Supporting Information

Symmetry Breaking of $A_3M_2X_9$-type Perovskites-Derivative Induced by Polar Quaternary Ammonium Cation: Achieving Efficient Nonlinear Optical Properties

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Table S1. Fractional atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $(BTA)_3Bi_2Cl_9$.

Atom	*x*	*y*	*z*	U_{eq}
Bi (1)	8325.2(2)	5772.0(2)	10057.2(2)	39.5 (7)
Bi (2)	5678.1(2)	6591.7(2)	9977.9(2)	38.8 (7)
Cl (1)	10105.3(15)	6232.7(9)	10474.2(12)	60.3(5)
Cl (2)	8741(2)	4880.6(10)	10896.4(16)	86.3(8)
Cl (3)	9027.2(18)	5308.9(10)	8829.8(13)	69.6(6)
Cl (4)	7199.2(15)	6390.8(8)	11242.0(10)	50.6(5)
Cl (5)	6227.5(15)	5371.1(8)	9693.1(10)	50.7(4)
Cl (6)	4072.1(16)	6266.3(9)	10724.6(12)	64.0(5)
Cl (7)	4578.1(17)	6763.1(10)	8708.0(11)	63.5(5)
Cl (8)	5548.9(16)	7660.9(8)	10395.3(12)	55.9(5)
Cl (9)	7558.6(16)	6803.2(9)	9167.7(11)	56.3(5)
N (1)	5562(4)	5408(2)	7126(3)	39.3(1)
C (14)	3541(7)	6125(4)	6215(5)	65(2)
C (15)	2963(8)	6626(5)	6078(6)	81(3)
C (16)	3429(10)	7138(5)	5943(6)	86(3)
C (17)	4482(10)	7168(4)	5925(6)	85(3)
C (18)	5086(7)	6674(4)	6079(5)	62(2)
C (19)	4616(6)	6142(3)	6222(4)	47.5(2)
C (20)	5248(6)	5590(3)	6300(4)	47.3(2)
C (21)	6212(6)	5883(3)	7542(4)	46.2(2)
C (22)	7247(6)	6020(4)	7198(5)	62(2)
C (23)	6176(7)	4846(3)	7048(4)	55(2)
C (24)	6565(8)	4579(4)	7812(5)	69(3)
C (25)	4640(6)	5322(3)	7615(4)	50.2(2)
C (26)	3927(9)	4819(4)	7353(6)	84(3)
N (2)	846(4)	7076(3)	8174(3)	43.7(1)
C (27)	2120(7)	7485(4)	9886(4)	60(2)
C (28)	2814(7)	7842(5)	10267(5)	73(3)
C (29)	2787(8)	8427(5)	10126(6)	81(3)
C (30)	2058(9)	8666(4)	9626(5)	77(3)
C (31)	1334(8)	8302(4)	9251(5)	65(2)
C (32)	1352(6)	7699(3)	9372(4)	47.1(2)
C (33)	567(6)	7299(3)	8979(4)	49.1(2)
C (34)	963(6)	7570(4)	7610(4)	50.1(2)
C (35)	-5(8)	7916(4)	7427(5)	79(3)
C (36)	-19(6)	6665(4)	7917(5)	64(2)

Table S1. Fractional atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $(BTA)_3Bi_2Cl_9$.

Atom	*x*	*y*	*z*	U_{eq}
C (37)	107(7)	6375(4)	7130(5)	75(3)
C (38)	1881(6)	6757(3)	8228(5)	53.7(19)
C (39)	1908(7)	6194(4)	8678(5)	75(3)
N (3)	750(6)	3590(3)	7937(5)	71.4(18)
C (1)	2166(13)	4900(6)	9817(8)	125(4)
C (2)	3136(12)	4840(6)	9647(7)	113(4)
C (3)	3563(12)	4363(7)	9337(7)	120(4)
C (4)	2898(10)	3924(6)	9055(6)	101(3)
C (5)	1851(8)	3981(4)	9112(5)	72(2)
C (6)	1455(11)	4423(6)	9526(7)	114(3)
C (7)	1154(9)	3505(4)	8768(6)	83(3)
C (8)	1602(9)	3519(5)	7364(7)	103(3)
C (9)	1983(10)	2843(6)	7326(8)	129(5)
C (10)	-105(9)	3145(5)	7707(7)	105(3)
C (11)	-1115(9)	3245(6)	8120(8)	122(4)
C (12)	216(11)	4186(5)	7746(9)	120(4)
C (13)	967(12)	4653(6)	7471(8)	138(5)

