Supplementary Information

Thermally stimuli-responsive materials with transformable double channels of nonlinear optical and dielectric

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Table S1. Crystal data and structure refinement for Compound **1** and **2**.

Temperature	**183 K**	**235 K**	**263 K**	**233 K**	**277 K**
Empirical formula	$2(C_5H_{13}FN)\cdot CdI_4$	$2(C_5H_{13}FN)\cdot CdI_4$	$CdI_4\cdot 2(C_5FN)$	$I_4Zn\cdot 2(C_5H_{13}FN)$	$I_4Zn\cdot 2(C_5FN)$
Formula weight	832.33	832.33	806.12	785.3	759.09
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	*Pnma*	$P2_12_12_1$	*Pnma*
a/ Å	9.4619 (10)	9.4851(2)	14.4331(7)	9.3191(3)	14.3356(6)
b/ Å	14.2560 (18)	14.3502(4)	9.4991(7)	14.1463 (4)	9.3530(5)
c/ Å	16.857 (2)	16.9573(10)	17.0349(14)	16.6946(5)	16.9232(9)
α/°	90	90	90	90	90
β/°	90	90	90	90	90
γ/°	90	90	90	90	90
Volume($Å^3$)	2273.9 (5)	2308.11(10)	2335.5(3)	2200.86(12)	2269.1(10)
Z	4	4	4	4	4
Radiation type	Mo-Ka	Mo-Ka	Mo-Ka	Mo-Ka	Mo-Ka
Absorption correction	Semi-empirical	Semi-empirical	Semi-empirical	Semi-empirical	Semi-empirical
F(000)	1512	1512	1408	1440	1336
GOF	1.03	1.09	1.13	1.05	1.13
R_1[a][I > 2σ(I)]	0.036	0.048	0.082	0.033	0.089
wR_2[b][I >	0.091	0.14	0.285	0.093	0.311

2σ(I)]

Table S2. Bond lengths (Å) and bond angles for compound **1** at 183 K.

Bond lengths (Å) and Bond angles			
I1—Cd1	2.7836 (10)	N2—C8	1.497 (10)
Cd1—I4	2.7690 (10)	N2—C7	1.500 (11)
Cd1—I3	2.7796 (10)	N2—C9	1.485 (11)
Cd1—I2	2.7509 (11)	N2—C6	1.489 (11)
N1—C4	1.501 (10)	F1—C5	1.352 (19)
N1—C2	1.500 (11)	C4—C5	1.494 (12)
N1—C1	1.487 (10)	F2—C10	1.37 (2)
N1—C3	1.487 (11)	C9—C10	1.511 (12)
I4—Cd1—I1	108.72 (3)	C3—N1—C2	109.4 (10)
I4—Cd1—I3	107.15 (3)	C8—N2—C7	110.7 (10)
I3—Cd1—I1	115.46 (4)	C9—N2—C8	112.4 (11)
I2—Cd1—I1	104.23 (3)	C9—N2—C7	110.7 (10)
I2—Cd1—I4	113.44 (4)	C9—N2—C6	107.8 (14)
I2—Cd1—I3	108.02 (4)	C6—N2—C8	107.1 (11)
C2—N1—C4	106.9 (9)	C6—N2—C7	107.7 (13)
C1—N1—C4	111.7 (9)	C5—C4—N1	117.1 (10)
C1—N1—C2	108.3 (10)	F1—C5—C4	113.8 (13)
C1—N1—C3	109.6 (12)	N2—C9—C10	116.4 (12)
C3—N1—C4	110.8 (11)	F2—C10—C9	109.9 (14)

Table S3. Bond lengths (Å) and bond angles for compound **1** at 263 K.

