Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Halide-Driven Polarity Tuning and Optimized SHG-Bandgap Balance in $(C_4H_{11}N_2)ZnX_3$ (X = Cl, Br, I)

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Table S1. Summary of Crystal Data and Structure Refinements for title compounds

Empirical formula	$C_4H_{11}Cl_3N_2Zn$	$C_4H_{11}Br_3N_2Zn$	$C_4H_{10}I_3N_2Zn$
Formula weight	258.87	392.25	532.21
Temperature/K	100(2)	293(2)	298.81(10)
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	*P*1	*P*1	*Cc*
a/Å	6.4270(2)	6.5788(4)	24.3787(5)
b/Å	6.4344(2)	6.6986(4)	7.0895(2)
c/Å	6.6193(2)	6.8678(3)	13.6140(3)
α/°	104.564(3)	105.815(4)	90
β/°	92.820(3)	93.252(4)	91.304(2)
γ/°	118.055(4)	116.169(6)	90
Volume/Å^3	229.271(16)	255.81(3)	2352.34(10)
Z	1	1	8
ρ_{calcg}/cm^3	1.875	2.546	3.006
μ/mm^{-1}	11.219	16.576	64.311
F(000)	130.0	184.0	1896
Radiation	Cu Kα (λ=1.54184)	Cu Kα (λ=1.54184)	Cu Kα (λ=1.54184)
Goodness-of-fit on F^2	1.057	1.059	1.041
Flack factor	0.00(4)	-0.06(9)	0.065(14)
R_1, wR_2 [I >2σ(I)][a]	0.0582, 0.1416	0.0657, 0.1618	0.0580, 0.1460
R_1, wR_2 (all data)[a]	0.0583, 0.1417	0.0659, 0.1623	0.0590, 0.1472

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, and $wR_2 = \{\sum w[(F_o)^2 - (Fc)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$.

Table S2. Fractional Atomic Coordinates (× 10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $(C_4H_{11}N_2)ZnX_3$ (X = Cl, Br, I).

$(C_4H_{11}N_2)ZnCl_3$				
Atom	**x**	**y**	**z**	**U(eq)**
Zn1	4694.9(12)	5998.7(12)	6769.4(11)	8.7(4)
Cl1	4551(3)	8796(3)	5367(3)	12.5(4)
Cl2	1214(3)	3422(4)	7470(3)	18.8(5)
Cl3	7777(3)	7865(3)	9613(3)	13.0(5)
N1	6939(12)	2793(12)	375(11)	10.6(13)
N2	5648(12)	3976(12)	4477(12)	10.4(13)
C1	4450(14)	1200(14)	703(13)	14.4(16)
C2	3857(14)	2764(15)	2448(13)	12.9(15)
C3	8109(14)	5521(14)	4111(13)	11.2(15)
C4	8773(15)	3993(17)	2404(14)	14.7(16)
$(C_4H_{11}N_2)ZnBr_3$				
Atom	**x**	**y**	**z**	**U(eq)**
Br1	5501.7(19)	1272.9(17)	4716.4(16)	44.1(4)
Br2	2022.7(19)	2163.1(19)	414.9(16)	45.1(4)
Br3	8684(3)	6679(3)	2631(3)	60.5(5)
Zn1	5209(3)	4062(3)	3325(2)	34.8(4)
N1	4271(16)	6050(17)	5609(14)	31.7(17)
N2	3149(19)	7300(20)	9609(15)	42(2)
C1	5470(20)	8780(20)	9250(20)	40(2)
C2	6050(20)	7270(20)	7551(18)	42(3)
C3	1320(20)	6140(30)	7680(20)	52(3)
C4	1962(19)	4650(30)	6015(18)	40(2)
$(C_4H_{11}N_2)ZnI_3$				
Atom	**x**	**y**	**z**	**U(eq)**
I1	6292.3(4)	8487.2(14)	8062.2(6)	48.0(3)
I2	7116.8(4)	12263.0(19)	6077.9(8)	61.0(3)
I3	5408.2(4)	13177.1(14)	6674.9(7)	50.0(3)
I4	3827.5(4)	6476.9(13)	5576.9(6)	48.1(3)
I5	4568.9(4)	2418.0(15)	3602.8(7)	52.9(3)
I6	2880.7(4)	1818.7(14)	4259.8(7)	48.2(3)
Zn1	6206.9(8)	10761(2)	6578.2(13)	40.1(4)
Zn2	3693.9(8)	4177(2)	4108.4(13)	39.8(4)
N1	6003(5)	9028(15)	5399(8)	38(2)
N2	5681(5)	5602(18)	4374(9)	48(3)
N3	3482(4)	5920(15)	2929(8)	37(2)
N4	3185(6)	9431(18)	1966(11)	51(3)
C1	3881(6)	7390(30)	2787(12)	49(3)
C2	2930(7)	6720(20)	2985(13)	50(3)
C3	2771(7)	7880(30)	2089(17)	64(5)
C4	3750(6)	8630(20)	1901(12)	47(3)

