Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

$(C_2H_5NH_3)_2BiCl_{5-x}Br_x$ Perovskites Containing 1D Chains: Effect of Br Substitution on Structural and Optical Properties

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Table S1. Selected bond angles of ethyl ammine unit as well as X–Bi–X unit of $(C_2H_5NH_3)_2BiCl_{5-x}Br_x$ at RT and LT.

$(C_2H_5NH_3)_2BiCl_{5-x}Br_x$	Space Group	C1–C2–N1 bond angle (degree) Ordered	C3–C4–N2 bond angle (degree) Disordered	Bi–Cl/Br–Bi bridged bond angle (degree)
x =0	C m c a	123.17	110.62	162.71
	P b c a	112.163	110.49	150.17
	A b a 2	110.059	110.599	148.332
x =1	C m c a	120.57	110.68	164.62
	A b a 2	115.005	115.685	150.211
x =2	C m c a	119.10	110.65	165.21
	A b a 2	131.534	112.695	155.647
x =3	C m c a	118.77	110.66	165.06
x =5	C m c a	118.61	110.67	164.30
	A b a 2	111.67	114.882	164.472

Table S2: Hydrogen bond distances (Å) of selected bonds in $(C_2H_5NH_3)_2BiCl_{5-x}Br_x$ compounds.

x	**N1–H–(Cl/Br)3**	**N2–H–(Cl/Br)2/(Cl/Br)5**
0	2.86	2.72
1.185	2.94	2.77
2.27	2.97	2.83
3.125	2.99	2.92
5	3.02	2.84
0_LT (90 K)	2.40	2.43
0_LT (160 K)	2.45	2.42
1.15_LT	2.75	2.87
2.12_LT	2.79	3.10
5_LT	2.84	3.15

Table S3. Bond length of different kind of Bi–Br bond (Å) in $(EA)_2BiCl_{5-x}Br_x$

Composition	Space Group	Bi–X1	Bi–X2	Bi–X3	Bi–X4	Bi–X5
x =0	C m c a	2.58	2.68	2.70	2.84	
	P b c a	2.54	2.59	2.68	2.83	2.71
	A b a 2	2.53	2.59	2.68	2.83	2.71
x =1	C m c a	2.636	2.725	2.765	2.858	
	A b a 2	2.60	2.60	2.71	2.85	2.78
x =2	C m c a	2.668	2.756	2.793	2.883	
	A b a 2	2.68	2.65	2.74	2.90	2.81
x =3	C m c a	2.693	2.783	2.812	2.920	
x =5	C m c a	2.715	2.822	2.83	3.004	
	A b a 2	2.73	2.69	2.82	3.00	2.84

Table S4. Polyhedral tilting angle in the $(C_2H_5NH_3)_2BiCl_{5-x}Br_x$ compounds.

x	**RT_Tilt angle (θ)**	**LT_Tilt angle (θ)**
0	76	71.97 (90 K), 72.22 (160 K)
1	76.74	72.33
2	77.20	75.48
3	77.42	------
5	77.50	77.50

Table S5: Elemental analysis of $(C_2H_5NH_3)_2BiCl_{5-x}Br_x$ compounds from EDX spectra.

Loaded Composition	**EDX Composition**
$(C_2H_5NH_3)_2BiCl_5$	$(C_2H_5NH_3)_2BiCl_{4.67(01)}$
$(C_2H_5NH_3)_2BiCl_4Br$	$(C_2H_5NH_3)_2BiCl_{3.8(02)}Br_{1.1(01)}$
$(C_2H_5NH_3)_2BiCl_3Br_2$	$(C_2H_5NH_3)_2BiCl_{2.56(01)}Br_{2.14(01)}$
$(C_2H_5NH_3)_2BiCl_2Br_3$	$(C_2H_5NH_3)_2BiCl_{1.65(02)}Br_{3.23(01)}$
$(C_2H_5NH_3)_2BiBr_5$	$(C_2H_5NH_3)_2BiBr_{5.06(03)}$

Table S6: Atomic positions obtained from Single Crystals of $(C_2H_5NH_3)_2BiCl_{5-x}Br_x$.

***x* = 0**							
Atom	**Wyck.**	**Site**	**S.O.F.**	**x/a**	**y/b**	**z/c**	**U [Å²]**
Bi1	8f	m..		1/2	0.36404(2)	0.36630(2)	
Cl1	16g	1		0.7515(2)	0.37926(8)	0.46200(11)	
Cl2	8f	m..		1/2	0.24584(10)	0.40254(16)	
Cl3	8f	m..		1/2	0.48324(10)	0.33111(15)	
Cl4	8e	.2.		1/4	0.34464(16)	1/4	
N2	8f	m..		1/2	0.4676(3)	0.1490(4)	
H2A	8f	m..	0.5	1/2	0.43849	0.11424	0.1050
H2B	16g	1	0.5	0.59607	0.46398	0.17746	0.1050
H2C	16g	1	0.5	0.40393	0.46398	0.17746	0.1050
C3	8f	m..		1/2	0.5785(6)	0.1488(7)	
H3A	8f	m..	0.5	1/2	0.61189	0.11404	0.3300
H3B	16g	1	0.5	0.39637	0.58068	0.17976	0.3300
H3C	16g	1	0.5	0.60363	0.58068	0.17976	0.3300
C4	8f	m..		1/2	0.5277(7)	0.1121(7)	
H4A	16g	1	0.5	0.60277	0.52863	0.07956	0.1850
H4B	16g	1	0.5	0.39723	0.52863	0.07956	0.1850
C1	16g	1	0.5	0.4531(16)	0.3260(6)	0.6862(7)	
H1A	16g	1	0.5	0.51744	0.35992	0.70633	0.1500
H1B	16g	1	0.5	0.34062	0.33969	0.66783	0.1500
H1C	16g	1	0.5	0.43510	0.29623	0.72487	0.1500
C2	16g	1	0.5	0.5585(15)	0.2975(7)	0.6218(7)	
H2D	16g	1	0.5	0.57819	0.32774	0.58303	0.1740
H2E	16g	1	0.5	0.67283	0.28421	0.64017	0.1740
N1	16g	1	0.5	0.4596(14)	0.2436(5)	0.5889(6)	
H1D	16g	1	0.5	0.52255	0.22766	0.55156	0.1680
H1E	16g	1	0.5	0.44297	0.21572	0.62429	0.1680
H1F	16g	1	0.5	0.35538	0.25600	0.57141	0.1680

***x* = 1.185**							
Atom	**Wyck.**	**Site**	**S.O.F.**	**x/a**	**y/b**	**z/c**	**U [Å²]**
Bi1	8f	m..		1/2	0.36490(2)	0.36705(2)	
Cl1	16g	1	0.737	0.75219(17)	0.37930(7)	0.46605(8)	
Cl3	8f	m..	0.693	1/2	0.48735(9)	0.33546(12)	
Cl2	8f	m..	0.756	1/2	0.24474(9)	0.40033(14)	
Cl4	8e	.2.	0.89	1/4	0.34758(15)	1/4	
N2	8f	m..		1/2	0.4680(4)	0.1500(4)	
H2A	8f	m..	0.5	1/2	0.43827	0.11641	0.1050
H2B	16g	1	0.5	0.59516	0.46511	0.17845	0.1050
H2C	16g	1	0.5	0.40484	0.46511	0.17845	0.1050
C3	8f	m..		1/2	0.5774(6)	0.1506(7)	
H3A	8f	m..	0.5	1/2	0.61099	0.11666	0.2800
H3B	16g	1	0.5	0.39736	0.57914	0.18153	0.2800
H3C	16g	1	0.5	0.60264	0.57914	0.18153	0.2800
C4	8f	m..		1/2	0.5257(7)	0.1118(8)	

H4A	16g	1	0.5	0.60199	0.52639	0.07953	0.1790
H4B	16g	1	0.5	0.39801	0.52639	0.07953	0.1790
Br4	8e	.2.	0.11	1/4	0.34758(15)	1/4	
Br2	8f	m..	0.244	1/2	0.24474(9)	0.40033(14)	
Br1	16g	1	0.263	0.75219(17)	0.37930(7)	0.46605(8)	
Br3	8f	m..	0.307	1/2	0.48735(9)	0.33546(12)	
N1	16g	1	0.5	0.4587(16)	0.2443(7)	0.5900(7)	
H1A	16g	1	0.5	0.52276	0.22804	0.55364	0.1480
H1B	16g	1	0.5	0.43945	0.21671	0.62532	0.1480
H1C	16g	1	0.5	0.35678	0.25677	0.57146	0.1480
C2	16g	1	0.5	0.5568(15)	0.2981(8)	0.6238(7)	
H2D	16g	1	0.5	0.66863	0.28465	0.64340	0.1780
H2E	16g	1	0.5	0.57932	0.32794	0.58521	0.1780
C1	16g	1	0.5	0.4504(18)	0.3268(7)	0.6862(7)	
H1D	16g	1	0.5	0.51381	0.36041	0.70663	0.1910
H1E	16g	1	0.5	0.34043	0.34066	0.66658	0.1910
H1F	16g	1	0.5	0.42960	0.29744	0.72467	0.1910

***x* = 2.27**							
Atom	**Wyck.**	**Site**	**S.O.F.**	**x/a**	**y/b**	**z/c**	**U [Å²]**
Bi1	8f	m..		1/2	0.36565(2)	0.63207(2)	
Cl1	16g	1	0.503	0.24687(18)	0.37941(7)	0.53193(8)	
Cl3	8f	m..	0.499	1/2	0.48891(9)	0.66264(12)	
Cl2	8f	m..	0.518	1/2	0.24411(9)	0.60112(14)	
Cl4	8e	.2.	0.718	3/4	0.34895(15)	3/4	
Br3	8f	m..	0.501	1/2	0.48891(9)	0.66264(12)	
Br1	16g	1	0.497	0.24687(18)	0.37941(7)	0.53193(8)	
Br4	8e	.2.	0.282	3/4	0.34895(15)	3/4	
Br2	8f	m..	0.482	1/2	0.24411(9)	0.60112(14)	
N2	8f	m..		1/2	0.4676(5)	0.8490(5)	
H2A	8f	m..	0.5	1/2	0.43753	0.88168	0.1070
H2B	16g	1	0.5	0.40557	0.46521	0.82048	0.1070
H2C	16g	1	0.5	0.59443	0.46521	0.82048	0.1070
C4	8f	m..		1/2	0.5242(8)	0.8881(9)	
H4A	16g	1	0.5	0.39866	0.52477	0.92027	0.1680
H4B	16g	1	0.5	0.60134	0.52477	0.92027	0.1680
C3	8f	m..		1/2	0.5762(7)	0.8483(8)	
H3A	8f	m..	0.5	1/2	0.60987	0.88182	0.2420
H3B	16g	1	0.5	0.60186	0.57771	0.81750	0.2420
H3C	16g	1	0.5	0.39814	0.57771	0.81750	0.2420
C1	16g	1	0.5	0.5510(19)	0.3257(8)	0.3153(9)	
H1A	16g	1	0.5	0.48403	0.35757	0.29336	0.1480
H1B	16g	1	0.5	0.65362	0.34221	0.33787	0.1480
H1C	16g	1	0.5	0.58366	0.29738	0.27744	0.1480
C2	16g	1	0.5	0.4420(16)	0.2938(9)	0.3748(11)	
H2D	16g	1	0.5	0.40755	0.32254	0.41271	0.1780
H2E	16g	1	0.5	0.33747	0.27764	0.35219	0.1780
N1	16g	1	0.5	0.5448(17)	0.2431(8)	0.4106(9)	

H1D	16g	1	0.5	0.47970	0.22505	0.44494	0.1860
H1E	16g	1	0.5	0.57509	0.21646	0.37586	0.1860
H1F	16g	1	0.5	0.63996	0.25802	0.43188	0.1860

***x* = 3.125**							
Atom	**Wyck.**	**Site**	**S.O.F.**	**x/a**	**y/b**	**z/c**	**U [Å²]**
Bi1	8f	m..		1/2	0.36660(2)	0.63095(2)	
Cl1	16g	1	0.336	0.24574(13)	0.37968(5)	0.53074(6)	
Cl3	8f	m..	0.308	1/2	0.49012(6)	0.66152(9)	
Cl2	8f	m..	0.327	1/2	0.24416(6)	0.60147(10)	
Cl4	8e	.2.	0.568	3/4	0.34957(10)	3/4	
C1	8f	m..		0	0.5756(6)	0.6512(7)	
H1A	8f	m..	0.5	0	0.60882	0.61736	0.2200
H1B	16g	1	0.5	-0.10092	0.57743	0.68183	0.2200
H1C	16g	1	0.5	0.10092	0.57743	0.68183	0.2200
N1	8f	m..		0	0.4681(4)	0.6519(5)	
H1D	8f	m..	0.5	0	0.43773	0.61995	0.1110
H1E	16g	1	0.5	0.09356	0.46608	0.68027	0.1110
H1F	16g	1	0.5	-0.09356	0.46608	0.68027	0.1110
C2	8f	m..		0	0.5233(6)	0.6122(8)	
H2A	16g	1	0.5	0.10043	0.52350	0.58020	0.1570
H2B	16g	1	0.5	-0.10043	0.52350	0.58020	0.1570
Br1	16g	1	0.664	0.24574(13)	0.37968(5)	0.53074(6)	
Br3	8f	m..	0.692	1/2	0.49012(6)	0.66152(9)	
Br4	8e	.2.	0.432	3/4	0.34957(10)	3/4	
Br2	8f	m..	0.673	1/2	0.24416(6)	0.60147(10)	
N2	16g	1	0.5	0.9548(16)	0.7446(7)	0.4109(8)	
H2C	16g	1	0.5	1.02129	0.72581	0.44358	0.1570
H2D	16g	1	0.5	0.86725	0.76201	0.43435	0.1570
H2E	16g	1	0.5	0.91431	0.71835	0.37812	0.1570
C4	16g	1	0.5	1.0606(15)	0.7924(9)	0.3704(10)	
H4A	16g	1	0.5	1.10617	0.82081	0.40615	0.1950
H4B	16g	1	0.5	1.15702	0.77363	0.34539	0.1950
C3	16g	1	0.5	0.950(2)	0.8254(8)	0.3141(9)	
H3A	16g	1	0.5	1.01841	0.85512	0.28935	0.1910
H3B	16g	1	0.5	0.90641	0.79738	0.27837	0.1910
H3C	16g	1	0.5	0.85565	0.84447	0.33903	0.1910

***x* = 5**							
Atom	**Wyck.**	**Site**	**S.O.F.**	**x/a**	**y/b**	**z/c**	**U [Å²]**
Bi1	8f	m..		1/2	0.63140(2)	0.62777(3)	
Br1	16g	1		0.24396(13)	0.61826(5)	0.52956(6)	
Br2	8f	m..		1/2	0.75513(6)	0.59895(11)	
Br3	8f	m..		1/2	0.50771(7)	0.66096(10)	
Br4	8e	.2.		3/4	0.64968(8)	3/4	
N1	8f	m..		1/2	0.5311(5)	0.8469(7)	
H1A	8f	m..	0.5	1/2	0.56132	0.87849	0.0990

