Supporting Information

Temperature-triggered Order-Disorder Phase Transition in Molecular-Ionic Material N-butyldiethanolammonium Picrate Monohydrate

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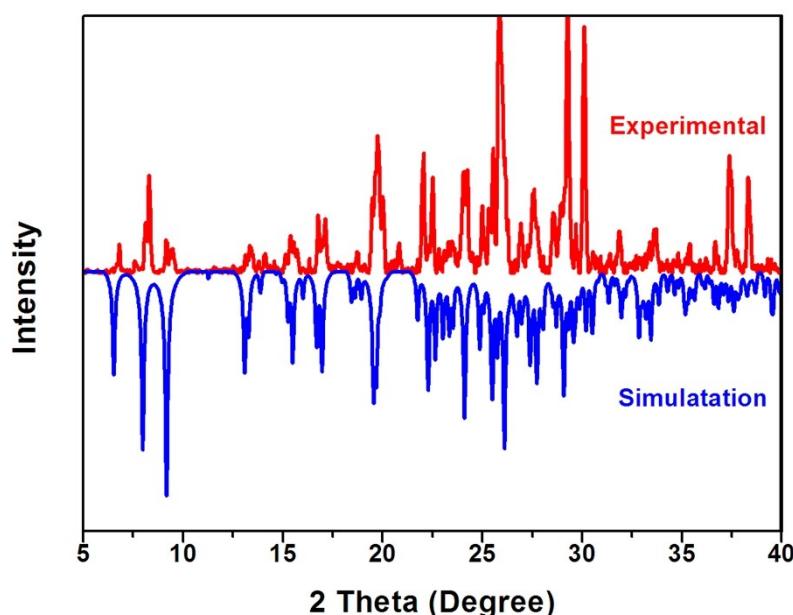Zhao and Junhua Luo*

Table of Contents:

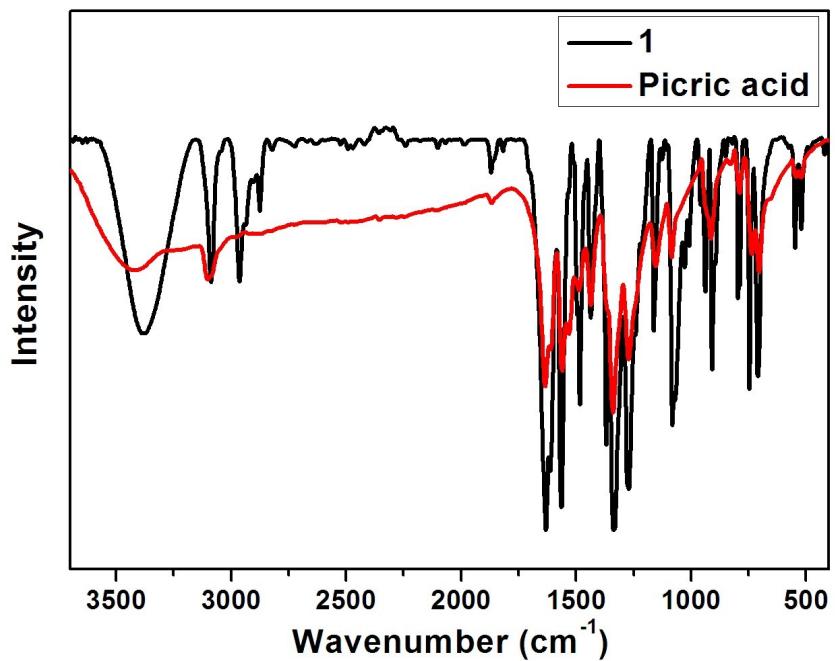**Figure S1.** Experimental and simulated X-ray powder diffraction patterns of ʙᴇᴀᴘᴍ at room temperature.

Figure S2. Infrared (IR) spectrum of compound ᴮᴱᴬᴾᴹ.

Figure S3. Crystal structure of picrate anion in ᴮᴱᴬᴾᴹ. (a) Picrate anion with little thermal ellipsoid at 100 K (LTP); (b) The O2, O5 and O6 are more fairish when split

into two occupied sites at 185 K (HTP). Hydrogen atoms are omitted for clarity.

Figure S4. DSC curve of deuterated sample of BEAPM.

Figure S5. Diagrams of the adjacent picrate anions viewed along the *a*-axis at (LTP) and (HTP) of **1**.The dashed lines represent π-π interactions between rings of the picrate anion.

