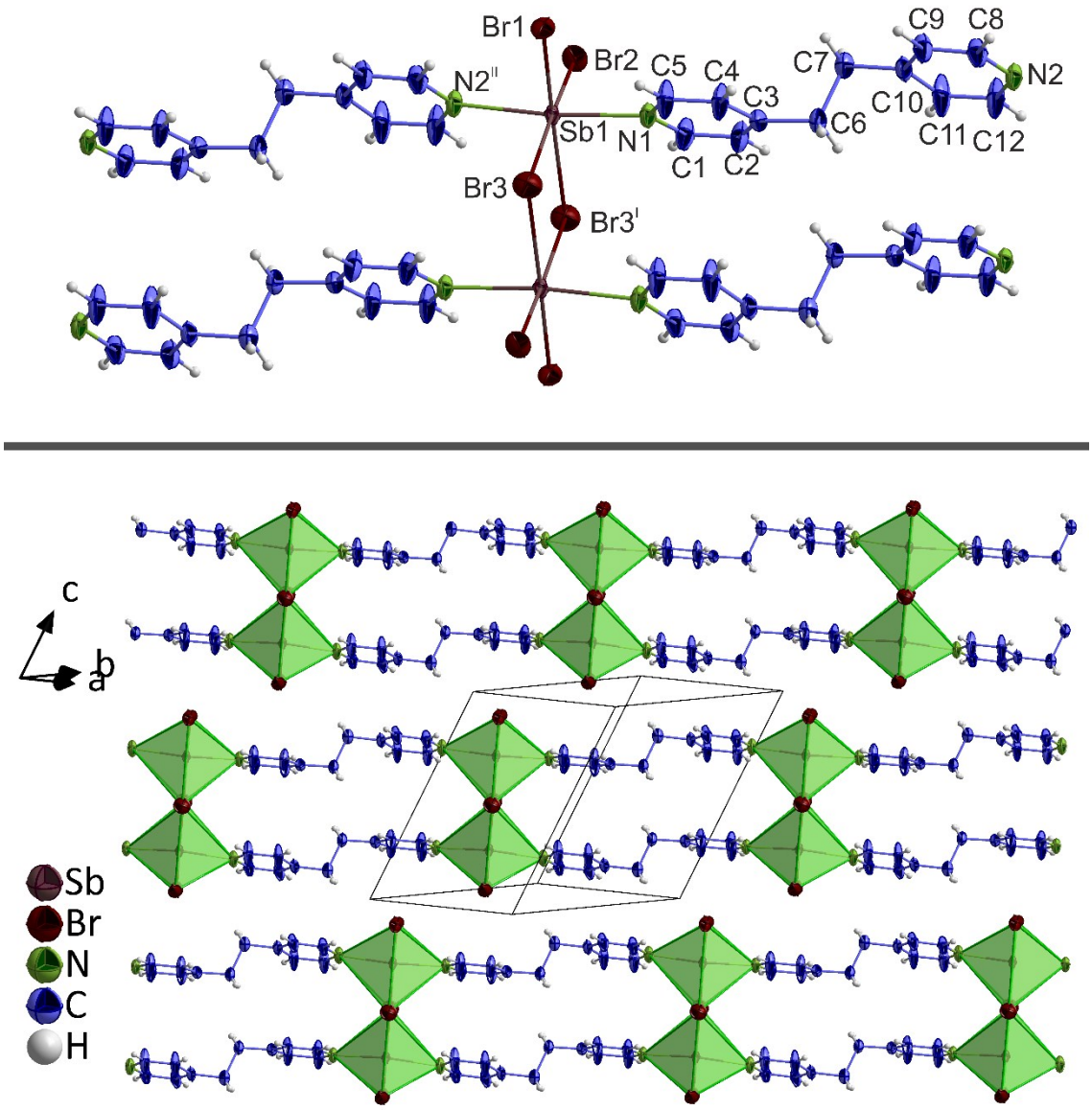

Figure S6. Depiction of the Sb coordination (top) and excerpt of the crystal structure displaying the linear double-strands in $^{1}_{\infty}[Sb_2Br_6(bpa)_2]$ (**2b**). Symmetry operations: I : 1-x, -y, 1-z; II: 1+x, 1+y, +z.

Table S9: Selected interatomic distances (in Å) and angles (in °) in **2c**.
Symmetry operations: I : 1-x, 2-y, 1-z; II: 1+x, 1+y, +z

Sb1 I3	3.2658(4)	I2 Sb1 I3	88.279(12)	N1 Sb1 I2	89.24(7)
Sb1 I2	2.8092(4)	I1 Sb1 I3	179.187(11)	N1 Sb1 $I3^{I}$	91.12(7)
Sb1 I1	2.8024(4)	I1 Sb1 I2	92.493(14)	$N2^{II}$ Sb1 I3	92.31(8)
Sb1 $I3^{I}$	3.2810(4)	I1 Sb1 $I3^{I}$	86.338(13)	$N2^{II}$ Sb1 I2	87.65(7)
Sb1 N1	2.422(3)	I1 Sb1 N1	89.42(7)	$N2^{II}$ Sb1 I1	87.98(8)
Sb1 $N2^{II}$	2.479(3)	$I3^{I}$ Sb1 I3	92.892(12)	$N2^{II}$ Sb1 $I3^{I}$	91.93(7)
		$I3^{I}$ Sb1 I2	178.772(11)	$N2^{II}$ Sb1 N1	175.86(10)
		N1 Sb1 I3	90.33(7))		

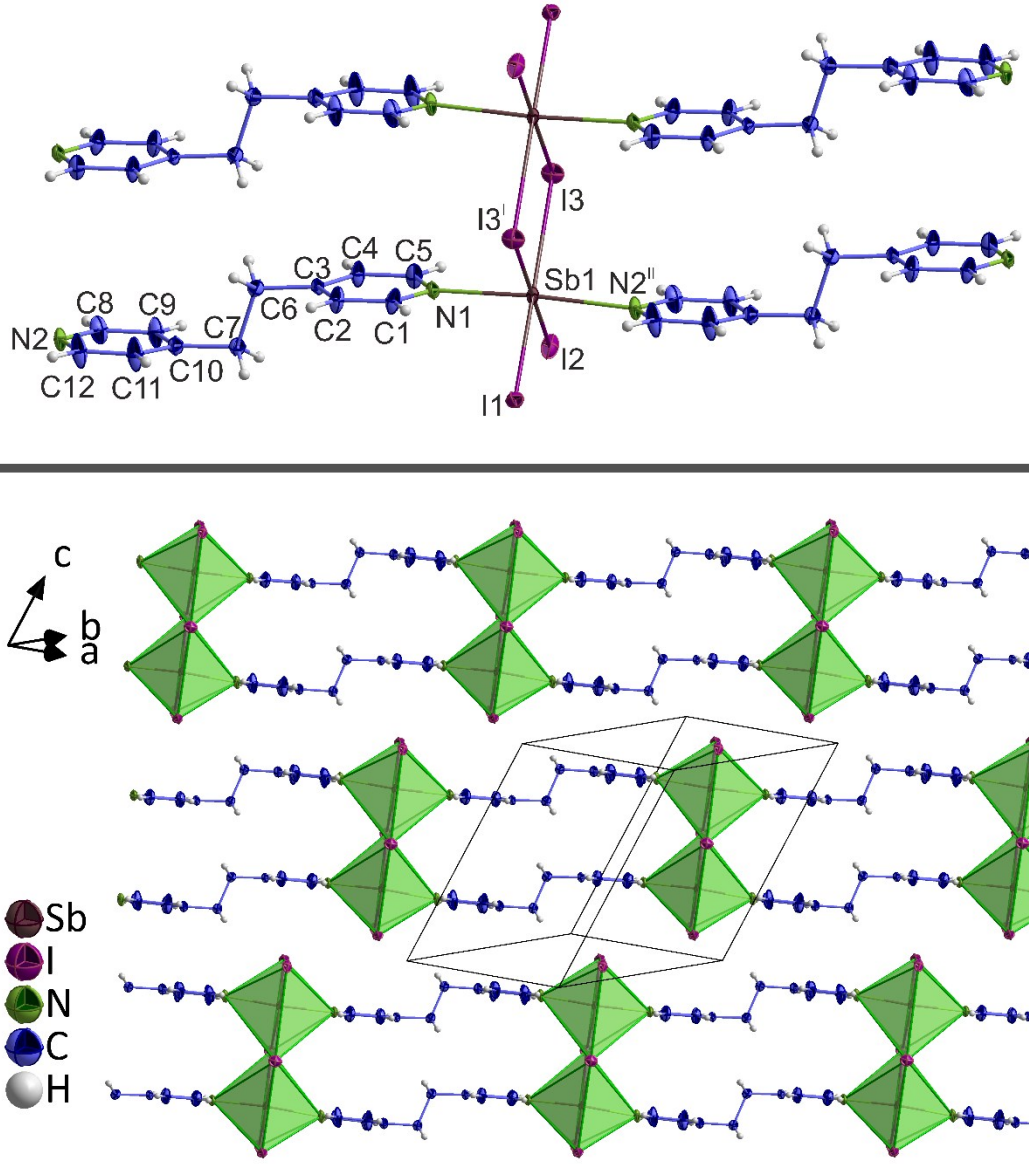

Figure S7. Depiction of the Sb coordination (top) and excerpt of the crystal structure displaying the linear double-strands in $^1_\infty[Sb_2I_6(bpa)_2]$ (**2c**). Symmetry operations: I : 1-x, 2-y, 1-z; II: 1+x, 1+y, +z.

Crystallographic details for 3a-c

Table S10 Crystallographic data for **3a-c**.

	3a	**3b**	**3c**
Empirical formula	$C_{10}H_8Cl_3N_2Sb$	$C_{10}H_8Br_3N_2Sb$	$C_{10}H_8I_3N_2Sb$
Formula weight /g·mol^{-1}	384.28	517.66	658.63
Crystal color and shape	colourless block	colourless block	yellow plate
Crystal size	0.257 × 0.212 × 0.079	0.257 × 0.212 × 0.079	0.175 × 0.153 × 0.062
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	P-1
a /Å	962.10(19)	1010.8(2)	762.51(5)
b /Å	1154.5(2)	1189.5(2)	998.46(6)
c /Å	1187.6(2)	1192.2(2)	1075.50(7)
α /°	90	90	117.048(3)
β /°	109.13(3)	109.549(5)	90.144(3)
γ /°	90	90	95.474(3)
V /Å^3	1246.2(5)	1350.8(5)	724.96(8)
Z	4	4	2
ρ_{calc} /g·cm^{-3}	2.048	2.545	3.017
F(000)	736.0	952.0	584.0
μ(Mo$_{K\alpha}$) /cm^{-1}	2.829	10.891	8.268
Temperature/K	100	100	100
2Θ range /°	4.482 - 56.71	4.276 - 56.658	4.258 - 56.552
No. of measured reflections	16387	23837	6188
No. of independent reflections	3106	3361	4422
R(int)	0.0516	0.0850	0.0850
R_1 ($I > 2\sigma(I)$)	0.0340	0.0314	0.0348
R_1 (all data)	0.0456	0.0491	0.0396
wR_2 (all data)	0.0867	0.0601	0.0877
S (all data)	1.063	1.018	1.003
$\Delta\rho_{max}$, $\Delta\rho_{min}$ /e· Å^{-3}	2.402 / -1.578	0.847 / -1.357	1.44 / -1.08

Table S11: Selected interatomic distances (in Å) and angles (in °) in **3a**.
Symmetry operations: I : 1+x,+y,-1+z

Sb1 Cl3	2.7376(11)	Cl2 Sb1 Cl3	169.57(3)	N1 Sb1 Cl2	87.25(8)
Sb1 Cl2	2.4717(10)	Cl1 Sb1 Cl3	86.78(4)	N2^I Sb1 Cl3	97.00(8)
Sb1 Cl1	2.3725(10)	Cl1 Sb1 Cl2	90.94(3)	N2^I Sb1 Cl2	92.82(8)
Sb1 N1	2.309(3)	Cl1 Sb1 N1	86.80(9)	N2^I Sb1 Cl1	83.08(8)
Sb1 N2^I	2.538(3)	N1 Sb1 Cl3	82.47(8)	N2^I Sb1 N1	169.88(10)