U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Table S2. Bond lengths for $(BTA)_3Bi_2Cl_9$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Bi (1)	Cl (1)	2.596(2)	N (2)	C (34)	1.501(9)
Bi (1)	Cl (2)	2.541(2)	N (2)	C (36)	1.509(9)
Bi (1)	Cl (3)	2.561(2)	N (2)	C (38)	1.520(9)
Bi (1)	Cl (4)	2.918(2)	C (27)	C (28)	1.358(12)
Bi (1)	Cl (5)	2.896 (2)	C (27)	C (32)	1.385(10)
Bi (1)	Cl (9)	2.957(2)	C (28)	C (29)	1.362(13)
Bi (2)	Cl (4)	2.895(2)	C (29)	C (30)	1.359(13)
Bi (2)	Cl (5)	2.929(2)	C (30)	C (31)	1.387(13)
Bi (2)	Cl (6)	2.592(2)	C (31)	C (32)	1.397(11)
Bi (2)	Cl (7)	2.577(2)	C (32)	C (33)	1.502(10)
Bi (2)	Cl (8)	2.557(2)	C (34)	C (35)	1.500(12)
Bi (2)	Cl (9)	2.889(2)	C (36)	C (37)	1.521(12)
N (1)	C (20)	1.516(8)	C (38)	C (39)	1.502(11)
N (1)	C (21)	1.529(9)	N (3)	C (7)	1.510(12)
N (1)	C (23)	1.520(9)	N (3)	C (8)	1.515(13)
N (1)	C (25)	1.499(9)	N (3)	C (10)	1.537(13)
C (14)	C (15)	1.382(12)	N (3)	C (12)	1.557(14)
C (14)	C (19)	1.384(11)	C (1)	C (2)	1.303(18)
C (15)	C (16)	1.342(14)	C (1)	C (6)	1.496(18)
C (16)	C (17)	1.360(15)	C (2)	C (3)	1.343(17)
C (17)	C (18)	1.390(12)	C (3)	C (4)	1.393(17)
C (18)	C (19)	1.387(11)	C (4)	C (5)	1.363(14)
C (19)	C (20)	1.507(10)	C (5)	C (6)	1.350(15)
C (21)	C (22)	1.517(11)	C (5)	C (7)	1.516(13)
C (23)	C (24)	1.512(10)	C (8)	C (9)	1.625(15)
C (25)	C (26)	1.529(11)	C (10)	C (11)	1.527(15)
N (2)	C (33)	1.532(9)	C (12)	C (13)	1.529(17)

Table S3. Bond angles for $(BTA)_3Bi_2Cl_9$.

