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

Supporting Information

Switchable Behaviors of Quadratic Nonlinear Optical Properties Originating from Bi-step Phase Transitions in a Molecule-Based Crystal

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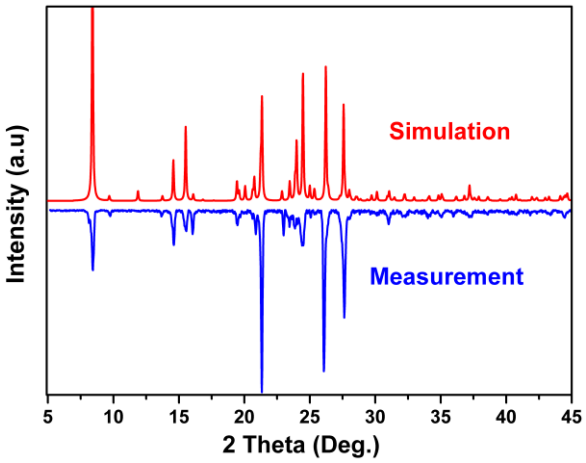

Figure S1. Experimental and simulated PXRD Patterns of **1**, verifying the phase purity

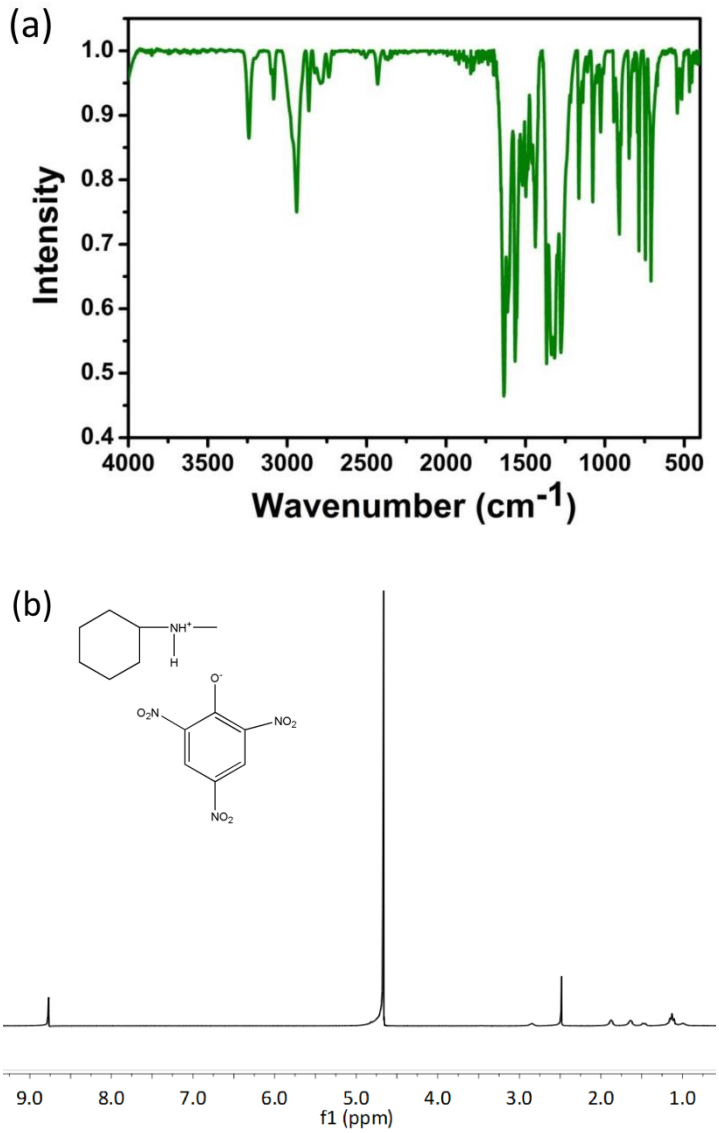

Figure S2. (a) IR Spectrum of 1, (b) ^{1}H NMR spectra measured in D_2O for **1**.