Table S12: Selected interatomic distances (in Å) and angles (in °) in **3b**.
Symmetry operations: I : 1-x, 1-y, -z; II: +x, +y, 1+z

Sb1 Br3	2.9012(7)	Br2 Sb1 Br3	171.420(17)	N1 Sb1 Br2	88.39(8)
Sb1 Br2	2.6276(6)	Br1 Sb1 Br3	88.99(2)	N1 Sb1 Br3^{I}	88.71(9)
Sb1 Br1	2.5304(6)	Br1 Sb1 Br2	91.96(2)	N2^{II} Sb1 Br3	94.33(8)
Sb1 Br3^{I}	3.3442(7)	Br1 Sb1 Br3^{I}	175.873(16)	N2^{II} Sb1 Br2	94.25(8)
Sb1 N1	2.325(3)	Br1 Sb1 N1	87.70(9)	N2^{II} Sb1 Br1	86.80(10)
Sb1 N2^{II}	2.563(4)	Br3^{I} Sb1 Br3	92.61(2)	N2^{II} Sb1 Br3^{I}	99.06(8)
		Br3^{I} Sb1 Br2	85.90(2)	N2^{II} Sb1 N1	171.95(11)
		N1 Sb1 Br3	83.13(8)		

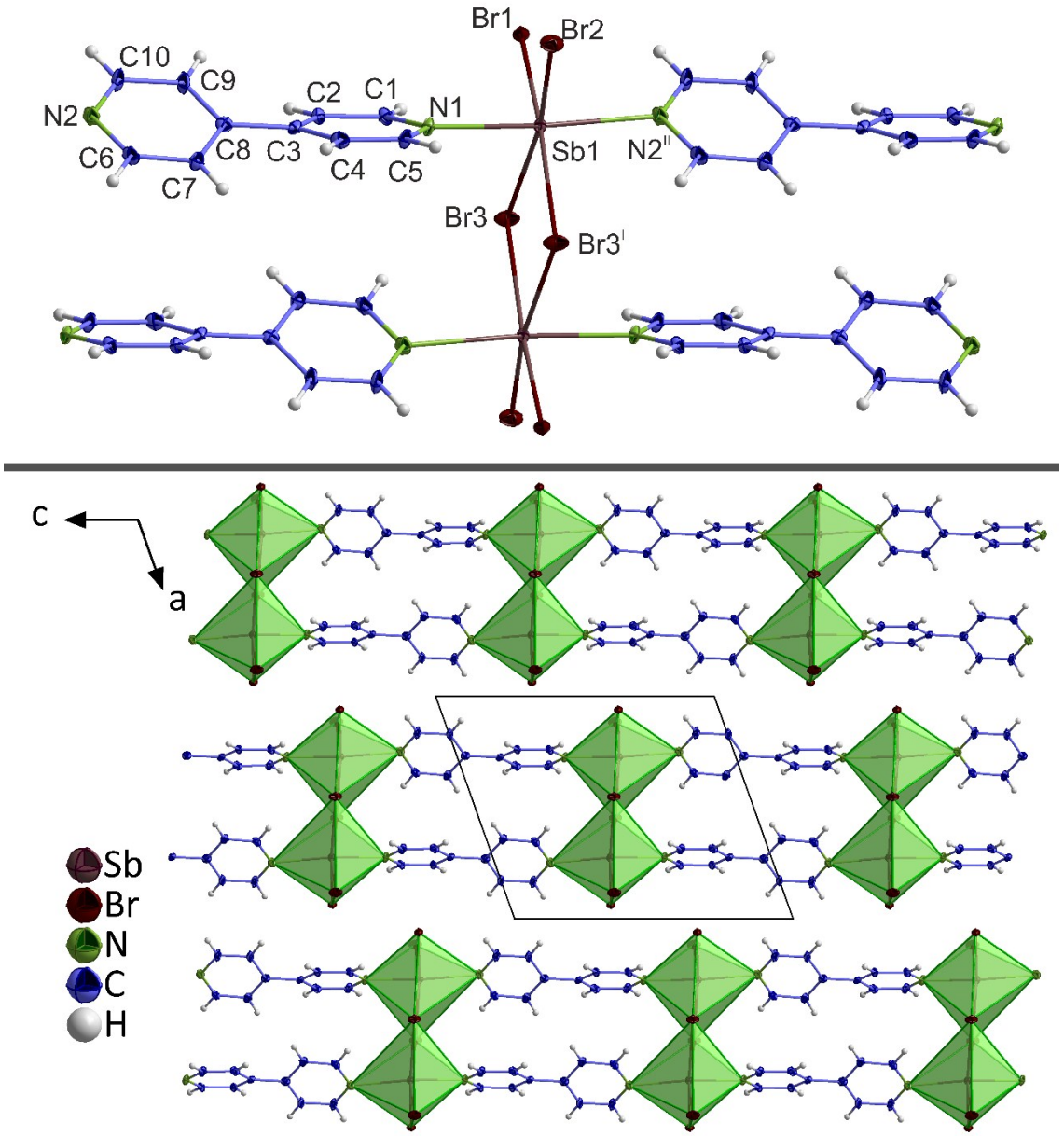

Figure S8. Depiction of the Sb coordination (top) and excerpt of the crystal structure displaying the linear double-strands in $^{1}_{\infty}[Sb_2Br_6(bipy)_2]$ (**3b**). Symmetry operations: I : 1-x, 1-y, -z; II: +x, +y, 1+z.

Table S13: Selected interatomic distances (in Å) and angles (in °) in **3c**.
Symmetry operations: I : 1-x, 1-y, 1-z; II: +x, +y, 1+z

Sb1 I3	3.1429(8)	I2 Sb1 I3	174.05(2)	N1 Sb1 I2	89.54(16)
Sb1 I2	2.8698(8)	I1 Sb1 I3	89.07(2)	N1 Sb1 $I3^{I}$	89.41(17)
Sb1 I1	2.7762(8)	I1 Sb1 I2	91.03(2)	$N2^{II}$ Sb1 I3	91.48(16)
Sb1 $I3^{I}$	3.4456(8)	I1 Sb1 $I3^{I}$	178.04(2)	$N2^{II}$ Sb1 I2	94.47(16)
Sb1 N1	2.410(6)	I1 Sb1 N1	89.03(17)	$N2^{II}$ Sb1 I1	88.84(16)
Sb1 $N2^{II}$	2.529(6)	$I3^{I}$ Sb1 I3	91.96(2)	$N2^{II}$ Sb1 $I3^{I}$	92.79(16)
		$I3^{I}$ Sb1 I2	87.77(2)	$N2^{II}$ Sb1 N1	175.5(2)
		N1 Sb1 I3	84.52(16)		

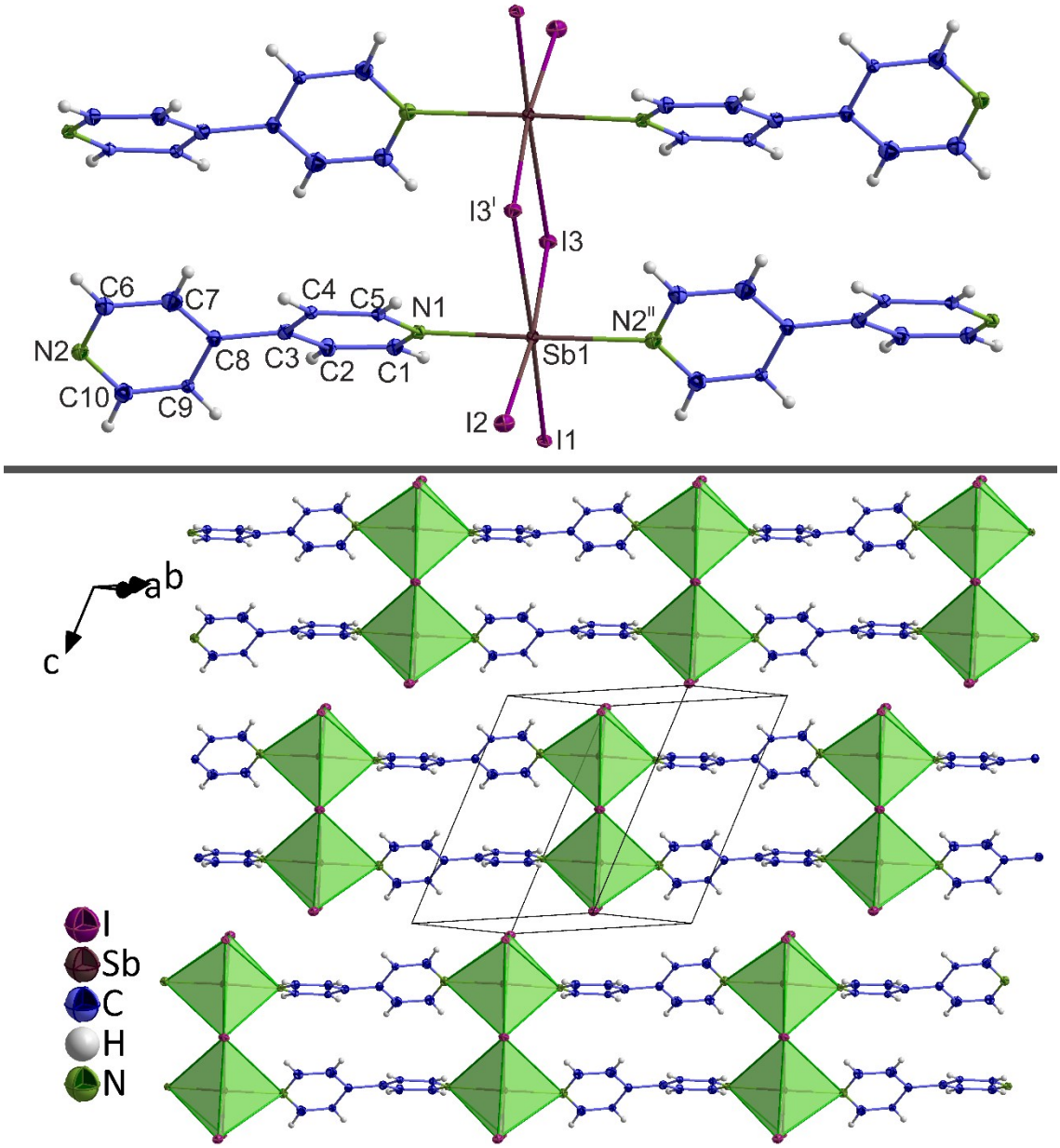

Figure S9. Depiction of the Sb coordination (top) and excerpt of the crystal structure displaying the linear double-strands in $^1_\infty[Sb_2I_6(bipy)_2]$ (**3c**). Symmetry operations: I : 1-x, 1-y, 1-z; II: +x, +y, 1+z.

Crystallographic details for 4a-c

Table S14 Crystallographic data for **4a**.

