Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

High-Temperature Enantiomeric Azobenzene-Based Photoisomerized Piezoelectrics: 4-(Phenyldiazenyl)anilinium) *D*- and *L*-Tartrate

*Xin Mu, Lei Xu, Yi-Yi Xu, Han-Yue Zhang** and *Ren-Gen Xiong*

Jiangsu Key Laboratory for Science and Applications of Molecular Ferroelectrics, Southeast University, Nanjing 211189, P.R. China.

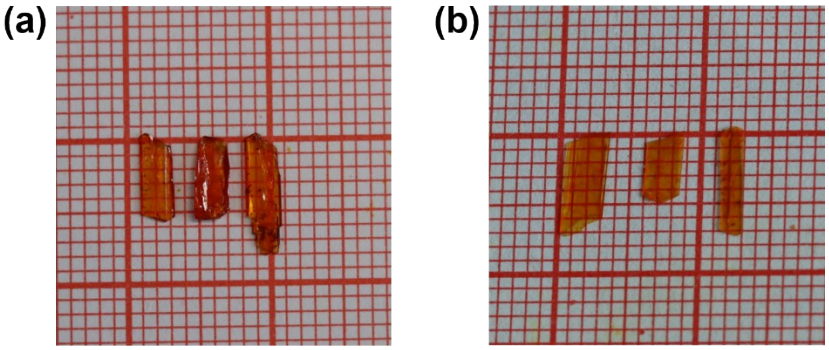

Figure S1. The crystal morphologies and sizes of (a) *D*-1 and (b) *L*-1.

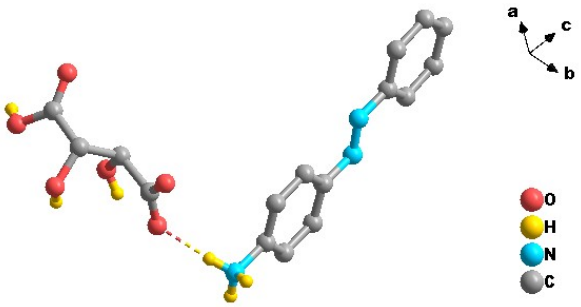

Figure S2. The basic unit of *rac*-1.

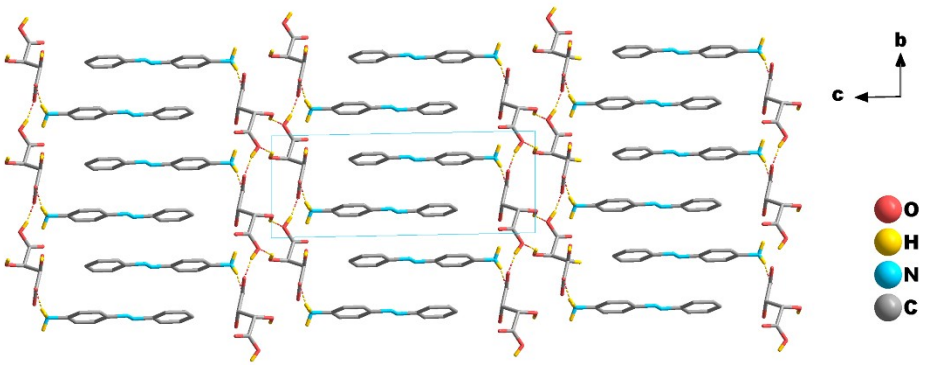

Figure S3. Packing views of *rac*-1 along the *a*-axis at 273 K.

