Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information for:

High-temperature phase transitions, switchable dielectric behaviors and barocaloric effects in three new organic molecule-based crystals

Rui-Xia Li, Lin Zhou, Ping-Ping Shi, Xuan Zheng, Ji-Xing Gao, Qiong Ye* and Da-Wei Fu*

Ordered Matter Science Research Center, Jiangsu Key Laboratory for Science and Applications of Molecular Ferroelectrics, Southeast University, Nanjing 211189, People's Republic of China.

E-mail: yeqiong@seu.edu.cn, dawei@seu.edu.cn

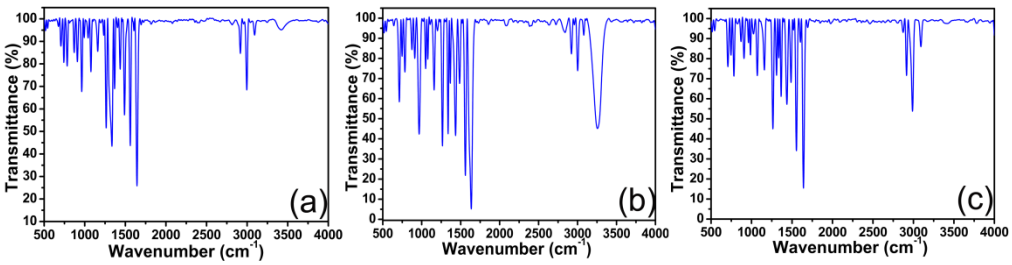

Figure S1. The IR spectrum of compounds **1** (a), **2** (b) and **3**(c).

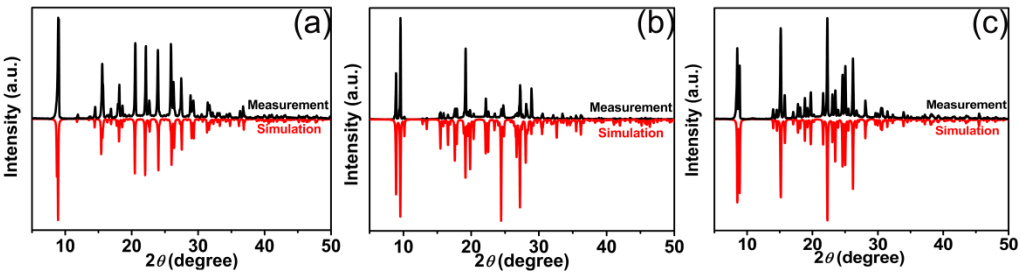

Figure S2. PXRD patterns of compounds **1** (a), **2** (b) and **3** (c) based on the measurement data (black line) at 298 K and the simulation data (red line) based on the crystal structures of **1** at 223 K, **2** at 298 K and **3** at 298 K, respectively.

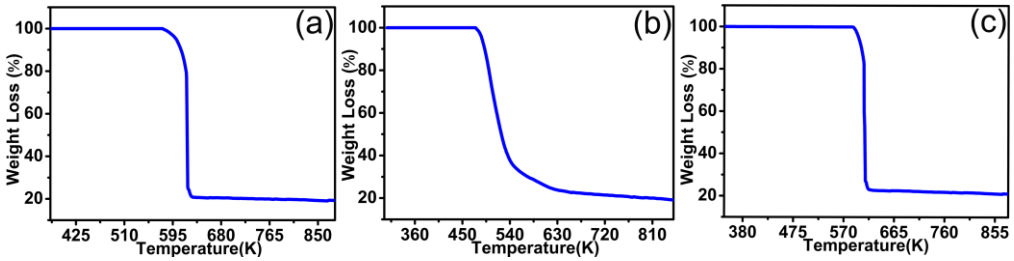

Figure S3. TGA curves of compound **1** (a), **2** (b) and **3** (c).

Table S1. Crystallographic data and structure refinements for compounds **1**, **2** and **3**.

