Supplementary Information (SI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2025

Supporting Information

Ligand substitution in organic–inorganic hybrid zinc iodides for second-harmonic generation

Juan Cheng,[a] Gangji Yi,[a] Ying Long,[b] Qinglan Zhong,[a] Guohong Zou,[a] Lindong Luan,*[b] and Zhien Lin*[a]

[a] College of Chemistry, Sichuan University, Chengdu, 610064, China.

[b] Department of Criminal Investigation, Sichuan Police College, Luzhou, 646000, China.

* To whom correspondence should be addressed. E-mail: luanld@scpolicec.edu.cn (L. Luan); zhienlin@scu.edu.cn (Z. Lin).

Table S1. Crystallographic data and structure refinement details for compound **1**–**4**

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_6H_{12}I_4N_4OZn$	$C_6H_9I_3N_4Zn$	$C_6H_8I_2N_4Zn$	$C_9H_{12}I_2N_6Zn$
Formula weight	729.17	583.24	455.33	523.42
Crystal system	triclinic	monoclinic	monoclinic	triclinic
Space group	$P\bar{1}$ (No. 2)	*Cc* (No. 9)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	7.8051(3)	14.4475(3)	8.3020(3)	9.4368(5)
b, Å	8.1621(3)	8.5738(3)	18.1309(7)	12.6632(7)
c, Å	16.1191(7)	12.6506(4)	8.5613(3)	15.0847(8)
α, degree	84.849(2)	90	90	78.004(2)
β, degree	77.258(2)	112.904(1)	98.050(1)	84.540(2)
γ, degree	64.2120(10)	90	90	70.980(2)
Volume, Å^3	901.82(6)	1443.48(8)	1275.97(8)	1666.26(16)
Z	2	4	4	4
D_c, g/cm^3	2.685	2.684	2.370	2.086
Reflections collected	23551	25634	25073	59369
Independent reflections	4136	3300	2922	7644
Final R_1, wR_2 [I>2σ (I)][a]	0.0294, 0.0643	0.0198, 0.0434	0.0292, 0.0600	0.0319, 0.0580
Final R_1, wR_2 [all data]	0.0364, 0.0679	0.0210, 0.0438	0.0433, 0.0654	0.0577, 0.0684

Table S2. Selected bond lengths (Å) and angles (deg) for compound **1**

I1−Zn1	2.6194(6)	I2−Zn1−I3	110.43(2)
I2−Zn1	2.6033(6)	I2−Zn1−I4	112.46(2)
I3−Zn1	2.6051(6)	I3−Zn1−I1	109.04(2)
I4−Zn1	2.6078(6)	I3−Zn1−I4	107.16(2)
N1−C1	1.286(10)	I4−Zn1−I1	109.08(2)
N1−C2	1.336(9)	C1−N1−C2	109.0(7)
N2−C1	1.306(10)	C1−N2−C3	108.1(6)
N2−C3	1.310(9)	N1−C1−N2	107.5(7)
C2−C3	1.284(9)	C3−C2−N1	106.5(6)
N3−C4	1.288(9)	C2−C3−N2	109.1(7)
N3−C6	1.335(10)	C4−N3−C6	108.5(6)
N4−C4	1.238(9)	C4−N4−C5	110.2(6)
N4−C5	1.323(9)	N4−C4−N3	109.1(6)
C5−C6	1.321(11)	C6−C5−N4	106.5(7)
I2−Zn1−I1	108.61(2)	C5−C6−N3	105.7(6)