H1B	16g	1	0.5	0.59206	0.53311	0.81879	0.0990
H1C	16g	1	0.5	0.40795	0.53311	0.81879	0.0990
C2	8f	m..		1/2	0.4753(8)	0.8867(11)	
H2A	16g	1	0.5	0.59883	0.47506	0.91834	0.1550
H2B	16g	1	0.5	0.40117	0.47506	0.91834	0.1550
C1	8f	m..		1/2	0.4228(7)	0.8475(10)	
H1D	8f	m..	0.5	1/2	0.38964	0.88077	0.2210
H1E	16g	1	0.5	0.40071	0.42111	0.81713	0.2210
H1F	16g	1	0.5	0.59930	0.42111	0.81713	0.2210
N2	16g	1	0.5	-0.044(2)	0.7421(9)	0.5933(11)	
H2C	16g	1	0.5	0.01638	0.72591	0.55706	0.1510
H2D	16g	1	0.5	-0.05916	0.71514	0.62856	0.1510
H2E	16g	1	0.5	-0.14365	0.75394	0.57619	0.1510
C4	16g	1	0.5	0.052(2)	0.7958(10)	0.6245(12)	
H4A	16g	1	0.5	0.16196	0.78302	0.64257	0.1770
H4B	16g	1	0.5	0.07066	0.82494	0.58599	0.1770
C3	16g	1	0.5	-0.047(3)	0.8243(10)	0.6866(12)	
H3A	16g	1	0.5	0.01441	0.85787	0.70548	0.1940
H3B	16g	1	0.5	-0.15535	0.83749	0.66855	0.1940
H3C	16g	1	0.5	-0.06421	0.79564	0.72503	0.1940

***x* = 0 (160 K)**						
Atom	**Wyck.**	**Site**	**S.O.F.**	**x/a**	**y/b**	**z/c**
Bi1	8c	1	0.63201(2)	0.49449(3)	0.63487(2)	
Cl1	8c	1	0.52648(14)	0.7251(3)	0.62031(11)	
Cl2	8c	1	0.54651(14)	0.2186(3)	0.61245(10)	
Cl3	8c	1	0.59196(15)	0.4539(3)	0.75113(12)	
Cl4	8c	1	0.72909(14)	0.7901(3)	0.65968(13)	
Cl5	8c	1	0.66989(18)	0.5203(3)	0.51643(13)	
N2	8c	1	0.8511(6)	0.4616(10)	0.5264(4)	
H2A	8c	1	0.87690	0.49159	0.55947	0.0440
H2B	8c	1	0.80541	0.51299	0.52725	0.0440
H2C	8c	1	0.84579	0.34287	0.52494	0.0440
N1	8c	1	0.5951(6)	0.0082(8)	0.7371(4)	
H1A	8c	1	0.55165	-0.04062	0.72453	0.0370
H1B	8c	1	0.59020	0.12702	0.73834	0.0370
H1C	8c	1	0.63235	-0.02092	0.71169	0.0370
C4	8c	1	0.8935(10)	0.5240(14)	0.4720(7)	
H4A	8c	1	0.94362	0.46936	0.47136	0.0640
H4B	8c	1	0.89999	0.65319	0.47385	0.0640
C2	8c	1	0.6135(6)	-0.0597(14)	0.7980(5)	
H2D	8c	1	0.61778	-0.18947	0.79655	0.0470
H2E	8c	1	0.57229	-0.02983	0.82531	0.0470
C3	8c	1	0.8507(11)	0.4744(16)	0.4150(8)	
H3A	8c	1	0.87868	0.51544	0.38047	0.1170
H3B	8c	1	0.84494	0.34640	0.41301	0.1170
H3C	8c	1	0.80139	0.52990	0.41550	0.1170
C1	8c	1	0.6868(10)	0.0181(13)	0.8220(8)	

H1D	8c	1	0.69662	-0.02937	0.86150	0.0980
H1E	8c	1	0.72795	-0.01323	0.79550	0.0980
H1F	8c	1	0.68248	0.14634	0.82425	0.0980

***x* = 0 (90 K)**							
Atom	**Wyck.**	**Site**	**S.O.F.**	**x/a**	**y/b**	**z/c**	**U [Å²]**
Bi1	8b	1		0.63322(2)	0.63702(2)	0.63507(6)	
Cl1	8b	1		0.52662(15)	0.62159(15)	0.8595(4)	
Cl2	8b	1		0.54935(16)	0.6140(2)	0.3580(4)	
Cl3	8b	1		0.59224(13)	0.75552(12)	0.5925(3)	
Cl4	8b	1		0.72653(14)	0.66254(13)	0.9362(4)	
Cl5	8b	1		0.67116(15)	0.51598(11)	0.6655(6)	
N1	8b	1		0.5941(4)	0.7425(4)	0.1553(15)	
H1A	8b	1		0.55079	0.72973	0.10583	0.0350
H1B	8b	1		0.63033	0.71455	0.13605	0.0350
H1C	8b	1		0.58742	0.74730	0.27229	0.0350
C2	8b	1		0.6913(5)	0.8241(5)	0.160(2)	
H2A	8b	1		0.70562	0.86272	0.10668	0.0500
H2B	8b	1		0.68435	0.82949	0.28586	0.0500
H2C	8b	1		0.73064	0.79416	0.13891	0.0500
C1	8b	1		0.6167(6)	0.8015(5)	0.0758(16)	
H1D	8b	1		0.57700	0.83184	0.09524	0.0360
H1E	8b	1		0.62338	0.79643	-0.05202	0.0360
C4	8b	1		0.6462(7)	0.4168(5)	0.197(4)	
H4A	8b	1		0.61398	0.38460	0.24195	0.1710
H4B	8b	1		0.66851	0.40377	0.08578	0.1710
H4C	8b	1		0.68580	0.42530	0.28152	0.1710
C3	8b	1		0.5989(5)	0.4752(5)	0.166(3)	
H3A	8b	1		0.55848	0.46648	0.08136	0.1340
H3B	8b	1		0.57580	0.48805	0.27744	0.1340
N2	8b	1		0.6486(4)	0.5270(3)	0.0940(13)	
H2D	8b	1		0.62031	0.56055	0.07684	0.0330
H2E	8b	1		0.68531	0.53535	0.17225	0.0330
H2F	8b	1		0.66928	0.51539	-0.00922	0.0330

***x* = 1.15 (90 K)**							
Atom	**Wyck.**	**Site**	**S.O.F.**	**x/a**	**y/b**	**z/c**	**U [Å²]**
Bi1	8b	1		0.63222(2)	0.63517(2)	0.6418(4)	
Br5	8b	1	0.359	0.66604(14)	0.51130(11)	0.6301(12)	
Br3	8b	1	0.22	0.59405(15)	0.75471(13)	0.648(2)	
Br2	8b	1	0.3	0.5295(4)	0.6207(4)	0.3954(8)	
Br4	8b	1	0.03	0.7280(2)	0.6585(2)	0.3416(6)	
N008	8b	1		0.5945(8)	0.7418(6)	0.130(5)	
H00A	8b	1		0.55116	0.73098	0.18206	0.0620
H00B	8b	1		0.58776	0.74445	0.01325	0.0620
H00C	8b	1		0.62991	0.71400	0.15366	0.0620
N009	8b	1		0.6478(7)	0.5266(6)	0.165(5)	

H00G	8b	1		0.61693	0.55785	0.18591	0.0580
H00H	8b	1		0.68223	0.52430	0.25157	0.0580
H00I	8b	1		0.67099	0.53187	0.06118	0.0580
C00A	8b	1		0.6889(9)	0.8226(8)	0.124(6)	
H00D	8b	1		0.70055	0.86128	0.17697	0.0830
H00E	8b	1		0.72908	0.79438	0.14941	0.0830
H00F	8b	1		0.68362	0.82722	-0.00204	0.0830
C00B	8b	1		0.6460(9)	0.4198(9)	0.129(9)	
H00J	8b	1		0.61231	0.38546	0.12877	0.1420
H00K	8b	1		0.67106	0.42274	0.01631	0.1420
H00L	8b	1		0.68319	0.41458	0.22166	0.1420
C00C	8b	1		0.6052(12)	0.4722(9)	0.161(9)	
H00M	8b	1		0.57897	0.46783	0.27341	0.0930
H00N	8b	1		0.56687	0.47596	0.06856	0.0930
C1	8b	1		0.6184(10)	0.7997(9)	0.198(3)	
H1A	8b	1		0.62406	0.79641	0.32651	0.0570
H1B	8b	1		0.57868	0.82919	0.17534	0.0570
Cl3	8b	1	0.78	0.59405(15)	0.75471(13)	0.648(2)	

***x* = 2.12 (90 K)**							
Atom	**Wyck.**	**Site**	**S.O.F.**	**x/a**	**y/b**	**z/c**	**U [Å²]**
Bi1	8b	1		0.63127(3)	0.63406(3)	0.3486(5)	
Br5	8b	1	0.64	0.66086(17)	0.50864(13)	0.3536(14)	
Br1	8b	1	0.46	0.5260(4)	0.6187(5)	0.0972(7)	
Br2	8b	1	0.57	0.5280(4)	0.6241(3)	0.6025(9)	
Br3	8b	1	0.36	0.6000(3)	0.7558(2)	0.348(2)	
Br4	8b	1	0.1	0.7327(5)	0.6514(5)	0.6467(12)	
Cl4	8b	1	0.9	0.7327(5)	0.6514(5)	0.6467(12)	
Cl2	8b	1	0.43	0.5280(4)	0.6241(3)	0.6025(9)	
Cl3	8b	1	0.64	0.6000(3)	0.7558(2)	0.348(2)	
Cl1	8b	1	0.54	0.5260(4)	0.6187(5)	0.0972(7)	
Cl5	8b	1	0.36	0.66086(17)	0.50864(13)	0.3536(14)	
N1	8b	1		0.8516(11)	0.5316(10)	0.346(6)	
H1A	8b	1		0.88234	0.56333	0.33727	0.0770
H1B	8b	1		0.81781	0.53273	0.25889	0.0770
H1C	8b	1		0.82779	0.53273	0.44989	0.0770
C4	8b	1		0.8478(16)	0.4216(14)	0.347(9)	
H4A	8b	1		0.87928	0.38631	0.33821	0.1530
H4B	8b	1		0.82214	0.42140	0.45917	0.1530
H4C	8b	1		0.81138	0.42139	0.25315	0.1530
C6	8b	1		0.895(2)	0.4765(15)	0.334(10)	
H6A	8b	1		0.93222	0.47594	0.42751	0.0990
H6B	8b	1		0.92146	0.47593	0.22151	0.0990
C3	8b	1		0.6845(14)	0.3241(13)	0.364(7)	
H3A	8b	1		0.69238	0.35747	0.28456	0.1150
H3B	8b	1		0.67626	0.33930	0.48164	0.1150
H3C	8b	1		0.72824	0.29837	0.36355	0.1150
N2	8b	1		0.592(2)	0.2457(16)	0.372(7)	

H2A	8b	1		0.55235	0.23547	0.30605	0.1550

***x*= 5 (90 K)**							
Atom	**Wyck.**	**Site**	**S.O.F.**	**x/a**	**y/b**	**z/c**	**U [Å²]**
Bi1	8b	1		0.37227(2)	0.36860(2)	0.3961(6)	
Br1	8b	1		0.4713(3)	0.3804(3)	0.1378(3)	
Br2	8b	1		0.4696(3)	0.3831(4)	0.6500(3)	
Br3	8b	1		0.40102(11)	0.24489(8)	0.3905(14)	
Br4	8b	1		0.2499(7)	0.3505(1)	0.6456(13)	
Br5	8b	1		0.33887(10)	0.49235(8)	0.4019(15)	
N2	8b	1		0.1531(7)	0.4683(6)	0.401(7)	
H2A	8b	1		0.12584	0.43834	0.36235	0.1010
H2B	8b	1		0.19543	0.46927	0.34507	0.1010
H2C	8b	1		0.16169	0.46311	0.51097	0.1010
C3	8b	1		0.1147(12)	0.5237(9)	0.376(6)	
H3A	8b	1		0.10443	0.52818	0.25593	0.1600
H3B	8b	1		0.06809	0.52156	0.43457	0.1600
C2	8b	1		0.1532(11)	0.5756(9)	0.433(5)	
H2D	8b	1		0.12392	0.61040	0.41182	0.1290
H2E	8b	1		0.16244	0.57230	0.55255	0.1290
H2F	8b	1		0.19884	0.57894	0.37360	0.1290
C1	8b	1		0.3174(13)	0.1740(11)	0.942(3)	
H1A	8b	1		0.30010	0.14033	0.87854	0.1970
H1B	8b	1		0.33861	0.16046	1.04664	0.1970
H1C	8b	1		0.27707	0.20018	0.96619	0.1970
C4	8b	1		0.3753(14)	0.2075(11)	0.839(2)	
H4A	8b	1		0.41570	0.18085	0.81317	0.1610
H4B	8b	1		0.35406	0.22064	0.73259	0.1610
N4	8b	1		0.4037(12)	0.2610(9)	0.937(3)	
H4C	8b	1		0.43721	0.27994	0.87485	0.1610
H4D	8b	1		0.36667	0.28568	0.95882	0.1610
H4E	8b	1		0.42372	0.24886	1.03340	0.1610

Table S7: Anisotropic displacement parameters (in Å²) of $(C_2H_5NH_3)_2BiCl_{5-x}Br_x$

***x* = 0**						
Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
Bi1	0.03825(17)	0.0641(2)	0.04213(18)	0.00000	0.00000	0.00853(12)
Cl1	0.070(1)	0.1244(14)	0.0737(11)	-0.0163(10)	-0.0285(8)	0.0033(9)
Cl2	0.133(2)	0.0561(14)	0.0923(17)	0.00000	0.00000	0.0161(13)
Cl3	0.193(3)	0.0550(14)	0.0764(16)	0.00000	0.00000	0.0095(12)
Cl4	0.126(3)	0.140(3)	0.155(3)	0.00000	-0.104(2)	0.00000
N2	0.116(7)	0.063(5)	0.083(5)	0.00000	0.00000	0.012(4)
C3	0.49(4)	0.053(8)	0.116(11)	0.00000	0.00000	-0.020(7)
C4	0.25(2)	0.115(12)	0.096(9)	0.00000	0.00000	0.029(9)

C1	0.071(13)	0.165(14)	0.138(12)	-0.008(9)	-0.015(8)	-0.058(10)
C2	0.093(14)	0.172(16)	0.169(15)	-0.009(10)	-0.011(10)	-0.063(12)
N1	0.051(11)	0.147(9)	0.138(9)	0.003(6)	0.005(6)	-0.063(8)

***x* = 1.185**						
Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
Bi1	0.03917(19)	0.0651(3)	0.0402(2)	0.00000	0.00000	0.00869(17)
Cl1	0.0709(9)	0.1314(15)	0.0782(10)	-0.0167(9)	-0.0286(7)	0.0061(8)
Cl3	0.173(2)	0.0620(14)	0.0797(15)	0.00000	0.00000	0.0145(12)
Cl2	0.126(2)	0.0637(16)	0.0989(17)	0.00000	0.00000	0.0192(13)
Cl4	0.109(2)	0.145(3)	0.130(3)	0.00000	-0.082(2)	0.00000
N2	0.123(8)	0.070(7)	0.068(5)	0.00000	0.00000	0.002(5)
C3	0.41(3)	0.056(10)	0.095(11)	0.00000	0.00000	-0.007(9)
C4	0.25(2)	0.096(12)	0.098(10)	0.00000	0.00000	0.033(10)
Br4	0.109(2)	0.145(3)	0.130(3)	0.00000	-0.082(2)	0.00000
Br2	0.126(2)	0.0637(16)	0.0989(17)	0.00000	0.00000	0.0192(13)
Br1	0.0709(9)	0.1314(15)	0.0782(10)	-0.0167(9)	-0.0286(7)	0.0061(8)
Br3	0.173(2)	0.0620(14)	0.0797(15)	0.00000	0.00000	0.0145(12)
N1	0.050(12)	0.157(12)	0.162(10)	0.021(8)	0.001(7)	-0.063(10)
C2	0.079(14)	0.177(19)	0.190(18)	0.011(10)	-0.016(10)	-0.050(14)
C1	0.087(17)	0.155(16)	0.139(14)	-0.03(1)	-0.025(9)	-0.048(12)