	4a	**4b**	**4c**
Empirical formula	$C_{12}H_{10}BiCl_3N_2$	$C_{12}H_{10}BiBr_3N_2$	$C_{12}H_{10}BiI_3N_2$
Formula weight /g·mol^{-1}	497.55	630.93	771.90
Crystal color and shape	colourless block	colourless block	orange plate
Crystal size	0.253 × 0.189 × 0.103	0.115 × 0.07 × 0.068	0.136 × 0.121 × 0.063
Crystal system	triclinic	triclinic	triclinic
Space group	*P*-1	*P*-1	*P*??
a /pm	880.98(7)	904.34(9)	898.14(5)
b /pm	924.39(8)	919.19(9)	964.54(5)
c /pm	992.41(8)	1011.119(10)	1070.022(6)
α /°	74.791(3)	77.649(3)	67.547(2)
β /°	65.696(3)	65.792(3)	84.936(2)
γ /°	74.641(3)	75.676(3)	78.170(2)
V /10^{6}· pm^3	699.36(10)	736.7(13)	838.59(8)
Z	2	2	2
ρ_{calc} /g·cm^{-3}	2.363	2.844	3.057
μ(Mo$_{K\alpha}$) /cm^{-1}	13.160	20.083	16.021
F(000)	460.0	568.0	676.0
Temperature/K	200	100	100
Min/max transmission	0.4449/0.7461	0.290434/0.430169	0.225030/0.430176
2Θ range /°	4.574 - 54.436	4.452 – 54.362	4.118 – 54.444
No. of measured reflections	29273	14978	39316
No. of independent reflections	3112	3275	3754
R(int)	0.0672	0.0731	0.0628
No. of parameters	164	164	164
R_1 ($I > 2\sigma(I)$)	0.0239	0.0273	0.0260
R_1 (all data)	0.0286	0.0335	0.0329
wR_2 (all data)	0.0542	0.0574	0.0496
S (all data)	1.068	1.044	1.057
$\Delta\rho_{max}$, $\Delta\rho_{min}$ /e· Å^{-3}	1.97/-1.21	1.24/-0.86	1.142 / -0.946

Table S15: Selected interatomic distances (in Å) and angles (in °) in **4a**.
Symmetry operations: I 1-x,+2-y, 1-z; II: 1+x, 1+y, +z

Bi1 Cl3	2.9099(12)	Cl2 Bi1 Cl3	174.68(4)	N1 Bi1 Cl2	91.43(9)
Bi1 Cl2	2.5320(11)	Cl1 Bi1 Cl3	88.20(4)	N1 Bi1 Cl3^{I}	88.88(9)
Bi1 Cl1	2.5272(16)	Cl1 Bi1 Cl2	97.11(4)	N2^{II} Bi1 Cl3	90.69(9)
Bi1 Cl3^{I}	2.9187(13)	Cl1 Bi1 Cl3^{I}	173.92(3)	N2^{II} Bi1 Cl2	89.25(9)
Bi1 N1	2.507(3)	Cl1 Bi1 N1	89.54(9)	N2^{II} Bi1 Cl1	90.46(9)
Bi1 N2^{II}	2.530(4)	Cl3^{I} Bi1 Cl3	85.88(3)	N2^{II} Bi1 Cl3^{I}	91.05(9)
		Cl3^{I} Bi1 Cl2	88.80(4)	N2^{II} Bi1 N1	179.31(12)
		N1 Bi1 Cl3	88.63(9)		

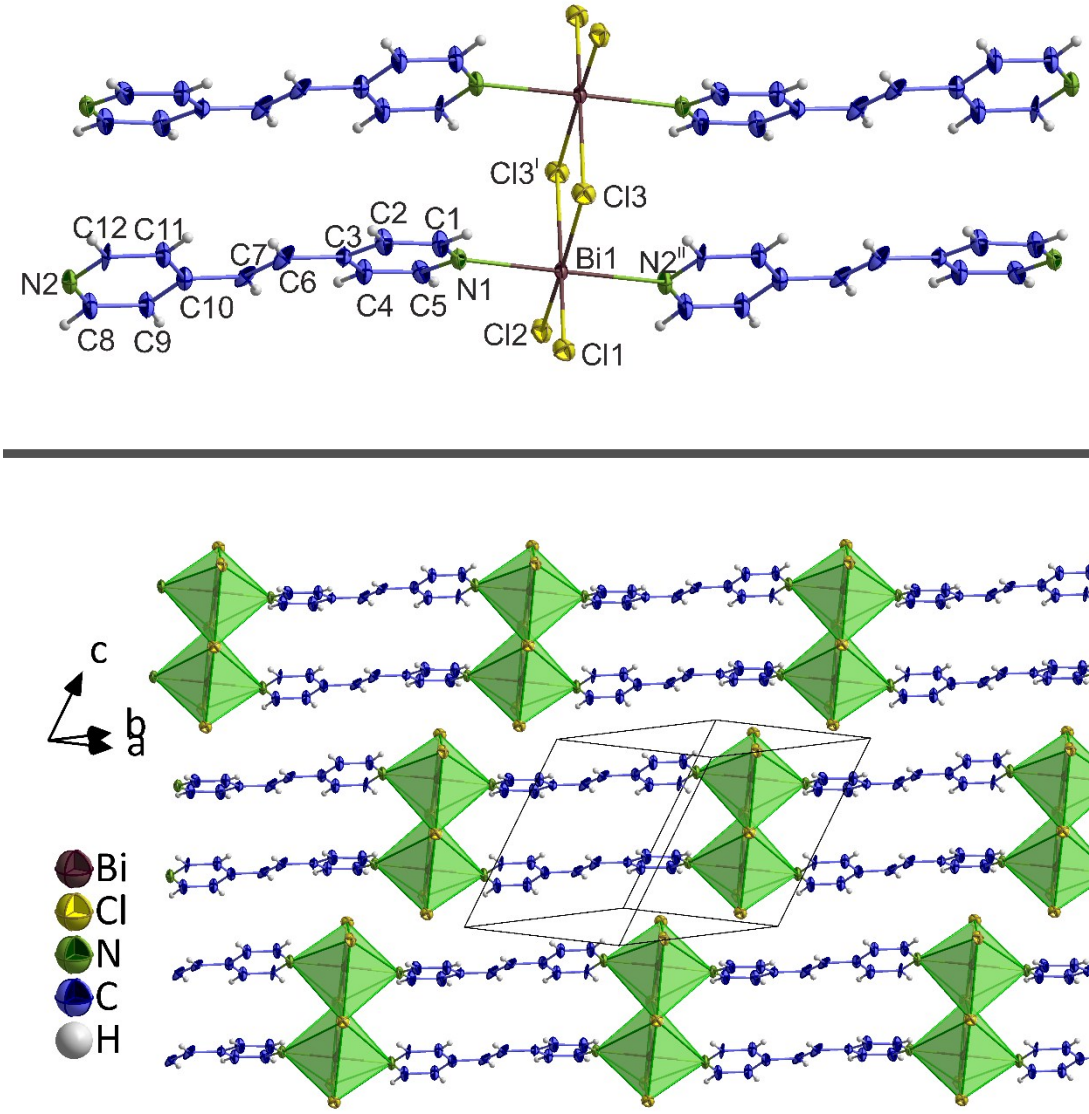

Figure S10. Depiction of the Bi coordination (top) and excerpt of the crystal structure displaying the linear double-strands in $^{1}_{\infty}[Bi_2Cl_6(bpe)_2]$ (**4a**). Symmetry operations: I : 1-x,+2-y, 1-z; II: 1+x, 1+y, +z.

Table S16: Selected interatomic distances (in Å) and angles (in °) in **4b**.
Symmetry operations: I: 2-x,2-y, 1-z, II: 1+x, 1+y, +z

Bi1 Br3	3.0459(7)	Br2 Bi1 Br3	87.72(2)	N1 Bi1 Br2	89.95(12)
Bi1 Br2	2.6756(7)	Br1 Bi1 Br3	173.96(2)	N1 Bi1 Br3^{I}	89.97(12)
Bi1 Br1	2.6709(7)	Br1 Bi1 Br2	96.71(2)	N2^{II} Bi1 Br3	85.88(12)
Bi1 Br3^{I}	3.0489(7)	Br1 Bi1 Br3^{I}	88.04(2)	N2^{II} Bi1 Br2	91.94(12)
Bi1 N1	2.556(5)	Br1 Bi1 N1	91.05(12)	N2^{II} Bi1 Br1	89.86(12)
Bi1 N2^{II}	2.520(5)	Br3^{I} Bi1 Br3	87.54(2)	N2^{II} Bi1 Br3^{I}	88.04(11)
		Br3^{I} Bi1 Br2	175.25(2)	N2^{II} Bi1 N1	177.79(16)
		N1 Bi1 Br3	93.06(12)		

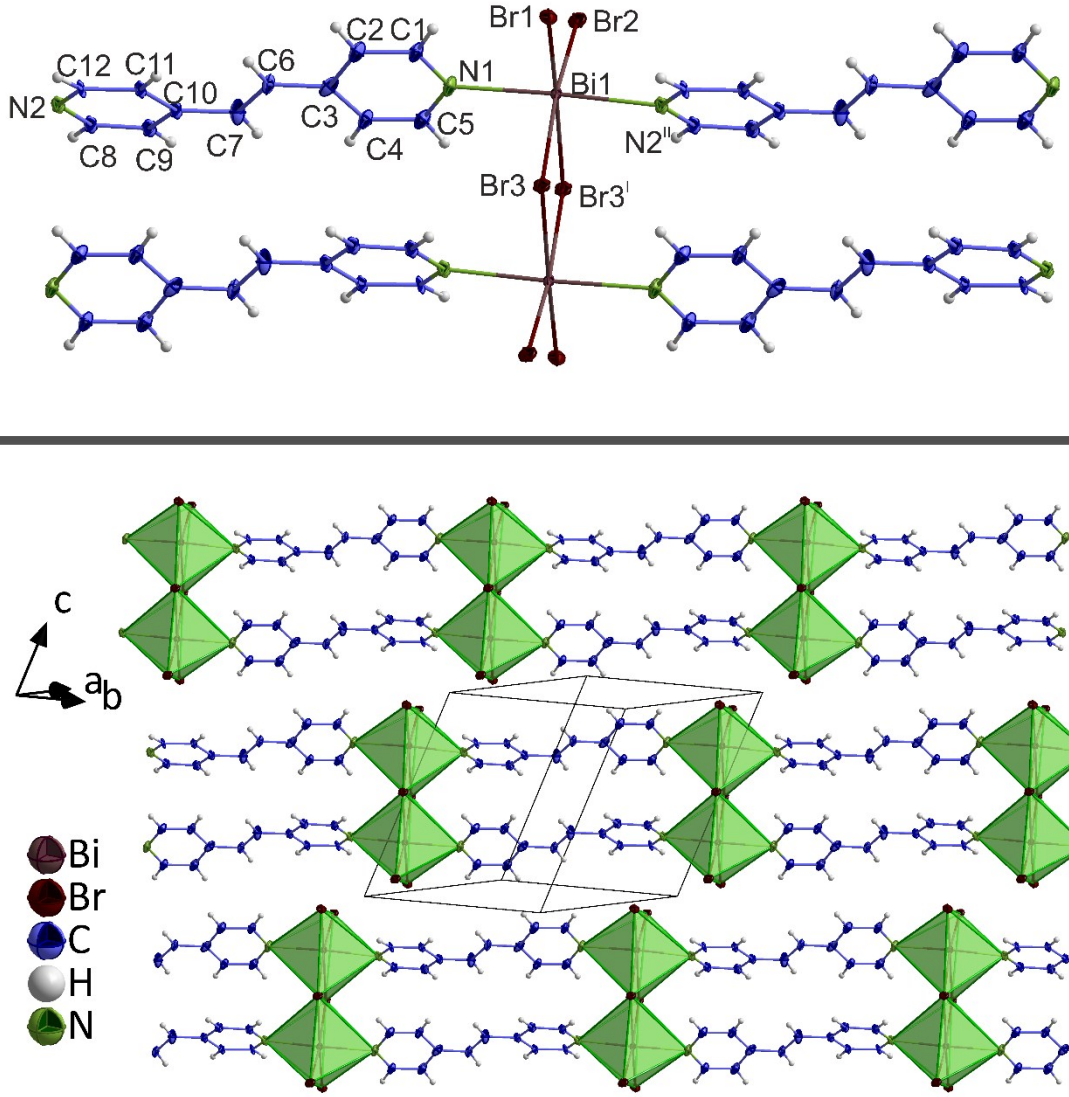

Figure S11. Depiction of the Bi coordination (top) and excerpt of the crystal structure displaying the linear double-strands in $^{1}_{\infty}[Bi_2Br_6(bpe)_2]$ (**4b**). Symmetry operations: I: 2-x,2-y, 1-z, II: 1+x, 1+y, +z.