C5	5441(6)	8350(20)	5375(11)	47(3)
C6	6373(7)	7410(30)	5292(12)	49(3)
C7	6273(6)	6310(30)	4374(11)	49(3)
C8	5287(6)	7220(30)	4453(13)	52(4)

Table S3. Bond Lengths for $(C_4H_{11}N_2)ZnX_3$ (X = Cl, Br, I).

$(C_4H_{11}N_2)ZnCl_3$

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn1	Cl1	2.2582(19)	N1	C4	1.502(12)
Zn1	Cl2	2.2291(19)	N2	C2	1.488(11)
Zn1	Cl3	2.2735(19)	N2	C3	1.493(9)
Zn1	N2	2.055(6)	C1	C2	1.521(11)
N1	C1	1.503(10)	C3	C4	1.519(10)

$(C_4H_{11}N_2)ZnBr_3$

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	Zn1	2.3896(19)	N1	C4	1.483(15)
Br2	Zn1	2.4068(18)	N2	C1	1.489(16)
Br3	Zn1	2.360(2)	N2	C3	1.499(18)
Zn1	N1	2.076(9)	C1	C2	1.509(17)
N1	C2	1.483(14)	C3	C4	1.513(18)

$(C_4H_{11}N_2)ZnI_3$

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I1	Zn1	2.590(2)	N2	C7	1.529(19)
I2	Zn1	2.568(2)	N2	C8	1.50(2)
I3	Zn1	2.600(2)	N3	C1	1.446(19)
I4	Zn2	2.596(2)	N3	C2	1.465(19)
I5	Zn2	2.580(2)	N4	C3	1.50(3)
I6	Zn2	2.6067(19)	N4	C4	1.496(19)
Zn1	N1	2.074(11)	C1	C4	1.52(2)
Zn2	N3	2.083(11)	C2	C3	1.51(2)
N1	C5	1.450(18)	C5	C8	1.530(19)
N1	C6	1.47(2)	C6	C7	1.49(2)

Table S4. Bond Angles for $(C_4H_{11}N_2)ZnX_3$ (X = Cl, Br, I).

$(C_4H_{11}N_2)ZnCl_3$

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl1	Zn1	Cl3	111.31(7)	C2	N2	Zn1	110.8(5)
Cl2	Zn1	Cl1	114.44(8)	C2	N2	C3	110.4(6)
Cl2	Zn1	Cl3	112.46(8)	C3	N2	Zn1	112.0(5)
N2	Zn1	Cl1	104.5(2)	N1	C1	C2	108.9(6)
N2	Zn1	Cl2	108.7(2)	N2	C2	C1	113.0(7)
N2	Zn1	Cl3	104.6(2)	N2	C3	C4	111.1(6)
C4	N1	C1	111.8(7)	N1	C4	C3	110.4(6)

$(C_4H_{11}N_2)ZnBr_3$							
Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
Br1	Zn1	Br2	111.50(8)	C2	N1	C4	110.3(9)
Br3	Zn1	Br1	114.89(10)	C4	N1	Zn1	113.0(7)
Br3	Zn1	Br2	112.51(9)	C1	N2	C3	111.9(10)
N1	Zn1	Br1	104.7(3)	N2	C1	C2	109.1(10)
N1	Zn1	Br2	104.7(3)	N1	C2	C1	113.1(11)
N1	Zn1	Br3	107.6(3)	N2	C3	C4	109.2(11)
C2	N1	Zn1	111.0(7)	N1	C4	C3	112.0(11)
$(C_4H_{11}N_2)ZnI_3$							
Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
I1	Zn1	I3	114.68(7)	C6	N1	Zn1	113.8(9)
I2	Zn1	I1	114.29(8)	C8	N2	C7	110.7(12)
I2	Zn1	I3	113.14(8)	C1	N3	Zn2	112.1(9)
N1	Zn1	I1	104.4(3)	C1	N3	C2	110.4(11)
N1	Zn1	I2	103.5(3)	C2	N3	Zn2	113.8(8)
N1	Zn1	I3	105.3(3)	C4	N4	C3	110.4(12)
I4	Zn2	I6	115.12(7)	N3	C1	C4	113.1(13)
I5	Zn2	I4	114.85(8)	N3	C2	C3	112.8(13)
I5	Zn2	I6	110.27(7)	N4	C3	C2	109.1(15)
N3	Zn2	I4	104.2(3)	N4	C4	C1	110.5(12)
N3	Zn2	I5	105.9(3)	N1	C5	C8	114.0(12)
N3	Zn2	I6	105.5(3)	N1	C6	C7	113.8(13)
C5	N1	Zn1	115.0(8)	C6	C7	N2	107.9(12)
C5	N1	C6	108.7(11)	N2	C8	C5	108.3(13)