***x* = 2.27**						
Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
Bi1	0.0422(3)	0.0633(3)	0.0470(3)	0.00000	0.00000	-0.0087(2)
Cl1	0.0723(9)	0.1297(15)	0.0810(11)	0.0168(9)	-0.0277(7)	-0.0057(8)
Cl3	0.167(2)	0.0576(14)	0.0819(15)	0.00000	0.00000	-0.0115(11)
Cl2	0.126(2)	0.0617(16)	0.1095(18)	0.00000	0.00000	-0.0174(12)
Cl4	0.106(2)	0.148(3)	0.127(3)	0.00000	-0.074(2)	0.00000
Br3	0.167(2)	0.0576(14)	0.0819(15)	0.00000	0.00000	-0.0115(11)
Br1	0.0723(9)	0.1297(15)	0.0810(11)	0.0168(9)	-0.0277(7)	-0.0057(8)
Br4	0.106(2)	0.148(3)	0.127(3)	0.00000	-0.074(2)	0.00000
Br2	0.126(2)	0.0617(16)	0.1095(18)	0.00000	0.00000	-0.0174(12)
N2	0.129(10)	0.070(8)	0.069(7)	0.00000	0.00000	0.000(6)
C4	0.231(18)	0.096(13)	0.092(11)	0.00000	0.00000	-0.025(10)
C3	0.32(2)	0.070(11)	0.096(12)	0.00000	0.00000	0.015(10)
C1	0.056(16)	0.16(2)	0.150(18)	0.034(12)	-0.028(10)	0.051(13)
C2	0.071(16)	0.17(2)	0.20(2)	-0.007(13)	-0.013(12)	0.065(15)
N1	0.044(14)	0.140(14)	0.189(14)	-0.023(9)	0.006(9)	0.067(11)

***x* = 3.125**						
Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
Bi1	0.03818(19)	0.0588(2)	0.04242(19)	0.00000	0.00000	-0.00906(16)
Cl1	0.0634(7)	0.1213(9)	0.0709(7)	0.0133(6)	-0.0251(5)	-0.0054(6)
Cl3	0.1641(18)	0.0551(9)	0.0748(11)	0.00000	0.00000	-0.0100(7)
Cl2	0.1219(15)	0.0552(10)	0.1038(13)	0.00000	0.00000	-0.0168(8)

Cl4	0.0893(15)	0.1347(19)	0.1049(17)	0.00000	-0.0617(13)	0.00000
C1	0.29(2)	0.058(8)	0.096(10)	0.00000	0.00000	0.003(7)
N1	0.140(9)	0.067(6)	0.070(6)	0.00000	0.00000	0.004(5)
C2	0.216(16)	0.074(9)	0.103(10)	0.00000	0.00000	0.022(8)
Br1	0.0634(7)	0.1213(9)	0.0709(7)	0.0133(6)	-0.0251(5)	-0.0054(6)
Br3	0.1641(18)	0.0551(9)	0.0748(11)	0.00000	0.00000	-0.0100(7)
Br4	0.0893(15)	0.1347(19)	0.1049(17)	0.00000	-0.0617(13)	0.00000
Br2	0.1219(15)	0.0552(10)	0.1038(13)	0.00000	0.00000	-0.0168(8)
N2	0.054(14)	0.160(13)	0.178(14)	0.015(8)	-0.014(9)	0.083(11)
C4	0.089(16)	0.20(2)	0.20(2)	0.005(13)	0.007(12)	0.074(14)
C3	0.086(19)	0.148(15)	0.149(16)	-0.025(11)	0.017(11)	0.060(12)

***x* = 5**						
Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
Bi1	0.0301(3)	0.0547(3)	0.0404(3)	0.00000	0.00000	0.0082(3)
Br1	0.0538(6)	0.1125(9)	0.0655(7)	-0.0119(6)	-0.0236(6)	0.0033(7)
Br2	0.1104(14)	0.0498(8)	0.0963(14)	0.00000	0.00000	0.014(1)
Br3	0.1663(18)	0.0495(9)	0.0729(12)	0.00000	0.00000	0.0079(9)
Br4	0.0678(11)	0.1190(13)	0.0883(13)	0.00000	-0.045(1)	0.00000
N1	0.107(11)	0.060(8)	0.08(1)	0.00000	0.00000	0.010(8)
C2	0.19(2)	0.085(13)	0.114(18)	0.00000	0.00000	0.052(15)
C1	0.30(3)	0.043(10)	0.097(16)	0.00000	0.00000	0.002(12)
N2	0.036(17)	0.165(18)	0.178(19)	0.017(10)	0.021(12)	-0.054(15)
C4	0.056(17)	0.20(2)	0.18(2)	0.008(14)	-0.013(15)	-0.037(19)
C3	0.07(2)	0.18(2)	0.13(2)	-0.030(16)	-0.027(14)	-0.059(18)

***x* = 0 (160 K)**						
Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
Bi1	0.0247(4)	0.0196(3)	0.0206(4)	0.00000(11)	0.00134(12)	-0.00087(11)
Cl1	0.0343(13)	0.0310(12)	0.0419(13)	0.0093(10)	-0.0032(10)	0.0043(11)
Cl2	0.0376(12)	0.0284(11)	0.0348(13)	-0.0067(10)	-0.0023(10)	-0.0078(10)
Cl3	0.0409(14)	0.0382(12)	0.0187(11)	-0.0026(12)	0.0036(10)	-0.0002(11)
Cl4	0.0432(13)	0.0384(13)	0.0493(17)	-0.0163(11)	0.0032(13)	-0.0048(12)
Cl5	0.0398(15)	0.0553(17)	0.0214(14)	0.0052(10)	0.0051(11)	-0.003(1)
N2	0.041(5)	0.048(5)	0.021(5)	-0.006(4)	-0.001(4)	0.006(4)
N1	0.038(6)	0.031(5)	0.023(5)	-0.002(3)	-0.001(4)	0.000(3)
C4	0.063(9)	0.066(9)	0.032(8)	-0.010(6)	0.027(7)	0.004(5)
C2	0.051(6)	0.035(5)	0.031(6)	-0.003(6)	-0.002(5)	0.004(5)
C3	0.050(8)	0.156(18)	0.029(8)	-0.010(8)	0.004(7)	0.005(7)
C1	0.074(11)	0.066(9)	0.056(10)	-0.010(6)	-0.027(9)	-0.001(6)

***x* = 0 (90 K)**						
Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
Bi1	0.00948(16)	0.02451(18)	0.01186(17)	0.00082(13)	0.0004(3)	-0.0058(3)
Cl1	0.0141(13)	0.0356(18)	0.0161(13)	0.0022(12)	0.0026(11)	-0.0025(14)
Cl2	0.0227(15)	0.069(2)	0.0105(13)	-0.0179(17)	-0.0016(12)	-0.0094(16)
Cl3	0.0172(11)	0.0307(13)	0.0166(15)	0.0055(10)	-0.0018(9)	-0.0003(10)
Cl4	0.0223(14)	0.0380(15)	0.0183(14)	-0.0023(12)	-0.012(1)	-0.0018(13)
Cl5	0.0227(12)	0.0224(12)	0.076(3)	0.0006(10)	0.0179(18)	-0.0143(18)
N1	0.021(4)	0.051(5)	0.015(5)	-0.016(4)	0.004(5)	-0.001(6)
C2	0.027(5)	0.041(6)	0.032(8)	-0.005(5)	0.001(7)	-0.002(7)
C1	0.028(6)	0.037(7)	0.025(6)	0.009(5)	0.001(5)	-0.003(5)
C4	0.035(8)	0.063(10)	0.24(3)	-0.016(7)	0.029(13)	0.017(15)
C3	0.095(11)	0.085(10)	0.15(2)	-0.074(9)	-0.050(15)	0.068(15)
N2	0.018(4)	0.030(5)	0.035(7)	-0.005(3)	-0.006(4)	0.007(4)

***x* = 1.15 (90 K)**						
Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
Bi1	0.01496(19)	0.0259(2)	0.0192(2)	0.00160(17)	0.0001(6)	0.0017(7)
Br5	0.0315(14)	0.0301(14)	0.095(3)	0.0085(10)	-0.027(3)	-0.006(3)
Br3	0.0282(15)	0.0311(16)	0.140(4)	0.0063(11)	0.011(5)	0.002(6)
Br2	0.078(4)	0.046(4)	0.079(6)	0.002(3)	-0.058(4)	-0.001(3)
Br4	0.031(2)	0.051(3)	0.030(2)	-0.0018(17)	0.0174(14)	-0.0030(19)
N008	0.043(7)	0.059(9)	0.054(11)	-0.016(6)	-0.009(15)	-0.020(18)
N009	0.021(6)	0.040(7)	0.084(19)	0.000(5)	-0.004(11)	-0.024(13)
C00A	0.041(8)	0.044(9)	0.081(19)	-0.015(7)	0.025(17)	-0.016(18)
C00B	0.028(9)	0.062(14)	0.19(3)	-0.016(9)	0.01(3)	-0.07(3)
C00C	0.062(12)	0.051(12)	0.12(3)	-0.039(10)	0.02(3)	-0.03(3)
C1	0.037(10)	0.057(13)	0.048(14)	0.007(9)	-0.003(7)	0.001(9)
Cl3	0.0282(15)	0.0311(16)	0.140(4)	0.0063(11)	0.011(5)	0.002(6)
Cl4	0.031(2)	0.051(3)	0.030(2)	-0.0018(17)	0.0174(14)	-0.0030(19)
Cl5	0.0315(14)	0.0301(14)	0.095(3)	0.0085(10)	-0.027(3)	-0.006(3)
Cl1	0.104(5)	0.079(6)	0.053(5)	-0.044(5)	0.049(4)	-0.016(3)
Cl2	0.078(4)	0.046(4)	0.079(6)	0.002(3)	-0.058(4)	-0.001(3)
Br1	0.104(5)	0.079(6)	0.053(5)	-0.044(5)	0.049(4)	-0.016(3)

***x* = 2.12 (90 K)**						
Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
Bi1	0.0309(5)	0.0413(6)	0.0527(6)	0.0040(2)	0.0005(8)	0.0005(10)
Br5	0.0473(18)	0.0364(19)	0.137(4)	0.0083(12)	0.018(4)	-0.002(5)
Br1	0.104(5)	0.101(6)	0.047(3)	-0.031(5)	-0.029(4)	0.006(3)
Br2	0.067(4)	0.074(5)	0.092(5)	0.008(3)	0.034(4)	0.006(3)
Br3	0.069(3)	0.038(3)	0.157(6)	0.0103(19)	-0.023(7)	-0.002(7)

Br4	0.071(6)	0.112(7)	0.087(7)	-0.026(5)	-0.044(4)	0.028(5)
Cl4	0.071(6)	0.112(7)	0.087(7)	-0.026(5)	-0.044(4)	0.028(5)
Cl2	0.067(4)	0.074(5)	0.092(5)	0.008(3)	0.034(4)	0.006(3)
Cl3	0.069(3)	0.038(3)	0.157(6)	0.0103(19)	-0.023(7)	-0.002(7)
Cl1	0.104(5)	0.101(6)	0.047(3)	-0.031(5)	-0.029(4)	0.006(3)
Cl5	0.0473(18)	0.0364(19)	0.137(4)	0.0083(12)	0.018(4)	-0.002(5)
N1	0.044(9)	0.056(14)	0.092(17)	0.005(9)	-0.01(2)	-0.03(2)
C4	0.064(16)	0.056(19)	0.19(4)	0.021(15)	0.06(3)	0.03(4)
C6	0.073(17)	0.055(18)	0.12(3)	0.009(15)	-0.02(3)	0.01(3)
C3	0.059(14)	0.07(2)	0.10(2)	-0.011(13)	0.02(3)	-0.03(3)
N2	0.11(2)	0.13(3)	0.14(3)	-0.09(2)	0.06(3)	-0.05(3)
C1	0.20(6)	0.33(10)	0.18(9)	-0.22(7)	0.09(6)	-0.06(7)

***x* = 5 (90 K)**						
Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
Bi1	0.0348(3)	0.0586(4)	0.0337(3)	0.0074(2)	-0.0009(11)	0.0048(11)
Br1	0.063(4)	0.101(3)	0.054(4)	0.004(3)	0.022(3)	0.005(3)
Br2	0.053(3)	0.135(4)	0.063(4)	0.002(4)	-0.025(3)	-0.022(4)
Br3	0.0901(12)	0.0523(10)	0.1140(18)	0.0142(8)	0.017(5)	0.000(5)
Br4	0.0829(11)	0.1255(16)	0.0709(11)	-0.006(6)	0.0453(10)	0.003(7)
Br5	0.0671(10)	0.0531(10)	0.169(3)	0.0078(8)	-0.020(4)	0.017(4)
N2	0.061(8)	0.071(10)	0.121(14)	0.002(7)	0.01(3)	0.02(4)
C3	0.108(17)	0.066(13)	0.22(4)	0.025(13)	-0.13(3)	-0.03(3)
C2	0.090(13)	0.068(13)	0.10(4)	0.015(11)	0.039(18)	0.003(15)
C1	0.14(2)	0.15(2)	0.11(3)	-0.049(16)	-0.007(16)	-0.047(18)
C4	0.19(2)	0.12(2)	0.09(2)	-0.015(16)	0.002(16)	-0.020(15)
N4	0.192(19)	0.120(17)	0.09(3)	-0.073(15)	-0.006(16)	0.034(15)

Table S8: Selected bond lengths obtained from Single Crystals of $(C_2H_5NH_3)_2BiCl_{5-x}Br_x$

***x* = 0**			
Atoms 1,2	**d 1,2 [Å]**	**Atoms 1,2**	**d 1,2 [Å]**
Bi1—Cl1^{i}	2.5773(16)	C3—C4	1.294(18)
Bi1—Cl1	2.5773(16)	C4—H4A	0.9700
Bi1—Cl2	2.678(2)	C4—H4B	0.9700
Bi1—Cl3	2.695(2)	C1—H1A	0.9600
Bi1—Cl4^{ii}	2.8384(6)	C1—H1B	0.9600
Bi1—Cl4	2.8384(6)	C1—H1C	0.9600
N2—H2A	0.8900	C1—C2	1.5320
N2—H2B	0.8900	C2—H2D	0.9700
N2—H2C	0.8900	C2—H2E	0.9700
N2—C4	1.477(15)	C2—N1	1.5191
C3—H3A	0.9600	N1—H1D	0.8900
C3—H3B	0.9600	N1—H1E	0.8900