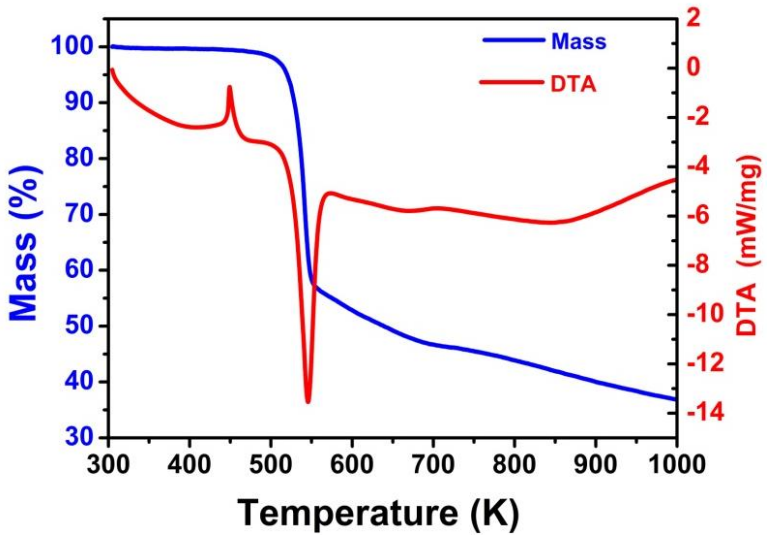

Figure S3. The TG/DTA curves of **1** with heating rate 10 K/min.

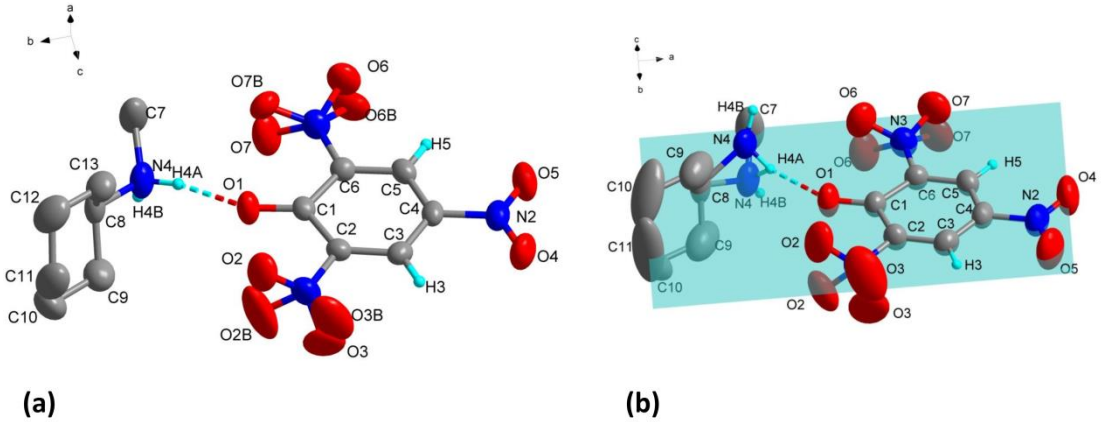

Figure S4. (a) N- methylcyclohexylaminium cation with little thermal ellipsoid at 260K (ITP); (b) highly-disordered N- methylcyclohexylaminium cation of 1 at 293 K. Hydrogen atoms are omitted for clarity.