Atom Atom Atom	Angle/°	Atom Atom Atom	Angle/°
Cl (1) Bi (1) Cl (4)	94.10(6)	C (14) C (19) C (18)	117.9(7)
Cl (1) Bi1(1) Cl (5)	173.14(6)	C (14) C (19) C (20)	120.9(8)
Cl (1) Bi (1) Cl (9)	95.10(6)	C (18) C (19) C (20)	120.9(7)
Cl (2) Bi (1) Cl (1)	90.49(8)	C (19) C (20) N (1)	115.7(6)
Cl (2) Bi (1) Cl (3)	93.51(8)	C (22) C (21) N (1)	115.9(6)
Cl (2) Bi (1) Cl (4)	95.33(8)	C (24) C (23) N (1)	114.7(6)
Cl (2) Bi (1) Cl (5)	92.23(7)	N (1) C (25) C (26)	114.5(6)
Cl (2) Bi (1) Cl (9)	172.24(7)	C (34) N (2) C (33)	111.4(6)
Cl (3) Bi (1) Cl (1)	93.14(7)	C (34) N (2) C (36)	112.1(6)
Cl (3) Bi (1) Cl (4)	168.52(7)	C (34) N (2) C (38)	106.7(5)
Cl (3) Bi (1) Cl (5)	92.98(7)	C (36) N (2) C (33)	105.7(5)
Cl (3) Bi (1) Cl (9)	91.56(7)	C (36) N (2) C (38)	110.7(6)
Cl (4) Bi (1) Cl (9)	78.93(5)	C (38) N (2) C (33)	110.2(5)
Cl (5) Bi (1) Cl (4)	79.39(5)	C (28) C (27) C (32)	122.0(8)
Cl (5) Bi (1) Cl (9)	81.63(5)	C (27) C (28) C (29)	119.7(9)
Cl (4) Bi (2) Cl (5)	79.23(5)	C (30) C (29) C (28)	121.3(9)
Cl (6) Bi (2) Cl (4)	96.43(6)	C (29) C (30) C (31)	118.9(9)
Cl (6) Bi (2) Cl (5)	90.74(6)	C (30) C (31) C (32)	121.2(8)
Cl (6) Bi (2) Cl (9)	172.72(7)	C (27) C (32) C (31)	116.8(8)
Cl (7) Bi (2) Cl (4)	170.65(6)	C (27) C (32) C (33)	121.2(7)
Cl (7) Bi (2) Cl (5)	97.57(6)	C (31) C (32) C (33)	121.9(7)
Cl (7) Bi (2) Cl (6)	92.38(7)	C (32) C (33) N (2)	115.4(6)
Cl (7) Bi (2) Cl (9)	90.47(7)	C (35) C (34) N (2)	115.2(7)
Cl (8) Bi (2) Cl (4)	89.55(6)	N (2) C (36) C (37)	115.1(7)
Cl (8) Bi (2) Cl (5)	168.20(6)	C (39) C (38) N (2)	116.3(6)
Cl (8) Bi (2) Cl (6)	94.17(7)	C (7) N (3) C (8)	111.8(8)
Cl (8) Bi (2) Cl (7)	92.94(7)	C (7) N (3) C (10)	111.7(8)
Cl (8) Bi (2) Cl (9)	92.37(6)	C (7) N (3) C (12)	116.2(9)
Cl (9) Bi (2) Cl (4)	80.42(5)	C (8) N (3) C (10)	107.1(8)
Cl (9) Bi (2) Cl (5)	82.24(6)	C (8) N (3) C (12)	106.5(8)
Bi (2) Cl (4) Bi (1)	83.99(5)	C (10) N (3) C (12)	102.8(9)
Bi (1) Cl (5) Bi (2)	83.80(5)	C (2) C (1) C (6)	115.4(14)
Bi (2) Cl (9) Bi (1)	83.42(5)	C (1) C (2) C (3)	126.0(16)
C (20) N (1) C (21)	111.1(5)	C (2) C (3) C (4)	117.8(15)
C (20) N (1) C (23)	105.5(5)	C (5) C (4) C (3)	120.1(13)
C (23) N (1) C (21)	111.5(6)	C (4) C (5) C (7)	118.4(10)
C (25) N (1) C (20)	112.0(6)	C (6) C (5) C (4)	120.5(12)

Table S3. Bond angles for $(BTA)_3Bi_2Cl_9$.

Atom Atom Atom	Angle/°	Atom Atom Atom	Angle/°
C (25) N (1) C (21)	105.2(5)	C (6) C (5) C (7)	120.8(11)
C (25) N (1) C (23)	111.5(6)	C (5) C (6) C (1)	118.8(13)
C (15) C (14) C (19)	120.6(9)	N (3) C (7) C (5)	116.6(8)
C (16) C (15) C (14)	120.8(10)	N (3) C (8) C (9)	110.9(9)
C (15) C (16) C (17)	120.2(9)	C (11) C (10) N (3)	113.4(10)
C (16) C (17) C (18)	120.3(10)	C (13) C (12) N (3)	113.4(11)
C (19) C (18) C (17)	120.1(9)		

Table S4. Hydrogen bond lengths (Å) for $(BTA)_3Bi_2Cl_9$.