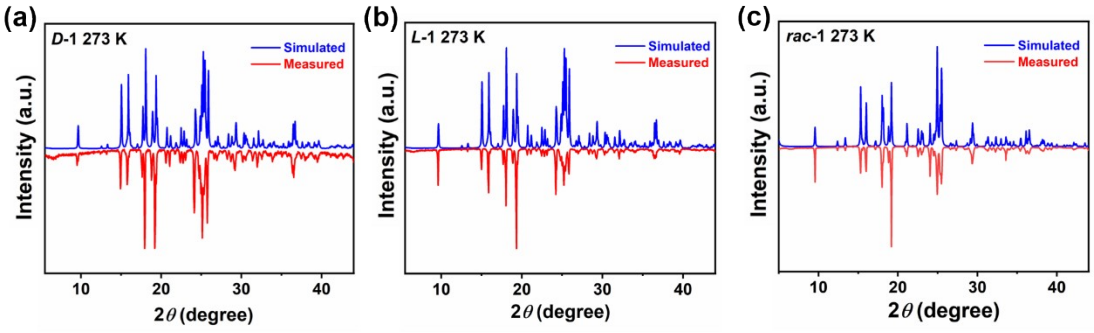

Figure S4. Experimental PXRD patterns and simulated ones from crystal structures of (a) *D*-1, (b) *L*-1, and (c) *rac*-1 at 273K.

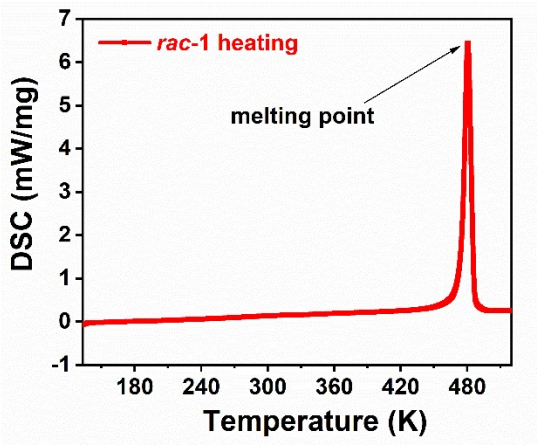

Figure S5. DSC curves of *rac*-1 in the heating mode.

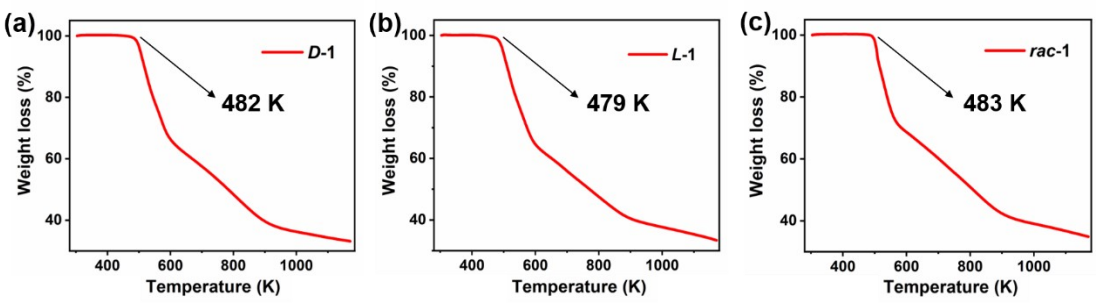

Figure S6. TGA curves of (a) *D*-1, (b) *L*-1, and (c) *rac*-1 in the temperature range of 280 K to 1180 K.

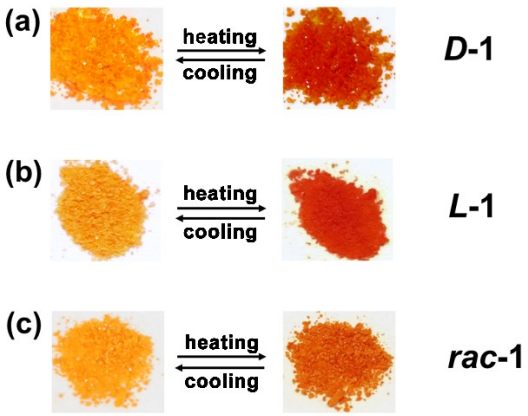

Figure S7. The color changes of the powder samples of (a) *D*-1, (b) *L*-1, and (c) *rac*-1 before and after the heating process.

