Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Perovskite-type organic-inorganic hybrid NLO switches tuned by guest cation

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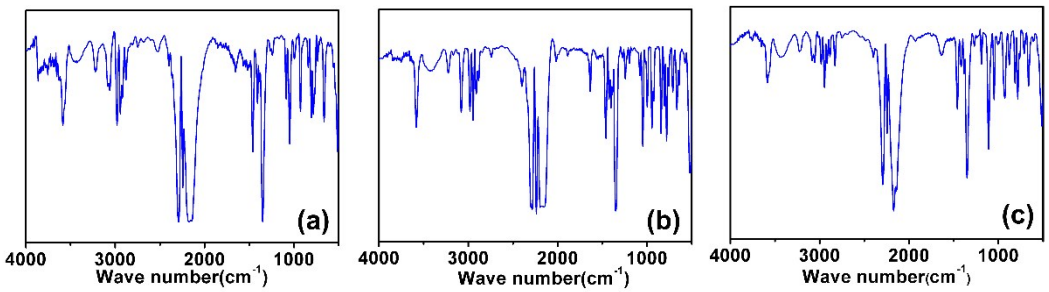

Figure S1. The IR spectrum of compounds **1**(a), **2**(b), **3**(c).

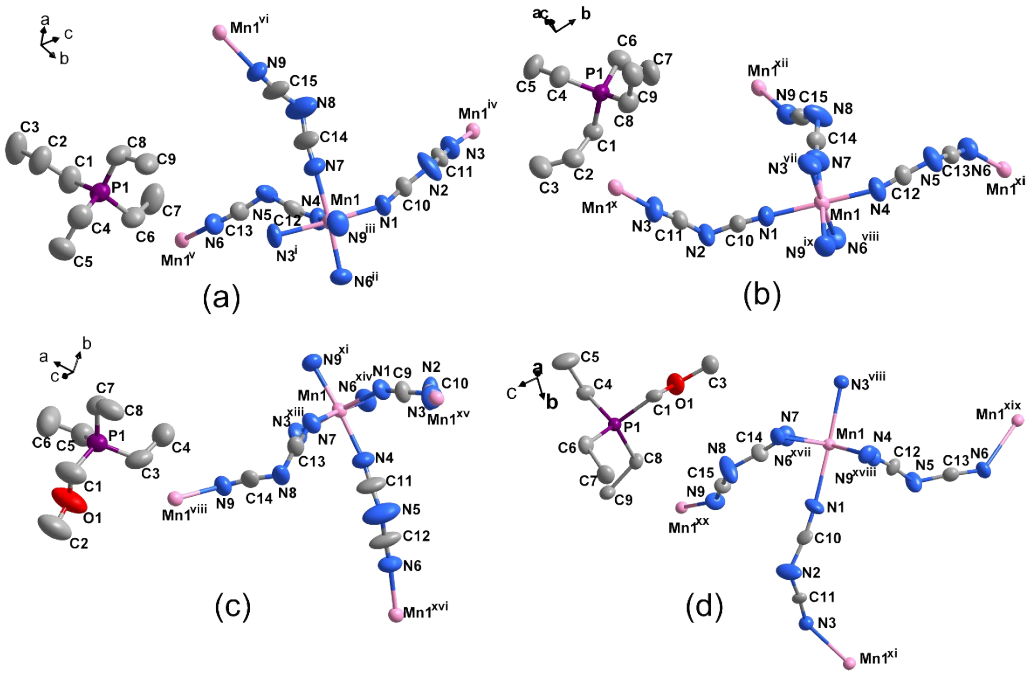

Figure S2. The asymmetric units of compounds **1**(a), **2**(b), **3**(c) at 293 K and **3**(d) at 173 K. Thermal ellipsoids for all atoms are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Symmetry codes:

(i) 0.5-*x*, 2-*y*, -0.5+*z*; (ii) -*x*, 0.5+*y*, 1.5-*z*; (iii) 1-*x*, 0.5+*y*, 1.5-*z*; (iv) 0.5-*x*, 2-*y*, 0.5+*z*; (v) -*x*, -0.5+*y*, 1.5-*z*; (vi) 1-*x*, -0.5+*y*, 1.5-*z*; (vii) 2-*x*, 0.5+*y*, 0.5-*z*; (viii) 1-*x*, -0.5+*y*, 0.5-*z*; (ix) *x*, 1.5-*y*, -0.5+*z*; (x) 2-*x*, -0.5+*y*, 0.5-*z*; (xi) 1-*x*, 0.5+*y*, 0.5-*z*; (xii) *x*, 1.5-*y*, 0.5+*z*. (xiii) 0.5-*x*, 1-*y*, 0.5+*z*; (xiv) -*x*, 0.5+*y*, 0.5-*z* ; (xv) 0.5-*x*, 1-*y*, -0.5+*z*; (xvi) –*x*, -0.5+*y*, 0.5-*z*; (xvii) *x, 0.5-y, 0.5+z;* (xviii) *-1+x, 0.5-y, -0.5+z*; (xix) *x*, *0.5-y, -0.5+z*; (xx) *1+x, 0.5-y, 0.5+z*.