Compound	**1**	**1**	**2**	**3**
Chemical Formula	$C_{11}H_{16}N_3O_7P$	$C_{11}H_{16}N_3O_7P$	$C_{10}H_{14}N_3O_8P$	$C_{14}H_{20}N_3O_7P$
Formula weight	333.24	333.24	335.21	373.30
Temperature (K)	223	333	298	298
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$	$P\bar{1}$	$P2_1/n$
a, Å	11.325(5)	11.412(2)	7.4008(15)	12.300(3)
b, Å	19.765(9)	19.766(4)	10.413(2)	19.943(4)
c, Å	6.921(3)	7.048(3)	10.972(2)	7.3103(15)
α, deg	90	90	109.76(3)	90
β, deg	100.830(8)	113.10(4)	99.84(3)	98.55(3)
γ, deg	90	90	104.20(3)	90
V, Å^3	1521.6(12)	1462.4(9)	741.0(4)	1773.3(7)
Z	4	4	2	4
Index ranges	$-14 \le h \ge 14$ $-25 \le k \ge 25$ $-8 \le l \ge 8$	$-13 \le h \ge 13$ $-23 \le k \ge 23$ $-8 \le l \ge 8$	$-8 \le h \ge 6$ $-10 \le k \ge 12$ $-13 \le l \ge 13$	$-14 \le h \ge 14$ $-23 \le k \ge 21$ $-8 \le l \ge 8$
D_{calcd}, g•cm^{-3}	1.455	1.514	1.502	1.398
μ, mm^{-1}	0.219	0.228	0.230	0.196
refns measured	11026	2380	4251	9960
independent reflns	3477	1300	2608	3125
reflns used	2788	700	1797	2239
Goodness-of-fit on F^2	1.119	1.099	1.076	1.051
Final R indices [$I >$ 2sigma(I)]	$R_1 = 0.0645$, $wR_2 = 0.1681$	$R_1 = 0.1055$, $wR_2 = 0.2832$	$R_1 = 0.0851$, $wR_2 = 0.2314$	$R_1 = 0.0775$, $wR_2 = 0.2229$

Table S2. Bond lengths (Å) and bond angles (°) of cations in compound **1** at 223 K, compounds **2** and **3** at 298 K.

Bond lengths(Å)	1	2	3	Bond angles(°)	1	2	3
C7-P1	1.785(3)	1.778(6)	1.776(5)	C7-P1-C8	109.29(18)	109.2(3)	108.7(3)

C8-P1	1.782(4)	1.782(5)	1.778(5)	C7-P1-C9	109.80(18)	111.0(3)	110.1(2)
C9-P1	1.778(3)	1.786(5)	1.771(5)	C8-P1-C9	109.74(18)	110.2(3)	108.4(3)
C10-P1	1.800(3)	1.811(5)	1.788(4)	C7-P1-C10	109.33(16)	110.8(3)	112.4(2)
C10-C11	1.545(5)		1.527(6)	C8-P1-C10	109.30(16)	108.1(3)	109.0(2)
C10-C14			1.524(4)	C9-P1-C10	109.36(16)	107.6(3)	108.16(19)
C10-O8		1.403(6)		C11-C10-P1	113.7(2)		113.9(3)
C11-C12			1.484(7)	O8-C10-P1		110.6(4)	
C12-C13			1.400(9)	C14-C10-P1			115.5(3)
C13-C14			1.473(8)	C10-C11-C12			105.0(4)
				C11-C12-C13			108.9(5)
				C12-C13-C14			110.6(5)
				C13-C14-C10			103.5(4)
				C14-C10-C11			104.2(4)

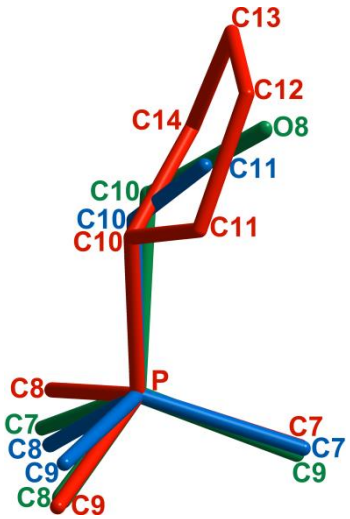

Figure S4. The overlapped view of cations in compounds **1**, **2** and **3**. The hydrogen atoms are omitted for clarity.