Table S5. Hydrogen Bonds for $(H_{11}C_4N_2)ZnX_3$ (X = Cl, Br, I)

$(C_4H_{11}N_2)ZnCl_3$						
D	**H**	**A**	**d(D-H)/Å**	**d(H-A)/Å**	**d(D-A)/Å**	**D-H-A/°**
N1	H1B	Cl3[1]	0.91	2.35	3.224(7)	161.9
N2	H2	Cl1[2]	1.00	2.32	3.282(7)	161.9
$(C_4H_{11}N_2)ZnBr_3$						
D	**H**	**A**	**d(D-H)/Å**	**d(H-A)/Å**	**d(D-A)/Å**	**D-H-A/°**
N1	H1	Br1[3]	0.98	2.53	3.464(10)	158.6
N2	H2B	Br2[4]	0.89	2.55	3.398(12)	159.6
$(C_4H_{11}N_2)ZnI_3$						
D	**H**	**A**	**d(D-H)/Å**	**d(H-A)/Å**	**d(D-A)/Å**	**D-H-A/°**
N1	H1	I1[5]	0.98	2.75	3.720(11)	170
N2	H2B	I3[6]	0.89	2.78	3.649(12)	166
N3	H3	I4[7]	0.98	2.80	3.740(11)	160
N4	H4B	I6[8]	0.89	2.79	3.645(15)	161

[1]+X, +Y, -1+Z; [2]+X, -1+Y, +Z; [3]+X, 1+Y, +Z; [4]+X, +Y, 1+Z; [5]+x, 2-y, -1/2+z; [6]+x, -1+y, z; [7]+x, 1-y, -1/2+z; [8]+x, 1+y, z.

Table S6. The assignments of the absorption peaks for $(H_{11}C_4N_2)ZnX_3$ (X = Cl, Br, I).

Assignment (cm^{-1})	$(C_4H_{11}N_2)ZnCl_3$	$(C_4H_{11}N_2)ZnBr_3$	$(C_4H_{11}N_2)ZnI_3$
ν(N-H)	3212, 3170	3205, 3159	3168, 3141
ν(C-H)	3035, 2785, 2785, 2364	3046, 2774 2424, 2365	3036, 2764 2358
ν(C-N)	1572	1566	1557
ν(C-C)	1450, 1400	1450, 1400	1447, 1395
ν(Zn-N)	1293, 1216, 871	1292, 1200 1080, 856	1292, 1200, 1083, 858
ν(Zn-X)	626, 484	625, 480	621, 474

Table S7. Calculated dipole moment for $ZnNCl_3$, $ZnNBr_3$, $ZnNI_3$ and net dipole moment for a unit cell in $(C_4H_{11}N_2)ZnCl_3$, $(C_4H_{11}N_2)ZnBr_3$ and $(C_4H_{11}N_2)ZnI_3$**.**

$(C_4H_{11}N_2)ZnCl_3$ (Z = 1)				
Polar unit	Dipole moment (D = Debyes)			
	x-component	y-component	z-component	Total magnitude
$Zn(1)NCl_3$	-0.87314	1.078438	1.529	2.064761
Net dipole moment (a unit cell)	-0.87314	1.078438	1.529	2.064761
Dipole moment per unit volume (Debyes/ $Å^3$)	0.009			
$(C_4H_{11}N_2)ZnBr_3$ (Z = 1)				
Polar unit	Dipole moment (D = Debyes)			
	x-component	y-component	z-component	Total magnitude
$Zn(1)NBr_3$	2.557298	-2.15943	-3.86643	5.113925
Net dipole moment (a unit cell)	2.557298	-2.15943	-3.86643	5.113925
Dipole moment per unit volume (Debyes/ $Å^3$)	0.020			
$(C_4H_{11}N_2)ZnI_3$ (Z = 8)				
Polar unit	Dipole moment (D = Debyes)			
	x-component	y-component	z-component	Total magnitude
$Zn(1)NI_3$	-1.74977	-4.12558	-4.9699	6.691941
$Zn(2)NI_3$	-1.74985	4.125606	-4.96989	6.691966
$Zn(3)NI_3$	-1.7533	4.123178	-4.96882	6.690582
$Zn(4)NI_3$	-1.75347	-4.12615	-4.9701	6.693403