C3—H3C	0.9600	N1—H1F	0.8900

***x* = 1.185**			
Atoms 1,2	**d 1,2 [Å]**	**Atoms 1,2**	**d 1,2 [Å]**
Bi1—Cl1|Br1^{i}	2.6358(12)	C3—H3B	0.9600
Bi1—Cl1|Br1	2.6358(12)	C3—H3C	0.9600
Bi1—Cl3|Br3	2.767(2)	C3—C4	1.338(18)
Bi1—Cl2|Br2	2.723(2)	C4—H4A	0.9700
Bi1—Cl4|Br4^{ii}	2.8596(5)	C4—H4B	0.9700
Bi1—Cl4|Br4	2.8596(5)	N1—H1A	0.8900
Bi1—Cl4|Br4	2.8596(5)	N1—H1B	0.8900
Bi1—Cl2|Br2	2.723(2)	N1—H1C	0.8900
Bi1—Cl1|Br1	2.6358(12)	N1—C2	1.5320
Bi1—Cl3|Br3	2.767(2)	C2—H2D	0.9700
N2—H2A	0.8900	C2—H2E	0.9700
N2—H2B	0.8900	C2—C1	1.5189
N2—H2C	0.8900	C1—H1D	0.9600
N2—C4	1.447(15)	C1—H1E	0.9600
C3—H3A	0.9600	C1—H1F	0.9600

***x* = 2.27**			
Atoms 1,2	**d 1,2 [Å]**	**Atoms 1,2**	**d 1,2 [Å]**
Bi1—Cl1|Br1	2.6680(13)	C4—H4B	0.9700
Bi1—Cl1|Br1^{i}	2.6680(13)	C4—C3	1.36(2)
Bi1—Br3|Cl3	2.7925(19)	C3—H3A	0.9600
Bi1—Cl2|Br2	2.757(2)	C3—H3B	0.9600
Bi1—Cl4|Br4	2.8842(5)	C3—H3C	0.9600
Bi1—Cl4|Br4^{ii}	2.8841(5)	C1—H1A	0.9600
Bi1—Br3|Cl3	2.7925(19)	C1—H1B	0.9600
Bi1—Cl1|Br1	2.6680(13)	C1—H1C	0.9600
Bi1—Cl4|Br4	2.8842(5)	C1—C2	1.5315
Bi1—Cl2|Br2	2.757(2)	C2—H2D	0.9700
N2—H2A	0.8900	C2—H2E	0.9700
N2—H2B	0.8900	C2—N1	1.5193
N2—H2C	0.8900	N1—H1D	0.8900
N2—C4	1.440(17)	N1—H1E	0.8900
C4—H4A	0.9700	N1—H1F	0.8900

***x* = 3.125**			
Atoms 1,2	**d 1,2 [Å]**	**Atoms 1,2**	**d 1,2 [Å]**
Bi1—Br1|Cl1^{i}	2.693(1)	N1—H1E	0.8900
Bi1—Br1|Cl1	2.693(1)	N1—H1F	0.8900
Bi1—Br3|Cl3	2.8120(14)	N1—C2	1.425(14)
Bi1—Br2|Cl2	2.7846(14)	C2—H2A	0.9700
Bi1—Cl4|Br4^{ii}	2.9200(4)	C2—H2B	0.9700
Bi1—Cl4|Br4	2.9200(4)	N2—H2C	0.8900
Bi1—Br1|Cl1	2.693(1)	N2—H2D	0.8900

Bi1—Br3|Cl3	2.8120(14)	N2—H2E	0.8900
Bi1—Cl4|Br4	2.9200(4)	N2—C4	1.5317
Bi1—Br2|Cl2	2.7846(14)	C4—H4A	0.9700
C1—H1A	0.9600	C4—H4B	0.9700
C1—H1B	0.9600	C4—C3	1.5198
C1—H1C	0.9600	C3—H3A	0.9600
C1—C2	1.363(17)	C3—H3B	0.9600
N1—H1D	0.8900	C3—H3C	0.9600

***x* = 5**			
Atoms 1,2	**d 1,2 [Å]**	**Atoms 1,2**	**d 1,2 [Å]**
Bi1—Br1	2.7159(10)	C1—H1D	0.9600
Bi1—Br1^{i}	2.716(1)	C1—H1E	0.9600
Bi1—Br2	2.8224(15)	C1—H1F	0.9600
Bi1—Br3	2.8377(15)	N2—H2C	0.8900
Bi1—Br4	3.0045(5)	N2—H2D	0.8900
Bi1—Br4^{ii}	3.0045(5)	N2—H2E	0.8900
N1—H1A	0.8900	N2—C4	1.5320
N1—H1B	0.8900	C4—H4A	0.9700
N1—H1C	0.8900	C4—H4B	0.9700
N1—C2	1.445(18)	C4—C3	1.5189
C2—H2A	0.9700	C3—H3A	0.9600
C2—H2B	0.9700	C3—H3B	0.9600
C2—C1	1.38(2)	C3—H3C	0.9600

***x* = 0 (160 K)**			
Atoms 1,2	**d 1,2 [Å]**	**Atoms 1,2**	**d 1,2 [Å]**
Bi1—Cl1	2.548(2)	N1—C2	1.477(14)
Bi1—Cl2	2.594(2)	C4—H4A	0.9700
Bi1—Cl3	2.688(3)	C4—H4B	0.9700
Bi1—Cl4	2.839(2)	C4—C3	1.52(2)
Bi1—Cl4^{i}	2.928(2)	C2—H2D	0.9700
Bi1—Cl5	2.715(3)	C2—H2E	0.9700
N2—H2A	0.8900	C2—C1	1.509(19)
N2—H2B	0.8900	C3—H3A	0.9600
N2—H2C	0.8900	C3—H3B	0.9600
N2—C4	1.491(16)	C3—H3C	0.9600
N1—H1A	0.8900	C1—H1D	0.9600
N1—H1B	0.8900	C1—H1E	0.9600
N1—H1C	0.8900	C1—H1F	0.9600

***x* = 0 (90 K)**			
Atoms 1,2	**d 1,2 [Å]**	**Atoms 1,2**	**d 1,2 [Å]**
Bi1—Cl1	2.538(3)	C1—H1E	0.9700
Bi1—Cl2	2.593(3)	C4—H4A	0.9600
Bi1—Cl3	2.685(3)	C4—H4B	0.9600

Bi1—Cl4	2.842(3)	C4—H4C	0.9600
Bi1—Cl4^{i}	2.931(3)	C4—C3	1.5320
Bi1—Cl5	2.715(3)	C3—H3A	0.9700
N1—H1A	0.8900	C3—H3B	0.9700
N1—H1B	0.8900	C3—N2	1.5194
N1—H1C	0.8900	N2—H2D	0.8900
N1—C1	1.465(13)	N2—H2E	0.8900
C2—H2A	0.9600	N2—H2F	0.8900
C2—H2B	0.9600	Cl5—H2D^{ii}	3.8464(27)
C2—H2C	0.9600	Cl5—H2D^{iii}	3.3489(42)
C2—C1	1.534(15)	Cl5—H2E^{iii}	3.8253(45)
C1—H1D	0.9700	Cl5—H2F^{iii}	2.4356(45)

***x* = *1.15* (90 K)**			
Atoms 1,2	**d 1,2 [Å]**	**Atoms 1,2**	**d 1,2 [Å]**
Bi1—Cl5|Br5	2.788(2)	N009—H00I	0.8900
Bi1—Cl3|Br3	2.712(3)	N009—C00C	1.41(2)
Bi1—Cl2|Br2	2.609(6)	C00A—H00D	0.9600
Bi1—Cl4|Br4	2.863(4)	C00A—H00E	0.9600
Bi1—Cl4|Br4^{i}	2.931(4)	C00A—H00F	0.9600
Bi1—Cl3|Br3	2.712(3)	C00A—C1	1.45(3)
Bi1—Cl4|Br4	2.863(4)	C00B—H00J	0.9600
Bi1—Cl5|Br5	2.788(2)	C00B—H00K	0.9600
Bi1—Cl1|Br1	2.606(6)	C00B—H00L	0.9600
Bi1—Cl2|Br2	2.609(6)	C00B—C00C	1.38(3)
Bi1—Cl1|Br1	2.606(6)	C00C—H00M	0.9700
N008—H00A	0.8900	C00C—H00N	0.9700
N008—H00B	0.8900	C1—H1A	0.9700
N008—H00C	0.8900	C1—H1B	0.9700
N008—C1	1.43(2)	H00I—Cl5|Br5^{ii}	3.2709(89)
N009—H00G	0.8900	H00G—Cl5|Br5^{ii}	4.3851(86)
N009—H00H	0.8900	H00H—Cl5|Br5^{ii}	4.6859(90)

***x* = *2.12* (90 K)**			
Atoms 1,2	**d 1,2 [Å]**	**Atoms 1,2**	**d 1,2 [Å]**
Bi1—Br5|Cl5	2.815(3)	C4—H4C	0.9600
Bi1—Cl1|Br1	2.682(6)	C4—C6	1.47(5)
Bi1—Br2|Cl2	2.659(7)	C6—H6A	0.9700
Bi1—Cl3|Br3	2.742(4)	C6—H6B	0.9700

Bi1—Cl4|Br4	2.905(9)	C3—H3A	0.9600
Bi1—Cl4|Br4^{i}	2.877(8)	C3—H3B	0.9600
Bi1—Cl4|Br4	2.905(9)	C3—H3C	0.9600
Bi1—Br2|Cl2	2.659(7)	C3—C1	1.39(6)
Bi1—Cl3|Br3	2.742(4)	N2—H2A	0.8900
Bi1—Cl1|Br1	2.682(6)	N2—H2B	0.8900
Bi1—Br5|Cl5	2.815(3)	N2—H2C	0.8900
N1—H1A	0.8900	N2—C1	1.22(8)
N1—H1B	0.8900	C1—H1D	0.9700
N1—H1C	0.8900	C1—H1E	0.9700
N1—C6	1.44(4)	Br5|Cl5—H1C	3.0907(38)
C4—H4A	0.9600	Br5|Cl5—H1A	4.1058(30)
C4—H4B	0.9600	Br5|Cl5—H1B	2.9191(39)

***x* = 5 (90 K)**			
Atoms 1,2	**d 1,2 [Å]**	**Atoms 1,2**	**d 1,2 [Å]**
Bi1—Br1	2.736(5)	C2—H2D	0.9600
Bi1—Br2	2.698(5)	C2—H2E	0.9600
Bi1—Br3	2.8247(17)	C2—H2F	0.9600
Bi1—Br4	3.005(9)	C1—H1A	0.9600
Bi1—Br4^{i}	3.006(9)	C1—H1B	0.9600
Bi1—Br5	2.8425(18)	C1—H1C	0.9600
N2—H2A	0.8900	C1—C4	1.5318
N2—H2B	0.8900	C4—H4A	0.9700
N2—H2C	0.8900	C4—H4B	0.9700
N2—C3	1.44(2)	C4—N4	1.5188
C3—H3A	0.9700	N4—H4C	0.8900
C3—H3B	0.9700	N4—H4D	0.8900
C3—C2	1.43(3)	N4—H4E	0.8900

Table S9: Selected bond angles obtained from Single Crystals of $(C_2H_5NH_3)_2BiCl_{5-x}Br_x$

***x* = 0**			
Atoms 1,2,3	**Angle 1,2,3 [°]**	**Atoms 1,2,3**	**Angle 1,2,3 [°]**
Cl1^{i}—Bi1—Cl1	95.16(9)	C4—C3—H3B	109.500
Cl1—Bi1—Cl2	88.07(5)	C4—C3—H3C	109.500
Cl1^{i}—Bi1—Cl2	88.07(6)	N2—C4—H4A	106.500
Cl1—Bi1—Cl3	91.60(5)	N2—C4—H4B	106.500
Cl1^{i}—Bi1—Cl3	91.60(5)	C3—C4—N2	123.2(12)
Cl1—Bi1—Cl4^{ii}	90.65(4)	C3—C4—H4A	106.500
Cl1—Bi1—Cl4	174.19(5)	C3—C4—H4B	106.500
Cl1^{i}—Bi1—Cl4	90.64(4)	H4A—C4—H4B	106.500
Cl1^{i}—Bi1—Cl4^{ii}	174.18(5)	H1A—C1—H1B	109.500
Cl2—Bi1—Cl3	179.50(8)	H1A—C1—H1C	109.500
Cl2—Bi1—Cl4^{ii}	91.74(8)	H1B—C1—H1C	109.500
Cl2—Bi1—Cl4	91.74(8)	C2—C1—H1A	109.500
Cl3—Bi1—Cl4^{ii}	88.63(8)	C2—C1—H1B	109.500

Cl3—Bi1—Cl4	88.63(8)	C2—C1—H1C	109.500
Cl4^{ii}—Bi1—Cl4	83.55(2)	C1—C2—H2D	109.500
Bi1—Cl4—Bi1^{iii}	162.72(14)	C1—C2—H2E	109.500
H2A—N2—H2B	109.500	H2D—C2—H2E	108.100
H2A—N2—H2C	109.500	N1—C2—C1	110.600
H2B—N2—H2C	109.500	N1—C2—H2D	109.500
C4—N2—H2A	109.500	N1—C2—H2E	109.500
C4—N2—H2B	109.500	C2—N1—H1D	109.500
C4—N2—H2C	109.500	C2—N1—H1E	109.500
H3A—C3—H3B	109.500	C2—N1—H1F	109.500
H3A—C3—H3C	109.500	H1D—N1—H1E	109.500
H3B—C3—H3C	109.500	H1D—N1—H1F	109.500
C4—C3—H3A	109.500	H1E—N1—H1F	109.500

(i) 1-x, y, z; (ii) 0.5+x, y, 0.5-z; (iii) -0.5+x, y, 0.5-z.

***x* = 1.185**			
Atoms 1,2,3	**Angle 1,2,3 [°]**	**Atoms 1,2,3**	**Angle 1,2,3 [°]**
Cl1|Br1^{i}—Bi1—Cl1|Br1	93.89(7)	Bi1^{iii}—Cl4|Br4—Bi1	164.60(13)
Bi1^{iii}—Cl4|Br4—Bi1	164.60(13)	H1A—N1—H1B	109.500
H2A—N2—H2B	109.500	H1A—N1—H1C	109.500
H2A—N2—H2C	109.500	H1B—N1—H1C	109.500
H2B—N2—H2C	109.500	C2—N1—H1A	109.500
C4—N2—H2A	109.500	C2—N1—H1B	109.500
C4—N2—H2B	109.500	C2—N1—H1C	109.500
C4—N2—H2C	109.500	N1—C2—H2D	109.500
H3A—C3—H3B	109.500	N1—C2—H2E	109.500
H3A—C3—H3C	109.500	H2D—C2—H2E	108.100
H3B—C3—H3C	109.500	C1—C2—N1	110.600
C4—C3—H3A	109.500	C1—C2—H2D	109.500
C4—C3—H3B	109.500	C1—C2—H2E	109.500
C4—C3—H3C	109.500	C2—C1—H1D	109.500
N2—C4—H4A	107.200	C2—C1—H1E	109.500
N2—C4—H4B	107.200	C2—C1—H1F	109.500
C3—C4—N2	120.6(12)	H1D—C1—H1E	109.500
C3—C4—H4A	107.200	H1D—C1—H1F	109.500
C3—C4—H4B	107.200	H1E—C1—H1F	109.500
H4A—C4—H4B	106.800		

(i) 1-x, y, z; (ii) 0.5+x, y, 0.5-z; (iii) -0.5+x, y, 0.5-z.