Table S17: Selected interatomic distances (in Å) and angles (in °) in **4c**.
Symmetry operations: I : -x, 1-y, 1-z; II: -1+x, -1+y, +z

Bi1 I3	3.2101(5)	I2 Bi1 I3	174.15(2)	N1 Bi1 I2	91.19(11)
Bi1 I2	2.9173(5)	I1 Bi1 I3	88.470(12)	N1 Bi1 $I3^{I}$	87.08(11)
Bi1 I1	2.8846(4)	I1 Bi1 I2	96.133(13)	$N2^{II}$ Bi1 I3	89.30(11)
Bi1 $I3^{I}$	3.3036(4)	I1 Bi1 $I3^{I}$	176.001(13)	$N2^{II}$ Bi1 I2	94.25(11)
Bi1 N1	2.513(5)	I1 Bi1 N1	91.06(11)	$N2^{II}$ Bi1 I1	90.63(11)
Bi1 $N2^{II}$	2.588(5)	$I3^{I}$ Bi1 I3	87.846(12)	$N2^{II}$ Bi1 $I3^{I}$	90.88(11)
		$I3^{I}$ Bi1 I2	87.449(13)	$N2^{II}$ Bi1 N1	174.1(2)
		N1 Bi1 I3	85.10(11)		

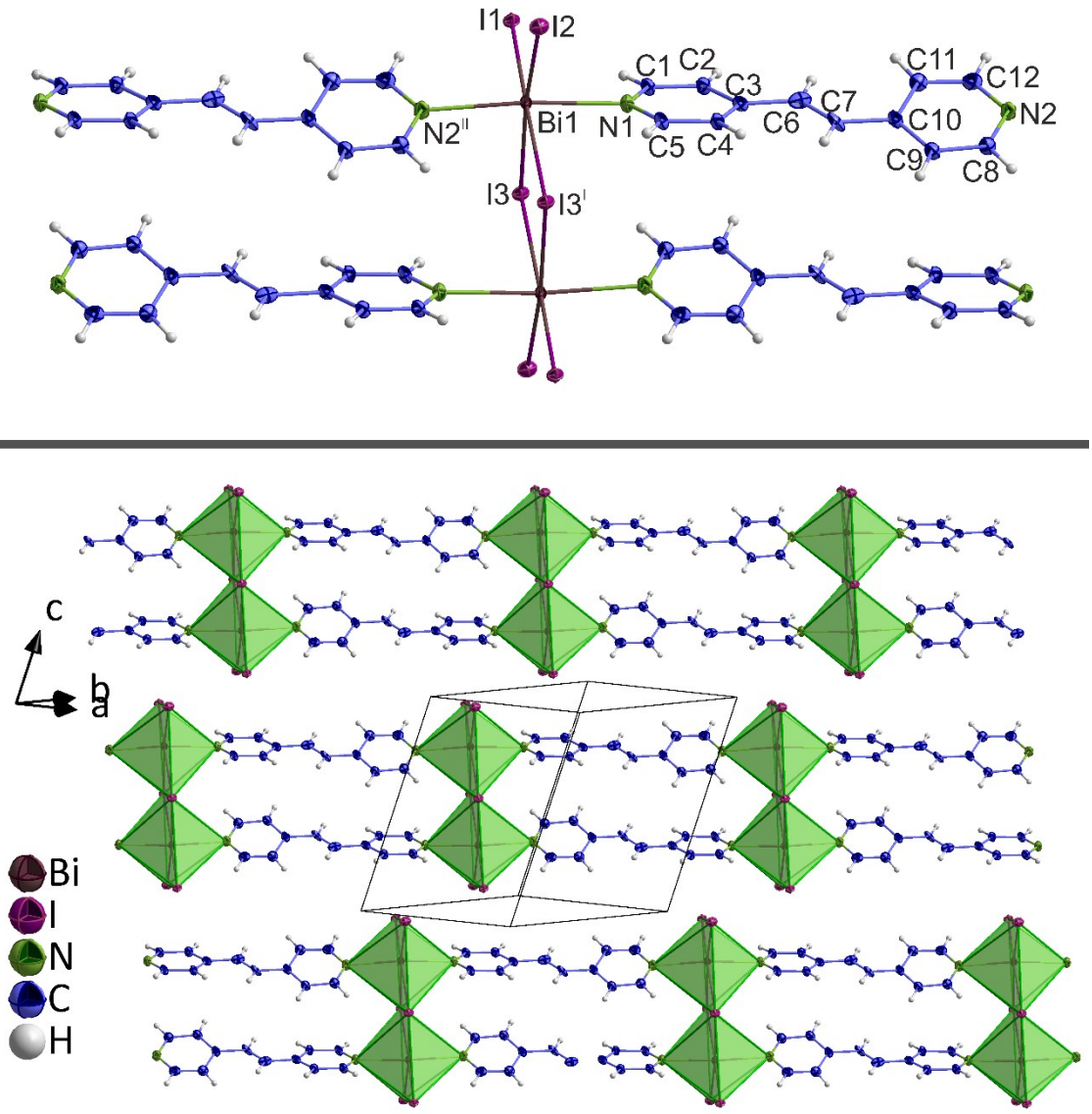

Figure S12. Depiction of the Bi coordination (top) and excerpt of the crystal structure displaying the linear double-strands in $^{1}_{\infty}[Bi_2I_6(bpe)_2]$ (**4c**). Symmetry operations: I : -x, 1-y, 1-z; II: -1+x, -1+y, +z.

Crystallographic details for 5a-c

Table S18 Crystallographic data for **5a-c**.

	5a	**5b**	**5c**
Empirical formula	$C_{12}H_{12}BiCl_3N_2$	$C_{12}H_{12}BiBr_3N_2$	$C_{12}H_{12}BiI_3N_2$
Formula weight /g·mol^{-1}	499.57	632.95	773.92
Crystal color and shape	colourless block	colourless block	yellow needle
Crystal size	0.236 × 0.142 × 0.106	0.105 × 0.064 × 0.037	0.136 × 0.121 × 0.063
Crystal system	triclinic	triclinic	triclinic
Space group	*P*??	*P*??	*P*??
a /pm	884.01(7)	894.83(4)	921.74(7)
b /pm	913.62(7)	945.11(4)	986.40(8)
c /pm	1050.82(9)	1052.23(6)	1106.19(8)
α /°	68.695(4)	69.645(3)	66.722(2)
β /°	71.645(4)	70.592(3)	73.097(2)
γ /°	75.065(3)	78.476(2)	84.010(2)
V /10^6· pm^3	740.55(11)	783.33(7)	883.91(12)
Z	2	2	2
ρ_{calc} /g·cm^{-3}	2.240	2.683	2.908
F(000)	464	572.0	680.0
μ(Mo$_{K\alpha}$) /cm^{-1}	12.428	18.915	15.200
Temperature/K	100	100	100
2Θ range /°	4.292- 54.444	4.308- 54.412	4.166 – 54.442
No. of measured reflections	28575	28354	30949
No. of independent reflections	3287	3504	3941
R(int)	0.0577	0.0861	0.0744
No. of parameters	163	164	164
R_1 ($I > 2\sigma(I)$)	0.0307	0.0361	0.0256
R_1 (all data)	0.0381	0.0478	0.0295
wR_2 (all data)	0.0749	0.0872	0.0586
S (all data)	1.090	1.024	1.032
$\Delta\rho_{max}$, $\Delta\rho_{min}$ /e· Å^{-3}	2.400 / -2.727	2.948 / -1.896	1.212 / -1.284

Table S19: Selected interatomic distances (in Å) and angles (in °) in **5a**.
Symmetry operations: I : 1-x, 2-y, 1-z; II: 1+x, 1+y, +z

Bi1 Cl3	2.8918(17)	Cl2 Bi1 Cl3	88.09(5)	N1 Bi1 Cl2	88.35(17)
Bi1 Cl2	2.5206(17)	Cl1 Bi1 Cl3	176.98(5)	N1 Bi1 Cl3^{I}	90.93(17)
Bi1 Cl1	2.5421(16)	Cl1 Bi1 Cl2	94.17(6)	N2^{II} Bi1 Cl3	90.83(14)
Bi1 Cl3^{I}	2.9278(18)	Cl1 Bi1 Cl3^{I}	92.59(5)	N2^{II} Bi1 Cl2	88.52(15)
Bi1 N1	2.499(5)	Cl1 Bi1 N1	89.65(14)	N2^{II} Bi1 Cl1	87.23(14)
Bi1 N2^{II}	2.512(5)	Cl3^{I} Bi1 Cl3	85.19(5)	N2^{II} Bi1 Cl3^{I}	92.58(15)
		Cl3^{I} Bi1 Cl2	173.20(5)	N2^{II} Bi1 N1	175.4(2)
		N1 Bi1 Cl3	92.41(14)		

Table S20: Selected interatomic distances (in Å) and angles (in °) in **5b**.
Symmetry operations: I : 1-x, 2-y, 1-z; II: 1+x, 1+y, +z

Bi1 Br3	3.0540(9)	Br2 Bi1 Br3	177.20(3)	N1 Bi1 Br2	90.97(16)
Bi1 Br2	2.6914(9)	Br1 Bi1 Br3	86.58(3)	N1 Bi1 $Br3^{I}$	90.02(17)
Bi1 Br1	2.6689(9)	Br1 Bi1 Br2	94.90(3)	$N2^{II}$ Bi1 Br3	89.41(16)
Bi1 $Br3^{I}$	3.0585(9)	Br1 Bi1 $Br3^{I}$	173.60(3)	$N2^{II}$ Bi1 Br2	88.19(16)
Bi1 N1	2.489(6)	Br1 Bi1 N1	88.24(17)	$N2^{II}$ Bi1 Br1	90.94(17)
Bi1 $N2^{II}$	2.529(6)	$Br3^{I}$ Bi1 Br3	87.31(2)	$N2^{II}$ Bi1 $Br3^{I}$	90.90(17)
		$Br3^{I}$ Bi1 Br2	91.29(3)	$N2^{II}$ Bi1 N1	178.8(2)
		N1 Bi1 Br3	91.45(16)		

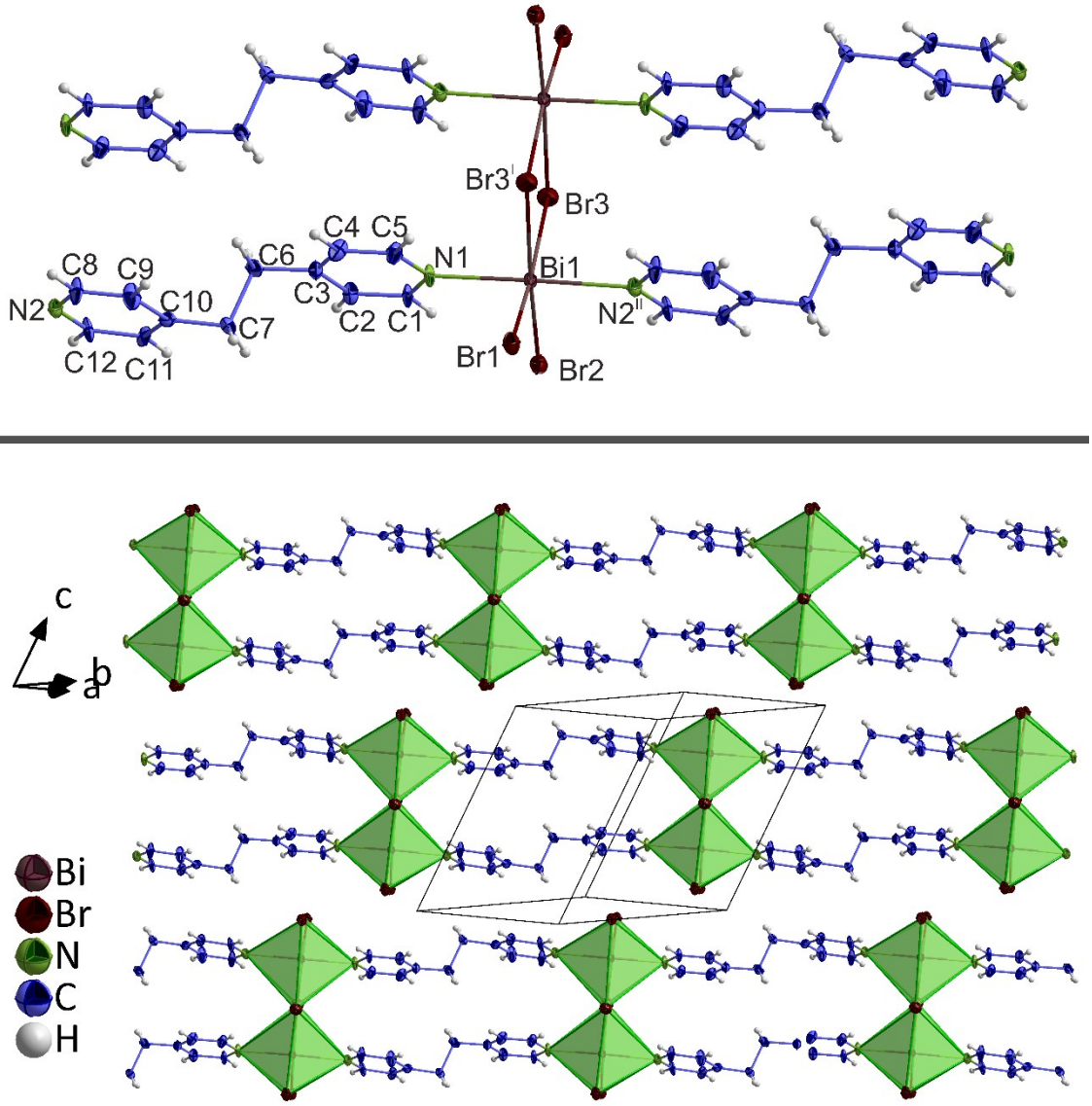

Figure S13. Depiction of the Bi coordination (top) and excerpt of the crystal structure displaying the linear double-strands in $^{1}_{\infty}[Bi_2Br_6(bpa)_2]$ (**5b**). Symmetry operations: I : 1-x, 2-y, 1-z; II: 1+x, 1+y, +z.