Table S3. Selected bond lengths (Å) and angles (deg) for compound **2**

I1−Zn1	2.6031(9)	I2−Zn1−I3	115.25(3)
I2−Zn1	2.5862(8)	N1−Zn1−I1	107.45(14)
I3−Zn1	2.6244(8)	N1−Zn1−I2	106.18(14)
Zn1−N1	2.012(5)	N1−Zn1−I3	105.30(14)
N1−C1	1.308(8)	C1−N1−Zn1	129.0(4)
N1−C3	1.369(8)	C1−N1−C3	105.1(5)
N2−C1	1.318(10)	C3−N1−Zn1	125.9(4)
N2−C2	1.333(10)	C1−N2−C2	108.4(6)
C2−C3	1.333(10)	N1−C1−N2	110.8(6)
N3−C4	1.283(13)	C3−C2−N2	106.4(6)
N3−C5	1.296(15)	C2−C3−N1	109.3(7)
N4−C4	1.247(12)	C4−N3−C5	108.3(8)
N4−C6	1.313(12)	C4−N4−C6	108.0(8)
C5−C6	1.316(15)	N4−C4−N3	109.9(9)
I1−Zn1−I3	108.63(3)	N3−C5−C6	106.4(8)
I2−Zn1−I1	113.41(3)	N4−C6−C5	107.2(9)

Table S4. Selected bond lengths (Å) and angles (deg) for compound **3**

I1−Zn1	2.5824(5)	N1−Zn1−N3	108.90(14)
I2−Zn1	2.5803(6)	N3−Zn1−I1	107.16(10)
Zn1−N1	2.000(3)	N3−Zn1−I2	108.66(11)
Zn1−N3	2.008(4)	C1−N1−Zn1	127.2(3)
N1−C1	1.304(6)	C1−N1−C3	104.8(4)
N1−C3	1.345(6)	C3−N1−Zn1	128.0(3)
N2−C1	1.326(7)	C2−N2−C1	108.4(5)
N2−C2	1.310(8)	C4−N3−Zn1	127.3(3)
N3−C4	1.313(6)	C4−N3−C6	104.3(4)
N3−C6	1.357(6)	C6−N3−Zn1	128.3(3)
N4−C4	1.327(7)	C4−N4−C5	107.0(5)
N4−C5	1.341(8)	N1−C1−N2	110.6(5)
C2−C3	1.338(7)	N2−C2−C3	106.0(5)
C5−C6	1.320(8)	C2−C3−N1	110.1(5)
I2−Zn1−I1	115.46(2)	N3−C4−N4	111.5(5)
N1−Zn1−I1	108.86(10)	C6−C5−N4	106.8(5)
N1−Zn1−I2	107.67(11)	C5−C6−N3	110.5(5)

Table S5. Selected bond lengths (Å) and angles (deg) for compound **4**

I1−Zn1	2.5364(6)	C3−N1−Zn1	127.8(3)
Zn1−N1	2.015(4)	C1−N2−C2	107.7(5)
Zn1−N3	2.005(4)	C4−N3−Zn1	127.3(4)
Zn1−N5	1.995(3)	C4−N3−C6	105.5(5)
N1−C1	1.294(6)	C6−N3−Zn1	127.2(4)
N1−C3	1.341(6)	C4−N4−C5	107.0(6)
N2−C1	1.316(7)	C7−N5−Zn1	125.8(3)
N2−C2	1.336(8)	C7−N5−C9	105.4(4)
N3−C4	1.313(6)	C9−N5−Zn1	128.6(3)
N3−C6	1.363(6)	C7−N6−C8	107.1(4)
N4−C4	1.328(8)	N1−C1−N2	111.4(5)
N4−C5	1.388(10)	C3−C2−N2	105.5(6)
N5−C7	1.318(5)	C2−C3−N1	110.5(5)
N5−C9	1.365(5)	N3−C4−N4	110.5(6)
N6−C7	1.319(6)	C6−C5−N4	105.8(6)
N6−C8	1.348(7)	C5−C6−N3	111.2(7)
C2−C3	1.329(7)	N5−C7−N6	111.4(4)
C5−C6	1.297(8)	C9−C8−N6	107.3(5)
C8−C9	1.340(7)	C8−C9−N5	108.7(4)
I2−Zn2	2.5298(6)	N7−Zn2−I2	113.57(10)
Zn2−N7	2.005(3)	N9−Zn2−I2	110.49(12)
Zn2−N9	1.998(4)	N9−Zn2−N7	107.19(15)
Zn2−N11	1.995(4)	N11−Zn2−I2	117.05(10)
N7−C10	1.312(5)	N11−Zn2−N7	103.57(14)
N7−C12	1.358(6)	N11−Zn2−N9	104.08(15)
N8−C10	1.324(6)	C10−N7−Zn2	127.5(3)
N8−C11	1.340(7)	C10−N7−C12	105.9(4)
N9−C13	1.329(6)	C12−N7−Zn2	126.5(3)
N9−C15	1.352(6)	C10−N8−C11	107.8(4)
N10−C13	1.329(7)	C13−N9−Zn2	126.8(3)
N10−C14	1.364(8)	C13−N9−C15	105.1(5)
N11−C16	1.303(6)	C15−N9−Zn2	127.9(4)
N11−C18	1.361(6)	C13−N10−C14	107.5(6)
N12−C16	1.317(7)	C16−N11−Zn2	126.8(4)
N12−C17	1.322(7)	C16−N11−C18	104.5(5)
C11−C12	1.345(7)	C18−N11−Zn2	128.8(3)
C14−C15	1.314(8)	C16−N12−C17	107.8(5)