***x* = 2.27**			
Atoms 1,2,3	**Angle 1,2,3 [°]**	**Atoms 1,2,3**	**Angle 1,2,3 [°]**
Cl4|Br4^{ii}—Bi1—Cl4|Br4	83.678(19)	H3B—C3—H3C	109.500
Bi1^{iii}—Cl4|Br4—Bi1	165.21(14)	H1A—C1—H1B	109.500
Bi1^{iii}—Cl4|Br4—Bi1	165.21(14)	H1A—C1—H1C	109.500
H2A—N2—H2B	109.500	H1B—C1—H1C	109.500
H2A—N2—H2C	109.500	C2—C1—H1A	109.500
H2B—N2—H2C	109.500	C2—C1—H1B	109.500
C4—N2—H2A	109.500	C2—C1—H1C	109.500

C4—N2—H2B	109.500	C1—C2—H2D	109.500
C4—N2—H2C	109.500	C1—C2—H2E	109.500
N2—C4—H4A	107.600	H2D—C2—H2E	108.100
N2—C4—H4B	107.600	N1—C2—C1	110.700
H4A—C4—H4B	107.000	N1—C2—H2D	109.500
C3—C4—N2	119.0(15)	N1—C2—H2E	109.500
C3—C4—H4A	107.600	C2—N1—H1D	109.500
C3—C4—H4B	107.600	C2—N1—H1E	109.500
C4—C3—H3A	109.500	C2—N1—H1F	109.500
C4—C3—H3B	109.500	H1D—N1—H1E	109.500
C4—C3—H3C	109.500	H1D—N1—H1F	109.500
H3A—C3—H3B	109.500	H1E—N1—H1F	109.500
H3A—C3—H3C	109.500		

(i) 1-x, y, z; (ii) -0.5+x, y, 1.5-z; (iii) 0.5+x, y, 1.5-z.

x = 3.125			
Atoms 1,2,3	**Angle 1,2,3 [°]**	**Atoms 1,2,3**	**Angle 1,2,3 [°]**
Br1|Cl1^{i}—Bi1—Br1|Cl1	94.33(5)	H2A—C2—H2B	107.100
Cl4|Br4^{ii}—Bi1—Cl4|Br4	83.361(14)	Bi1^{iii}—Cl4|Br4—Bi1	165.03(9)
Bi1^{iii}—Cl4|Br4—Bi1	165.03(9)	H2C—N2—H2D	109.500
H1A—C1—H1B	109.500	H2C—N2—H2E	109.500
H1A—C1—H1C	109.500	H2D—N2—H2E	109.500
H1B—C1—H1C	109.500	C4—N2—H2C	109.500
C2—C1—H1A	109.500	C4—N2—H2D	109.500
C2—C1—H1B	109.500	C4—N2—H2E	109.500
C2—C1—H1C	109.500	N2—C4—H4A	109.500
H1D—N1—H1E	109.500	N2—C4—H4B	109.500
H1D—N1—H1F	109.500	H4A—C4—H4B	108.100
H1E—N1—H1F	109.500	C3—C4—N2	110.600
C2—N1—H1D	109.500	C3—C4—H4A	109.500
C2—N1—H1E	109.500	C3—C4—H4B	109.500
C2—N1—H1F	109.500	C4—C3—H3A	109.500
C1—C2—N1	118.7(12)	C4—C3—H3B	109.500
C1—C2—H2A	107.600	C4—C3—H3C	109.500
C1—C2—H2B	107.600	H3A—C3—H3B	109.500
N1—C2—H2A	107.600	H3A—C3—H3C	109.500
N1—C2—H2B	107.600	H3B—C3—H3C	109.500

(i) 1-x, y, z; (ii) -0.5+x, y, 1.5-z; (iii) 0.5+x, y, 1.5-z.

x = 5			
Atoms 1,2,3	**Angle 1,2,3 [°]**	**Atoms 1,2,3**	**Angle 1,2,3 [°]**
Br1—Bi1—Br1^{i}	96.18(5)	C1—C2—H2A	107.700
Br1^{i}—Bi1—Br2	89.08(4)	C1—C2—H2B	107.700
Br1—Bi1—Br2	89.08(4)	C2—C1—H1D	109.500
Br1^{i}—Bi1—Br3	91.98(4)	C2—C1—H1E	109.500
Br1—Bi1—Br3	91.98(4)	C2—C1—H1F	109.500
Br1^{i}—Bi1—Br4	90.85(3)	H1D—C1—H1E	109.500

Br1^{i}—Bi1—Br4^{ii}	172.93(3)	H1D—C1—H1F	109.500
Br1—Bi1—Br4^{ii}	90.85(3)	H1E—C1—H1F	109.500
Br1—Bi1—Br4	172.93(3)	H2C—N2—H2D	109.500
Br2—Bi1—Br3	178.42(5)	H2C—N2—H2E	109.500
Br2—Bi1—Br4	90.23(5)	H2D—N2—H2E	109.500
Br2—Bi1—Br4^{ii}	90.23(5)	C4—N2—H2C	109.500
Br3—Bi1—Br4	88.57(5)	C4—N2—H2D	109.500
Br3—Bi1—Br4^{ii}	88.57(5)	C4—N2—H2E	109.500
Br4—Bi1—Br4^{ii}	82.120(15)	N2—C4—H4A	109.500
Bi1—Br4—Bi1^{iii}	164.33(7)	N2—C4—H4B	109.500
H1A—N1—H1B	109.500	H4A—C4—H4B	108.100
H1A—N1—H1C	109.500	C3—C4—N2	110.600
H1B—N1—H1C	109.500	C3—C4—H4A	109.500
C2—N1—H1A	109.500	C3—C4—H4B	109.500
C2—N1—H1B	109.500	C4—C3—H3A	109.500
C2—N1—H1C	109.500	C4—C3—H3B	109.500
N1—C2—H2A	107.700	C4—C3—H3C	109.500
N1—C2—H2B	107.700	H3A—C3—H3B	109.500
H2A—C2—H2B	107.100	H3A—C3—H3C	109.500
C1—C2—N1	118.5(17)	H3B—C3—H3C	109.500

(i) 1-x, y, z; (ii) -0.5+x, y, 1.5-z; (iii) 0.5+x, y, 1.5-z.

***x* = *0* (160 K)**			
Atoms 1,2,3	**Angle 1,2,3 [°]**	**Atoms 1,2,3**	**Angle 1,2,3 [°]**
Cl1—Bi1—Cl2	95.10(8)	N2—C4—H4A	109.600
Cl1—Bi1—Cl3	90.39(8)	N2—C4—H4B	109.600
Cl1—Bi1—Cl4^{i}	168.70(8)	N2—C4—C3	110.5(12)
Cl1—Bi1—Cl4	86.46(8)	H4A—C4—H4B	108.100
Cl1—Bi1—Cl5	90.47(8)	C3—C4—H4A	109.600
Cl2—Bi1—Cl3	86.72(7)	C3—C4—H4B	109.600
Cl2—Bi1—Cl4	178.43(8)	N1—C2—H2D	109.200
Cl2—Bi1—Cl4^{i}	96.11(8)	N1—C2—H2E	109.200
Cl2—Bi1—Cl5	90.74(8)	N1—C2—C1	112.2(10)
Cl3—Bi1—Cl4^{i}	88.82(8)	H2D—C2—H2E	107.900
Cl3—Bi1—Cl4	93.37(8)	C1—C2—H2D	109.200
Cl3—Bi1—Cl5	177.38(7)	C1—C2—H2E	109.200
Cl4—Bi1—Cl4^{i}	82.33(3)	C4—C3—H3A	109.500
Cl5—Bi1—Cl4	89.15(8)	C4—C3—H3B	109.500
Cl5—Bi1—Cl4^{i}	90.82(8)	C4—C3—H3C	109.500
Bi1—Cl4—Bi1^{ii}	150.17(11)	H3A—C3—H3B	109.500
H2A—N2—H2B	109.500	H3A—C3—H3C	109.500
H2A—N2—H2C	109.500	H3B—C3—H3C	109.500
H2B—N2—H2C	109.500	C2—C1—H1D	109.500
C4—N2—H2A	109.500	C2—C1—H1E	109.500
C4—N2—H2B	109.500	C2—C1—H1F	109.500
C4—N2—H2C	109.500	H1D—C1—H1E	109.500
H1A—N1—H1B	109.500	H1D—C1—H1F	109.500
H1A—N1—H1C	109.500	H1E—C1—H1F	109.500

H1B—N1—H1C	109.500	Cl5^{ii}—Cl4—Cl5	72.223(70)
C2—N1—H1A	109.500	Cl3^{ii}—Cl4—Cl3^{i}	77.093(53)
C2—N1—H1B	109.500	Cl3^{ii}—Cl4—Cl3	114.330(77)
C2—N1—H1C	109.500		

(i) 1.5-x, -0.5+y, z; (ii) 1.5-x, 0.5+y, z.

***x* = *0* (90 K)**			
Atoms 1,2,3	**Angle 1,2,3 [°]**	**Atoms 1,2,3**	**Angle 1,2,3 [°]**
Cl1—Bi1—Cl2	94.87(10)	C1—C2—H2C	109.500
Cl1—Bi1—Cl3	90.38(9)	N1—C1—C2	110.1(9)
Cl1—Bi1—Cl4^{i}	168.89(9)	N1—C1—H1D	109.600
Cl1—Bi1—Cl4	85.77(9)	N1—C1—H1E	109.600
Cl1—Bi1—Cl5	89.91(11)	C2—C1—H1D	109.600
Cl2—Bi1—Cl3	86.38(11)	C2—C1—H1E	109.600
Cl2—Bi1—Cl4	179.36(9)	H1D—C1—H1E	108.200
Cl2—Bi1—Cl4^{i}	96.18(8)	H4A—C4—H4B	109.500
Cl2—Bi1—Cl5	91.17(13)	H4A—C4—H4C	109.500
Cl3—Bi1—Cl4^{i}	89.13(8)	H4B—C4—H4C	109.500
Cl3—Bi1—Cl4	93.61(8)	C3—C4—H4A	109.500
Cl3—Bi1—Cl5	177.56(10)	C3—C4—H4B	109.500
Cl4—Bi1—Cl4^{i}	83.19(3)	C3—C4—H4C	109.500
Cl5—Bi1—Cl4	88.83(11)	C4—C3—H3A	109.500
Cl5—Bi1—Cl4^{i}	91.05(9)	C4—C3—H3B	109.500
Bi1—Cl4—Bi1^{ii}	148.34(11)	H3A—C3—H3B	108.100
H1A—N1—H1B	109.500	N2—C3—C4	110.600
H1A—N1—H1C	109.500	N2—C3—H3A	109.500
H1B—N1—H1C	109.500	N2—C3—H3B	109.500
C1—N1—H1A	109.500	C3—N2—H2D	109.500
C1—N1—H1B	109.500	C3—N2—H2E	109.500
C1—N1—H1C	109.500	C3—N2—H2F	109.500
H2A—C2—H2B	109.500	H2D—N2—H2E	109.500
H2A—C2—H2C	109.500	H2D—N2—H2F	109.500
H2B—C2—H2C	109.500	H2E—N2—H2F	109.500
C1—C2—H2A	109.500	Cl5—Cl4—Cl5^{ii}	71.979(69)
C1—C2—H2B	109.500		

(i) 1.5-x, y, -0.5+z; (ii) 1.5-x, y, 0.5+z; (iii) x, y, 1+z.

***x* = *1.15* (90 K)**			
Atoms 1,2,3	**Angle 1,2,3 [°]**	**Atoms 1,2,3**	**Angle 1,2,3 [°]**
Cl5|Br5—Bi1—Cl4|Br4^{i}	90.39(13)	H00E—C00A—H00F	109.500
Cl3|Br3—Bi1—Cl4|Br4^{i}	91.8(2)	C1—C00A—H00D	109.500
Cl2|Br2—Bi1—Cl4|Br4^{i}	165.5(2)	C1—C00A—H00E	109.500
Cl4|Br4—Bi1—Cl4|Br4^{i}	82.90(4)	C1—C00A—H00F	109.500
Cl3|Br3—Bi1—Cl4|Br4^{i}	91.8(2)	H00J—C00B—H00K	109.500
Cl4|Br4—Bi1—Cl4|Br4^{i}	82.90(4)	H00J—C00B—H00L	109.500
Cl5|Br5—Bi1—Cl4|Br4^{i}	90.39(13)	H00K—C00B—H00L	109.500
Cl1|Br1—Bi1—Cl4|Br4^{i}	101.6(2)	C00C—C00B—H00J	109.500

Cl2|Br2—Bi1—Cl4|Br4^{i}	165.5(2)	C00C—C00B—H00K	109.500
Cl1|Br1—Bi1—Cl4|Br4^{i}	101.6(2)	C00C—C00B—H00L	109.500
Bi1—Cl4|Br4—Bi1^{iii}	150.22(17)	N009—C00C—H00M	108.400
H00A—N008—H00B	109.500	N009—C00C—H00N	108.400
H00A—N008—H00C	109.500	C00B—C00C—N009	115.7(18)
H00B—N008—H00C	109.500	C00B—C00C—H00M	108.400
C1—N008—H00A	109.500	C00B—C00C—H00N	108.400
C1—N008—H00B	109.500	H00M—C00C—H00N	107.400
C1—N008—H00C	109.500	N008—C1—C00A	115.0(19)
H00G—N009—H00H	109.500	N008—C1—H1A	108.500
H00G—N009—H00I	109.500	N008—C1—H1B	108.500
H00H—N009—H00I	109.500	C00A—C1—H1A	108.500
C00C—N009—H00G	109.500	C00A—C1—H1B	108.500
C00C—N009—H00H	109.500	H1A—C1—H1B	107.500
C00C—N009—H00I	109.500	Bi1—Cl4|Br4—Bi1^{iii}	150.22(17)
H00D—C00A—H00E	109.500	Cl5|Br5^{iii}—Cl4|Br4—Cl5|Br5	72.331(84)
H00D—C00A—H00F	109.500		

(i) 1.5-x, y, 0.5+z; (ii) x, y, -1+z; (iii) 1.5-x, y, -0.5+z.

	x* = *2.12 **(90 K)**		
Atoms 1,2,3	**Angle 1,2,3 [°]**	**Atoms 1,2,3**	**Angle 1,2,3 [°]**
Br5|Cl5—Bi1—Cl4|Br4^{i}	89.0(2)	N1—C6—H6A	109.000
Cl1|Br1—Bi1—Cl4|Br4^{i}	102.9(3)	N1—C6—H6B	109.000
Br2|Cl2—Bi1—Cl4|Br4^{i}	165.8(3)	C4—C6—H6A	109.000
Cl3|Br3—Bi1—Cl4|Br4^{i}	92.2(3)	C4—C6—H6B	109.000
Cl4|Br4^{i}—Bi1—Cl4|Br4	82.84(8)	H6A—C6—H6B	107.800
Br2|Cl2—Bi1—Cl4|Br4^{i}	165.8(3)	H3A—C3—H3B	109.500
Cl3|Br3—Bi1—Cl4|Br4^{i}	92.2(3)	H3A—C3—H3C	109.500
Cl1|Br1—Bi1—Cl4|Br4^{i}	102.9(3)	H3B—C3—H3C	109.500
Br5|Cl5—Bi1—Cl4|Br4^{i}	89.0(2)	C1—C3—H3A	109.500
Bi1^{ii}—Cl4|Br4—Bi1	155.6(4)	C1—C3—H3B	109.500
Bi1^{ii}—Cl4|Br4—Bi1	155.6(4)	C1—C3—H3C	109.500
H1A—N1—H1B	109.500	H2A—N2—H2B	109.500
H1A—N1—H1C	109.500	H2A—N2—H2C	109.500
H1B—N1—H1C	109.500	H2B—N2—H2C	109.500
C6—N1—H1A	109.500	C1—N2—H2A	109.500
C6—N1—H1B	109.500	C1—N2—H2B	109.500
C6—N1—H1C	109.500	C1—N2—H2C	109.500
H4A—C4—H4B	109.500	C3—C1—H1D	104.400
H4A—C4—H4C	109.500	C3—C1—H1E	104.400
H4B—C4—H4C	109.500	N2—C1—C3	131.(9)
C6—C4—H4A	109.500	N2—C1—H1D	104.400
C6—C4—H4B	109.500	N2—C1—H1E	104.400
C6—C4—H4C	109.500	H1D—C1—H1E	105.600
N1—C6—C4	113.(3)	Br5|Cl5—Cl4|Br4—Br5|Cl5^{ii}	75.479(168)