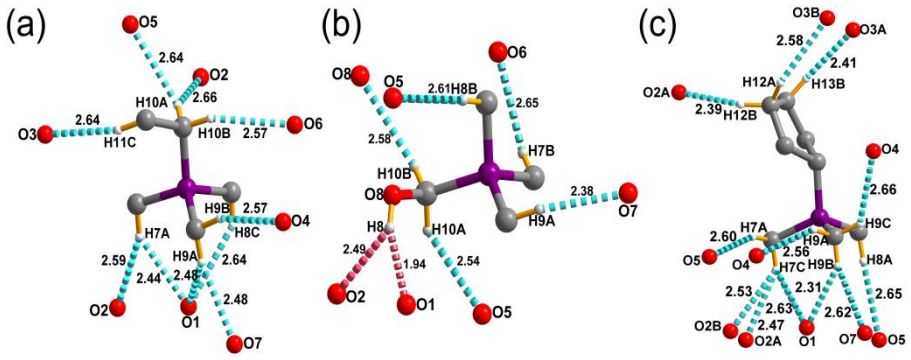

Figure S5. For compounds **1** (a), **2** (b) and **3** (c), the hydrogen bonds surrounding the cations are shown with dashed lines and the distances are indicated in Å. Other atoms which are not involved in the hydrogen-bonding interactions are omitted for clarity.

Table S3. Parameters of hydrogen bonds in compounds **1**, **2** and **3**.

Compound	D-H•••A	H•••A(Å)	D•••A(Å)	D-H•••A(°)
1	C(7)-H(7A)•••O(1)#1	2.44	3.226(4)	139.0
	C(7)-H(7A)•••O(2)#1	2.59	3.485(5)	155.3
	C(8)-H(8C)•••O(1)#1	2.64	3.383(4)	134.6
	C(9)-H(9A)•••O(1)#1	2.48	3.250(4)	136.8
	C(9)-H(9A)•••O(7)#1	2.48	3.387(4)	156.6
	C(9)-H(9B)•••O(4)#2	2.57	3.477(5)	158.3
	C(10)-H(10A)•••O(2)#3	2.66	3.512(4)	147.4
	C(10)-H(10A)•••O(5)	2.64	3.354(4)	130.4
	C(10)-H(10B)•••O(6)#4	2.57	3.442(4)	149.5
	C(11)-H(11C)•••O(3)#5	2.64	3.569(5)	164.0
2	C(7)-H(7B)•••O(6)#6	2.64	3.515(8)	150.9
	C(8)-H(8B)•••O(5)	2.61	3.565(8)	174.3
	C(9)-H(9A)•••O(7)#7	2.39	3.278(8)	153.6
	C(10)-H(10A)•••O(5)#8	2.54	3.395(7)	146.8
	C(10)-H(10B)•••O(8)#6	2.59	3.322 (6)	132.7
	O(8)-H(8)•••O(1)#9	1.94	2.728(5)	161.2
	O(8)-H(8)•••O(2)#9	2.49	2.969(8)	118.1
3	C(7)-H(7A)•••O(5) #10	2.60	3.501(7)	156.4
	C(7)-H(7C)•••O(1)#11	2.63	3.330(6)	130.0
	C(7)-H(7C)•••O(2A)#11	2.47	3.32(2)	148.2
	C(7)-H(7C)•••O(2B)#11	2.53	3.233(2)	130.5
	C(8)-H(8A)•••O(5)#12	2.65	3.581(6)	163.7
	C(9)-H(9A)•••O(4)#10	2.56	3.415(6)	147.8
	C(9)-H(9B)•••O(1)#11	2.31	3.142(5)	144.1
	C(9)-H(9B)•••O(7)#11	2.62	3.465(7)	146.5
	C(9)-H(9C)•••O(4)	2.66	3.352(5)	129.8
	C(12)-H(12A)•••O(3B)	2.58	3.443(1)	148.4
	C(12)-H(12B)•••O(2A)#13	2.39	3.248(2)	148.0
	C(13)-H(13B)•••O(3A)	2.41	3.303(2)	153.4