D—H	d(D—H)	d(H…A)	d(D…A)	∠(D—H…A)(°)	A
C(7)-H(7B)	0.970	2.896	3.513	122.46	Cl (8) #1
C(8)-H(8B)	0.970	2.809	3.744	162.12	Cl (1) #2
C(10)-H(10B)	0.970	2.843	3.633	139.18	Cl(7)#1
C(12)-H(12B)	0.970	2.744	3.560	142.15	Cl(3)#3
C(21)-H(21A)	0.970	2.865	3.588	132.14	C(l7)
C(21)-H(21B)	0.970	2.922	3.874	167.19	Cl (5)
C(22)-H(22B)	0.960	2.987	3.652	127.56	Cl(2)#4
C(24)-H(24A)	0.960	2.925	3.615	129.68	Cl(4)#4
C(24)-H(24C)	0.960	2.988	3.926	165.88	Cl (3)
C(33)-H(33B)	0.970	2.659	3.610	166.93	Cl(1)#3
C(35)-H(35A)	0.960	2.906	3.627	132.74	Cl(6)#5
C(36)-H(36B)	0.970	2.837	3.710	150.27	Cl(3)#3
C(37)-H(37A)	0.960	2.867	3.770	157.17	Cl(8)#5
C(38)-H(38B)	0.970	2.883	3.535	125.46	Cl (7)

Symmetry transformations used to generate equivalent atoms: #1 *x*-1/2, *y*-1/2, *z*; #2 *x*-1, -*y*+1, *z*-1/2; #3 *x*-1, *y*, *z*; #4 *x*, -*y*+1, *z*-1/2; #5 *x*-1/2, -*y*+3/2, *z*-1/2.

Table S5. Infrared vibration peaks (cm^{-1}) of $(BTA)_3Bi_2Cl_9$.

Wavenumber (cm^{-1})	Assignment
3057	ν(CH)
2991	$\nu_{as}(CH_3)$
2939	$\nu_{as}(CH_2)$
1585	ν(C=C)+ δ(CH)
1470	$\delta_s(CH_3)$
1384	$\omega(CH_2)+\delta_{as}(CH_3)$
1153	δ(CH)
1007	δ(C-N-C) + ν(C-C)
796	$\nu_3(NC_4)$
753	γ(CH)
705	$\nu(CH_2\text{-}N)$

Table S6. Comparison of structural feature and NLO properties for low-toxic lead-free hybrid metal halides.

Materials	Space group	Structural feature	Band gap (eV)	SHG response	Ref.
$(PBA)_4BiBr_7·H_2O$	*C*2	0D $[BiBr_6]^{3-}$ octahedra	3.52	0.4×KDP@1064 nm	1
$(PBA)_4BiI_7·H_2O$	*C*2	0D $[BiI_6]^{3-}$ octahedra	2.29	2.3×AGS@2090 nm	2
$(PBA)_4InBr_7·H_2O$	*C*2	0D $[InBr_6]^{3-}$ octahedra	4.05	0.6×KDP@1064 nm	2
$(C_4H_{16}N_3)BiBr_6$	$P2_12_12_1$	0D $[BiBr_6]^{3-}$ octahedron	2.72	0.6×KDP	3
$[NH_3CH_2CH_2F]_3BiCl_6$	$P2_12_12$	0D $[BiCl_6]^{3-}$ octahedron	/	PM; 0.6×KDP@1064 nm	4
$[(C_2H_5)_4N]InCl_4$	$P6_3mc$	0D $[InCl_4]^{-}$ tetrahedron	4.3	PM; 0.5×KDP@1064 nm	5
$[(C_2H_5)_4N]InCl_2Br_2$	$P6_3mc$	0D $[InCl_2Br_2]^{-}$ tetrahedron	3.55	PM; 0.7×KDP@1064 nm	5
$[(C_2H_5)_4N]InBr_4$	$P6_3mc$	0D $[InBr_4]^{-}$ tetrahedron	2.85	PM; 0.8×KDP@1064 nm	5
$(4\text{-}BrC_6H_4CH_2NH_3)_2MnBr_4$	$P2_12_12_1$	0D $[MnBr_4]^{2-}$ tetrahedra	/	PM; 0.3×KDP@1064 nm	6
[(R)-3-hydroxy-pyrrolidinium]$_5Sb_4Br_{17}$	$P2_12_12_1$	0D $[Sb_4Br_{16}]^{4-}$ tetranuclear clusters	3.0	0.79×KDP@1064 nm	6
$[C_5H_{12}N]SnCl_3$	$P2_12_12_1$	0D $[SnClr_6]^{2-}$ octahedra	3.647	PM; 1.1×KDP@1064 nm	7
$[NH_2(CH_2CH_3)_2]_3BiCl_6$	*R*3c	0D $[BiCl_6]^{3-}$ octahedron	3.26	PM; 1.9× KDP@1064 nm	8