((i) 1.5-x, y, -0.5+z; (ii) 1.5-x, y, 0.5+z.

x= 5 (90 K)			
Atoms 1,2,3	**Angle 1,2,3 [°]**	**Atoms 1,2,3**	**Angle 1,2,3 [°]**
Br1—Bi1—Br3	87.8(2)	C2—C3—H3B	108.600
Br1—Bi1—Br4	172.7(3)	C3—C2—H2D	109.500
Br1—Bi1—Br4^{i}	90.7(3)	C3—C2—H2E	109.500
Br1—Bi1—Br5	93.4(2)	C3—C2—H2F	109.500
Br2—Bi1—Br1	96.14(6)	H2D—C2—H2E	109.500
Br2—Bi1—Br3	90.4(2)	H2D—C2—H2F	109.500
Br2—Bi1—Br4^{i}	173.1(3)	H2E—C2—H2F	109.500
Br2—Bi1—Br4	91.1(3)	H1A—C1—H1B	109.500
Br2—Bi1—Br5	90.7(2)	H1A—C1—H1C	109.500
Br3—Bi1—Br4^{i}	89.70(15)	H1B—C1—H1C	109.500
Br3—Bi1—Br4	90.88(14)	C4—C1—H1A	109.500
Br3—Bi1—Br5	178.32(5)	C4—C1—H1B	109.500
Br4—Bi1—Br4^{i}	82.055(15)	C4—C1—H1C	109.500
Br5—Bi1—Br4	87.82(16)	C1—C4—H4A	109.500
Br5—Bi1—Br4^{i}	89.06(15)	C1—C4—H4B	109.500
Bi1—Br4—Bi1^{ii}	164.47(8)	H4A—C4—H4B	108.100
H2A—N2—H2B	109.500	N4—C4—C1	110.600
H2A—N2—H2C	109.500	N4—C4—H4A	109.500
H2B—N2—H2C	109.500	N4—C4—H4B	109.500
C3—N2—H2A	109.500	C4—N4—H4C	109.500
C3—N2—H2B	109.500	C4—N4—H4D	109.500
C3—N2—H2C	109.500	C4—N4—H4E	109.500
N2—C3—H3A	108.600	H4C—N4—H4D	109.500
N2—C3—H3B	108.600	H4C—N4—H4E	109.500
H3A—C3—H3B	107.500	H4D—N4—H4E	109.500
C2—C3—N2	115.(2)	Br5^{ii}—Br4—Br5	77.491(198)
C2—C3—H3A	108.600		

(i) 0.5-x, y, -0.5+z; (ii) 0.5-x, y, 0.5+z.

SEM

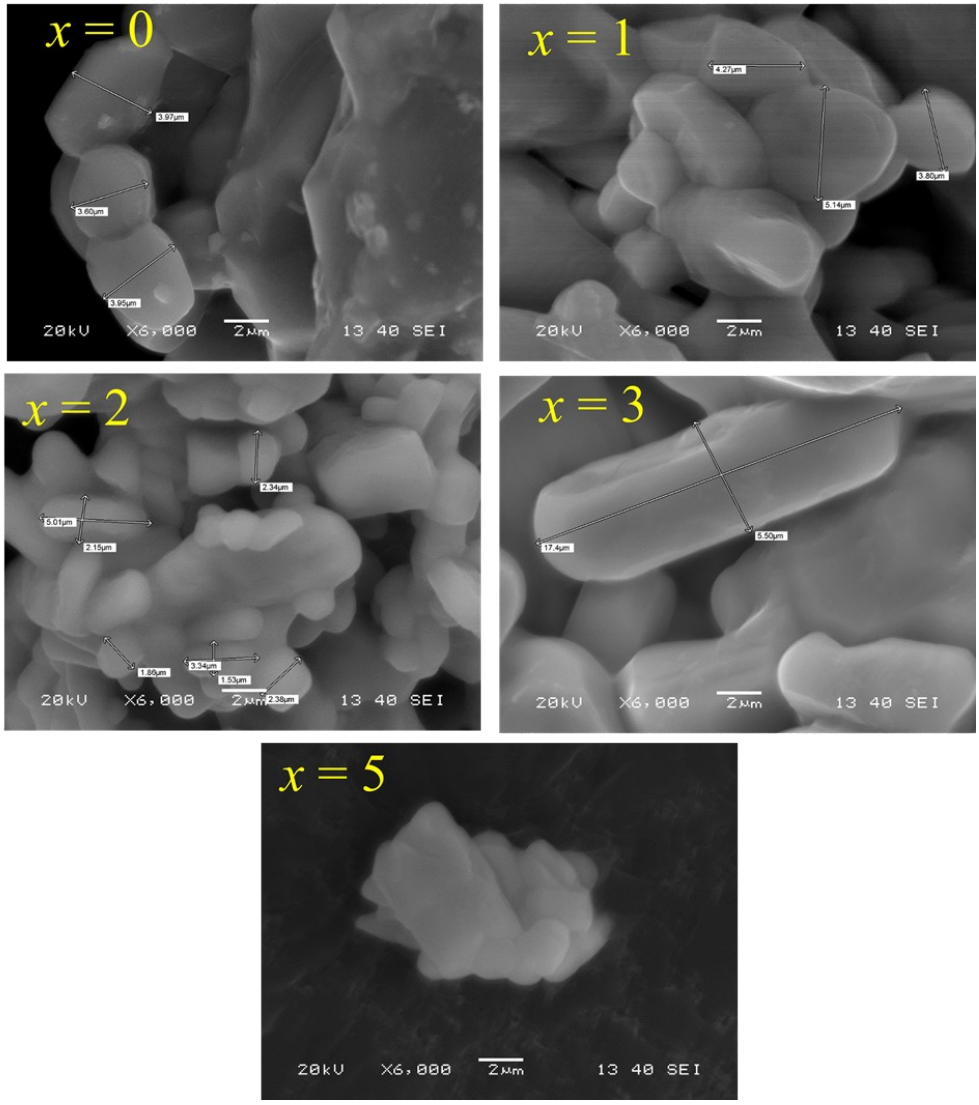


Figure S1: SEM images of $(C_2H_5NH_3)_2BiCl_{5-x}Br_x$ series.

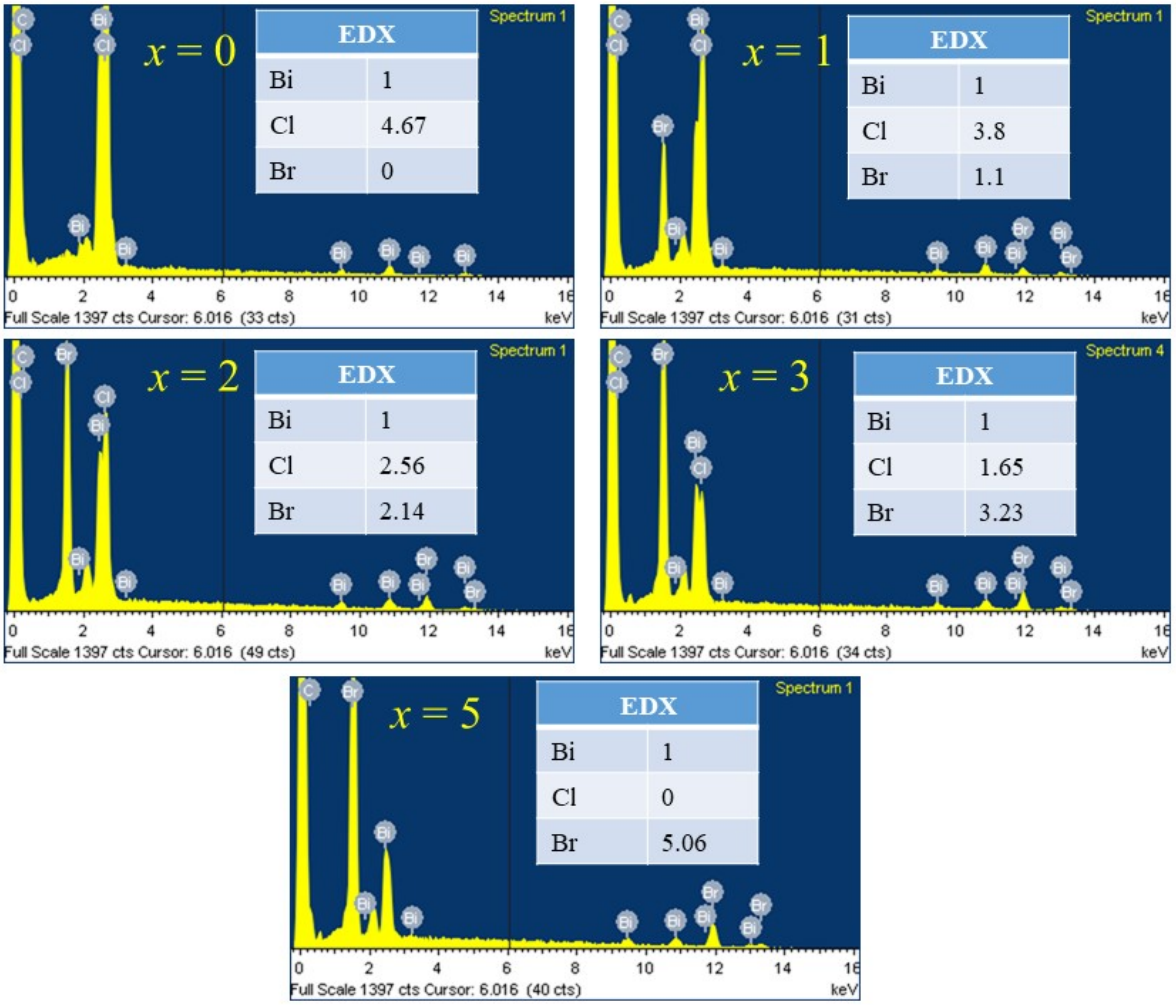


Figure S2: EDX spectra from SEM study of $(C_2H_5NH_3)_2BiCl_{5-x}Br_x$ series.

TGA

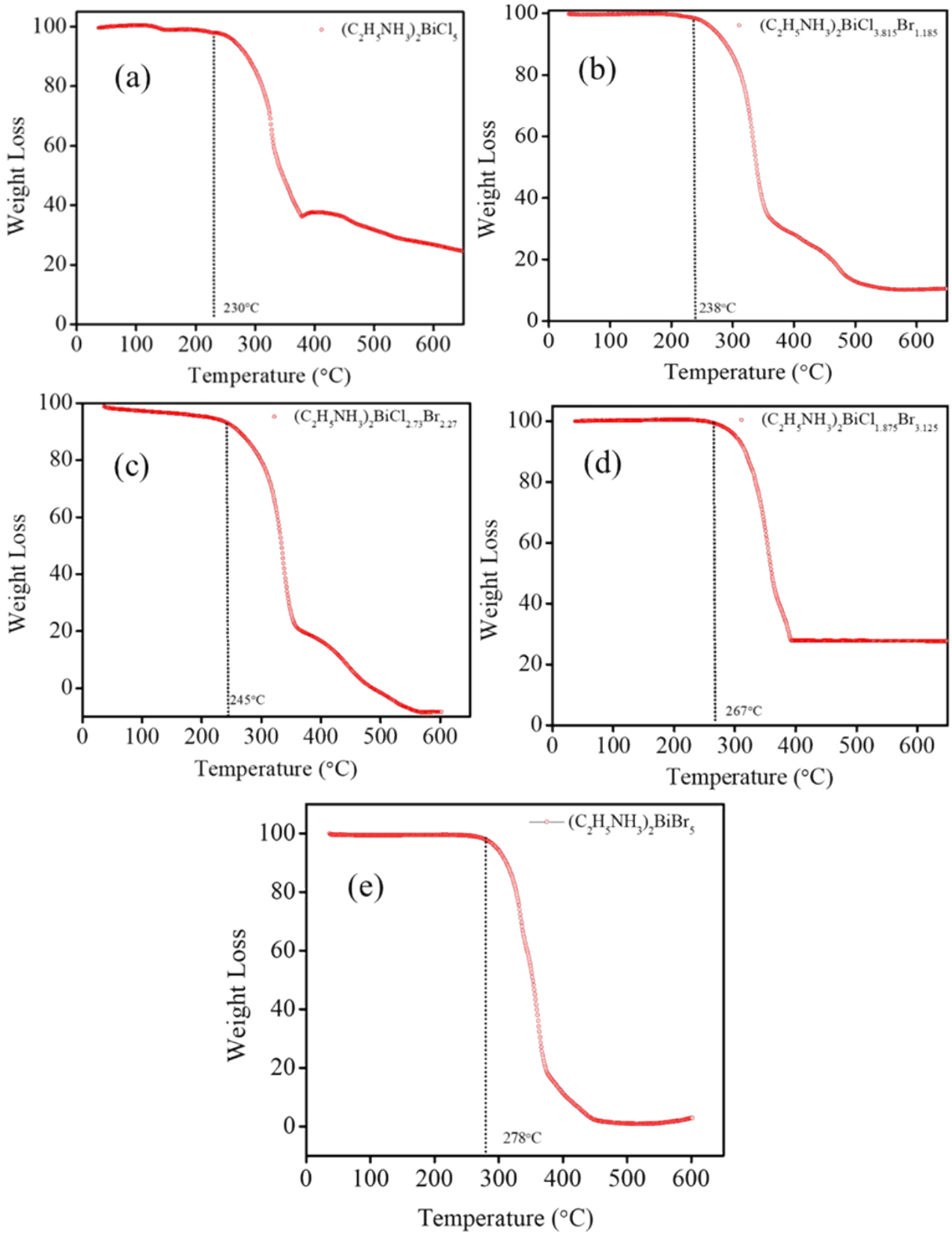


Figure S3: TGA data of $(C_2H_5NH_3)_2BiCl_{5-x}Br_x$ series.