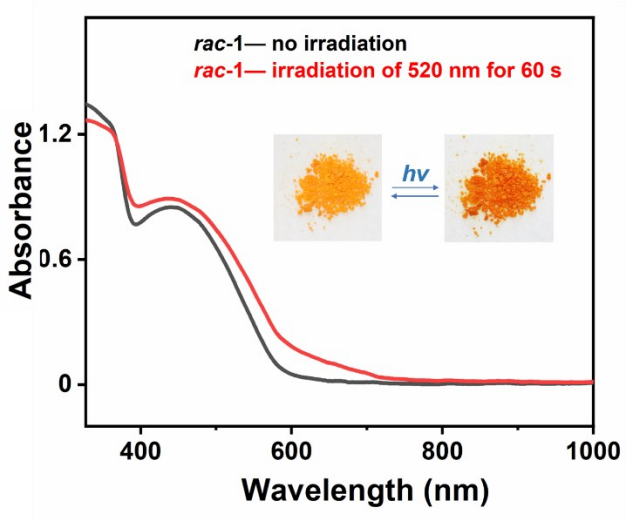

Figure S8. Solid-state UV-vis absorption spectra of *rac*-1 at 293 K before and after the irradiation of 520 nm for 60 s. (Insets: color changes of the powder samples before and after the irradiation).

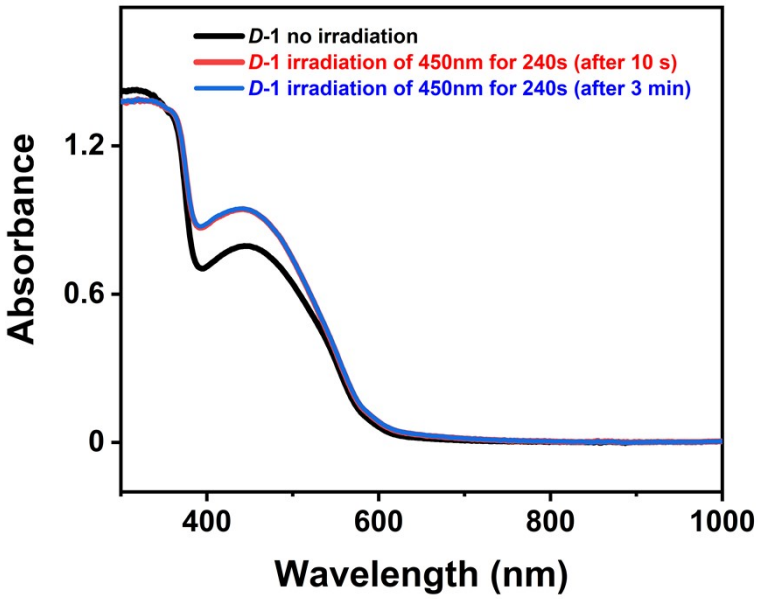

Figure S9. Solid-state UV-vis absorption spectra of *D*-1 after 450 nm irradiation for 240 s recorded at 10 s and 3 minutes.

Table S1. Crystal data for *D*-1, *L*-1 and *rac*-1 at 273 K, respectively.

Compound	***D*-1**	***L*-1**	***rac*-1**
Temperature		**273K**	
Formula	$C_{64}H_{68}N_{12}O_{24}$	$C_{64}H_{68}N_{12}O_{24}$	$C_{16}H_{17}N_3O_6$
Formula weight	1389.30	1389.30	347.32
Crystal system	triclinic	triclinic	triclinic
Space group	*P*1	*P*1	$P\bar{1}$
a, *b*, *c* (Å)	7.41810(10) 12.2977(2) 19.2802(3)	7.41880(10) 12.2962(2) 19.2868(4)	6.0753(4) 7.4995(5) 18.4956(8)
α, *β*, *γ* (°)	103.6720(10) 97.1770(10) 106.8510(10)	103.691(10) 97.174(10) 106.8560(10)	90.993(4) 90.184(4) 108.846(6)
Volume / ($Å^3$)	1599.84(4)	1600.15(5)	801.99(8)
Z	1	1	2
F (000)	728.0	728.0	364.0
Radiation λ(Cu Kα) (Å)	1.54184	1.54184	1.54184
2 Theta range (°)	4.822 to 151.986	7.844 to 152.084	4.778 to 164.956
Limiting indices	-9 ≤ h ≤ 9 -15 ≤ k ≤ 12 -23 ≤ l ≤ 23	-9 ≤ h ≤ 9 -15 ≤ k ≤ 14 -23 ≤ l ≤ 24	-7 ≤ h ≤ 7 -9 ≤ k ≤ 9 -23 ≤ l ≤ 18
Reflections collected	20397	17820	7086
Data/restraints/parameter	8744/3/923	7811/3/916	3088/0/230
GOF	1.148	1.526	1.070
Final R indicates [$I > 2\sigma(I)$]	R_1 = 0.0408 wR_2 = 0.1356	R_1 = 0.0476 wR_2 = 0.1707	R_1 = 0.0761 wR_2 = 0.2129
R indices (all data)	R_1 = 0.0437 wR_2 = 0.1391	R_1 = 0.0493 wR_2 = 0.1725	R_1 = 0.0852 wR_2 = 0.2326
Largest diff peak and hole, e/ $Å^{-3}$	0.17/-0.21	0.28/-0.26	0.64/-0.49
Flack parameter	0.00(9)	0.11(8)	
CCDC number	2102666	2102665	2102663