C17−C18	1.340(8)	N7−C10−N8	110.8(5)
N1−Zn1−I1	114.34(10)	N8−C11−C12	106.7(5)
N3−Zn1−I1	110.41(12)	C11−C12−N7	108.9(5)
N3−Zn1−N1	104.62(15)	N10−C13−N9	110.2(5)
N5−Zn1−I1	117.89(10)	C15−C14−N10	106.1(5)
N5−Zn1−N1	103.76(14)	C14−C15−N9	111.1(6)
N5−Zn1−N3	104.56(15)	N11−C16−N12	111.8(5)
C1−N1−Zn1	127.1(4)	N12−C17−C18	106.5(6)
C1−N1−C3	105.0(4)	C17−C18−N11	109.4(5)

Table S6. Dipole moments for ZnI_4 tetrahedron of compound **1** (*D* = Debyes).

compound **1**				
Polar unit (a unit cell)	Dipole moment (*D*)			
	x-component	y-component	z-component	total magnitude
ZnI_4	-0.409	-0.741	0.627	1.053
ZnI_4	0.409	0.741	-0.627	1.053
ZnI_4	-0.409	-0.741	0.627	1.053
ZnI_4	0.409	0.741	-0.627	1.053
	U_x	U_y	U_z	U_t
total	0.000	0.000	0.000	0.000
Cell Volume	901.82(6) Å^3			

Table S7. Dipole moments for ZnI_3N tetrahedron of compound **2** (*D* = Debyes).

compound **2**				
Polar unit (a unit cell)	Dipole moment (*D*)			
	x-component	y-component	z-component	total magnitude
ZnI_3N	-2.263	7.484	2.196	8.121
ZnI_3N	-2.263	7.484	2.196	8.121
ZnI_3N	-2.263	-7.484	2.196	8.121
ZnI_3N	-2.263	-7.484	2.196	8.121
	U_x	U_y	U_z	U_t
total	-9.052	0.000	8.784	12.613
Cell Volume	1443.48(8) Å^3			

Table S8. Dipole moments for ZnI_2N_2 tetrahedron of compound **3** (*D* = Debyes).

compound **3**				
Polar unit (a unit cell)	Dipole moment (*D*)			
	x-component	y-component	z-component	total magnitude
ZnI_2N_2	-2.683	4.534	-10.220	11.498
ZnI_2N_2	-2.684	-4.532	-10.220	11.498
ZnI_2N_2	2.684	4.532	10.220	11.498
ZnI_2N_2	2.686	-4.530	10.220	11.497
	U_x	U_y	U_z	U_t
total	0.003	0.004	0.000	0.005
Cell Volume	1275.97(8) Å^3			