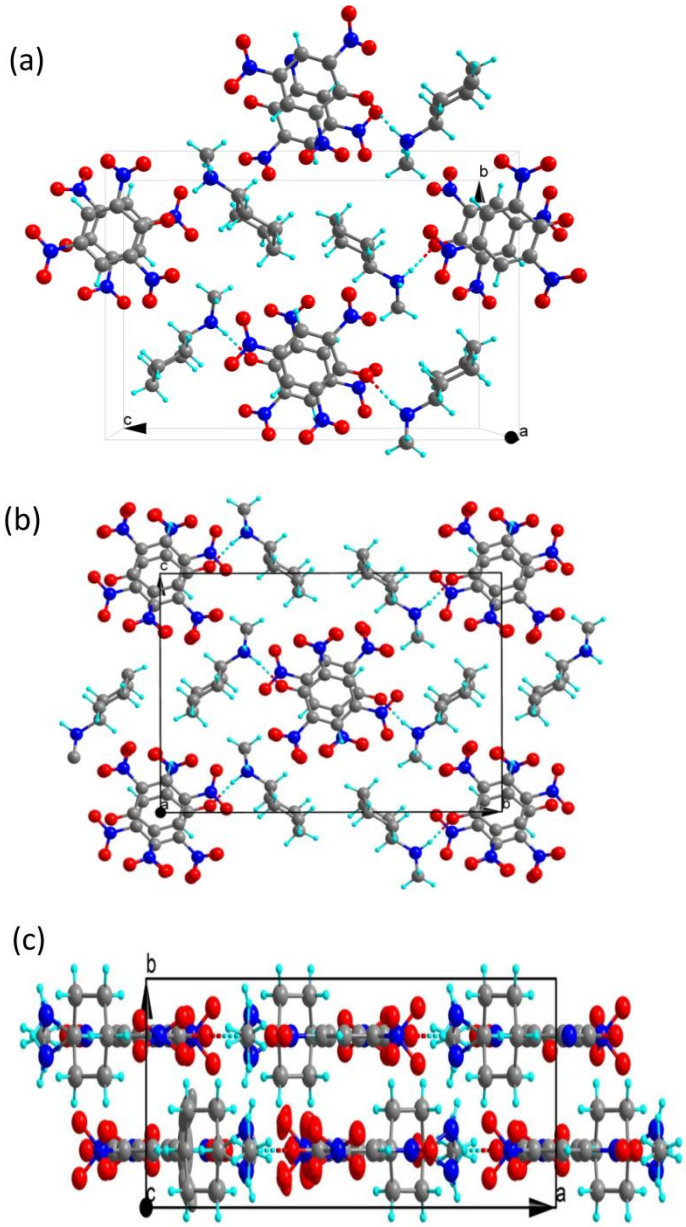

Figure S5. Crystal packing views of 1 along the a-axis direction in its LTP (a), along the a-axis direction in its ITP (b) and along the c-axis direction in its HTP (c)**.**

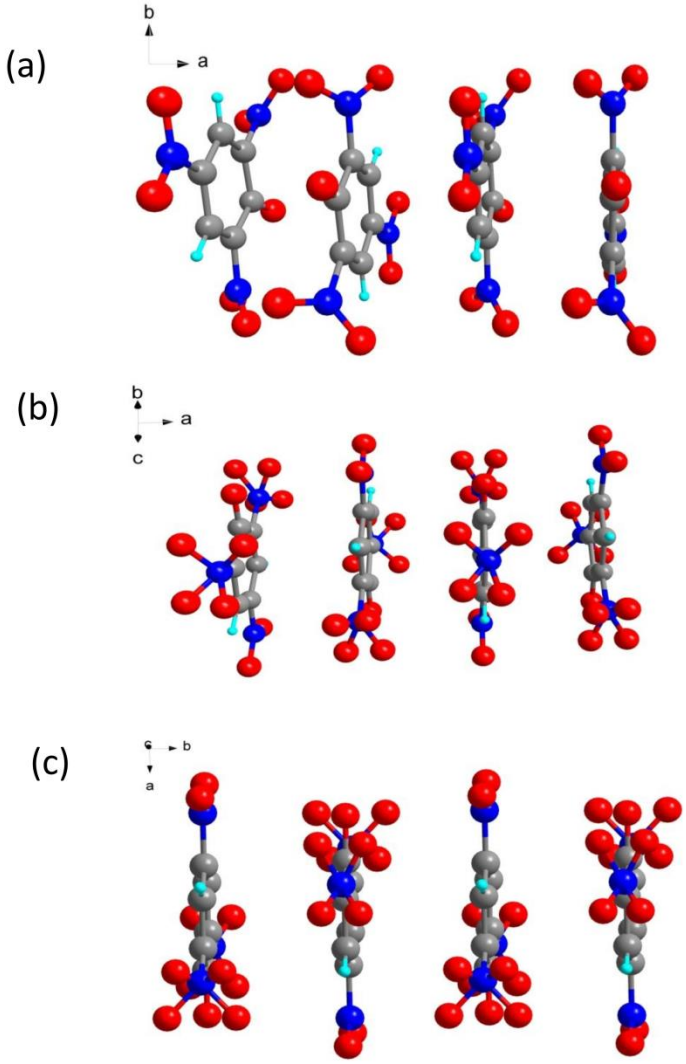

Figure S6. Diagrams of the adjacent picrate anions viewed along the *c*-axis at (LTP), (ITP) and (HTP) of **1.**