Table S2. Crystal data for *D*-1, *L*-1 and *rac*-1 at 323 K, respectively.

Compound	***D*-1**	***L*-1**
Temperature	**323K**	
Formula	$C_{32}H_{34}N_6O_{12}$	$C_{32}H_{34}N_6O_{12}$
Formula weight	694.65	694.65
Crystal system	triclinic	triclinic
Space group	*P*1	*P*1
a, *b*, *c* (Å)	7.41960(10) 6.21250(10) 18.4272(2)	7.41890(10) 6.21150(10) 18.42891(5)
α, *β*, *γ* (°)	89.9300(10) 91.1130(10) 71.8020(10)	89.944(2) 91.118(2) 71.795(2)
Volume / (Å^3)	806.73(2)	806.57(3)
Z	1	1
F (000)	364.0	364.0
Radiation λ(Cu Kα) (Å)	1.54184	1.54184
2 Theta range (°)	12.56 to 152.04	9.6 to 151.738
Limiting indices	-8 ≤ h ≤ 9 -6 ≤ k ≤ 7 -22 ≤ l ≤ 22	-9 ≤ h ≤ 9 -7 ≤ k ≤ 6 -20 ≤ l ≤ 23
Reflections collected	8495	8058
Data/restraints/parameter	3967/3/459	4021/7/461
GOF	1.038	1.083
Final R indicates [I >2σ(I)]	R_1 = 0.0281 wR_2 = 0.0771	R_1 = 0.0565 wR_2 = 0.1836
R indices (all data)	R_1 = 0.0282 wR_2 = 0.0772	R_1 = 0.0566 wR_2 = 0.1837
Largest diff peak and hole, e/ Å^{-3}	0.16/-0.12	0.30/-0.26
Flack parameter	0.10(7)	0.06(14)
CCDC number	2102622	2102664

Table S3. Hydrogen bond lengths (Å) and angles (º) for *D*-1, *L*-1 and *rac*-1, respectively.