Symmetry code: #1-x+1/2, y-1/2, -z+1/2. #2 -x+3/2, y-1/2, -z+1/2. #3 -x+1, -y+1, -z+1. #4 x+1/2, -y+1/2, z+1/2. #5 -x+1, -y+1, -z. #6 -x+1, -y, -z+1. #7 x, y+1, z. #8 x-1, y, z. #9 -x+1, -y, -z+2. #10 -x+1, -y, -z+1. #11 x-1, y, z.#12 -x+1, -y, -z+2. #13 x-1/2, 1/2-y, z-1/2.

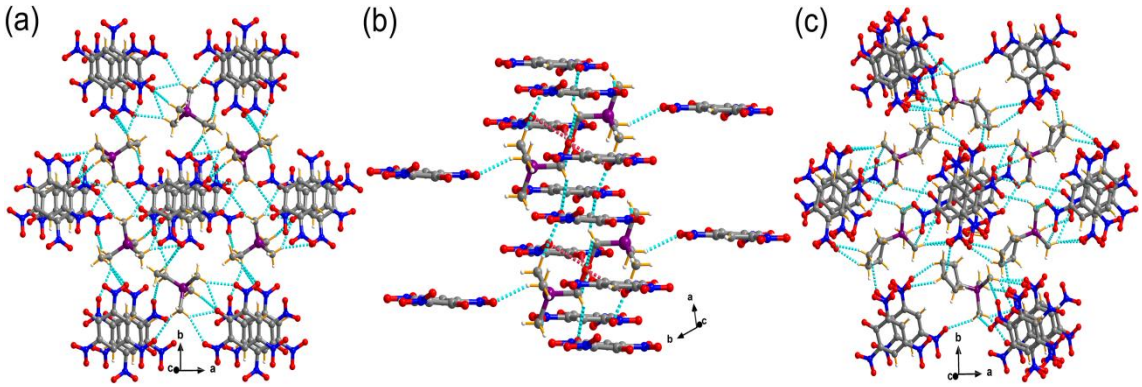

Figure S6. Packing diagrams of **1** (a), **2** (b), and **3** (c) viewed down the c axis, with the hydrogen bonds shown as dashed lines.

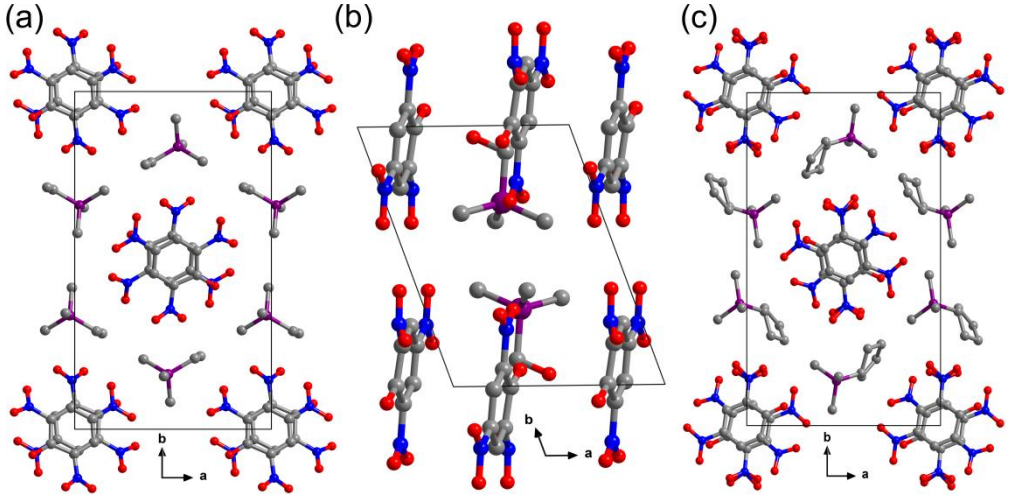

Figure S7. The packing structures of compounds **1**(a), **2**(b) and **3**(c).