Table S9. Dipole moments for $ZnIN_3$ tetrahedron of compound **4** (*D* = Debyes).

compound **4**				
Polar unit (a unit cell)	Dipole moment (*D*)			
	x-component	y-component	z-component	total magnitude
$ZnIN_3$	1.624	-4.288	9.155	10.239
$ZnIN_3$	-1.624	4.288	-9.155	10.239
$ZnIN_3$	6.378	-7.435	-1.488	9.908
$ZnIN_3$	-6.378	7.435	1.488	9.908
$ZnIN_3$	6.378	-7.435	-1.488	9.908
$ZnIN_3$	-6.378	7.435	1.488	9.908
	U_x	U_y	U_z	U_t
total	0.000	0.000	0.000	0.000
Cell Volume	1666.26(16) Å^3			

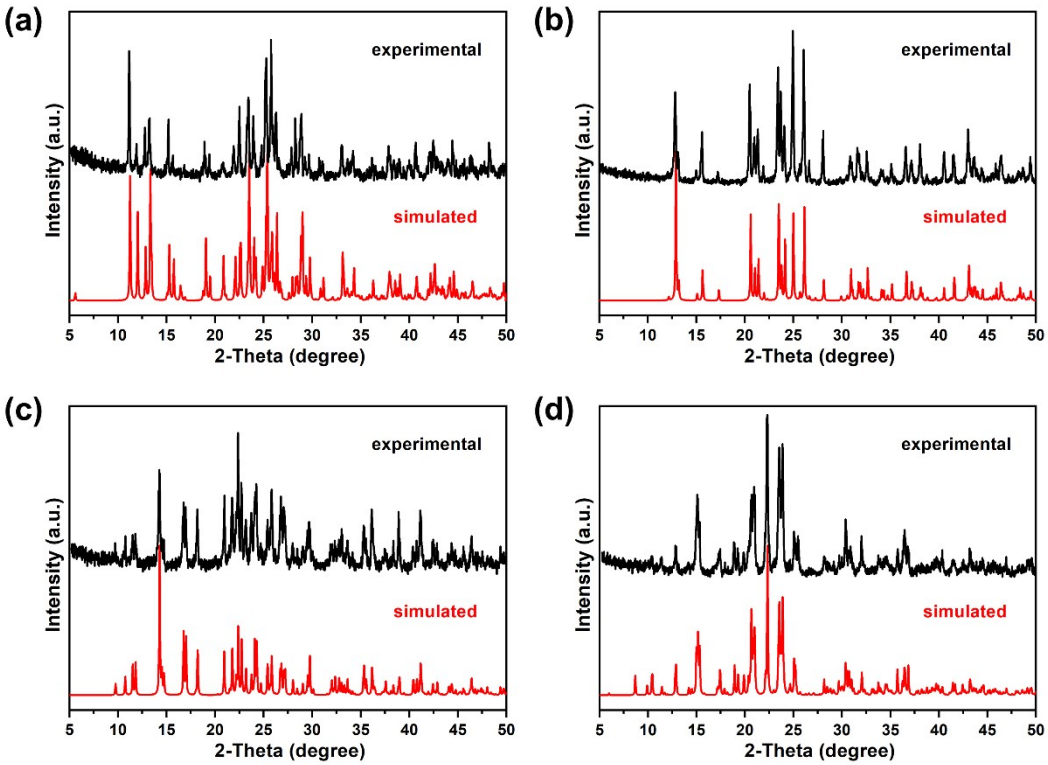

Fig. S1 Simulated and experimental powder XRD patterns for compound **1**(a), **2** (b), **3** (c), and **4** (d).