Table S6. Comparison of structural features and NLO properties for low-toxic lead-free hybrid metal halides.

Materials	Space group	Structural feature	Band gap (eV)	SHG response	Ref.
$[NH_2(CH_2CH_3)_2]_3BiBr_6$	*R*3c	0D $[BiBr_6]^{3-}$ octahedron	2.81	PM; 3.2×KDP@1064 nm	8
$(R\text{-}MPEA)_2SnBr_6$	$P2_1$	0D $[SnBr_6]^{2-}$ octahedra	2.68	PM; 18×α-SiO_2@980 nm	9
$[(R)\text{-}C_8H_{12}N)_4][Bi_2Br_{10}]$	$P2_1$	0D edge-sharing $[Bi_2Br_{10}]^{4-}$ dimers.	2.88	NPM; 20×α-SiO_2@1064 nm	10
$(R\text{-}MBA)BiI_4$	$P2_12_12_1$	1D edge-sharing $[BiI_6]^{3-}$ octahedra	/	1.56×$LiNbO_3$@1550 nm	11
$(R\text{-}MBA)_2CuCl_4$	*C*2	2D $[CuCl_4]^{2-}$ tetrahedra	2.93	28.75 pmV^{-1}@800 nm	12
$N(CH_3)_4]ZnCl_3$	$Pmc2_1$	$[ZnCl_4]^{2-}$ tetrahedra	3.4	NPM; 15×α-SiO_2@1064 nm	13
$[(CH_3)_3NH]_3Bi_2I_9$	*R3c*	face-sharing $[Bi_2I_9]^{3-}$ dimers	2.0	0.65×KDP	14
$(BTA)_3Bi_2Cl_9$	*Cc*	0D face-sharing $[Bi_2Cl_9]^{3-}$dimers and BTA^+ cations	3.21	1.36×KDP	This work

D: dimensionality.

Table S7. The *x*/*y*/*z*-projections of local dipole moment (D) of $[BiCl_6]^{3-}$ octahedrons and BTA^+ groups in one-unit cell of $(BTA)_3Bi_2Cl_9$.

Ion	μ_x	μ_y	μ_z
BTA^+	107.433	0	-115.774
BTA^+	-46.898	-0.006	-289.918
BTA^+	347.993	-0.011	87.909
$[BiCl_6]^{3-}$	34.592	0.012	0.321
$[BiCl_6]^{3-}$	-31.994	0.001	-1.428