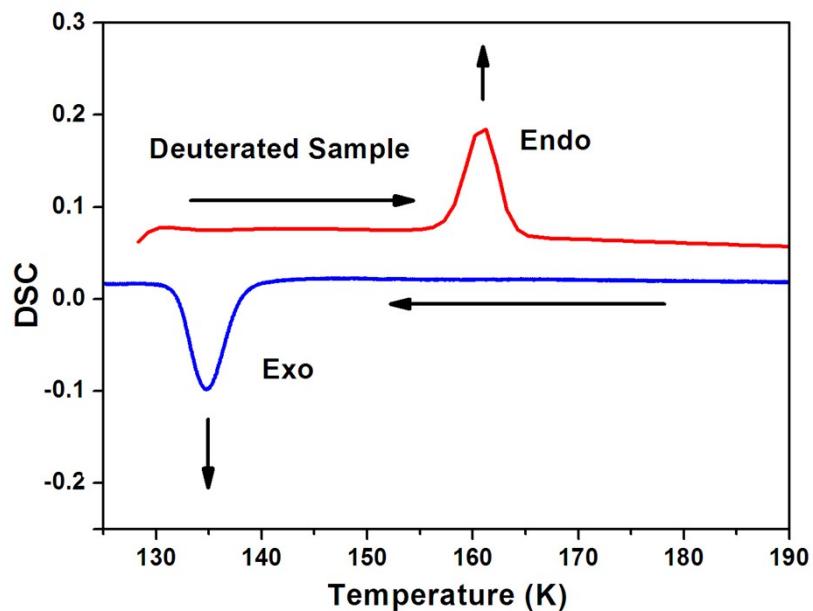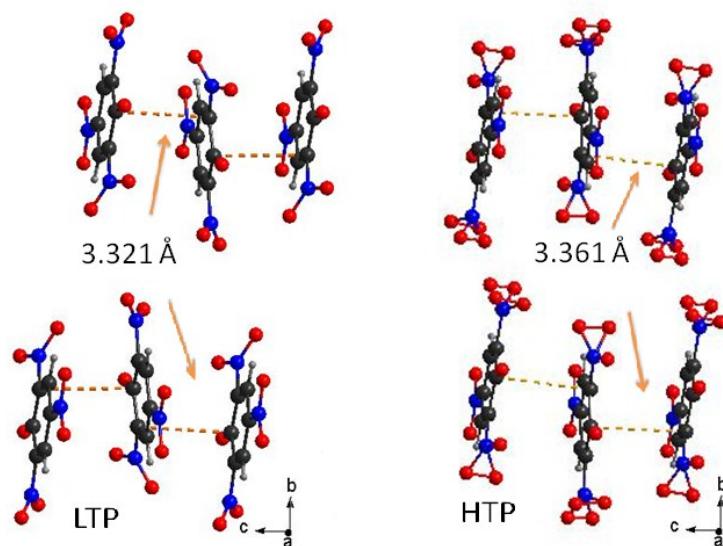**Table S1.** Crystal Data and structure refinement details of BEAPM at 175 and 330 K respectively.

Sum formula	$C_{14}H_{22}N4O_{10}$	$C_{14}H_{22}N4O_{10}$
Formula weight	408.36	408.36
Temperature (K)	185	100
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	13.5233(2)	13.5048(2)
b/Å	19.2674(2)	19.1864(3)
c/Å	7.1034(10)	7.0567(10)
α/ deg	90.0	90.0
β/ deg	91.585(10)	91.40(2)
γ/ deg	90.0	90
Volume (Å^3)	1850.15(2)	1827.91(5)
Z	4	4
D_{calcd}, g cm^{-1}	1.462	1.477
F(000)	860.0	856.0
wR_2 (on F_o^2,$I>2\sigma(I)$)	0.1621(3276)	0.1145(3202)
Goodness-of-fit on F^2	1.082	1.095
Completeness (%)	99.9	98.9
T_{min}/T_{max}	0.642/0.813	0.663/0.682
R_1 [on F_o^2, $I>2\sigma(I)$]	0.086(2975)	0.0413(3056)

$\alpha R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(|F_o|^2 - |F_c|^2) / \Sigma|F_o|^2]^{1/2}$

Table S2. Hydrogen-bond geometry (Å, deg) at 100 K and 185 K in compound

BEAPM

185 K	*D*—H	H…A	*D*…A	*D*—H…A
O10—H4...O1	0. 850	2.4486	2.99	122.651
N4—HA...O10	0.930	1.9224	2.841	169.028
O10—HD...O7	0.850	1.9150	3.119	159.485
O9—H9….O5	0.840	2.4122	3.014	129.233
O9—H9.....O7	0.840	1.9407	2.724	154.747
O10—HE...O9	0.851	2.2171	3.084	173.665
O8—H8...O10	0.840	1.9621	2.983	166.054
100 K				
O10—H4...O1	0. 850	2.3924	2.959	124. 579
N4—HA...O10	0.930	1.9252	2.844	169.118
O10—HE...O7	0.850	1.9090	2.714	157.486
O8—H8.....O6	0.841	2.3801	3.064	133.092
O8—H8.....O7	0.840	1.9456	2.7076	150.225

O10—HE...O8	0.850	2.2079	3.0836	168.252
O9—H9....O10	0.840	2.7556	2.7814	163.932
O10—HD...O9	0.850	2.7729	2.9858	96.124