Dielectric Measurement:

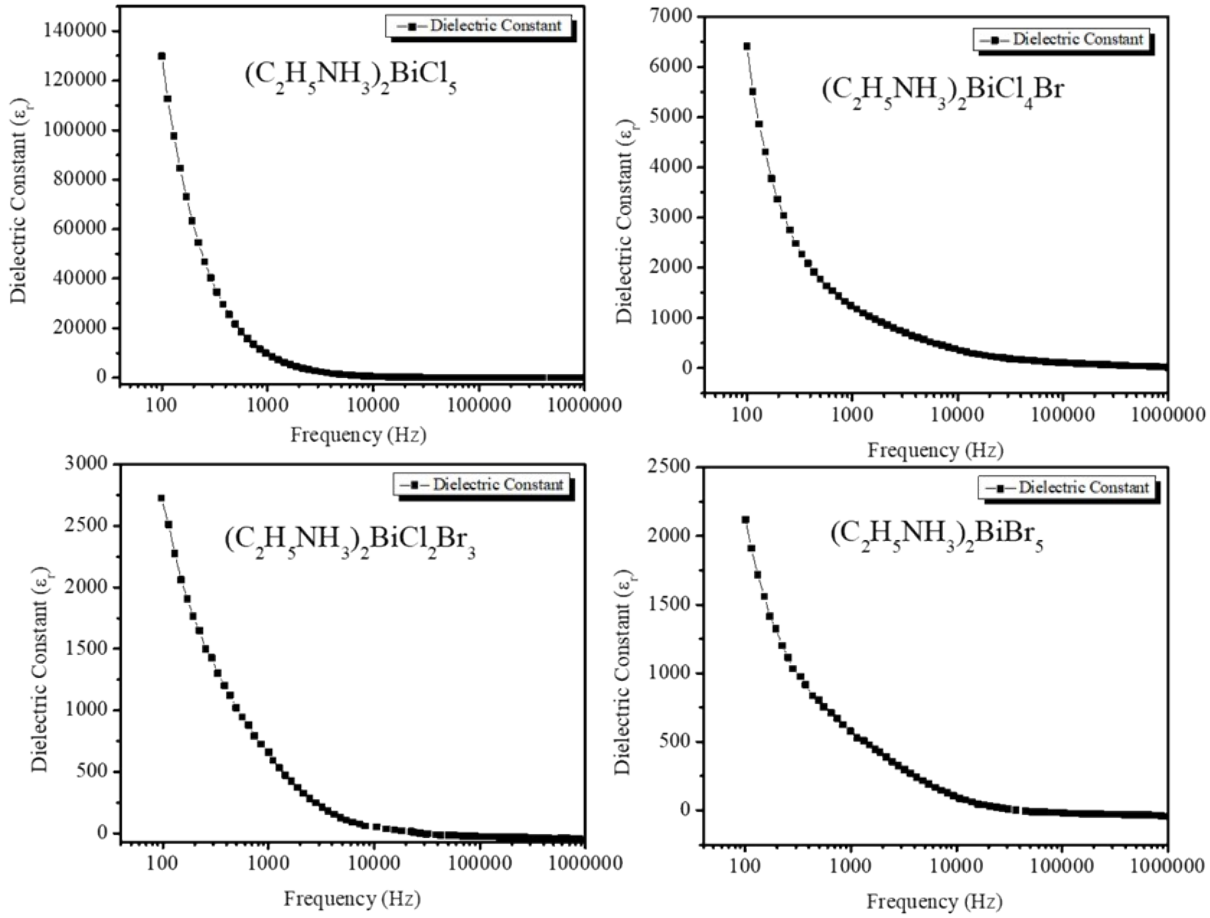


Figure S4: Dielectric constant Vs frequency at room temperature for selected compositions from $(C_2H_5NH_3)_2BiCl_{5-x}Br_x$ series.

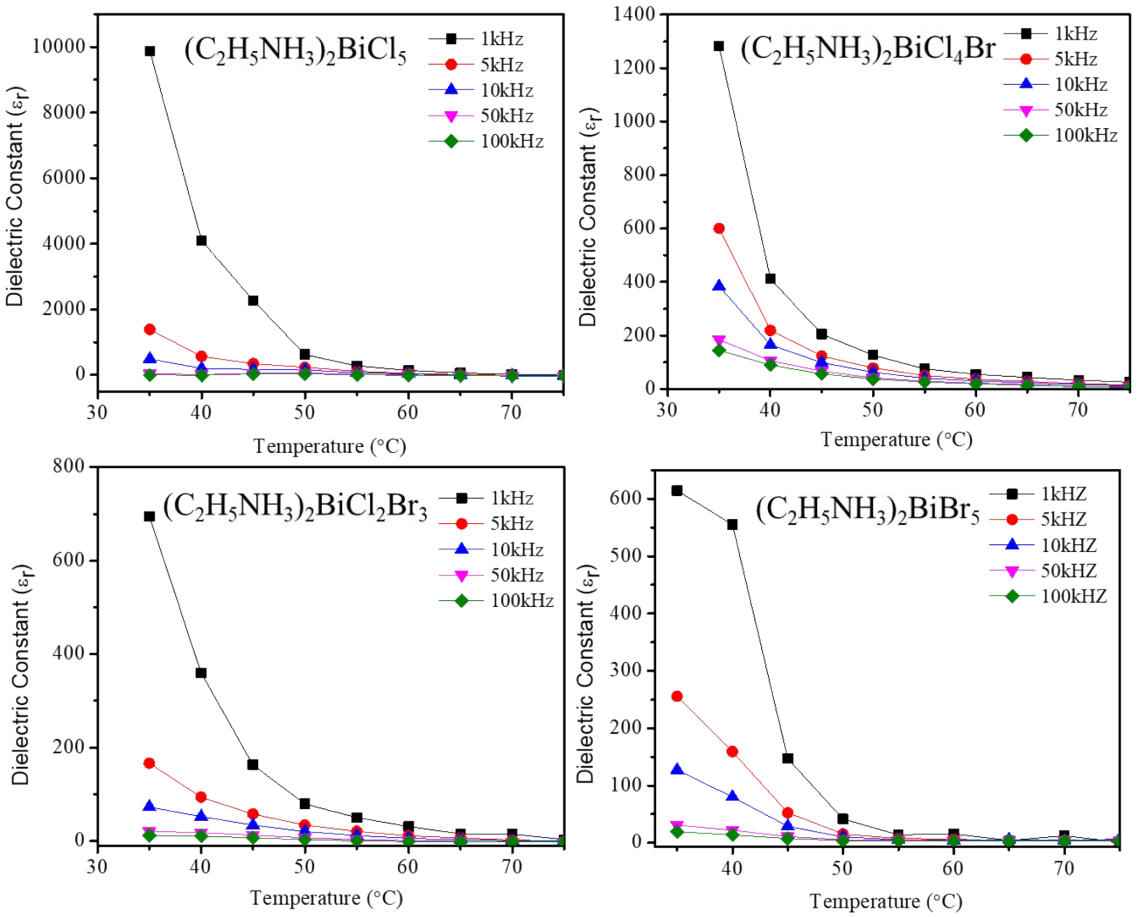


Figure S5: Dielectric constant Vs temperature at various frequencies for selected compositions from $(C_2H_5NH_3)_2BiCl_{5-x}Br_x$ series.

Raman:

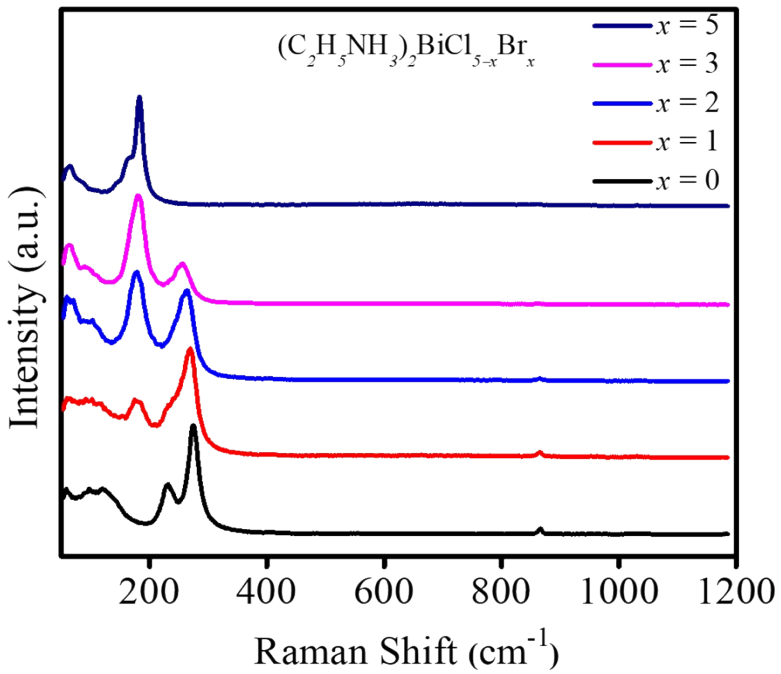


Figure S6: Raman bands of $(C_2H_5NH_3)_2BiCl_{5-x}Br_x$ series showing no bands after 350 cm^{-1}

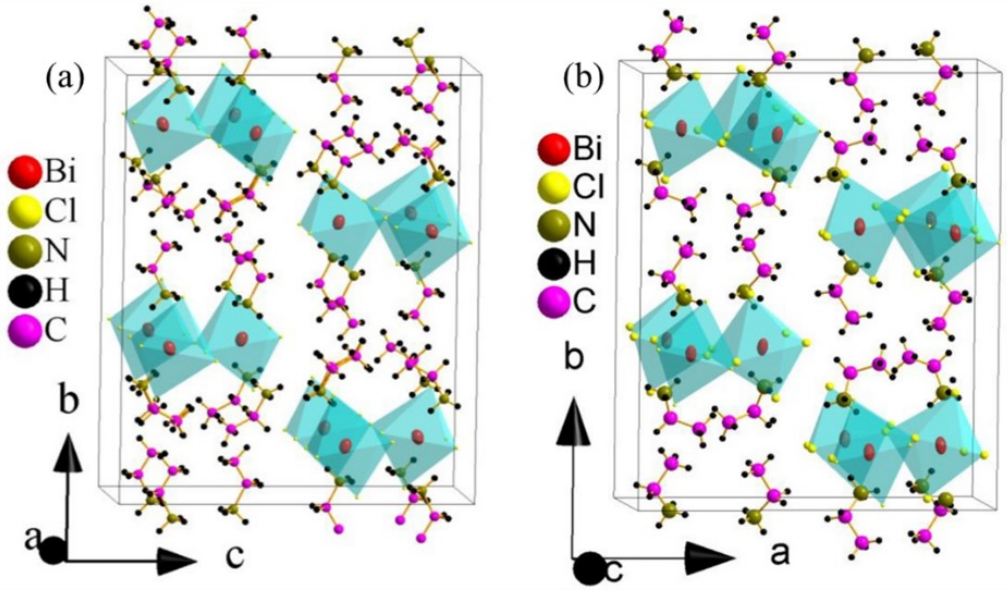
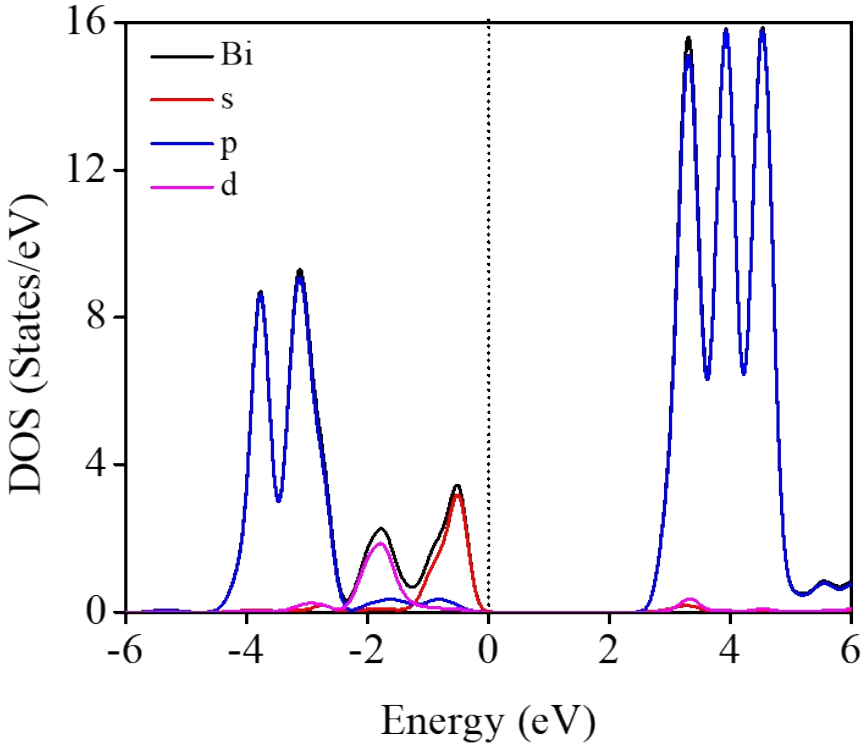
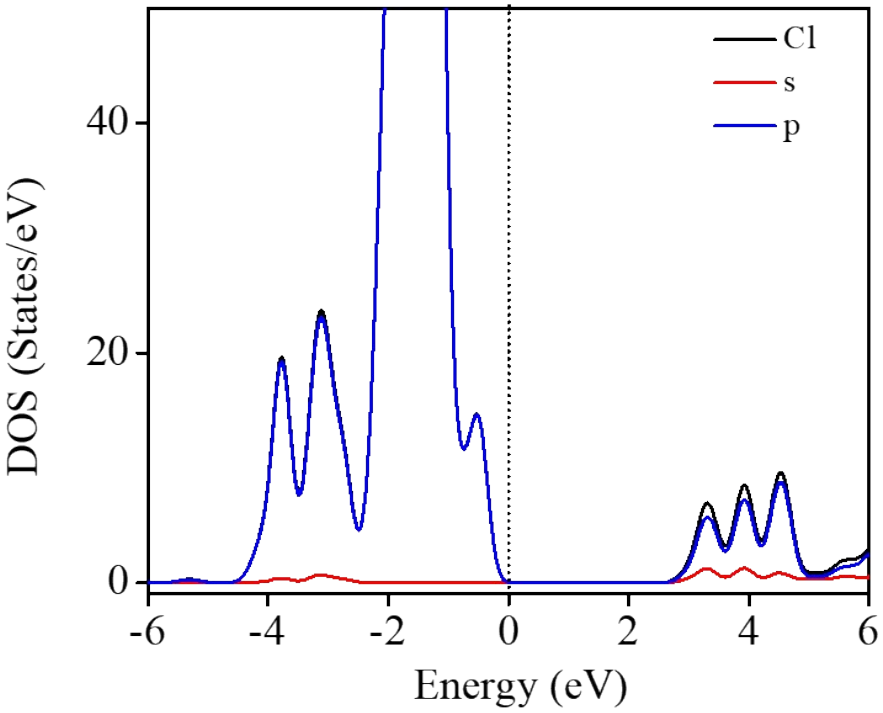


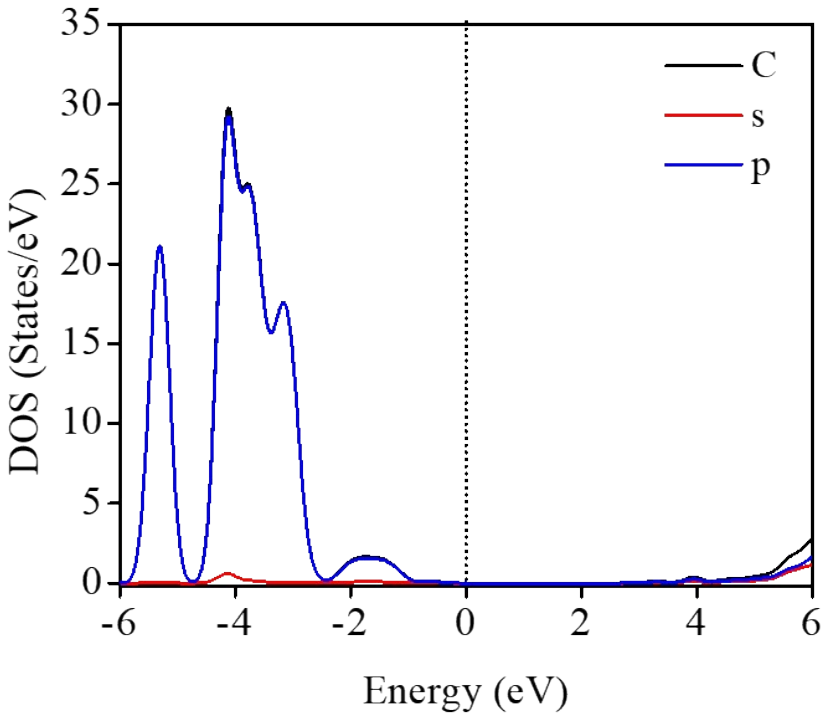
Figure S7. Crystal Structure of (a) RT Phase (Space gr. C*mca*), (b) LT Phase (Space gr. A*ba2*) of $(C_2H_5NH_3)_2BiCl_5$.

