Supplementary Information

Synthesis and SHG Properties of the Melamine-Based Material $(C_3N_6H_7)ZnX_3(C_3N_6H_6)$ (X = Cl, Br)

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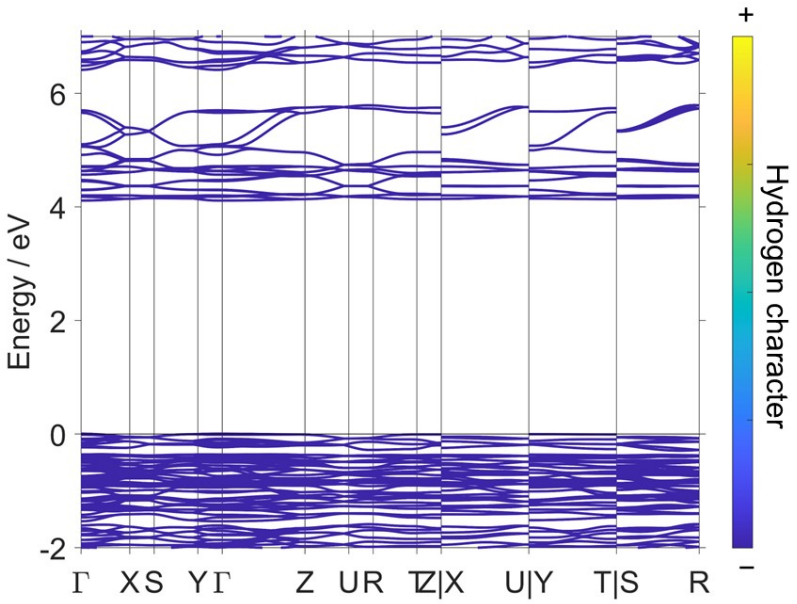

Figure S1. The electronic band structure of orthorhombic $(C_3N_6H_7)ZnCl_3(C_3N_6H_6)$, as calculated using DFT. Bands are coloured according to their hydrogen character. Special points in the Brillouin zone (Γ = (0 0 0), X = (0.5 0 0), S = (0.5 0.5 0), Y = (0 0.5 0), Z = (0 0 0.5), U = (0.5 0 0.5), R = (0.5 0.5 0.5)) were chosen following Y. Hinuma, G. Pizzi, Y. Kumagai, F. Oba, I. Tanaka, Band structure diagram paths based on crystallography, Comp. Mat. Sci. 128, 140 (2017).

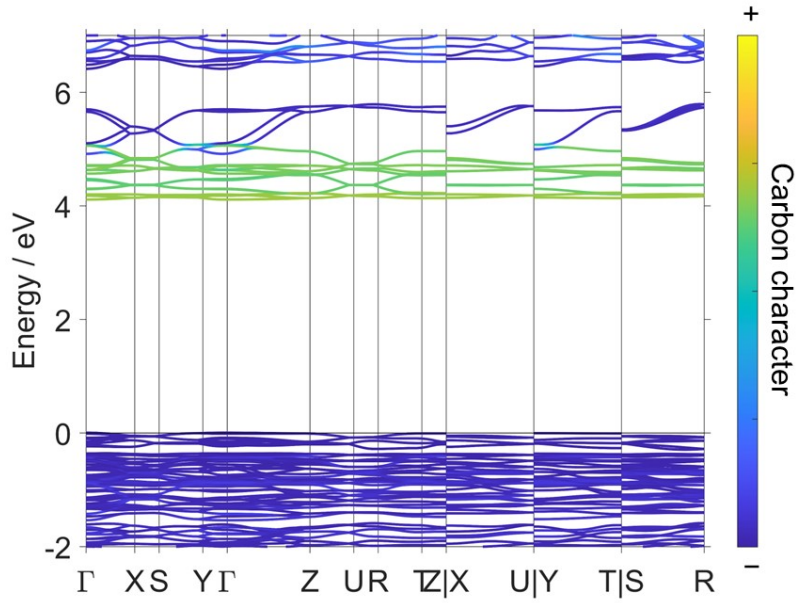

Figure S2. The electronic band structure of orthorhombic $(C_3N_6H_7)ZnCl_3(C_3N_6H_6)$, as calculated using DFT. Bands are coloured according to their carbon character. Special points in the Brillouin zone (Γ = (0 0 0), X = (0.5 0 0), S = (0.5 0.5 0), Y = (0 0.5 0), Z = (0 0 0.5), U = (0.5 0 0.5), R = (0.5 0.5 0.5)) were chosen following Y. Hinuma, G. Pizzi, Y. Kumagai, F. Oba, I. Tanaka, Band structure diagram paths based on crystallography, Comp. Mat. Sci. 128, 140 (2017).