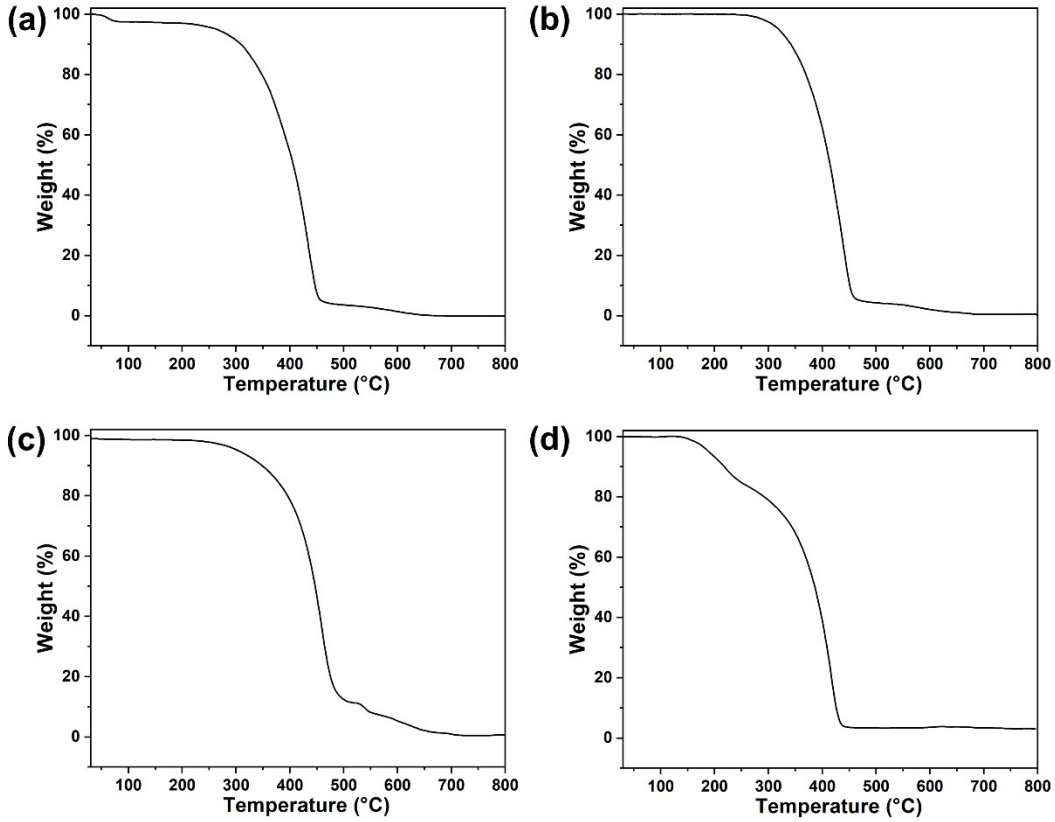

Fig. S2 TGA curves of compounds **1**(a), **2** (b), **3** (c), and **4** (d).

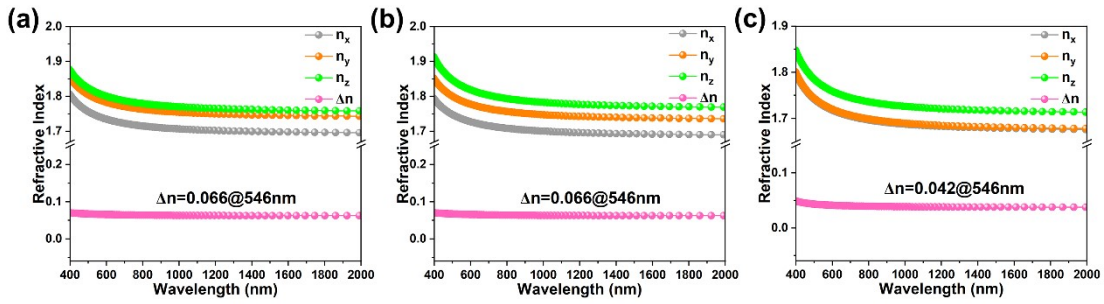

Fig. S3 Calculated linear refractive indices of compounds **1**(a), **3** (b), and **4** (c).