$Zn(5)NI_3$	-1.61051	4.887684	-5.18566	7.305772
$Zn(6)NI_3$	-1.60722	-4.8901	-5.18685	7.307508
$Zn(7)NI_3$	-1.6094	4.888934	-5.18538	7.306159
$Zn(8)NI_3$	-1.61066	-4.89074	-5.18696	7.308775
Net dipole moment (a unit cell)	-13.4442	0	-40.6236	42.79043
Dipole moment per unit volume (Debyes/ $Å^3$)	0.018			

Table S8. The angles between the crystallography axes (i.e. *a*, *b* and *c*) and the principal dielectric axes (i.e. x, y and z) in triclinic Cl and Br compounds.

Angle	*a*-O-x	*b*-O-x	*c*-O-x	*a*-O-y	*b*-O-y	*c*-O-y	*a*-O-z	*b*-O-z	*c*-O-z
Cl	62.06	58.58	122.887	138.383	33.962	76.503	61.920	101.583	36.229
Br	66.429	50.786	118.697	134.269	46.881	63.387	53.558	111.397	41.047

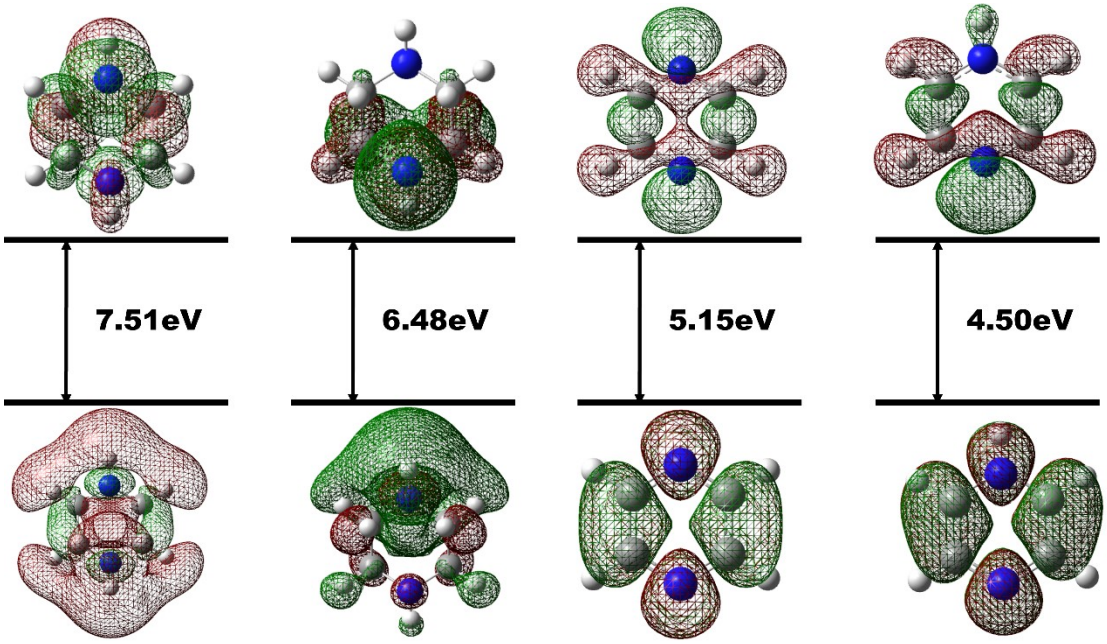

Figure S1. Calculated HOMO-LUMO gaps of non-π-conjugated $C_4H_{10}N_2$ and $(C_4H_{11}N_2)^+$ as well as π-conjugated $C_4H_4N_2$ and $(C_4H_5N_2)^+$.