Table S21: Selected interatomic distances (in Å) and angles (in °) in **5c**.
Symmetry operations: I : 1-x, 2-y, 1-z; II: 1+x, 1+y, +z

Bi1 I3	3.2594(4)	I2 Bi1 I3	177.061(13)	N1 Bi1 I2	88.36(11)
Bi1 I2	2.8858(5)	I1 Bi1 I3	86.962(13)	N1 Bi1 $I3^{I}$	91.46(11)
Bi1 I1	2.8758(5)	I1 Bi1 I2	94.715(15)	$N2^{II}$ Bi1 I3	90.94(11)
Bi1 $I3^{I}$	3.2557(5)	I1 Bi1 $I3^{I}$	176.244(13)	$N2^{II}$ Bi1 I2	91.48(11)
Bi1 N1	2.548(4)	I1 Bi1 N1	89.41(11)	$N2^{II}$ Bi1 I1	89.76(11)
Bi1 $N2^{II}$	2.520(4)	$I3^{I}$ Bi1 I3	89.395(12)	$N2^{II}$ Bi1 $I3^{I}$	89.38(11)
		$I3^{I}$ Bi1 I2	88.963(14)	$N2^{II}$ Bi1 N1	179.14(15)
		N1 Bi1 I3	89.24(11)		

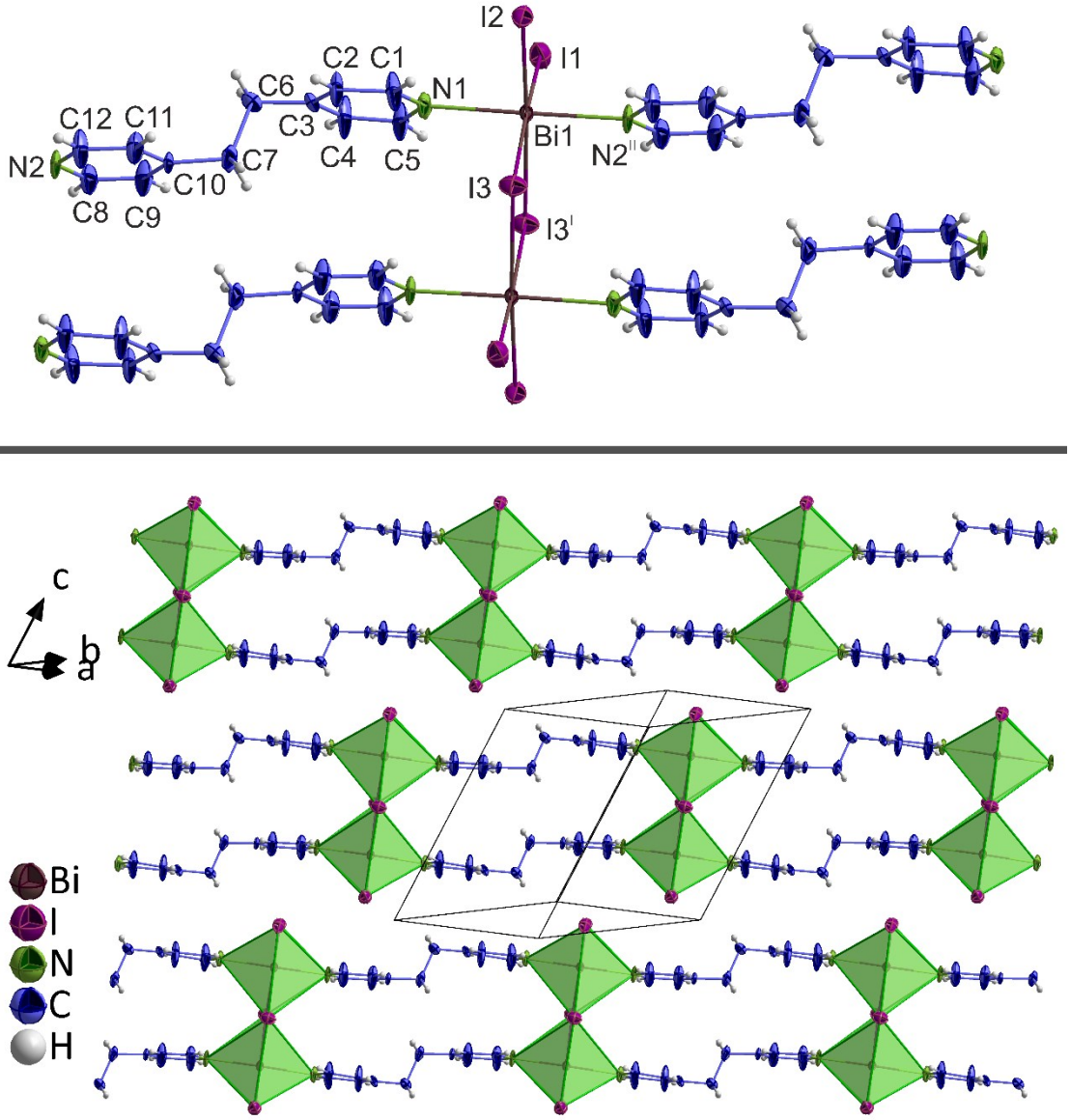

Figure S14. Depiction of the Bi coordination (top) and excerpt of the crystal structure displaying the linear double-strands in $^{1}_{\infty}[Bi_2I_6(bpa)_2]$ (**5c**). Symmetry operations: I : 1-x, 2-y, 1-z; II: 1+x, 1+y, +z.

Table S22: Comparison of interatomic distances of compounds **1**-**5** with literature known reference compounds.

Compound	M-X interatomic distance [pm]	M-N interatomic distance [pm]	Reference compound	M-X interatomic distance [pm]	M-N interatomic distance [pm]
1a	253-291	251-253	$^{1}_{\infty}[Bi_2Cl_6(bipy)_2]$[1]	251-291	252-254
2a	252-293	250-251	$^{2}_{\infty}[Bi_2Cl_6(pyz)_4]$[2]	256-305	249-275
3a	241-301	235-250	$[(CH_3)_3NH]_3[Sb_2Cl_9]$[3]	240-319	/
4a	240-313	233-250			
4a'	241-300	235-252	$[Sb(2AcpNO_2Ph)(DMSO)Cl_2]$[4]	254-265	226-255
5a	237-274	231-254			
1b	267-305	251-254	$^{1}_{\infty}[Bi_2Br_6(bipy)_2]$[1]	264-308	245-259
2b	267-305	248-256	$Bi_2Br_6(2\text{-bipy})_2$[5]	268-303	242-251
3b	257-316	238-253	$[(CH_3)_4N]_3[Sb_2Br_9]xBr_2$[6]	263-304	/
4b	258-314	240-247			
5b	253-334	233-256	$[Sb(2AcpNO_2Ph)(DMSO)Cl_2]$[4]	254-265	226-255
1c	288-330	251-258	$^{1}_{\infty}[Bi_2I_6(bipy)_2]$[1]	287-333	253-259
2c	287-326	251-254	$Bi_2I_6(3\text{-methylpyridine})_4$[7]	292-324	252-258
3c	278-341	239-252	*cis*-$(Me_4Sb)_2[Ph_2Sb_2I_6]$[8]	286-332	/
4c	280-328	242-248			
5c	278-345	241-253	$[Sb(2AcpNO_2Ph)(DMSO)Cl_2]$[4]	254-265	226-255

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Powder X-Ray Diffractometry

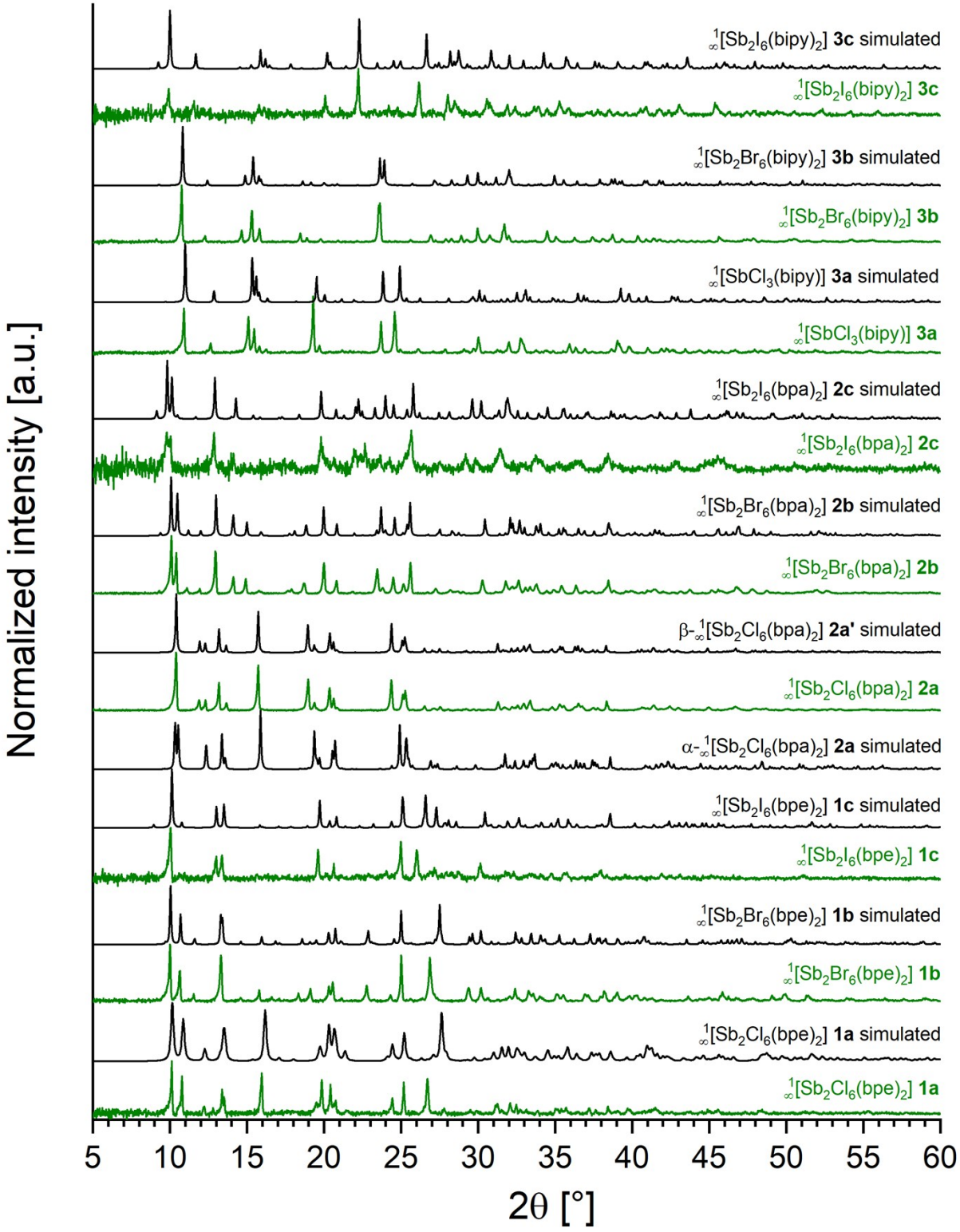

Figure S15. Comparison of obtained diffractograms (blue) and simulated diffractograms from single-crystal date (black) for compounds **1**-**3**.