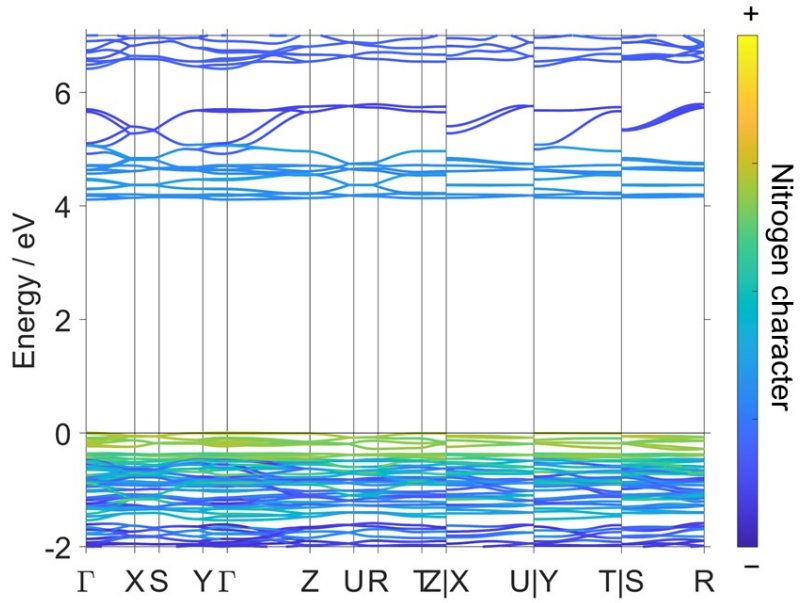

Figure S3. The electronic band structure of orthorhombic $(C_3N_6H_7)ZnCl_3(C_3N_6H_6)$, as calculated using DFT. Bands are coloured according to their nitrogen character. Special points in the Brillouin zone (Γ = (0 0 0), X = (0.5 0 0), S = (0.5 0.5 0), Y = (0 0.5 0), Z = (0 0 0.5), U = (0.5 0 0.5), R = (0.5 0.5 0.5)) were chosen following Y. Hinuma, G. Pizzi, Y. Kumagai, F. Oba, I. Tanaka, Band structure diagram paths based on crystallography, Comp. Mat. Sci. 128, 140 (2017).