Partial DOS:

$(C_2H_5NH_3)_2BiCl_5$




Cl
s
p
DOS (States/eV)
40
20
0
-6
-4
-2
0
2
4
6
Energy (eV)


C
s
p
DOS (States/eV)
35
30
25
20
15
10
5
0
-6
-4
-2
0
2
4
6
Energy (eV)

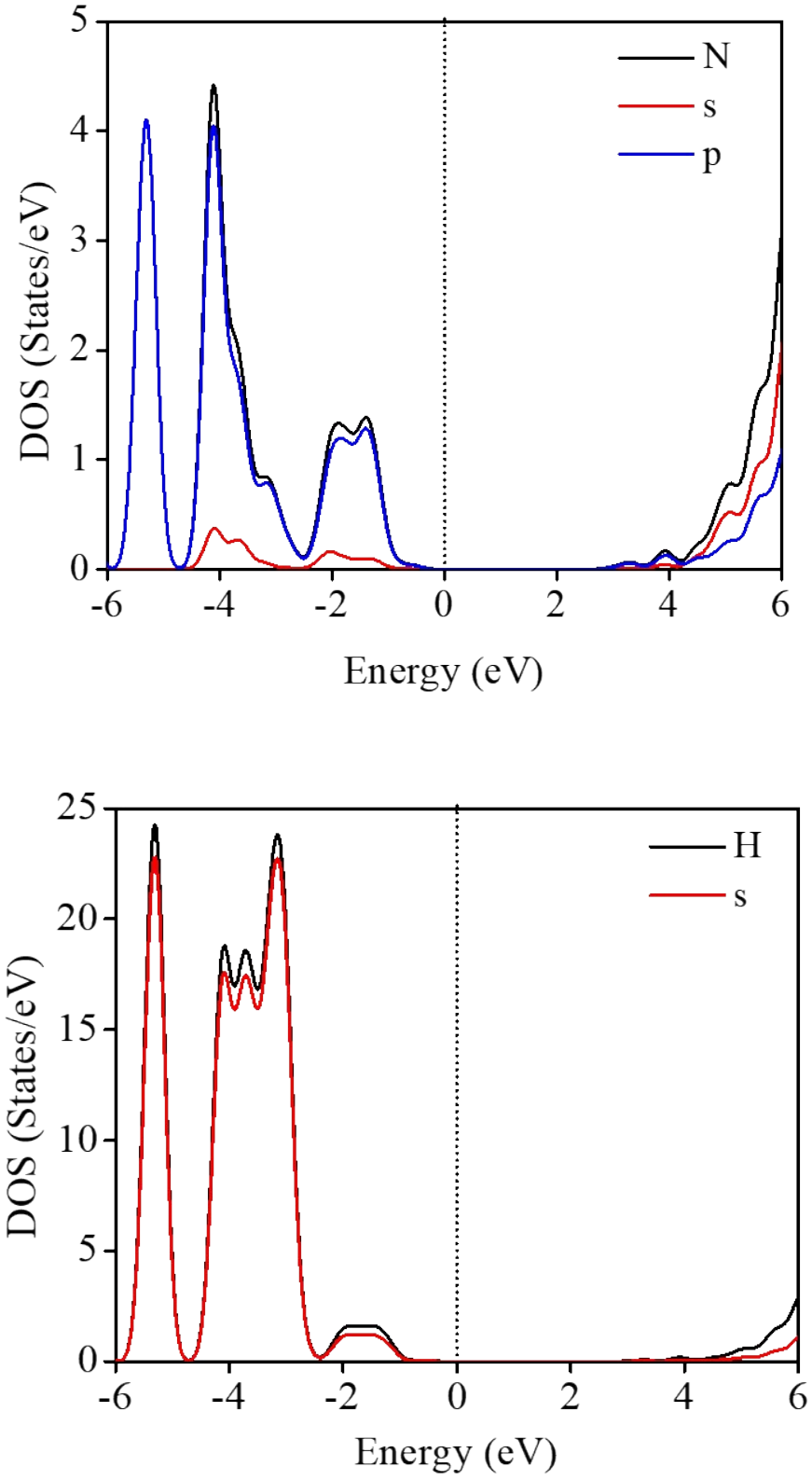
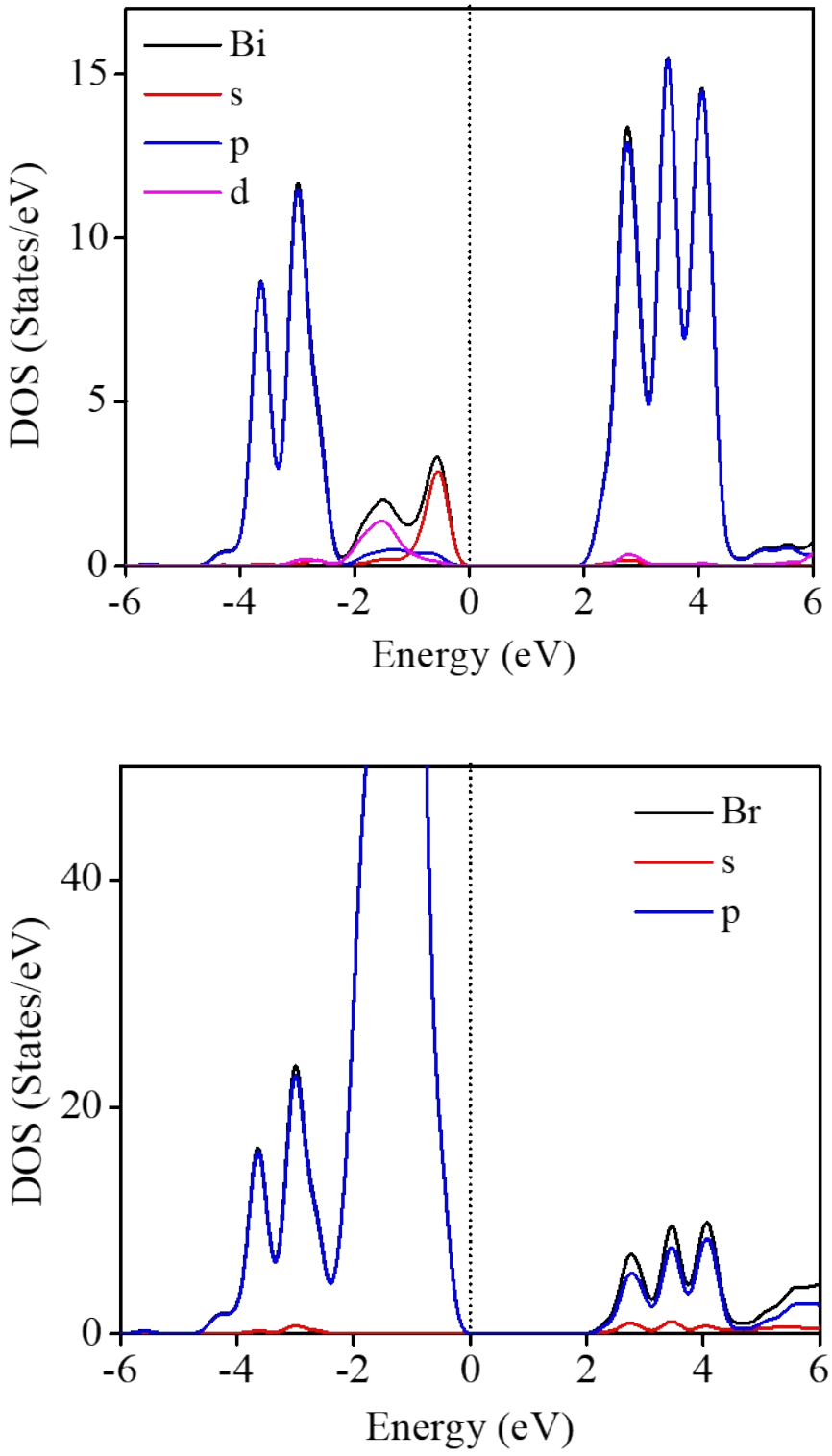
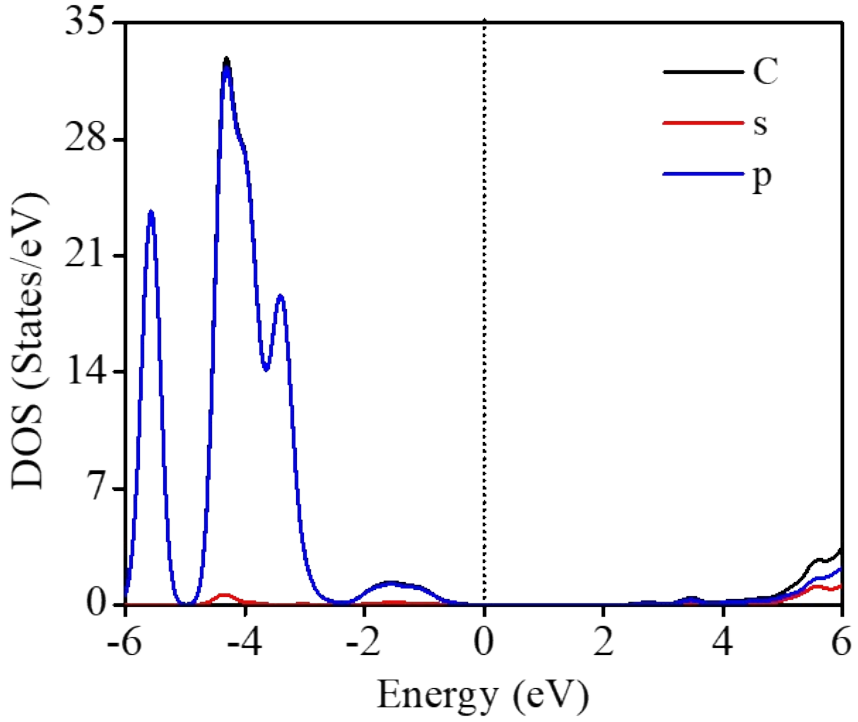
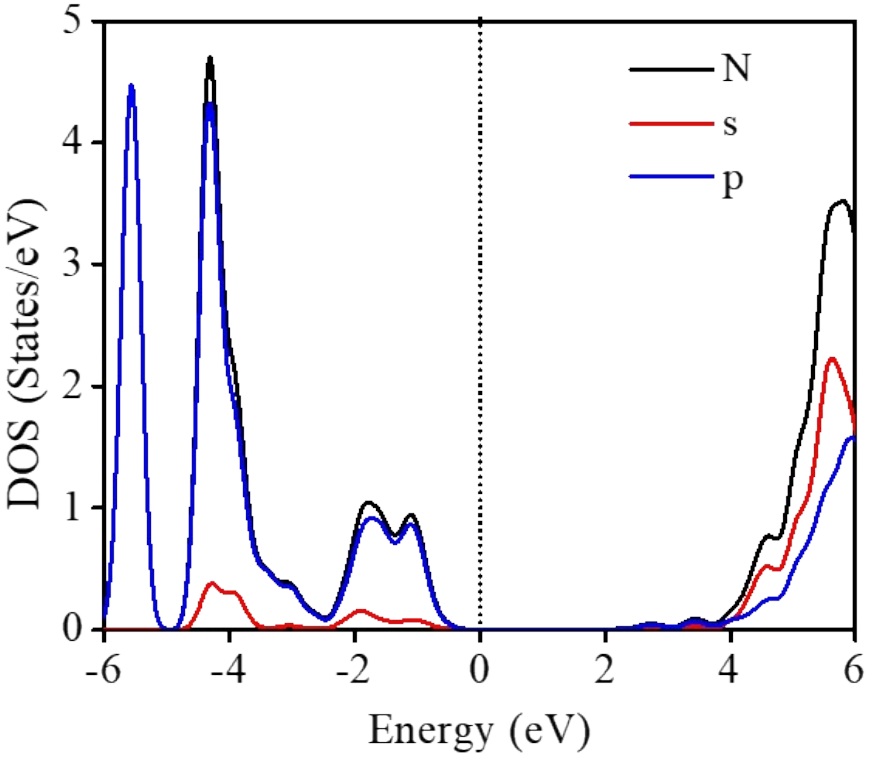


Figure S8: Partial DOS of $(C_2H_5NH_3)_2BiCl_5$ compound.

$(C_2H_5NH_3)_2BiBr_5$




35
28
21
14
7
0
DOS (States/eV)
-6
-4
-2
0
2
4
6
Energy (eV)
C
s
p


5
4
3
2
1
0
DOS (States/eV)
-6
-4
-2
0
2
4
6
Energy (eV)
N
s
p

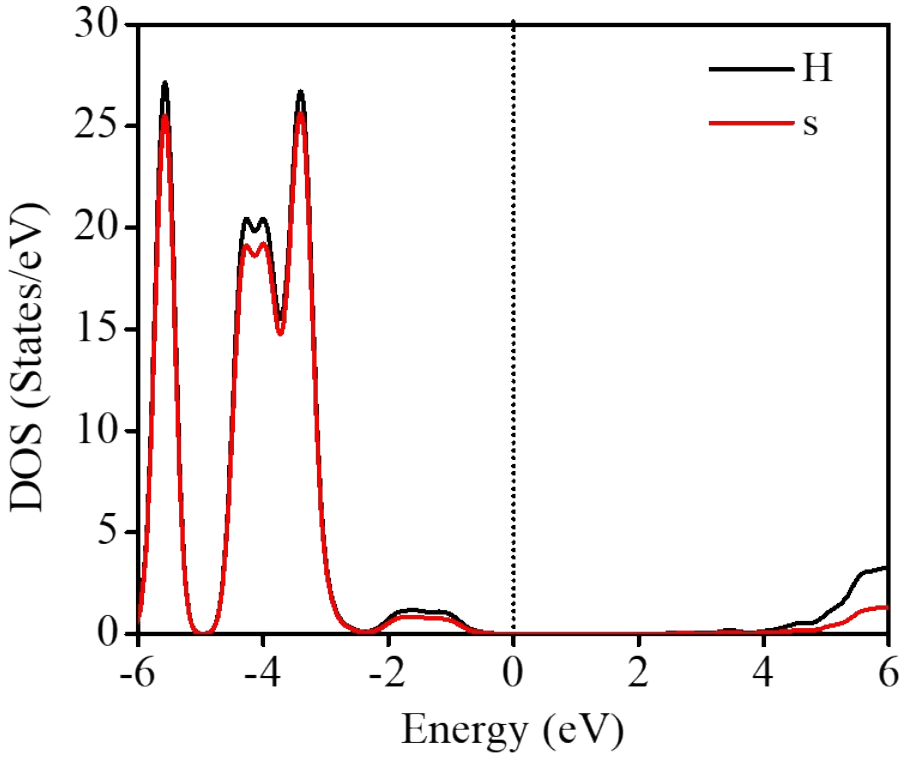


Figure S9: Partial DOS of $(C_2H_5NH_3)_2BiBr_5$ compound.