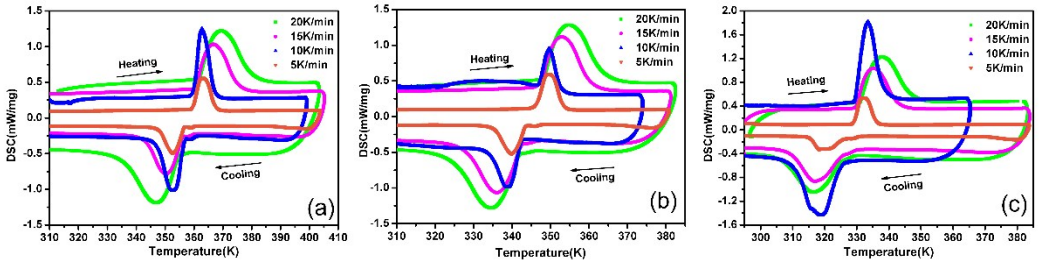

Figure S3. DSC curves of compounds **1**(a), **2**(b), **3**(c) obtained at different sweeping rates (20 K/min, 15 K/min, 10 K/min and 5 K/min) above room temperature in the cooling and heating cycles.

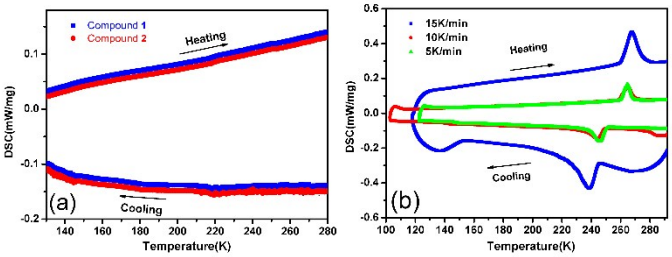

Figure S4. DSC curves of compounds **1** and **2**(a), **3**(b) obtained below room temperature in the cooling and heating cycles.

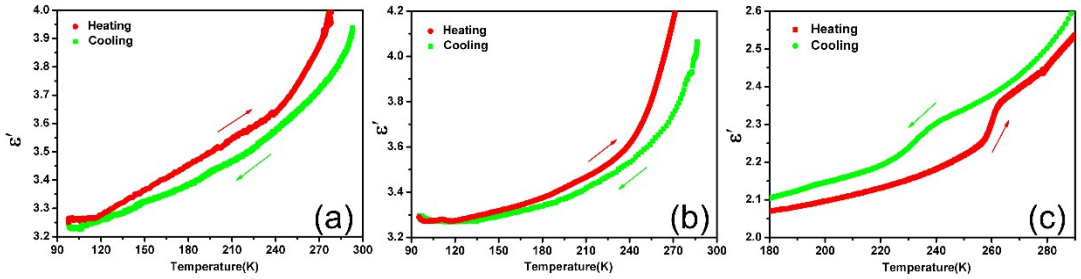

Figure S5. Temperature-variable dielectric constant measured at 1 MHz of compounds **1**(a), **2**(b), **3**(c).

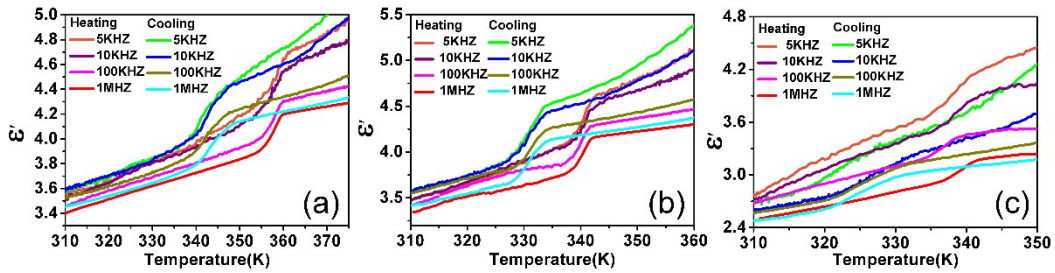

Figure S6. The dielectric constant (ε′) of compounds **1**(a), **2**(b), **3**(c) at different frequencies in the heating and cooling processes.

Table S1. Crystal data, data collection and reduction parameter of crystals of **1, 2, 3** at 293 K.and **3** at 173 K.