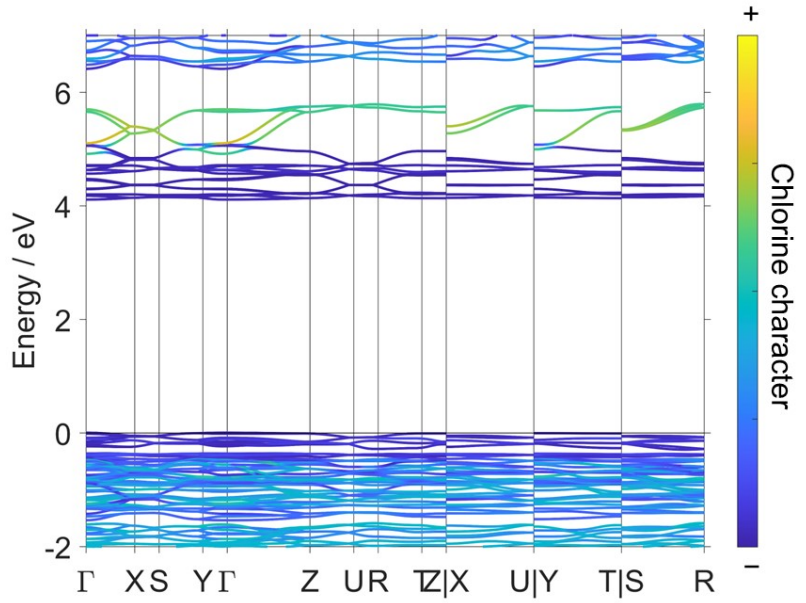

Figure S4. The electronic band structure of orthorhombic $(C_3N_6H_7)ZnCl_3(C_3N_6H_6)$, as calculated using DFT. Bands are coloured according to their chlorine character. Special points in the Brillouin zone (Γ = (0 0 0), X = (0.5 0 0), S = (0.5 0.5 0), Y = (0 0.5 0), Z = (0 0 0.5), U = (0.5 0 0.5), R = (0.5 0.5 0.5)) were chosen following Y. Hinuma, G. Pizzi, Y. Kumagai, F. Oba, I. Tanaka, Band structure diagram paths based on crystallography, Comp. Mat. Sci. 128, 140 (2017).

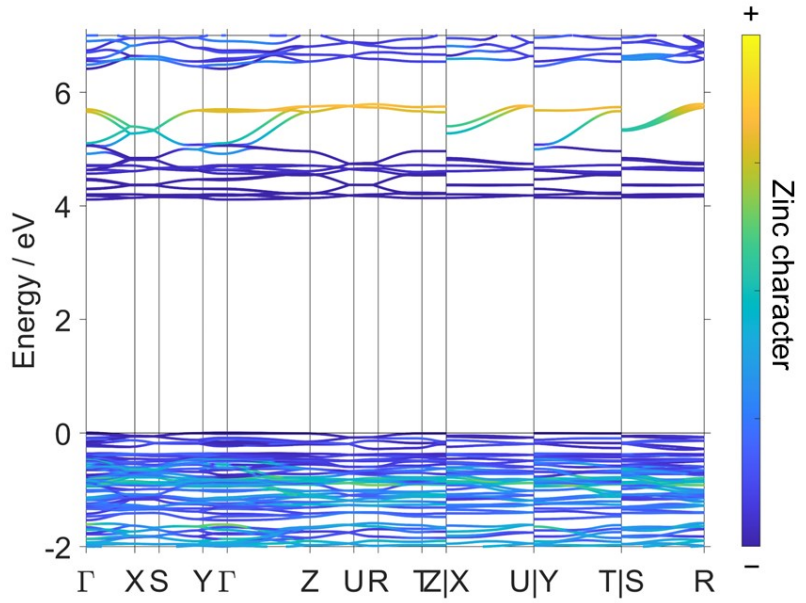

Figure S5. The electronic band structure of orthorhombic $(C_3N_6H_7)ZnCl_3(C_3N_6H_6)$, as calculated using DFT. Bands are coloured according to their zinc character. Special points in the Brillouin zone (Γ = (0 0 0), X = (0.5 0 0), S = (0.5 0.5 0), Y = (0 0.5 0), Z = (0 0 0.5), U = (0.5 0 0.5), R = (0.5 0.5 0.5)) were chosen following Y. Hinuma, G. Pizzi, Y. Kumagai, F. Oba, I. Tanaka, Band structure diagram paths based on crystallography, Comp. Mat. Sci. 128, 140 (2017).

Table S1: Hydrogen Bond information for **monoclinic (MelH)$ZnCl_3$(Mel)**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N4	H4a	N9	0.98(5)	2.00(5)	2.966(3)	170(4)
N4	H4b	Cl2	0.99(4)	2.27(4)	3.197(3)	156(3)
N5	H5a	Cl3[1]	0.87(5)	2.49(5)	3.279(3)	151(4)
N6	H6a	Cl1	0.98(4)	2.39(4)	3.293(3)	153(3)
N6	H6b	N8[2]	0.98(4)	2.00(4)	2.983(3)	175(3)
N7	H7	Cl1[3]	0.96(4)	2.59(4)	3.257(2)	127(3)
N10	H10a	Cl1[4]	0.98(4)	2.43(4)	3.306(3)	149(3)
N10	H10b	N3[5]	0.95(5)	2.08(5)	3.026(4)	177(4)
N11	H11a	Cl1[6]	0.98(5)	2.55(5)	3.412(3)	147(3)
N11	H11b	Cl2[6]	1.05(4)	2.43(4)	3.285(2)	138(3)
N12	H12a	N2	1.01(5)	1.98(5)	2.992(3)	178(4)
N12	H12b	Cl3[7]	0.94(4)	2.54(4)	3.348(3)	144(3)