Table S4. Equivalent isotropic displacement parameters (Uiso) for compound **1** at 223 K and 333 K.

1 (223 K)		**1 (333 K)**	
Atom	U_{iso}(Å^2 x 10^^{3})	Atom	U_{iso}(Å^2 x 10^^{3})
C(1)	27(1)	C(1)	214(4)
C(2)	26(1)	C(2)	203(3)
C(3)	29(1)	C(3)	229(4)
C(4)	27(1)	C(4)	230(5)
C(5)	28(1)	C(5)	252(5)
C(6)	28(1)	C(6)	415(8)
C(7)	46(1)	C(7)	217(4)
C(8)	44(1)	C(8)	299(4)
C(9)	46(1)	C(9)	357(8)
C(10)	34(1)	N(1)	272(4)

C(11)	43(1)	N(2)	262(6)
N(1)	34(1)	O(1)	534(13)
N(2)	36(1)	O(2)	414(6)
N(3)	38(1)	O(3)	451(6)
O(1)	39(1)	O(4)	363(6)
O(2)	54(1)	P(1)	224(2)
O(3)	63(1)		
O(4)	52(1)		
O(5)	49(1)		
O(6)	69(1)		
O(7)	61(1)		
P(1)	28(1)		

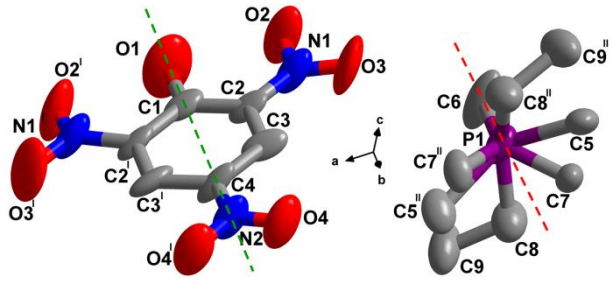

Figure S8. Molecular structures of **1** (a) at 333 K, thermal ellipsoids for all atoms are shown at the 10% probability level. Hydrogen atoms were omitted for clarity. Symmetry codes: (I) (-x, y,-2.5-z); (II) (-1-x, y, -2.5-z).

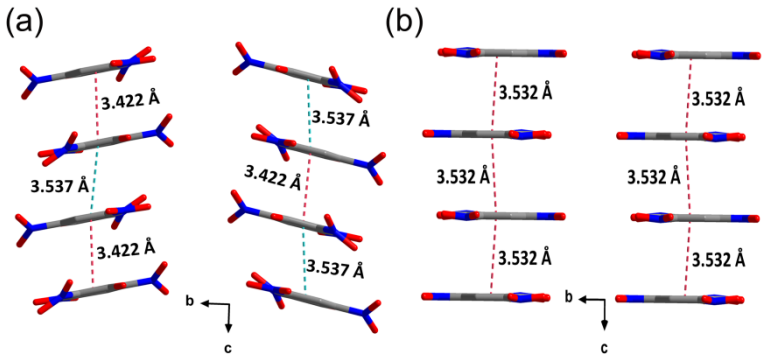

Figure S9. The diagrams of picrate anions in compounds **1**(a) at 223 K, **1**(b) at 333 K.

Table S5. The high-temperature cell parameters of compounds **2** and **3**.