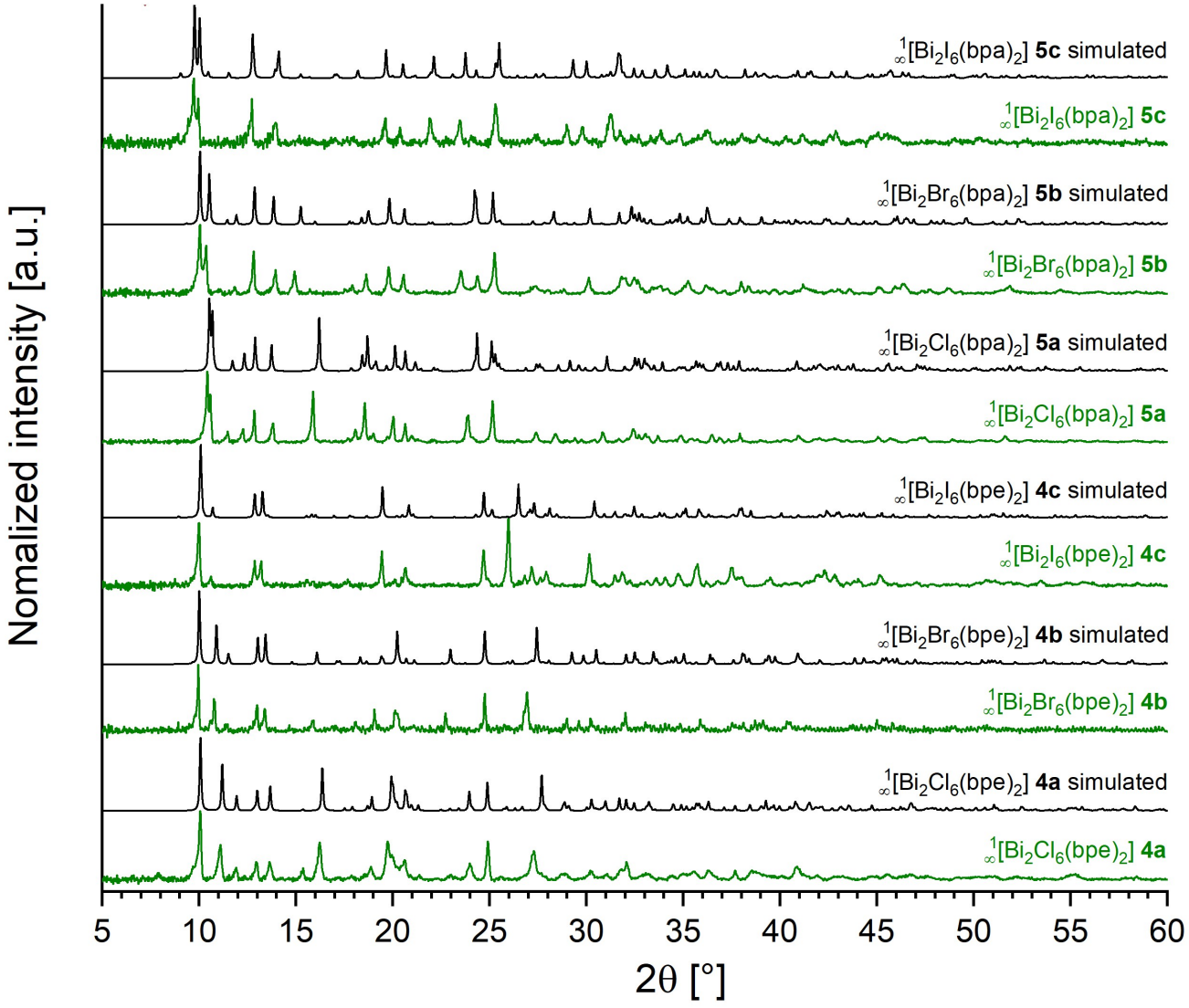

Figure S16. Comparison of obtained diffractograms (blue) and simulated diffractograms from single-crystal date (black) for compounds **4-5**.

Small differences in reflection positions and intensities between obtained and simulated diffractograms arise due to small differences in the crystal structures depending on the temperature. This effect was investigated in detail for compound **2a**. While the simulation of **2a** (100K) shows the mentioned differences (cf. figure S15), the simulation of **2a'** (300K) is perfectly matching the obtained diffractogram. As all other single crystal analyses were carried out at reduced temperatures (100K or 200K), the simulated diffractograms show similar small differences in comparison with the experimental diffractograms that were obtained at room-temperature.

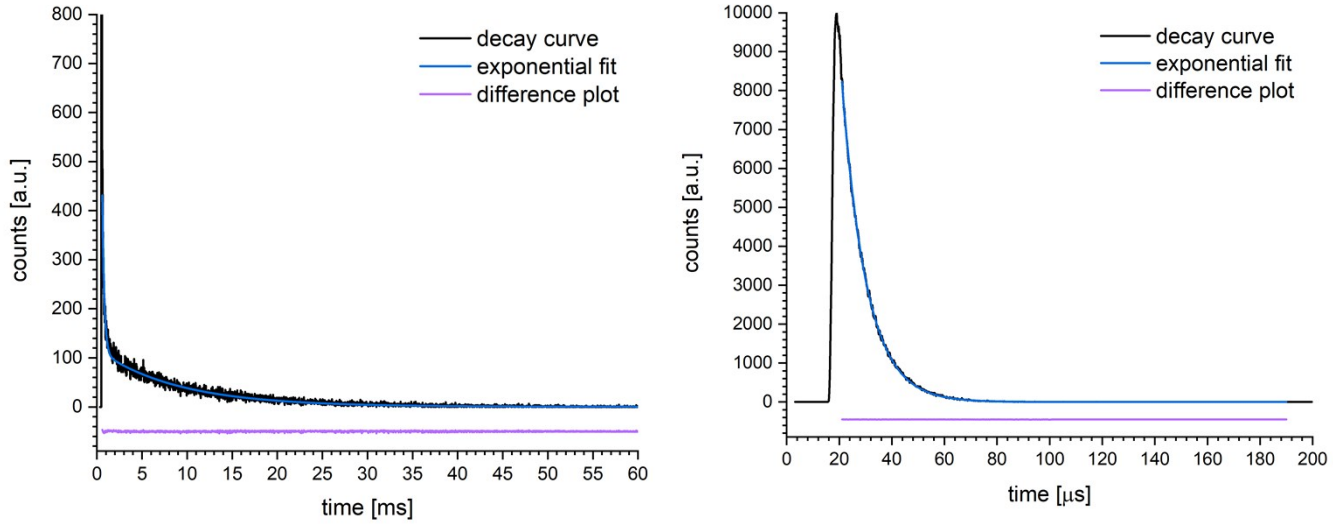

Figure S17. Decay curves (black), exponential fit curves (blue) and difference plot (violet) of emission at 674 nm of $_{\infty}[Sb_2Cl_6(bpe)_2]$ (**1a**, left) and emission at 684 nm of $_{\infty}[Sb_2Cl_6(bpa)_2]$ (**2a**, right).

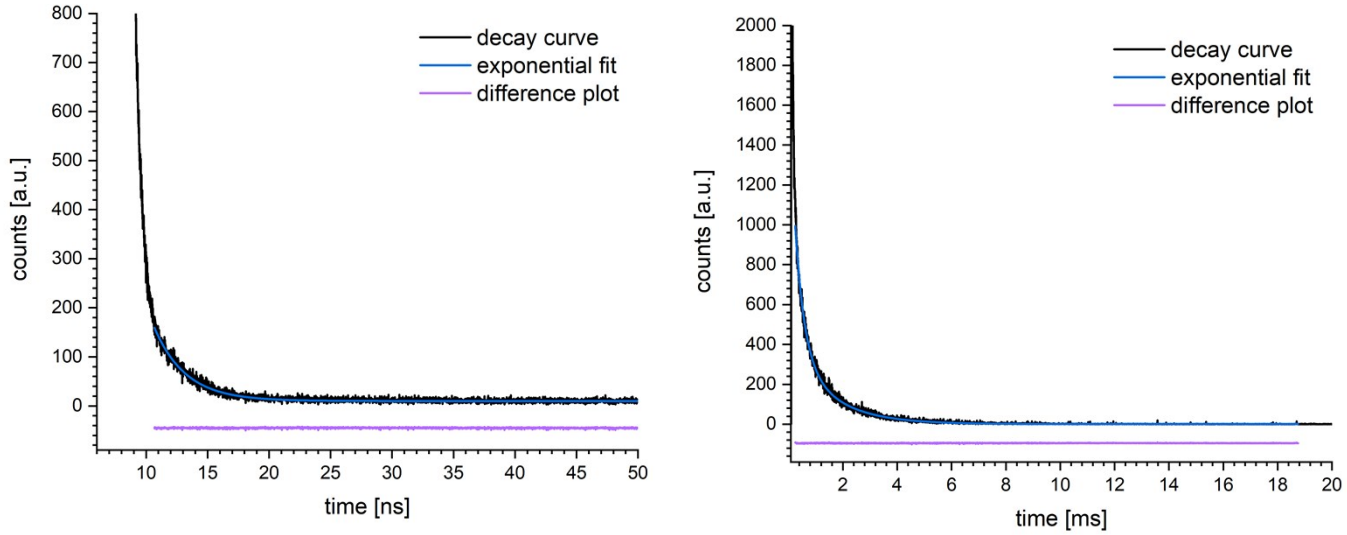

Figure S18. Decay curves (black), exponential fit curves (blue) and difference plot (violet) of emission at 443 nm (left) and at 572 nm (right) of $_{\infty}[Bi_2Cl_6(bpe)_2]$ (**4a**).

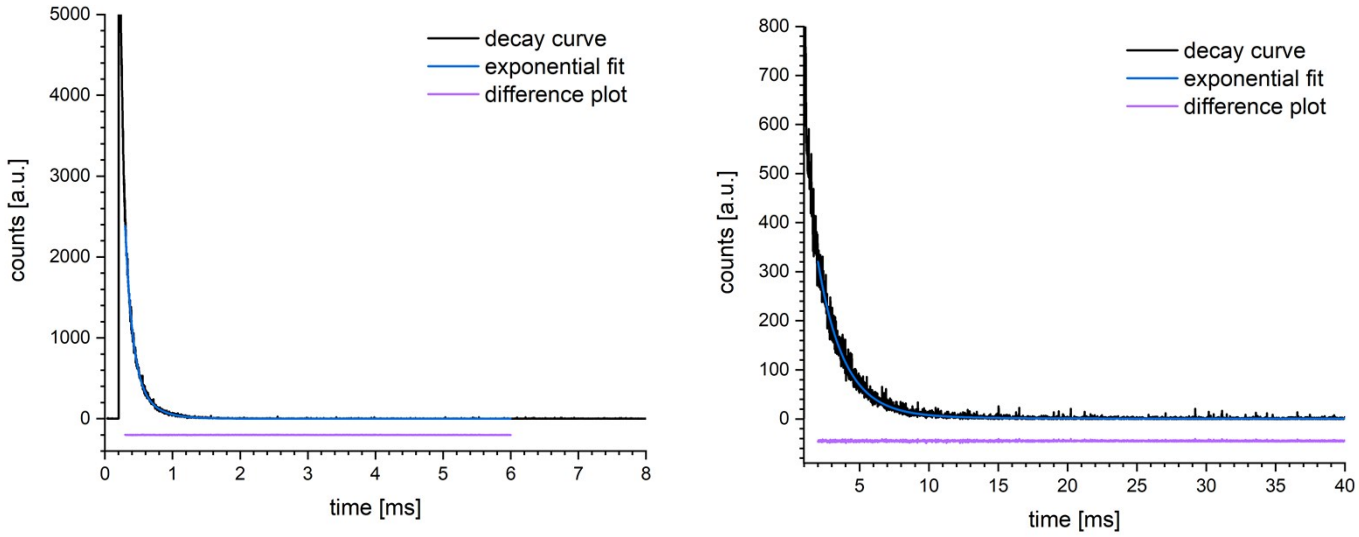

Figure S19. Decay curves (black), exponential fit curves (blue) and difference plot (violet) of emission at 430 nm (left) and at 565 nm (right) of $_{\infty}[Bi_2Cl_6(bpa)_2]$ (**5a**).