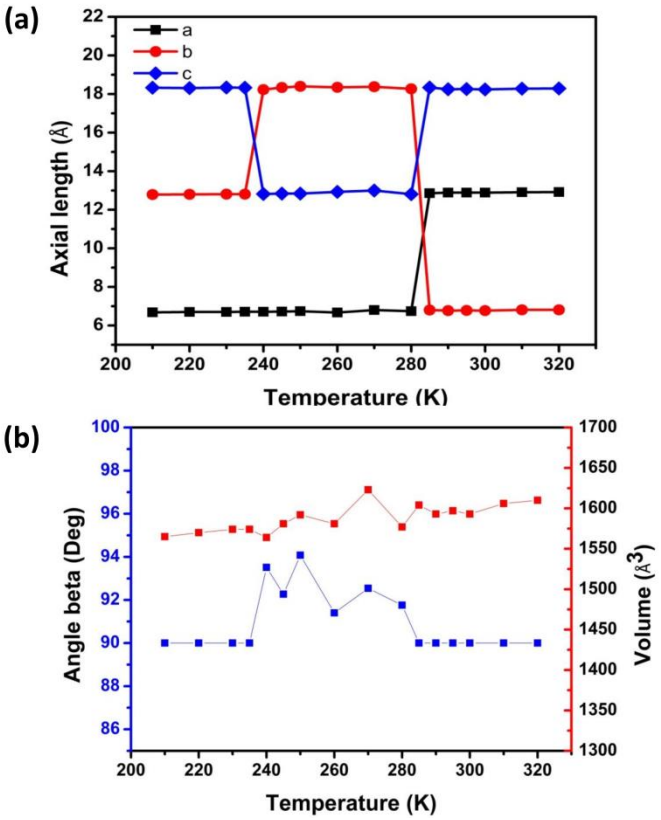

Figure S7. Temperature dependence of (a) cell parameter changes for three axis lengths and (b) crystal volume and monoclinic b angle in the range from 210 to 320 K of 1.

Tables

Table S1 Crystallographic data and details of data collection and refinement for **1**

Phase	**LTP**	**ITP**	**HTP**
Temperature (K)	205	260	293
Empirical formula	$C_{13}H_{18}N_4O_7$	$C_{13}H_{18}N_4O_7$	$C_{13}H_{18}N_4O_7$
Formula weight	342.31	342.31	342.31
Crystal system,	orthorhombic	monoclinic	orthorhombic
space group	$P2_12_12_1$	$P2_1/n$	Pnma
a (Å)	6.67620(10)	6.7455(2)	18.2587(3)
b (Å)	12.7767(2)	18.3207(6)	6.7913(2)
c (Å)	18.3011(3)	12.8506(5)	12.8788(3)
V(Å^3)	1561.08(4)	1585.19(9)	1596.98(7)
Z	4	4	4
Calculated density (mg/Å^3)	1.456	1.434	1.424
F(000)	720.0	720.0	720.0
Limiting indices	$-7 \le h \le 7$, $-10 \le k \le 15$, $-15 \le l \le 21$	$-8 \le h \le 8$, $-22 \le k \le 22$, $0 \le l \le 15$	$-22 \le h \le 15$, $-5 \le k \le 7$, $-15 \le l \le 14$
Reflections collected/unique	4847/2533 [R_{int} = 0.0137, R_{sigma} = 0.0188]	3078/3078 [R_{int} = 0.0170, R_{sigma} = 0.0169]	4977/1672 [R_{int} = 0.0160, R_{sigma} = 0.0191]
Completeness	99%	97%	96%
Data / restraints/parameters	2533/0/218	3078/74/262	1672/4/162
Goodness-of-fit on F^2	1.037	1.020	1.008
Final R indices [I>2sigma(I)]	R_1 = 0.0319, wR_2 = 0.0842	R_1 = 0.0723, wR_2 = 0.1359	R_1 = 0.0621, wR_2 = 0.1029

Table S2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 1 at 205 K. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	2394(3)	2791.0(12)	6437.4(7)	37.4(4)
C3	2300(3)	1186.5(15)	4800.7(11)	27.1(4)
O5	2484(3)	2379.9(14)	3049.8(8)	50.6(5)
C6	2276(3)	3287.6(15)	5177(1)	25.5(4)
C5	2329(3)	3010.9(16)	4454.7(11)	26.9(4)
N3	2267(3)	4404.9(14)	5332.0(9)	32.0(4)
C1	2265(3)	2556.2(15)	5778.3(10)	25.0(4)
O4	2365(3)	749.7(14)	3336.8(9)	51.3(5)
C4	2320(3)	1959.8(16)	4267.8(10)	27.3(4)
N2	2378(3)	1680.9(15)	3503.8(10)	35.1(4)
N1	2215(3)	654.2(15)	6063.3(10)	38.0(4)
O2	1072(3)	734.2(15)	6581.4(9)	52.3(5)
O6	3131(3)	4994.6(13)	4905(1)	49.4(5)
O7	1368(3)	4707.6(13)	5874.2(10)	51.9(5)
O3	3292(5)	-96.2(18)	5962.1(13)	84.1(8)
N4	1597(3)	4238.7(15)	7526.9(9)	35.8(4)
C8	2040(3)	3649.9(17)	8222.9(10)	31.9(5)
C13	4029(4)	3091(2)	8176.9(13)	41.4(6)
C9	349(4)	2895(2)	8383.3(14)	45.2(6)
C7	2846(5)	5190.0(19)	7421.3(13)	48.2(6)
C10	741(5)	2350(2)	9109.3(17)	55.6(7)
C11	2753(5)	1788(2)	9102.0(16)	58.6(8)
C12	4439(4)	2531(2)	8897.5(16)	53.6(7)
C2	2247(3)	1486.1(15)	5517.3(11)	26.5(4)