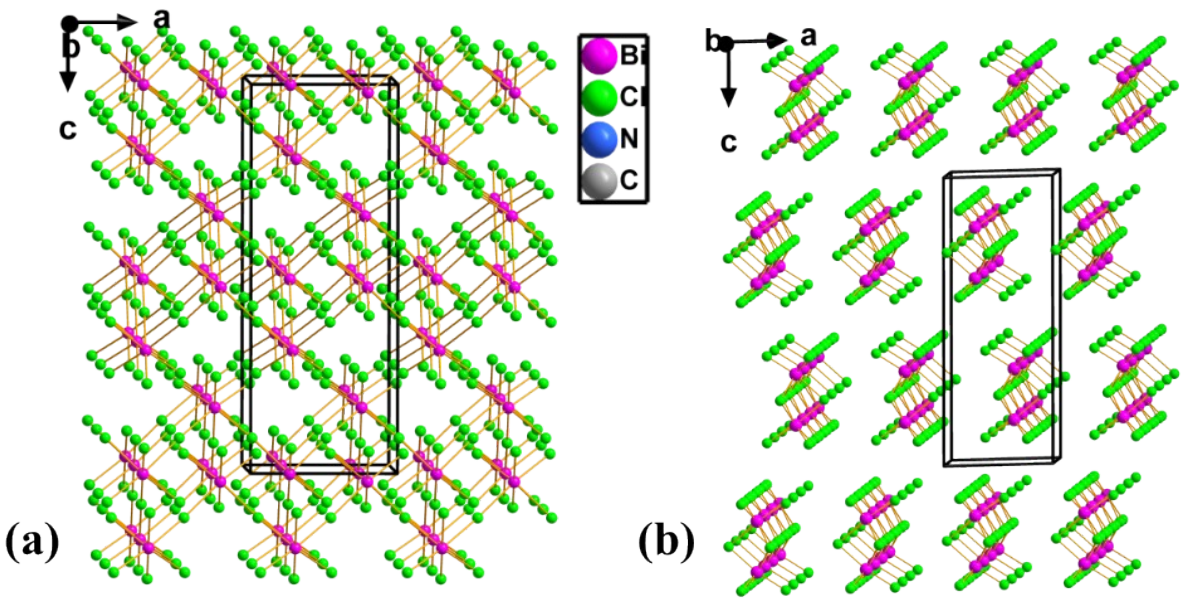

Figure S1. The crystal structures of $(CH_3NH_3)_3Bi_2Cl_9$ (a, orthorhombic *Pnma*) and $(CH_3)_4N)_3Bi_2Cl_9$ (b, hexagonal $P6_3/mmc$). Noted the C, N and H atoms were omitted for clarity.

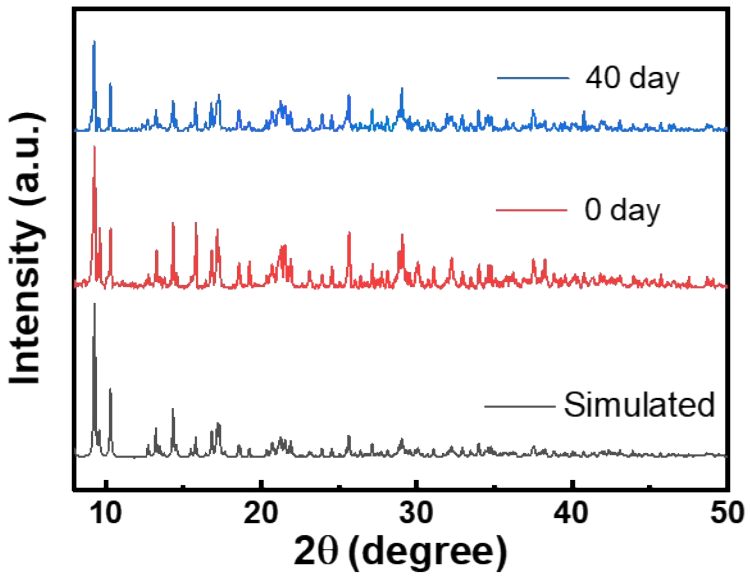

Figure S2. The powder X-ray diffraction patterns of $(BTA)_3Bi_2Cl_9$, including simulated and experimental ones (Blue: after exposed in air for 40 days and dried at 120 ℃).