Bond lengths (Å) and Bond angles			
Cd1—I1	2.768 (2)	C3—C4	1.517 (10)
Cd1—I3	2.7577 (17)	C3—C4ii	1.517 (10)
Cd1—I3i	2.7577 (17)	C3—C4'ii	1.517 (10)
Cd1—I2	2.774 (3)	C3—C4'	1.517 (10)
N2—C7	1.486 (10)	C8—F2	1.378 (10)
N2—C5i	1.491 (10)	F1—F1ii	1.1 (3)
N2—C5	1.491 (10)	F1—C4ii	1.8 (2)
N2—C6	1.490 (10)	F1—C4	1.380 (10)
N1—C3	1.501 (10)	C4—F1ii	1.8 (2)
N1—C1	1.499 (10)	C4—C4ii	1.2 (7)
N1—C2ii	1.503 (9)	C8'—C8'i	1.7 (2)
N1—C2	1.503 (9)	C8'—F2'	1.14 (10)
C7—C8	1.509 (10)	F1'—C4'	1.380 (10)
C7—C8'	1.41 (11)	C4'—C4'ii	1.3 (7)
C7—C8'i	1.41 (11)		
I1—Cd1—I2	116.41 (9)	N1—C3—C4ii	123 (8)

I3—Cd1—I1	106.48 (6)	N1—C3—C4	123 (8)
I3i—Cd1—I1	106.48 (6)	N1—C3—C4'ii	127 (6)
I3—Cd1—I3i	113.39 (10)	N1—C3—C4'	127 (6)
I3i—Cd1—I2	107.15 (6)	C4—C3—C4ii	48 (10)
I3—Cd1—I2	107.15 (6)	C4'—C3—C4'ii	51 (10)
C7—N2—C5	108.1 (16)	F2—C8—C7	115.8 (11)
C7—N2—C5i	108.1 (16)	F1ii—F1—C4	92 (10)
C7—N2—C6	119 (3)	F1ii—F1—C4ii	49 (9)
C5—N2—C5i	102 (3)	C4—F1—C4ii	43 (10)
C6—N2—C5	109.0 (18)	C3—C4—F1ii	94 (10)
C6—N2—C5i	109.0 (18)	F1—C4—C3	115.2 (11)
C3—N1—C2	111.7 (9)	F1—C4—F1ii	38 (10)
C3—N1—C2ii	111.7 (9)	C4ii—C4—C3	66 (10)
C1—N1—C3	112.7 (10)	C4ii—C4—F1ii	49 (9)
C1—N1—C2ii	111.9 (9)	C4ii—C4—F1	88 (10)
C1—N1—C2	111.9 (9)	C7—C8'—C8'i	52 (5)
C2ii—N1—C2	96 (3)	F2'—C8'—C7	131 (9)
N2—C7—C8	132 (2)	F2'—C8'—C8'i	95 (6)
C8'i—C7—N2	118 (5)	F1'—C4'—C3	115.2 (12)
C8'—C7—N2	118 (5)	C4'ii—C4'—C3	64 (10)
C8'i—C7—C8'	75 (9)	C4'ii—C4'—F1'	101 (10)

Symmetry codes: (i) x, −y+3/2, z; (ii) x, −y+1/2, z.

Table S4. Bond lengths (Å) and bond angles for compound **1** at 235 K.

Bond lengths (Å) and Bond angles			
Cd1—I1	2.7775 (8)	N8—C0AA	1.503 (8)
Cd1—I2	2.7614 (9)	N8—C1AA	1.506 (8)
Cd1—I4	2.7587 (10)	N8—C4AA	1.506 (12)
Cd1—I3	2.7737 (9)	N8—C3AA	1.485 (12)
N1—C3	1.504 (10)	C9—F2	1.37 (3)
N1—C4	1.502 (10)	C9—C4AA	1.501 (18)
N1—C1	1.520 (12)	C0AA—N8—C1AA	109.1 (9)
N1—C2	1.488 (13)	C0AA—N8—C4AA	109.9 (9)
F1—C5	1.276 (17)	C1AA—N8—C4AA	119.3 (10)
C4—C5	1.504 (10)	C3AA—N8—C0AA	99.9 (10)
I2—Cd1—I1	107.96 (3)	C3AA—N8—C1AA	104.1 (10)
I2—Cd1—I3	107.39 (3)	C3AA—N8—C4AA	112.6 (10)
I4—Cd1—I1	105.39 (3)	F2—C9—C4AA	105.6 (18)
I4—Cd1—I2	113.22 (3)	C9—C4AA—N8	113.7 (14)
I4—Cd1—I3	107.57 (3)	C2—N1—C3	114.4 (12)
I3—Cd1—I1	115.48 (3)	C2—N1—C4	110.1 (10)
C3—N1—C4	110.3 (8)	C2—N1—C1	109.8 (10)
C3—N1—C1	106.3 (9)	C5—C4—N1	115.4 (9)

C4—N1—C1	105.4 (7)	F1—C5—C4	117.9 (12)

Table S5. Bond lengths (Å) and bond angles for compound **2** at 233 K.