[1]1+x,+y,+z; [2]+x,+y,-1+z; [3]1-x,-1/2+y,1-z; [4]1+x,+y,1+z; [5]+x,+y,1+z; [6]-x,-1/2+y,1-z; [7]1-x,1/2+y,1-z

Table S2: Hydrogen Bond information for **orthorhombic (MelH)$ZnCl_3$(Mel)**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N4	H4A	N3[1]	0.88	2.11	2.986(6)	179.0
N4	H4B	Cl2	0.88	2.45	3.258(5)	153.3
N5	H5A	Cl2[2]	0.88	2.60	3.378(5)	148.7
N5	H5B	Cl1[2]	0.88	2.56	3.278(5)	138.8
N6	H6A	N2[3]	0.88	2.08	2.956(6)	174.8
N6	H6B	Cl1	0.88	2.40	3.193(5)	149.6
N7	H7	Cl2[4]	0.88	2.73	3.275(5)	121.1
N10	H10A	N9[1]	0.88	2.14	3.012(7)	172.7
N10	H10B	Cl2[5]	0.88	2.55	3.345(6)	151.2
N11	H11A	Cl3A[2]	0.88	2.50	3.301(6)	151.7
N11	H11A	Cl3B[2]	0.88	2.27	2.99(3)	139.5
N11	H11B	Cl1[6]	0.88	2.68	3.500(5)	155.5

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N12	H12A	N8[3]	0.88	2.08	2.962(6)	175.3
N12	H12B	Cl3A	0.88	2.61	3.419(6)	152.6
N12	H12B	Cl3B	0.88	2.49	3.32(2)	157.7

[1]1/2+x,3/2-y,+z; [2]1/2-x,1/2+y,-1/2+z; [3]-1/2+x,3/2-y,+z; [4]+x,+y,-1+z; [5]1-x,1-y,-1/2+z; [6]1/2+x,3/2-y,-1+z

Table S3: Hydrogen Bond information for **(MelH)ZnBr$_3$(Mel)**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N4	H4A	N3[1]	0.88	2.11	2.983(5)	174.4
N4	H4B	Br1	0.88	2.53	3.330(4)	151.2
N5	H5B	Br1[2]	0.88	2.71	3.441(4)	141.0
N6	H6A	N2[3]	0.88	2.14	3.017(5)	177.6
N6	H6B	Br2	0.88	2.55	3.365(3)	155.0
N7	H7	Br2[4]	0.88	2.87	3.410(4)	121.3
N10	H10A	N9[1]	0.88	2.07	2.953(5)	175.8
N10	H10B	Br3B	0.88	2.60	3.434(11)	158.5
N11	H11A	Br3A[2]	0.88	2.63	3.410(4)	148.1
N11	H11A	Br3B[2]	0.88	2.44	3.163(13)	139.2
N12	H12A	N8[3]	0.88	2.14	3.021(5)	173.6
N12	H12B	Br2[5]	0.88	2.68	3.483(4)	153.0

[1]-1/2+x,3/2-y,+z; [2]1/2-x,1/2+y,-1/2+z; [3]1/2+x,3/2-y,+z; [4]+x,+y,-1+z; [5]1-x,1-y,-1/2+z

Table S4: Hydrogen Bond information for **Zn$_3$(OH)$_2$Cl$_4$(Mel)$_3$**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
O1	H1	Cl2[1]	0.91(2)	2.27(3)	3.0652(11)	145(2)
O2	H2	Cl3[2]	0.94(2)	2.25(2)	3.0923(10)	149.1(18)
N4	H4a	Cl1	0.96(3)	2.28(3)	3.2309(16)	170.9(18)
N4	H4b	Cl2[3]	0.96(2)	2.38(2)	3.2915(14)	157.3(16)
N5	H5a	N14[4]	0.99(2)	2.09(3)	3.0737(19)	178(2)
N5	H5b	Cl1[5]	0.95(3)	2.47(3)	3.2725(14)	142.2(19)
N6	H6a	N15[5]	0.96(2)	2.15(2)	3.1124(18)	177.7(16)
N6	H6b	O1	0.98(3)	2.34(3)	3.2392(18)	151.8(17)