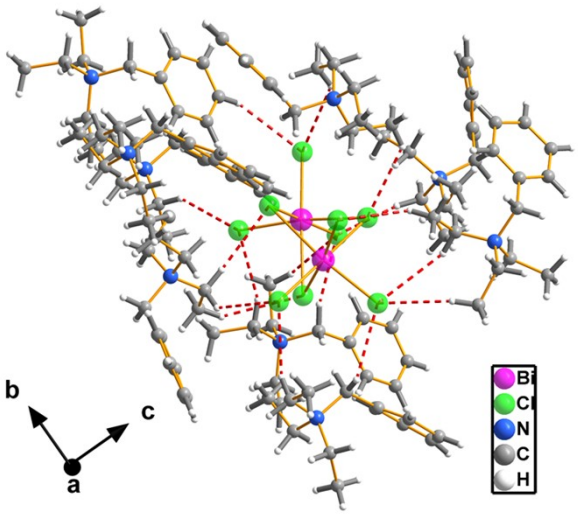

Figure S3. Structure showing the hydrogen bonds between the hydrogen atoms in BTA^{+} cations and the chlorine atoms in $[Bi_2Cl_9]^{3-}$ in the *bc*-plane.

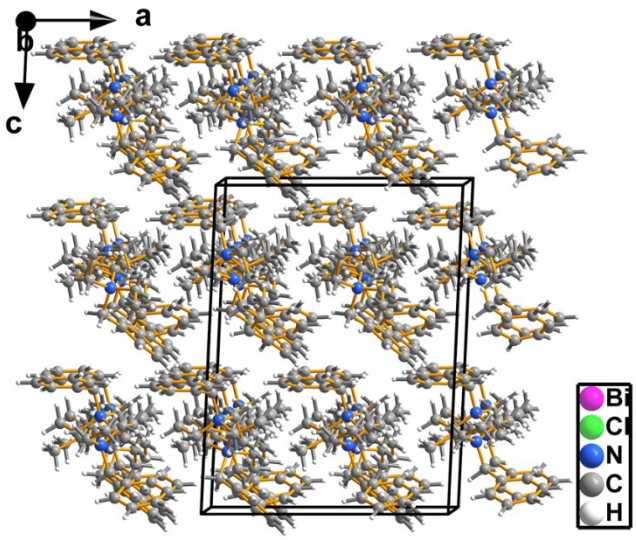

Figure S4. Uniformly arranged organic cations viewed along the *b*-axis.