Compound	**1**	**2**	**3**	**3**
Chemical Formula	$C_{15}H_{22}MnN_9P$	$C_{15}H_{20}MnN_9P$	$C_{14}H_{20}MnN_9OP$	$C_{14}H_{20}MnN_9OP$
Formula weight	414.33	412.31	416.30	416.30
Temperature	293 K	293 K	293 K	173 K
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$	$P2_12_12_1$	$P2_1/c$
a, Å	10.496(2)	10.098(2)	10.694(2)	10.391(13)
b, Å	12.396(3)	12.156(2)	12.092(2)	15.81(2)
c, Å	16.254(3)	17.119(3)	16.108(3)	15.482(15)
α, deg	90.00	90.00	90.00	90.00
β, deg	90.00	96.32(3)	90.00	127.560(19)
γ, deg	90.00	90.00	90.00	90.00
V, Å^3	2114.9(7)	2088.6(7)	2083.0(7)	2016(4)
Z	4	4	4	4
Index ranges	-13 ≤ *h* ≥ 10 -21 ≤ *l* ≥ 21 -15 ≤ *k* ≥ 15	-13 ≤ *h* ≥ 13 -21 ≤ *l* ≥ 21 -15 ≤ *k* ≥ 11	-12 ≤ *h* ≥ 13 -20 ≤ *l* ≥ 20 -15 ≤ *k* ≥ 15	-12 ≤ *h* ≥ 12 -18 ≤ *l* ≥18 -18 ≤ *k* ≥ 18
μ, cm^{-1}	0.72	0.73	0.73	0.76
reflns measured	14796	14172	14569	16461
independent reflns	4818	4638	4760	3334
reflns used	2656	3275	2752	2602
Goodness-of-fit on F^2	1.04	1.02	1.03	1.13
Final *R* indices [*I* > 2sigma(*I*)]	R_1 =0.055, wR_2 = 0.138	R_1 = 0.048, wR_2 = 0.132	R_1 = 0.060, wR_2 = 0.154	R_1 = 0.134, wR_2 = 0.3438

Table S2. The key bond lengths and angels of compounds **1, 2** and **3** at 293 K.

Bond lengths	**1**	**2**	**3**	Bond angles	**1**	**2**	**3**
Mn1—N1	2.206(4)	2.221(3)	2.199(4)	Mn1—N1—C10	155.1(4)	178.2(3)	152.6(4)
Mn1—N4	2.258(4)	2.208(3)	2.231(5)	Mn1—N4—C12	124.8(4)	160.2(3)	168.5(6)
Mn1—N7	2.222(5)	2.221(3)	2.270(4)	Mn1—N7—C14	167.2(6)	174.1(4)	123.4(4)
Mn1—N3	2.240(4)	2.214(3)	2.224(5)	N1—Mn1—N4	91.08(15)		88.60(2)
Mn1—N6	2.215(4)	2.227(3)	2.194(5)	N1—Mn1—N6	94.28(18)		90.07(19)
Mn1—N9	2.195(5)	2.216(3)	2.213(5)	N1—Mn1—N9	91.07(17)	86.73(12)	
C1—C2	1.460(9)	1.469(5)		N1—Mn1—N7	88.78(18)	90.86(14)	92.04(17)
C2—C3	1.503(9)	1.337(4)		N4—Mn1—N3	86.32(16)	87.80(14)	88.60(2)
C4—C5	1.500(1	1.472(3)	1.521(11)	N4—Mn1—N6	90.02(17)	91.16(13)	90.70(2)
C6—C7	1.494(9)	1.544(3)	1.472(10)	N4—Mn1—N7	87.59(18)	89.73(14)	87.01(19)
C8—C9	1.518(9)	1.492(5)	1.498(9)	N6—Mn1—N9	91.20(2)	92.01(15)	91.80(2)
C1—P1	1.793(6)	1.806(4)	1.800(7)	N7—Mn1—N9	91.10(2)		90.36(18)
C4—P1	1.785(7)	1.828(4)	1.816(8)	P1—C1—C2	116.0(5)	113.9(3)	
C6—P1	1.807(6)	1.774(4)	1.790(7)	C1—C2—C3	115.2(7)	123.6(4)	

C8—P1	1.799(7)	1.805(4)	1.802(6)	N4—Mn1—N9		92.70(13)	
C1—O1			1.373(9)	N3—Mn1—N9		92.51(15)	
C3—O1			1.370(8)	N3—Mn1—N7		88.38(16)	86.89(17)
				N3—Mn1—N1		91.31(14)	
				N7—Mn1—N6		87.14(16)	
				P1—C1—O1			107.5(6)
				C1—O1—C3			113.5(7)
				C1—P1—C6	108.4(3)	110.9(3)	108.7(4)
				C1—P1—C8	110.3(4)	109.8(2)	109.0(4)
				C1—P1—C4	111.5(3)	110.7(4)	109.4(7)
				C4—P1—C6	109.8(3)	108.4(2)	110.8(3)
				C4—P1—C8	107.4(3)	107.0(2)	107.5(4)
				C6—P1—C8	109.5(3)	110.1(4)	111.0(2)
				C10—N2—C11	121.4(4)	121.6(3)	120.8(5)
				C12—N2—C13	120.5(5)	119.9(3)	122.6(7)
				C14—N2—C15	122.7(6)	121.5(3)	121.0(5)
				N1—C10—N2	172.1(5)	173.2(4)	172.1(6)
				N2—C11—N3	174.3(5)	172.1(4)	174.0(6)
				N4—C12—N5	172.7(6)	172.8(3)	170.9(9)
				N5—C13—N6	174.3(6)	174.1(4)	171.0(8)
				N7—C14—N8	170.1(8)	173.1(4)	173.3(6)
				N8—C15—N9	171.1(8)	172.1(4)	173.2(7)