Bond lengths (Å) and Bond angles			
I002—Zn05	2.6139 (10)	F10—C18	1.350 (15)
I004—Zn05	2.5442 (11)	F7—C16—C12	115.4 (11)
Zn05—I1	2.5824 (10)	F10—C18—C9	115.6 (11)
Zn05—I2	2.6045 (11)	N5—C8	1.522 (13)
N4—C12	1.467 (13)	N5—C13	1.444 (12)
N4—C11	1.483 (14)	N5—C15	1.493 (15)
N4—C0AA	1.505 (12)	C9—C18	1.429 (18)
N4—C19	1.506 (15)	C12—C16	1.503 (18)
N5—C9	1.506 (11)	F7—C16	1.346 (15)
I004—Zn05—I002	108.35 (4)	C11—N4—C0AA	109.8 (8)
I004—Zn05—I1	105.52 (4)	C11—N4—C19	108.6 (9)
I004—Zn05—I2	112.15 (4)	C0AA—N4—C19	103.9 (9)
I1—Zn05—I002	114.23 (4)	C9—N5—C8	107.4 (8)
I1—Zn05—I2	109.22 (4)	C13—N5—C9	112.0 (8)
I2—Zn05—I002	107.47 (4)	C13—N5—C8	109.8 (9)
C12—N4—C11	115.0 (8)	C13—N5—C15	110.5 (11)
C12—N4—C0AA	110.9 (8)	C15—N5—C9	109.0 (9)
C12—N4—C19	107.9 (10)	C15—N5—C8	108.0 (9)
N4—C12—C16	116.3 (11)	C18—C9—N5	118.5 (10)

Table S6. Bond lengths (Å) and bond angles for compound **2** at 277 K.

Bond lengths (Å) and Bond angles			
I1—Zn1	2.575 (3)	C8—F2'	1.378 (10)
I3—Zn1	2.5825 (18)	C4—F1	1.372 (10)
I2—Zn1	2.595 (3)	C4—F1i	1.372 (10)
N1—C3	1.494 (7)	C4—F1'	1.382 (10)
N1—C2	1.490 (6)	C4—F1'i	1.382 (10)
N1—C1	1.497 (6)	N2—C7	1.505 (7)
N1—C1i	1.497 (6)	N2—C5	1.524 (5)
C3—C4	1.509 (7)	N2—C5i	1.524 (5)
C8—C7	1.510 (7)	N2—C6	1.507 (7)
C8—F2	1.369 (10)	F1—F1i	0.93 (8)
I1—Zn1—I3	107.11 (7)	F1i—C4—C3	115.4 (10)
I1—Zn1—I3i	107.11 (7)	F1—C4—F1i	40 (4)
I1—Zn1—I2	114.91 (11)	F1—C4—F1'i	25 (2)
I3—Zn1—I3i	112.49 (11)	F1i—C4—F1'i	64 (2)
I3i—Zn1—I2	107.67 (7)	F1'i—C4—C3	110.4 (9)
I3—Zn1—I2	107.67 (7)	F1'—C4—C3	110.4 (9)
C3—N1—C1i	112.0 (6)	F1'—C4—F1'i	89 (3)
C3—N1—C1	112.0 (6)	C7—N2—C5	109.4 (5)

C2—N1—C3	113.8 (7)	C7—N2—C5i	109.4 (5)
C2—N1—C1	113.1 (6)	C7—N2—C6	110.8 (7)
C2—N1—C1i	113.1 (6)	C5i—N2—C5	109.1 (7)
C1—N1—C1i	90.8 (15)	C6—N2—C5i	109.0 (6)
N1—C3—C4	130.2 (10)	C6—N2—C5	109.0 (6)
F2—C8—C7	115.7 (10)	N2—C7—C8	134.2 (9)
F2'—C8—C7	110.9 (9)	F1i—F1—C4	70.1 (18)
F1—C4—C3	115.4 (10)		

Symmetry code: (i) x, $-y+3/2$, z.