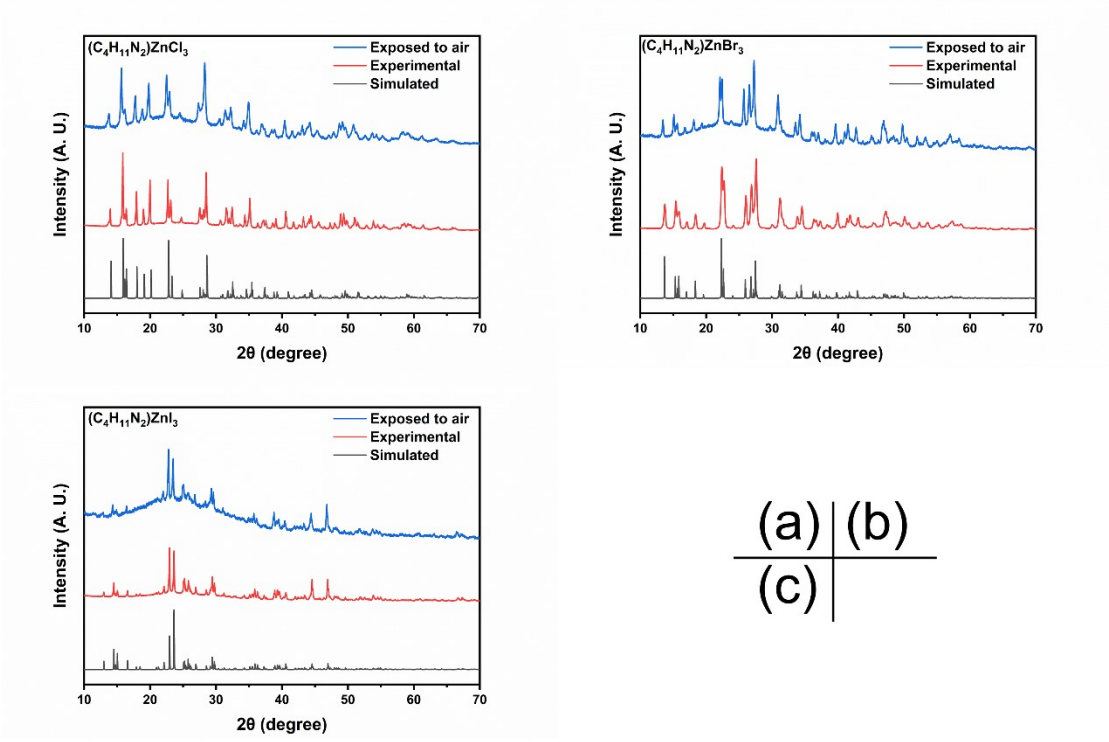

Figure S2. Simulated, measured and exposed to air powder X-ray diffraction patterns for $(C_4H_{11}N_2)ZnX_3$ (X = Cl a, Br b, I c).