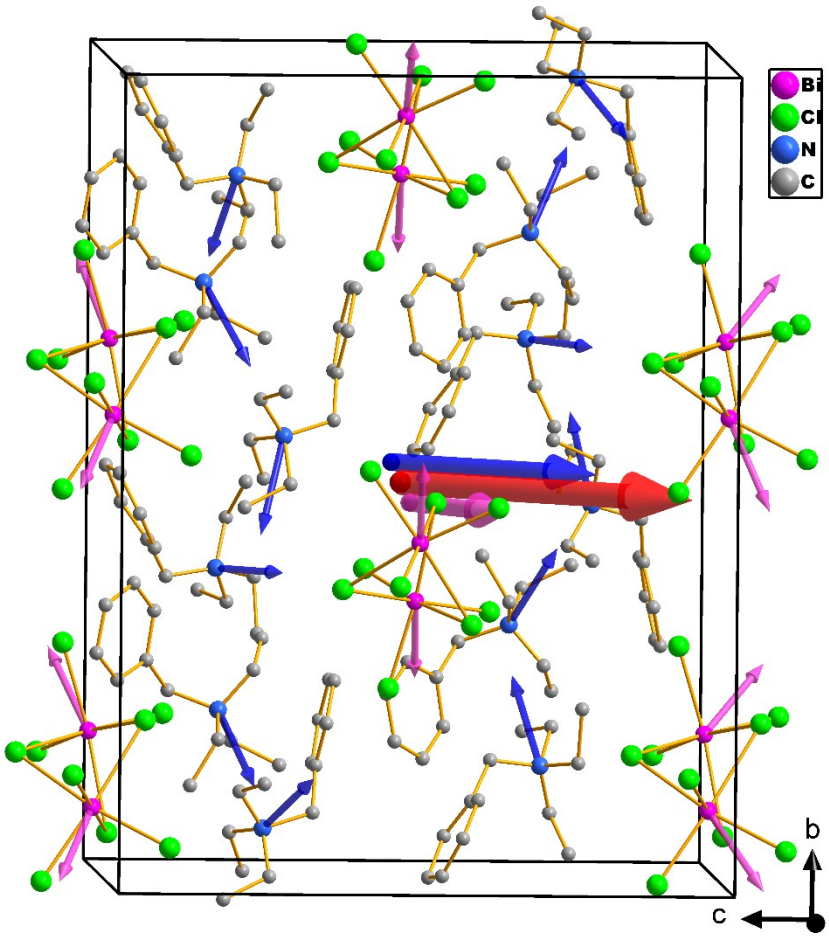

Figure S5. Dipole moments of $[Bi_2Cl_9]^{3-}$ and BTA^+ groups in one-unit cell. Blue: BTA^+; purple: $[BiCl_6]^{3-}$. The blue, purple and red arrows in the middle present the total dipole moments of the organic parts, the inorganic parts and the whole unite cell, respectively.

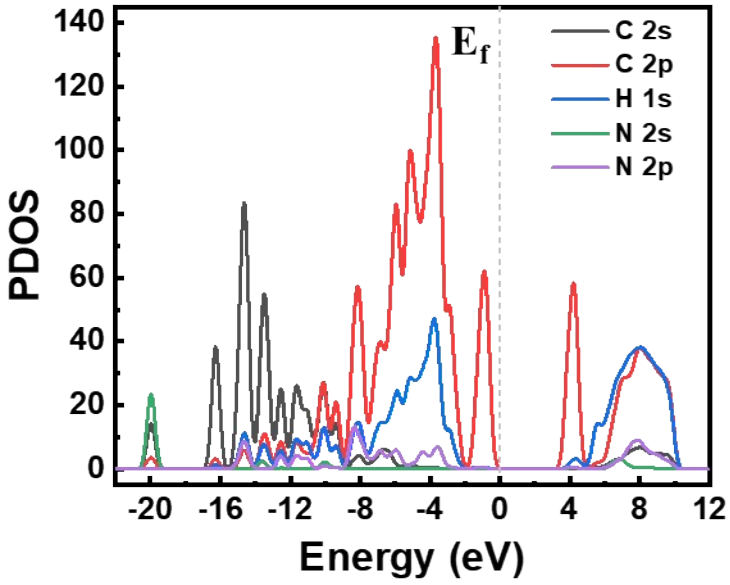

Figure S6. Partial density of states of C, N, and H atoms in $(BTA)_3Bi_2Cl_9$.

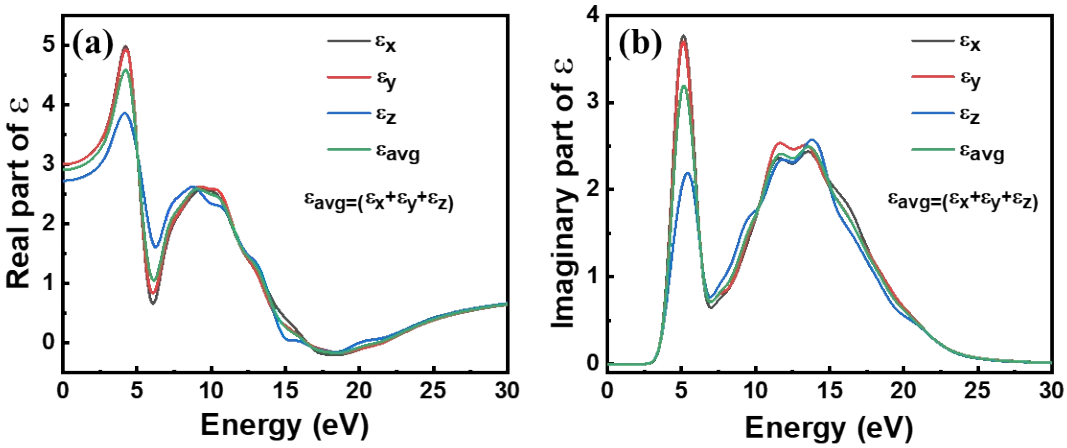

Figure S7. The calculated real and imaginary parts of the dielectric function polarized along the three directions for $(BTA)_3Bi_2Cl_9$.

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