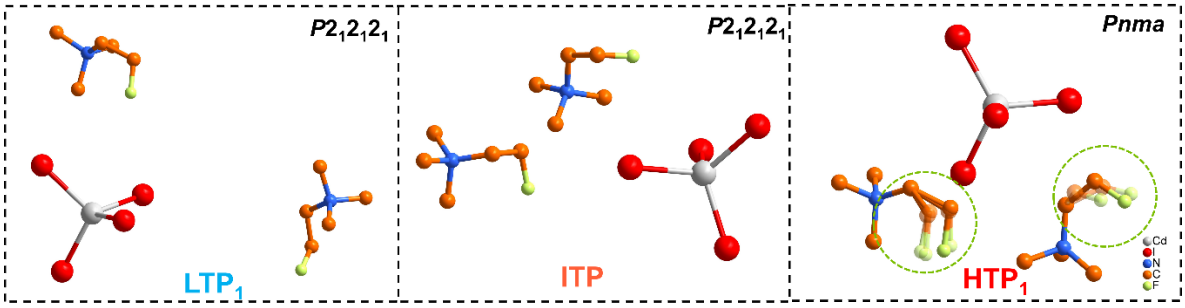

Fig. S1 Molecular structure of compound **1** at LTP_1, ITP and HTP_1.

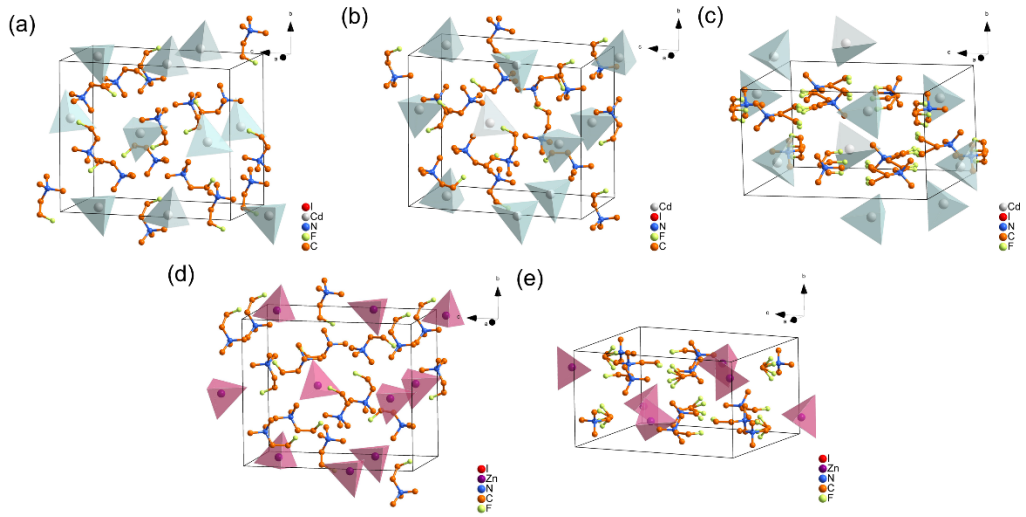

Fig. S2 Unit cell packing view of compound **1** at LTP_1 (a), ITP (b) and HTP_1 (c). Unit cell packing view of compound **2** at LTP_2 (d) and HTP_2 (e).