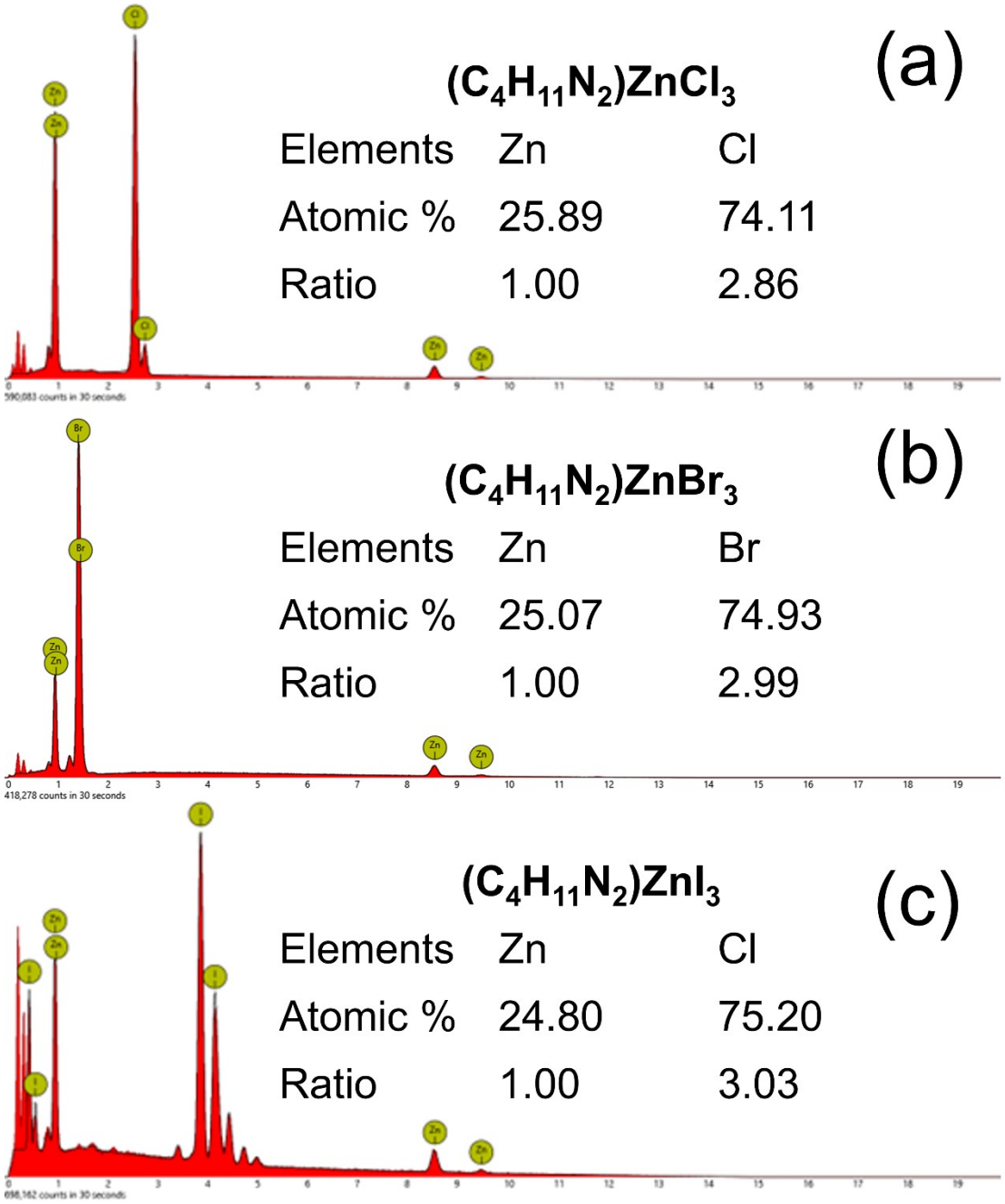

Figure S3. EDS for $(C_4H_{11}N_2)ZnX_3$ (X = Cl a, Br b, I c).

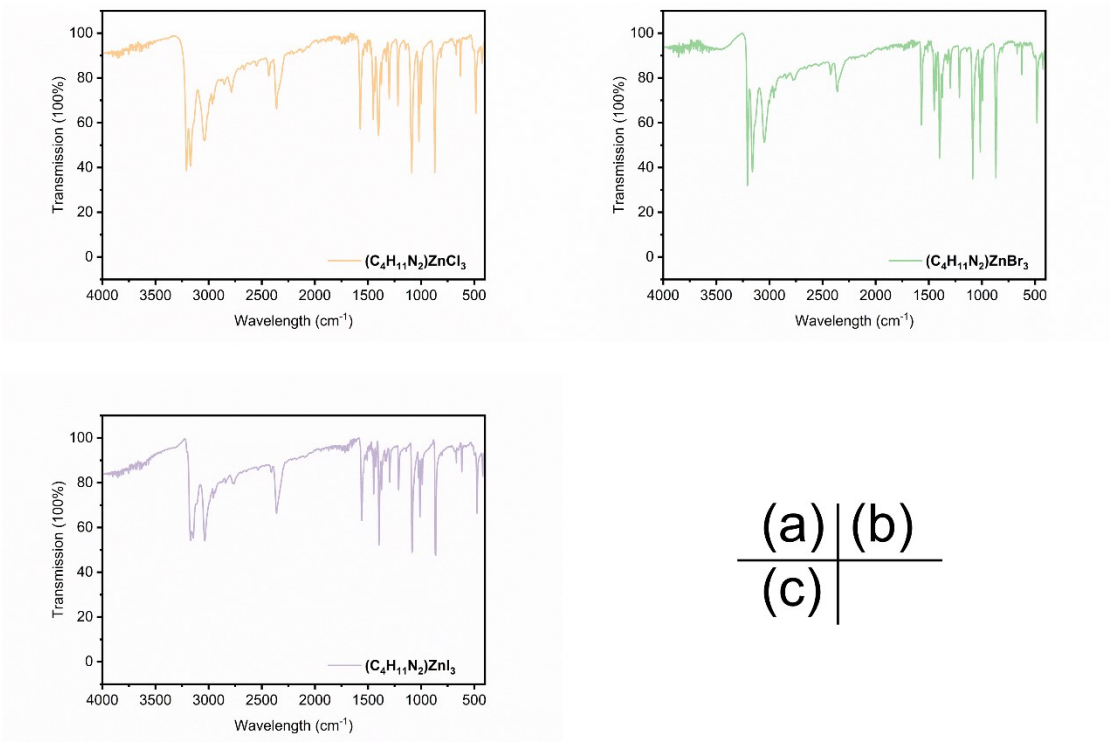

Figure S4. IR spectra for $(C_4H_{11}N_2)ZnX_3$ (X = Cl a, Br b, I c).