	2	**3**
a(Å)	11.20893	20.94900
b(Å)	9.86901	11.93100
c(Å)	6.80324	7.38200
α(°)	90.0	90.0
β(°)	92.6	100.1
γ(°)	90.0	90.0

V(Å^3)	751.82	1816.47

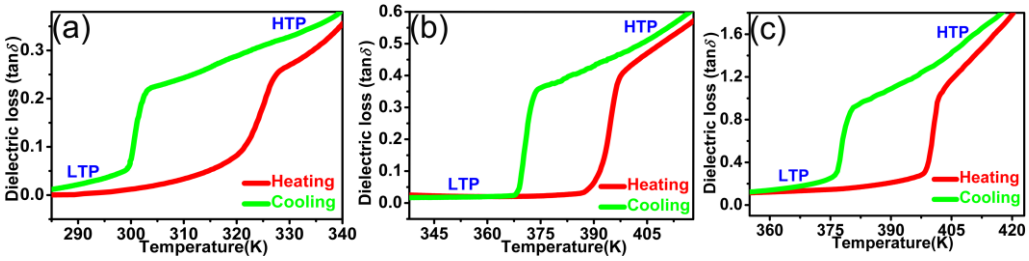

Figure S10. Temperature-variable dielectric loss (tanδ) measured at 1 MHz of compounds **1** (a), **2** (b) and **3** (c).

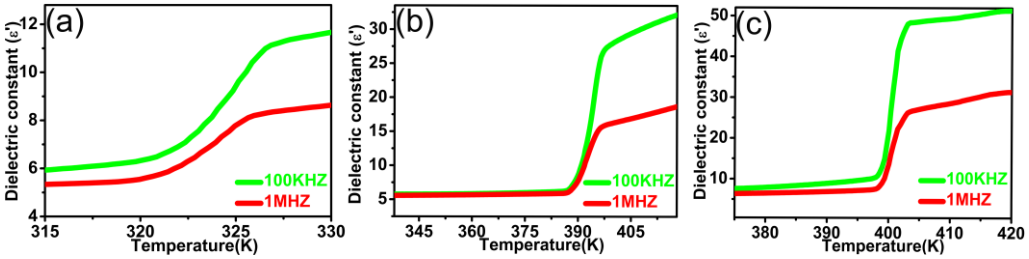

Figure S11. The dielectric constant (ε') for compounds **1**(a), **2**(b) and **3**(c) measured in the heating modes at 100 kHz and 1 MHz.

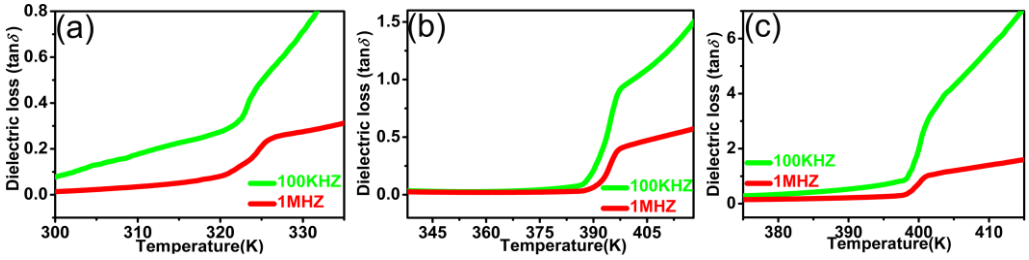

Figure S12. The dielectric loss (tanδ) for compounds **1**(a), **2**(b) and **3**(c) measured in the heating modes at 100 kHz and 1 MHz.