Figure S20. Decay curve (black), exponential fit curve (blue) and difference plot (violet) of emission at 502 nm of $_{\infty}[SbCl_3(bipy)]$ (**3a**).

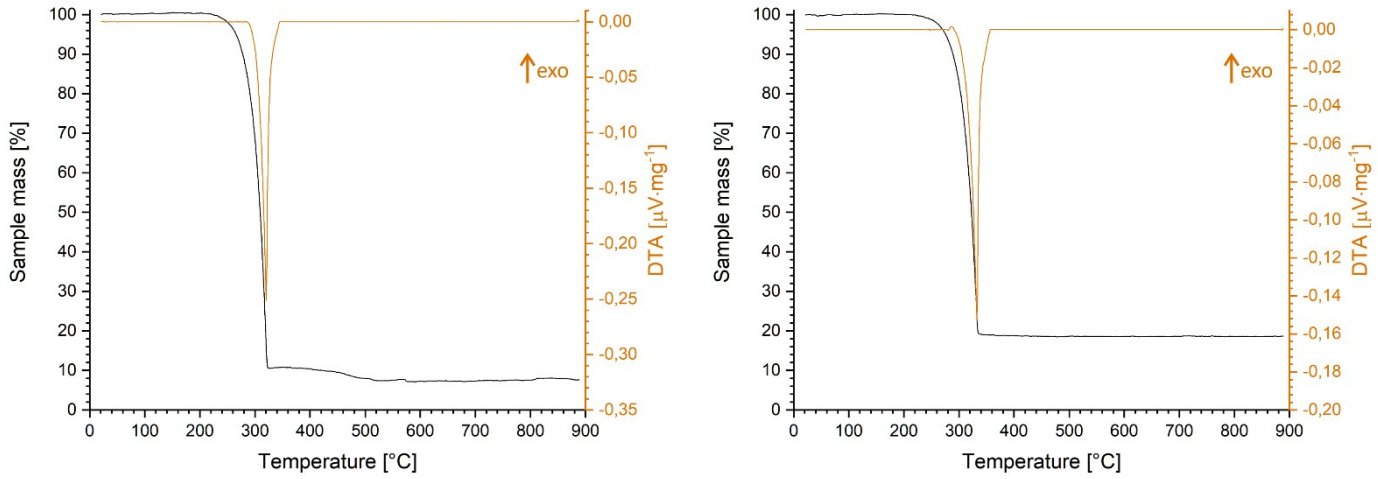

Figure S21. DTA- (black) and TG-curve of $_\infty[Sb_2Cl_6(bpe)_2]$ (**1a**, left) and of $_\infty[Sb_2Br_6(bpe)_2]$ (**1b**, right).

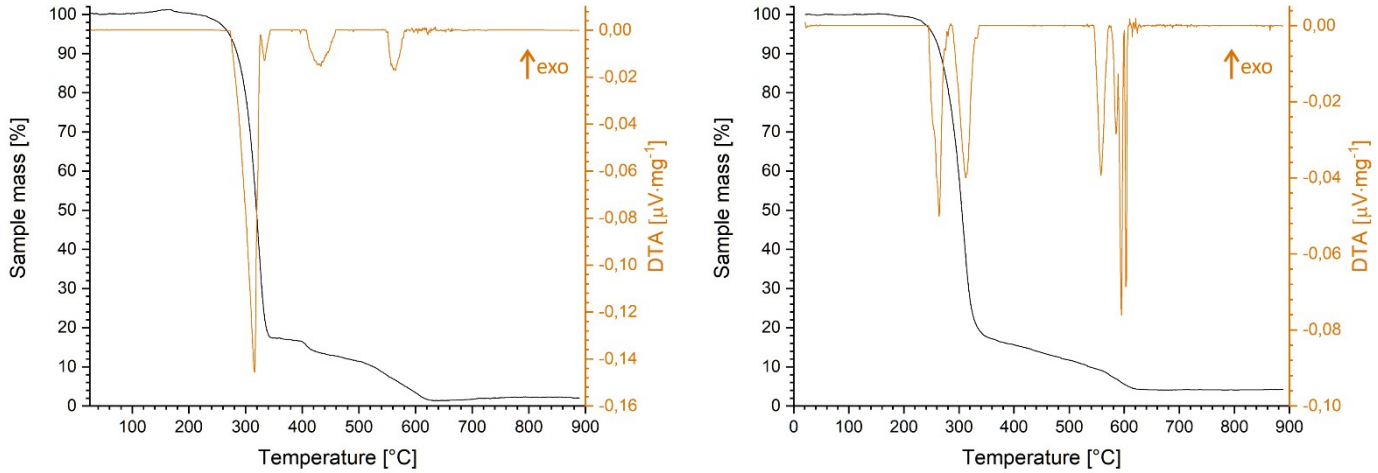

Figure S22. DTA- (black) and TG-curve of $_\infty[Sb_2I_6(bpe)_2]$ (**1c**, left) and of $_\infty[Sb_2Cl_6(bpa)_2]$ (**2a**, right).

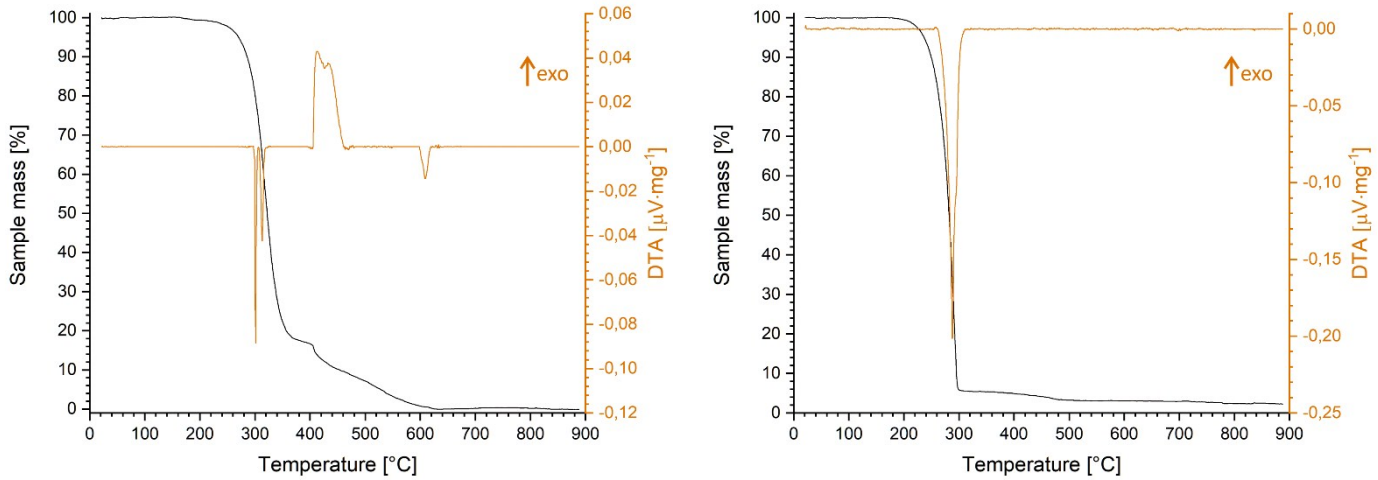

Figure S23. DTA- (black) and TG-curve of $_{\infty}[Sb_2Br_6(bpa)_2]$ (**2b**, left) and of $_{\infty}[SbCl_3(bipy)]$ (**3a**, right).

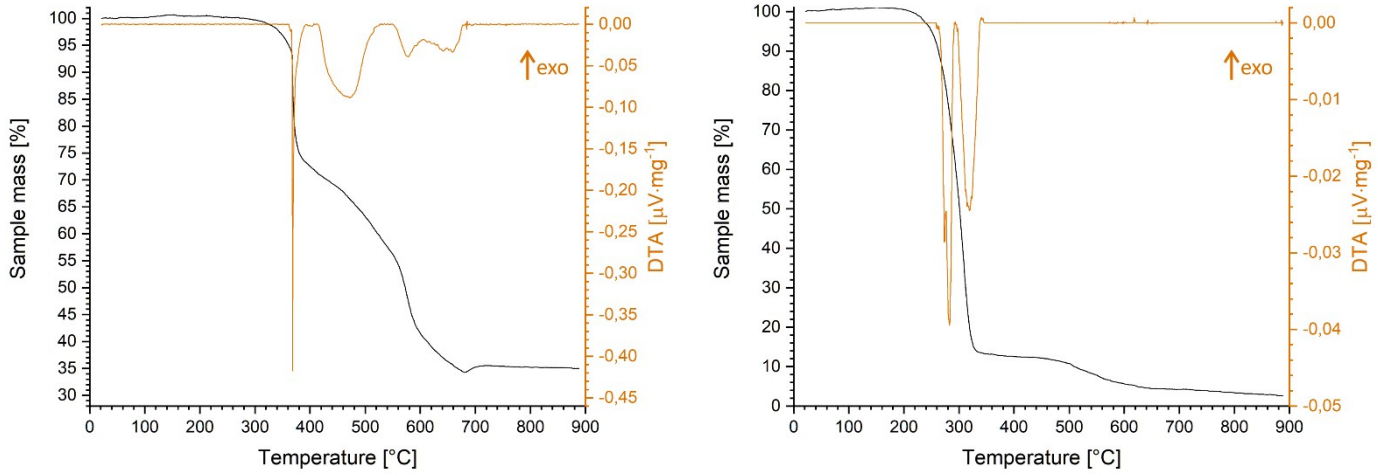

Figure S24. DTA- (black) and TG-curve of $_{\infty}[Sb_2Br_6(bipy)_2]$ (**3b**, left) and of $_{\infty}[Sb_2I_6(bipy)_2]$ (**3c**, right).

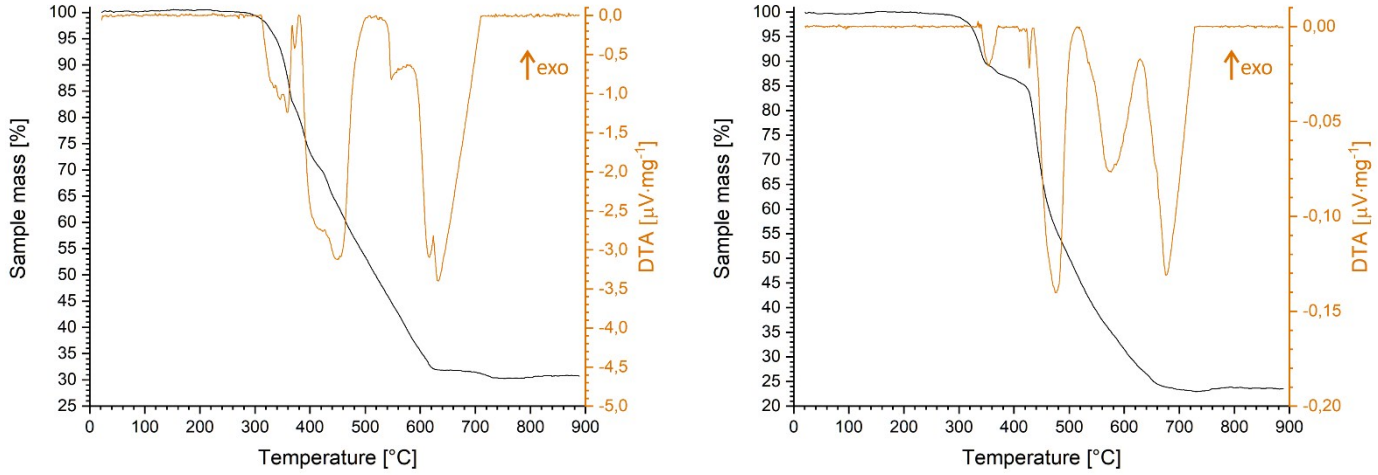

Figure S25. DTA- (black) and TG-curve of $_{\infty}[Bi_2I_6(bpe)_2]$ (**4c**, left) and of $_{\infty}[Bi_2I_6(bpa)_2]$ (**5c**, right).