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N10	H10b	Cl3[2]	0.98(2)	2.34(2)	3.2847(15)	162.2(18)
N11	H11a	Cl3[6]	1.00(2)	2.43(2)	3.2843(14)	144.1(17)
N11	H11b	N20[7]	0.94(3)	2.05(3)	2.9913(18)	172(2)
N12	H12a	N21[8]	0.96(3)	2.02(3)	2.9714(18)	171.0(19)
N16	H16a	Cl2[1]	1.00(2)	2.45(2)	3.3677(15)	152.0(19)
N17	H17a	Cl2[9]	0.99(2)	2.44(2)	3.2903(14)	143.3(17)
N17	H17b	N2[10]	0.93(2)	2.05(2)	2.9824(19)	175.3(18)
N18	H18a	N3[11]	0.97(2)	2.08(3)	3.0378(18)	169.0(19)
N18	H18b	O1	0.99(2)	2.64(2)	3.4763(19)	142.9(16)
N22	H22a	Cl3[12]	0.94(2)	2.48(2)	3.3597(15)	154.5(17)
N22	H22b	Cl4	0.99(2)	2.30(2)	3.2651(16)	162.8(18)
N23	H23a	N8[13]	0.94(2)	2.08(2)	3.0191(18)	176.7(18)
N23	H23b	Cl4[14]	0.95(2)	2.57(2)	3.3963(14)	145.9(17)
N24	H24a	N9[14]	0.96(2)	2.10(2)	3.0602(18)	174.0(18)
N24	H24b	O2	0.99(2)	2.17(2)	3.1102(18)	158.6(17)

[1]1-x,1-y,1-z; [2]1-x,1-y,-z; [3]1-x,2-y,1-z; [4]1+x,1+y,+z; [5]1+x,+y,+z; [6]1-x,2-y,-z; [7]-1+x,1+y,+z; [8]+x,1+y,+z; [9]-x,1-y,1-z; [10]-1+x,-1+y,+z; [11]-1+x,+y,+z; [12]2-x,1-y,-z; [13]1+x,-1+y,+z; [14]+x,-1+y,+z

Table S5: Selected Zn–*X* (*X* = N, O, Cl, Br) bond lengths (Å). Values are refined distances with estimated standard deviations in parentheses.

Compound	Atom 1	Atom 2	Distance / Å
monoclinic (MelH)$ZnCl_3$(Mel)			
	Zn1	Cl1	2.2836(6)
	Zn1	Cl2	2.2716(7)
	Zn1	Cl3	2.2633(6)
	Zn1	N1	2.053(2)
orthorhombic (MelH)$ZnCl_3$(Mel)			
	Zn1	Cl1	2.269(1)
	Zn1	Cl2	2.280(1)
	Zn1	Cl3a	2.261(2)
	Zn1	Cl3b	2.240(3)
	Zn1	N1	2.050(4)
(MelH)$ZnBr_3$(Mel)			
	Zn1	Br1	2.403(8)
	Zn1	Br2	2.4177(9)
	Zn1	Br3a	2.391(2)
	Zn1	Br3b	2.374(2)
$Zn_3(OH)_2Cl_4(Mel)_3$			
	Zn1	Cl1	2.2616(3)
	Zn1	Cl2	2.3151(4)
	Zn1	O1	1.925(1)
	Zn1	N1	2.031(1)
	Zn2	O1	1.947(1)
	Zn2	O2	1.9456(9)
	Zn2	N7	2.058(1)
	Zn2	N13	2.045(1)
	Zn3	Cl3	2.3159(3)
	Zn3	Cl4	2.2458(3)
	Zn3	O2	1.9352(9)
	Zn3	N19	2.035(1)