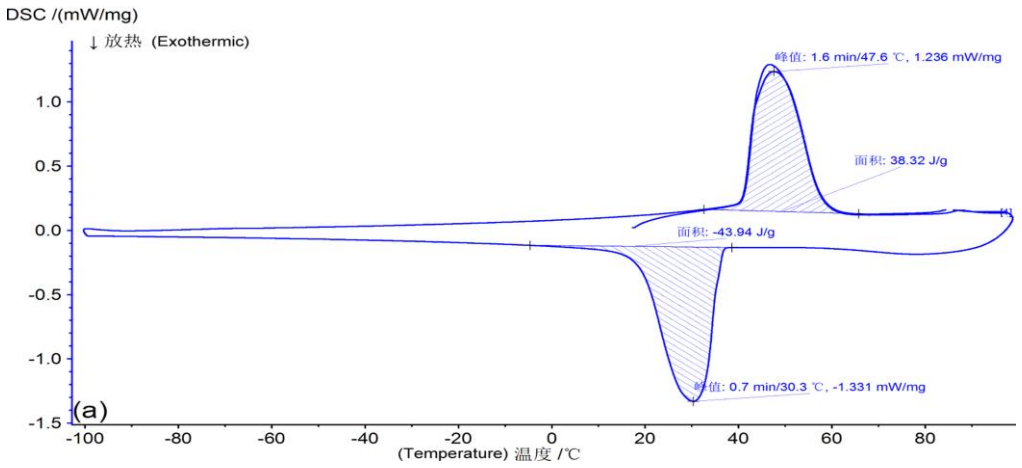

Figure S13. The original measured DSC image of compound **1**.

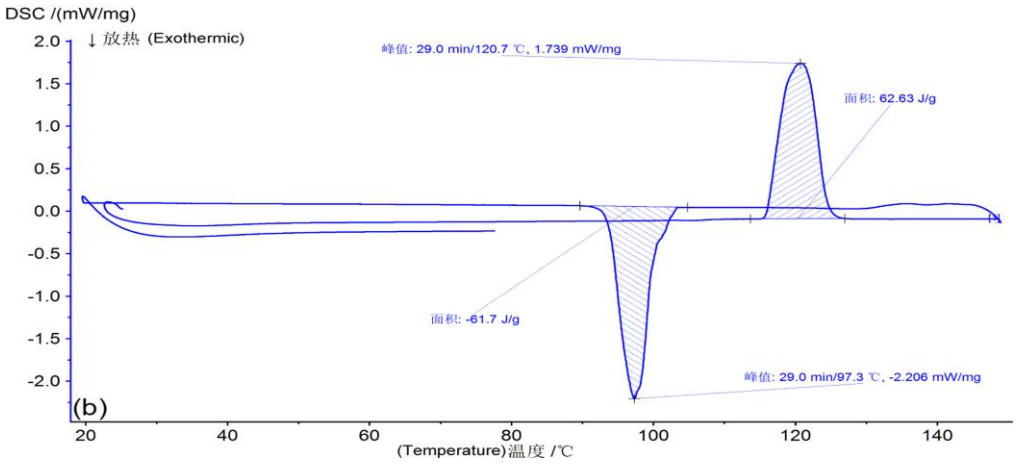

Figure S14. The original measured DSC image of compound **2**.

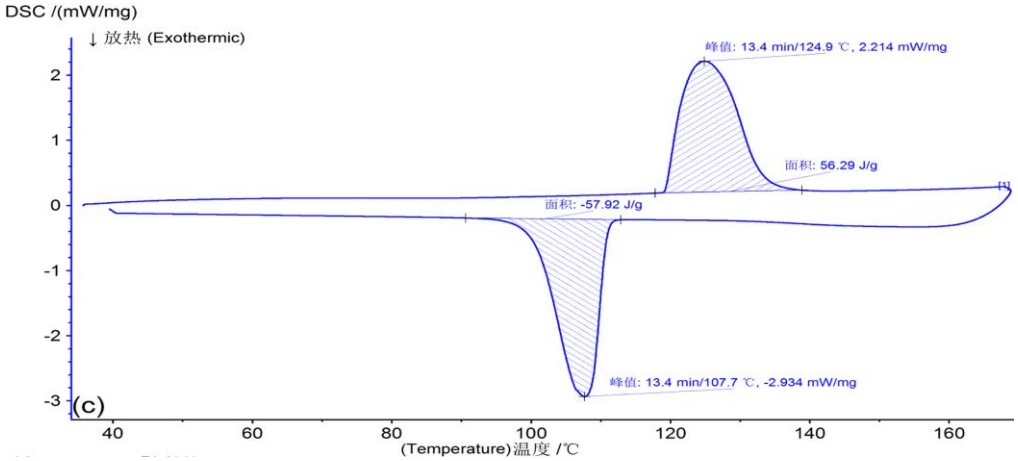

Figure S15. The original measured DSC image of compound **3**.