D*—H···*A	***D*—H**	**H···A**	***D*···A**	***D*—H—A/°**
		***D*-1 273 K**		
O001—H001···O00J	0.82	1.71	2.523(2)	174.5
O005—H005···O00K	0.82	2.20	2.882(3)	141.4
O006—H006···O00G	0.82	1.70	2.524(2)	176.6
O007—H007···O00K	0.82	1.80	2.589(2)	162.2
O008—H008···O00E	0.82	1.80	2.600(2)	163.2
O009—H009···O00E	0.82	2.19	2.883(3)	142.0
O00A—H00O···O00B	0.82	2.16	2.760(3)	129.9
O00F—H00M···O003	0.82	2.17	2.776(3)	131.1
O00M—H00P···O00D	0.82	2.18	2.886(3)	144.4
N00O—H00A···O00H	0.89	1.84	2.713(3)	166.6
N00O—H00B···O00A	0.89	1.94	2.795(3)	160.5
N00O—H00C···O00J	0.89	1.91	2.789(3)	168.9
N00P—H00D···O00I	0.89	1.86	2.730(3)	166.0
N00P—H00E···O00F	0.89	1.94	2.789(3)	160.1
N00P—H00F···O00G	0.89	1.90	2.785(3)	171.0
N00R—H00G···O00D	0.89	1.92	2.801(3)	168.8
N00R—H00I···O002	0.89	1.96	2.830(3)	166.2
N00S—H00J···O00C	0.89	1.89	2.769(3	170.5
N00S—H00L···O004	0.89	1.97	2.842(3)	165.2
O004—H004···O00C	0.78(7)	2.05（7）	2.602(3)	128(6)
O002—H002···O00D	0.76(8)	2.03（8）	2.601(3)	132(7)
		***D*-1 323 K**		
O6—H6D···O1	0.82	1.78	2.5888(18)	166.8
O9—H9A···O12	0.82	2.17	2.784(2)	131.5
O10—H10···O1	0.82	2.18	2.884(2)	144.2
O11—H11A···O8	0.82	1.70	2.523(2)	175.4
N3—H3B···O4	0.89	2.00	2.858(2)	162.9
N3—H3C···O2	0.89	1.91	2.788(2)	167.8
N6—H6A···O8	0.89	1.85	2.722(2)	170.9
N6—H6B···O7	0.89	1.93	2.790(2)	166.3
N6—H6C···O9	0.89	2.00	2.860(2)	160.5
		***L*-1 273 K**		
O001—H001···O00K	0.82	2.17	2.882(3)	145.5
O003—H003···O00F	0.82	2.16	2.881(3)	147.2
O004—H004···O00I	0.82	2.16	2.771(3)	131.8
O006—H006···O00K	0.82	1.78	2.588(3)	167.5
O007—H007···O00E	0.82	1.71	2.518(3)	166.6
O008—H008···O00H	0.82	1.71	2.522(3)	169.5
O009—H009···O00C	0.82	2.15	2.757(3)	130.5
O00A—H00M···O00F	0.82	1.80	2.600(3)	164.0

O00O—H00O···O00B	0.82	2.23	2.889(4)	138.2
N00P—H00A···O00E	0.89	1.91	2.789(4)	169.3
N00P—H00B···O009	0.89	1.94	2.791(3)	160.6
N00P—H00C···O00G	0.89	1.86	2.722(3)	162.6
N00Q—H00D···O00H	0.89	1.90	2.786(4)	170.6
N00Q—H00E···O004	0.89	1.93	2.784(3)	160.1
N00Q—H00F···O00J	0.89	1.87	2.734(3)	162.2
N00R—H00H···O00B	0.86	1.95	2.796(3)	167.1
N00R—H00I···O002	0.86	1.99	2.835(3)	165.1
N00S—H00K···O00D	0.89	1.89	2.766(3)	168.8
N00S—H00L···O005	0.89	1.98	2.849(4)	164.5
		***L*-1 323 K**		
O5—H5A···O1	0.82	1.78	2.582(4)	163.9
O9—H9A···O12	0.82	2.17	2.772(5)	130.3
O10—H10···O1	0.82	2.15	2.873(5)	147.4
N3—H3A···O9	0.89	1.93	2.783(5)	159.7
N3—H3B···O7	0.89	1.84	2.723(5)	168.6
N3—H3C···O8	0.89	1.90	2.783(5)	169.6
N6—H6B···O2	0.97	1.82	2.780(5)	171.1
N6—H6C···O3	0.97	1.91	2.852(6)	163.2
O11—H11···O8	0.82	1.74	2.525(5)	160.1
		***rac*-1 273K**		
O1—H1···O7	0.82	1.81	2.536(3)	146.2
O8—H8···O10	0.82	2.17	2.793(3)	132.4
O9—H9···O1	0.82	2.19	2.891(3)	144.3
N25—H25A···O6	0.89	1.87	2.745(3)	165.2
N25—H25B···O8	0.89	1.99	2.849(3)	161.9
N25—H25C···O7	0.89	1.91	2.790(3)	169.3