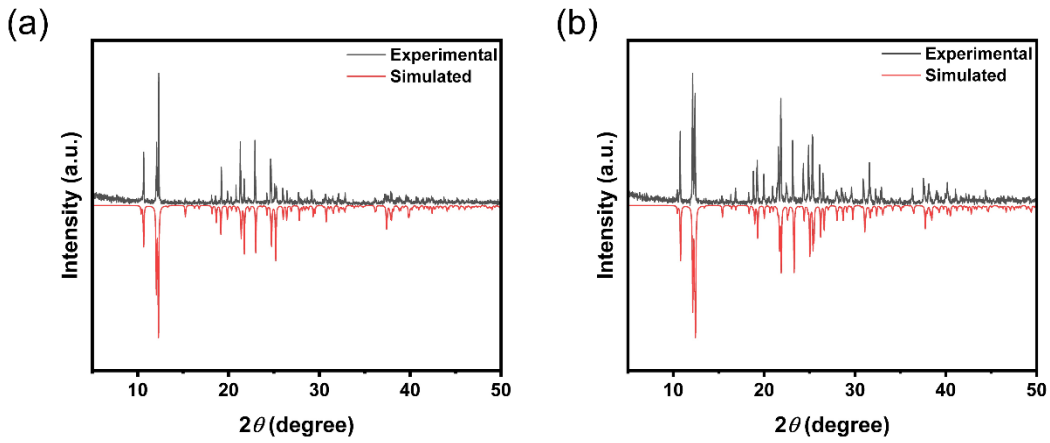

Fig. S3 Simulated and experimental PXRD patterns of compound **1** (a) and **2** (b) powders at room temperature.

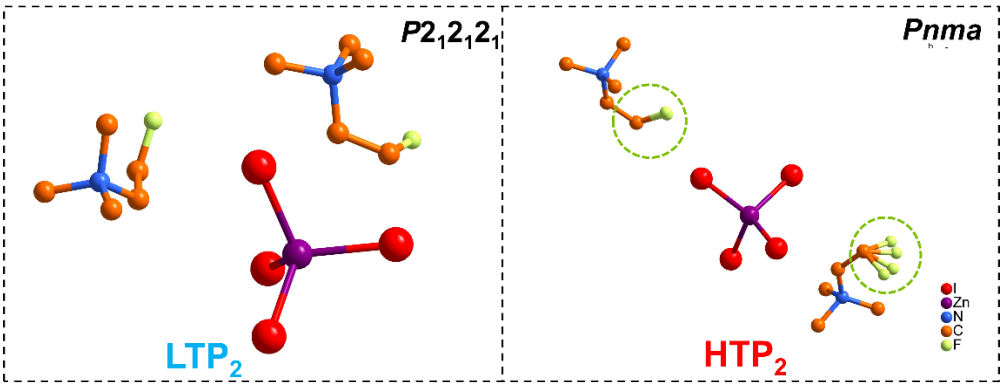

Fig. S4 Molecular structure of compound **2** at LTP_2, ITP and HTP_2.

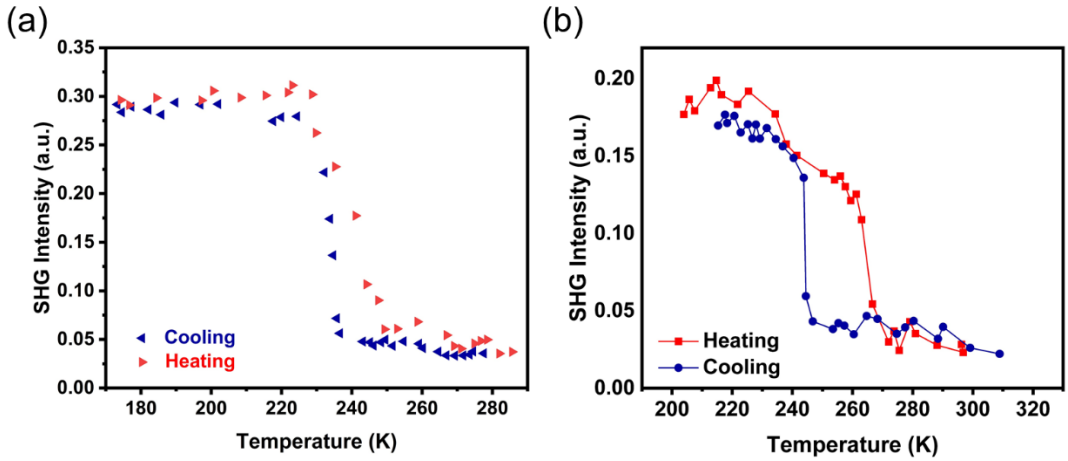

Fig. S4 Variable temperature SHG test of compound **1** (a) and compound **2** (b).