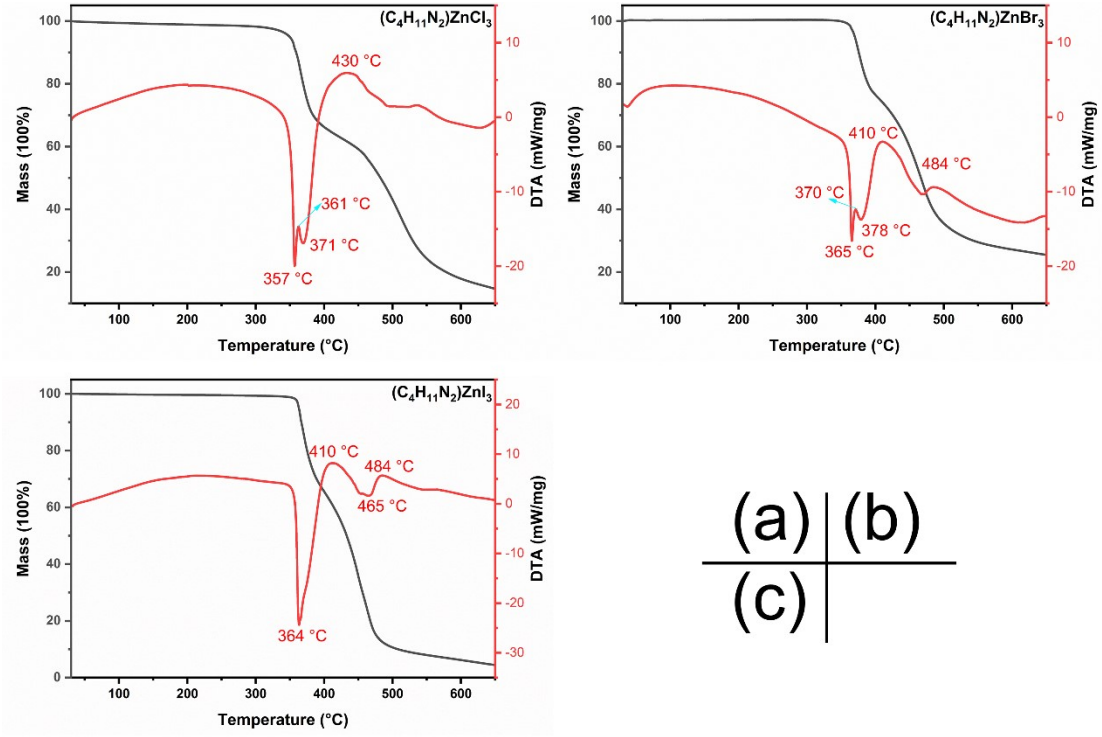

Figure S5. TG-DTA curves for $(C_4H_{11}N_2)ZnX_3$ (X = Cl a, Br b, I c).

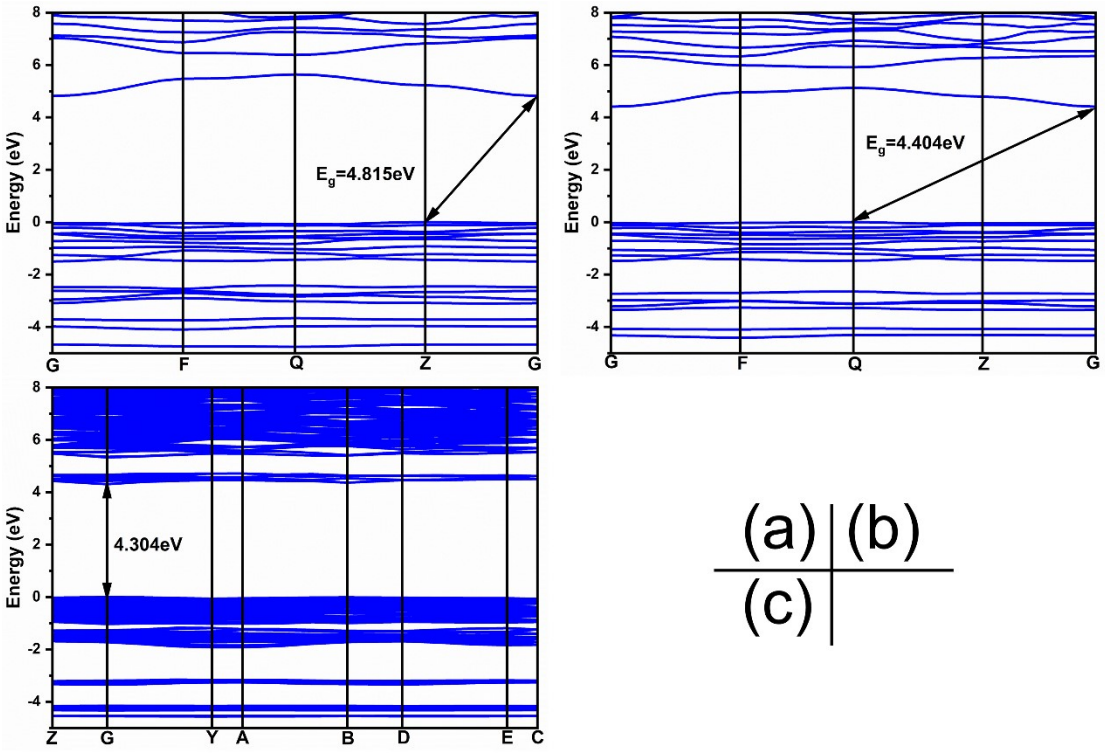

Figure S6. Calculated bandgaps for $(C_4H_{11}N_2)ZnX_3$ (X = Cl a, Br b, I c).