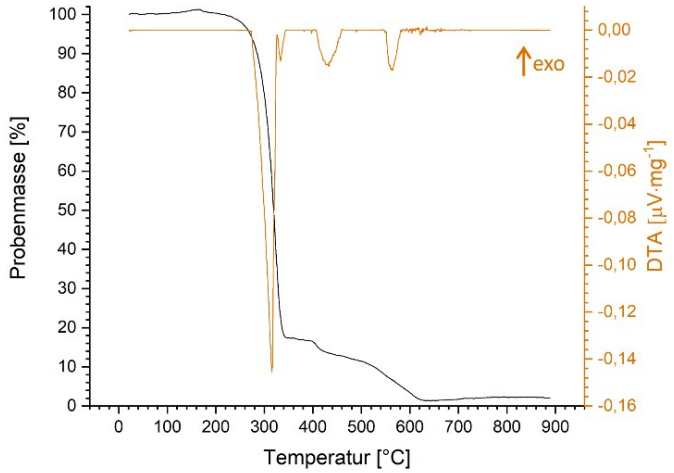

Figure S26. DTA- (black) and TG-curve of $_{\infty}[Bi_2Cl_6(bpa)_2]$ (**5a**).

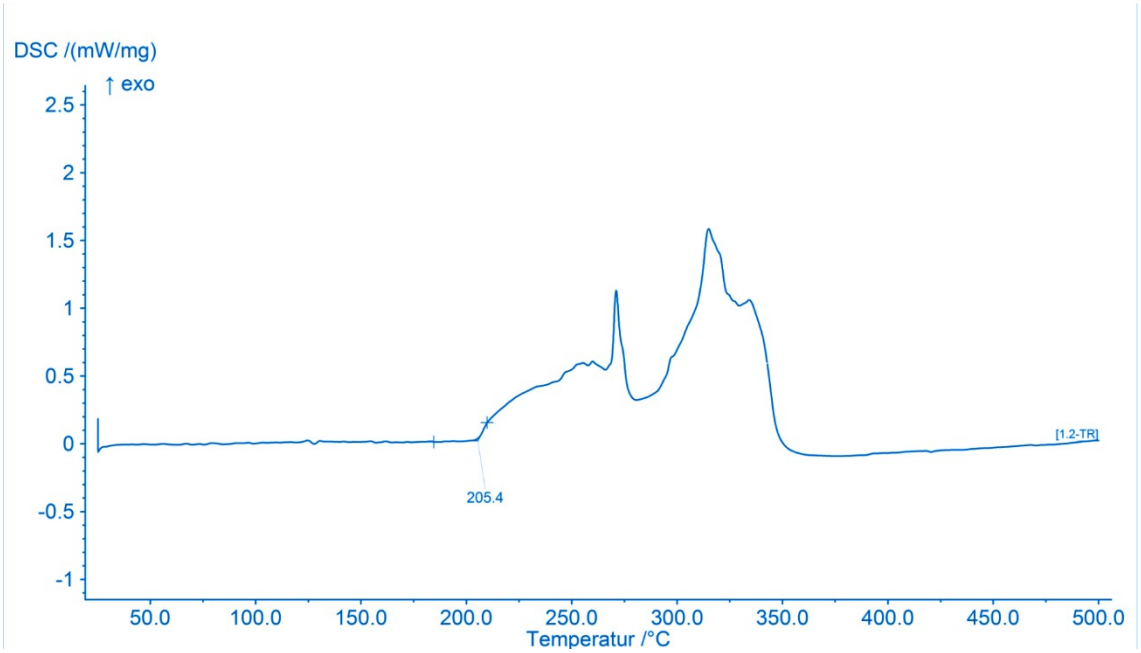

Figure S27. DSC-curve of $_{\infty}[Bi_2Cl_6(bpe)_2]$ (**4a**).

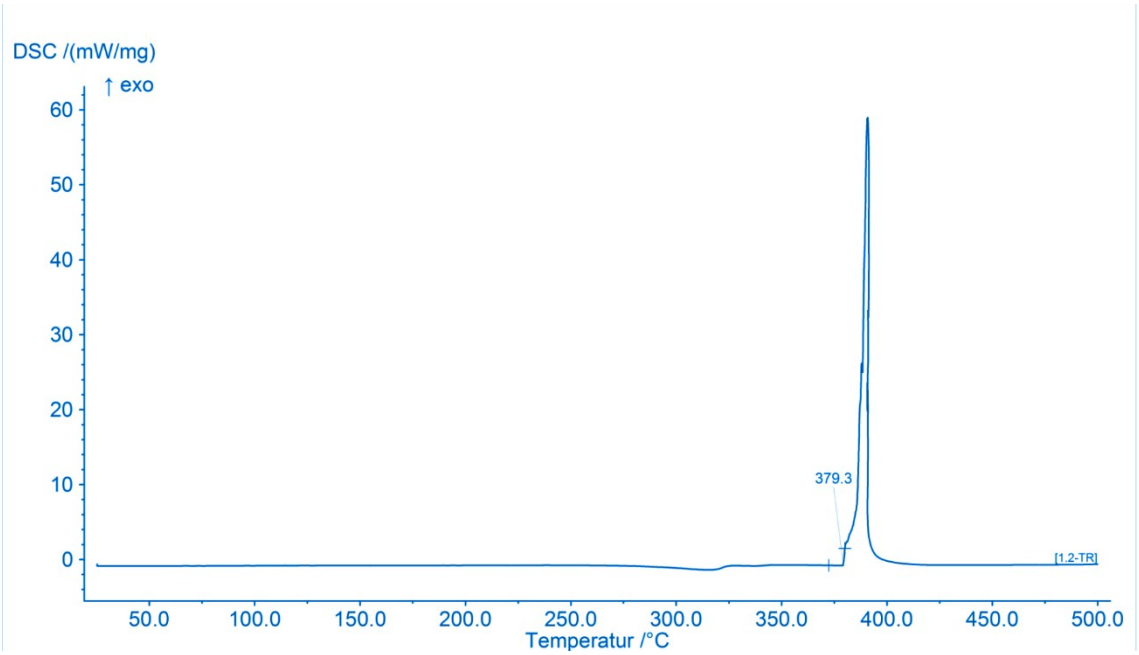

Figure S28. DSC-curve of $_{\infty}[Bi_2Br_6(bpe)_2]$ (**4b**).

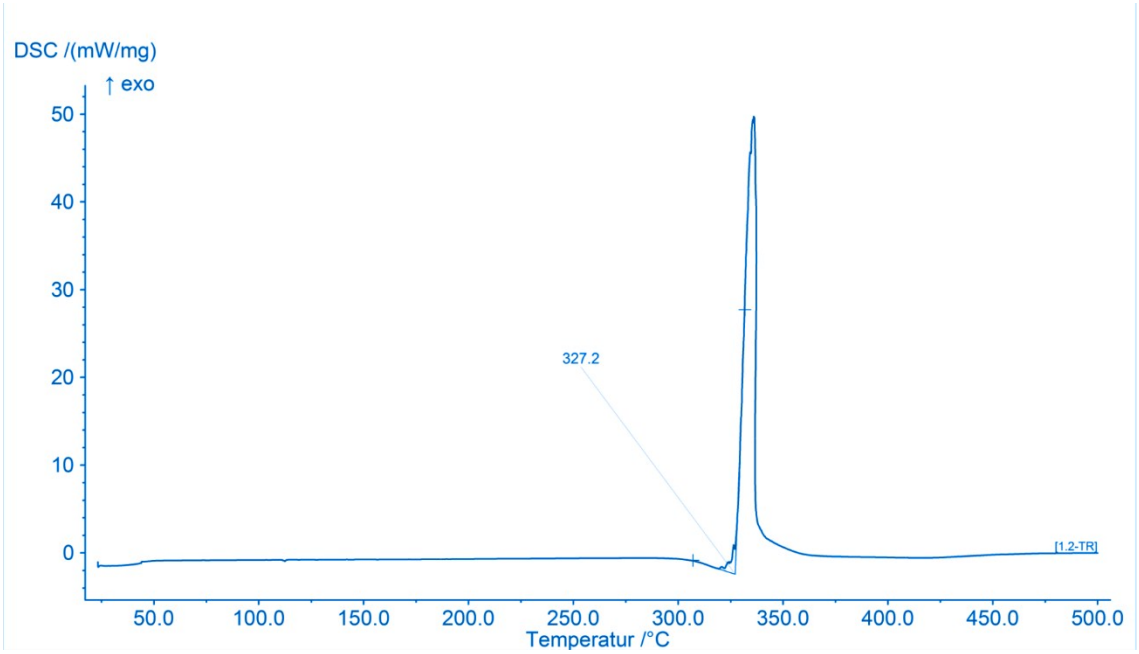

Figure S29. DSC-curve of $_{\infty}[Bi_2Br_6(bpa)_2]$ (**5b**).

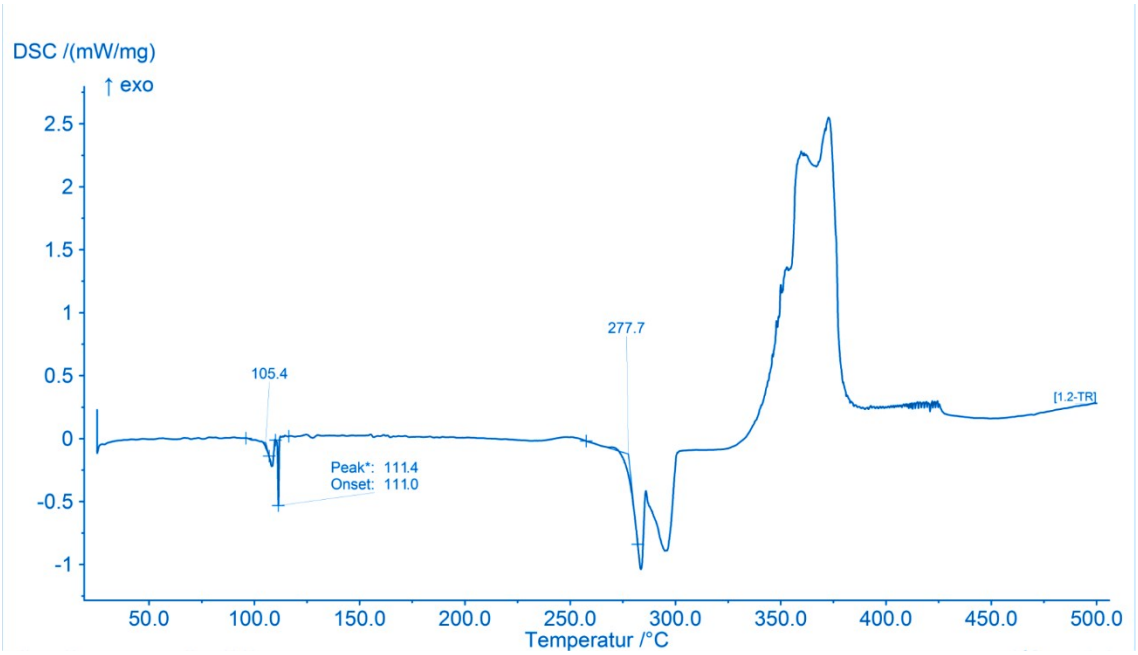

Figure S30. DSC-curve of $_{\infty}[Sb_2I_6(bpa)_2]$ (**2c**).