Table S3 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 1 at 260 K. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
O1	2604(4)	6449.3(11)	4722.8(17)	61.1(7)
O4	2474(5)	3366.7(14)	6769(2)	88.9(10)
O5	2244(5)	3073.9(13)	5152(2)	81.3(9)
O2	3924(8)	6604(2)	6777(3)	78.5(16)
O3	1784(14)	5992(4)	7593(6)	132(3)
O6	3067(11)	4883(3)	2534(3)	78.5(15)
O7	1701(12)	5905(2)	2800(3)	90(2)
O2B	1920(60)	6649(9)	6738(13)	169(12)
O3B	3160(40)	5900(14)	7722(15)	118(9)
O6B	1800(30)	4812(9)	2576(11)	75(4)
O7B	3250(30)	5922(7)	2854(9)	61(4)
N1	2782(6)	6088.1(17)	6860(2)	65.1(8)
N2	2404(4)	3527.5(15)	5849(2)	59.4(7)
N3	2451(5)	5335.0(15)	3122(2)	55.7(7)
C1	2588(4)	5795.8(15)	4964(2)	39.2(6)
C2	2637(4)	5540.2(15)	6030(2)	41.0(6)
C3	2568(4)	4826.4(16)	6331(2)	45.0(7)
C4	2486(4)	4291.0(15)	5567(2)	42.2(6)
C5	2468(4)	4474.1(15)	4524(2)	42.9(7)
C6	2500(4)	5189.0(15)	4237(2)	39.9(6)
N4	1748(6)	7542.7(16)	3289(2)	67.3(9)
C7	2810(8)	7472(2)	2322(3)	91.3(16)
C8	2233(6)	8229.7(16)	3907(2)	55.9(9)
C9	710(6)	8325(2)	4695(3)	76.9(11)
C10	1118(9)	9034(2)	5304(4)	104.0(18)
C11	3209(9)	9059(3)	5765(3)	96.3(16)
C12	4700(8)	8923(3)	4984(4)	91.3(15)
C13	4278(6)	8215(2)	4401(3)	68(1)

Table S4 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 1 at 293 K. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
O1	3552.1(11)	2500	294.0(19)	82.8(8)
O2	3371(2)	3726(8)	-1727(3)	123.8(19)
O3	3998(3)	1676(11)	-2589(4)	175(4)
O4	6932.1(14)	2500	-193(3)	112.0(12)
O5	6622.1(15)	2500	-1787(3)	123.4(13)
O6	4108.3(19)	1703(7)	2178(2)	106(2)
O7	5149(2)	1840(7)	2438(3)	101(2)
N1	3891(2)	2500	-1822(3)	95.9(12)
N2	6469.3(16)	2500	-875(3)	82.4(9)
N3	4678.6(17)	2500	1869(2)	75.9(9)
C1	4206.4(15)	2500	45(2)	56.0(8)
C2	4452.1(16)	2500	-1017(2)	59.7(8)
C3	5164.8(17)	2500	-1322(3)	61.6(8)
C4	5706.5(16)	2500	-578(3)	59.8(8)
C5	5533.5(16)	2500	455(3)	58.8(8)
C6	4816.5(16)	2500	757(2)	55.8(7)
N4	2440(2)	1611(7)	1685(3)	79.3(14)
C7	2524(2)	2500	2692(3)	132(2)
C8	1760.8(18)	2500	1083(3)	90.9(15)
C9	1725(2)	733(6)	453(3)	134.1(15)
C10	1015(3)	748(11)	-117(4)	214(4)
C11	953(5)	2500	-756(5)	256(10)