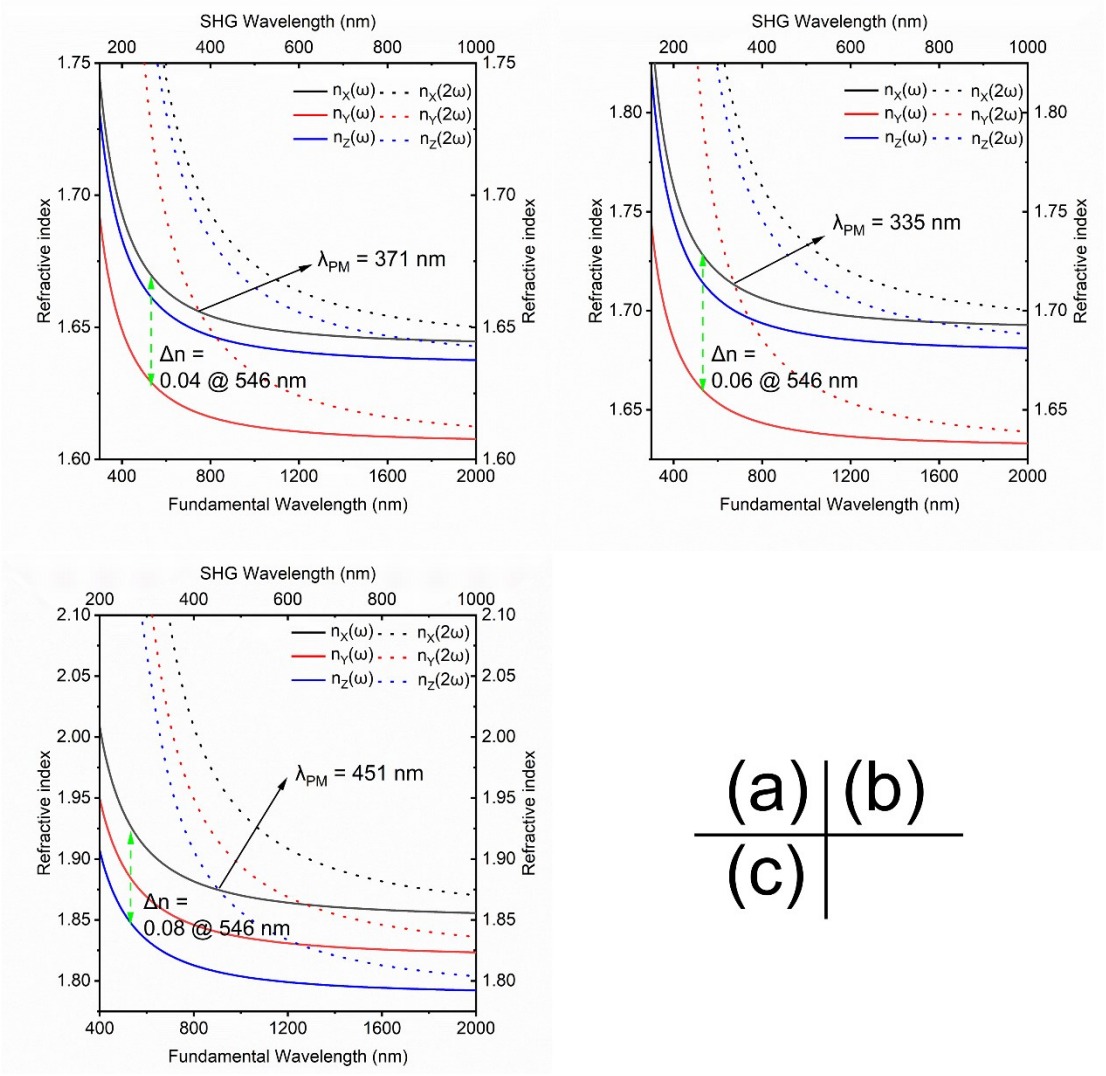

Figure S7. Calculated birefringence for $(C_4H_{11}N_2)ZnX_3$ (X = Cl a, Br b, I c).