

SUPPLEMENTARY MATERIALS

Ferroelasticity and Piezoelectricity of organic-inorganic hybrid materials with one-dimensional anionic structure.

So similar, yet so different

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1. Dilatometric measurement:

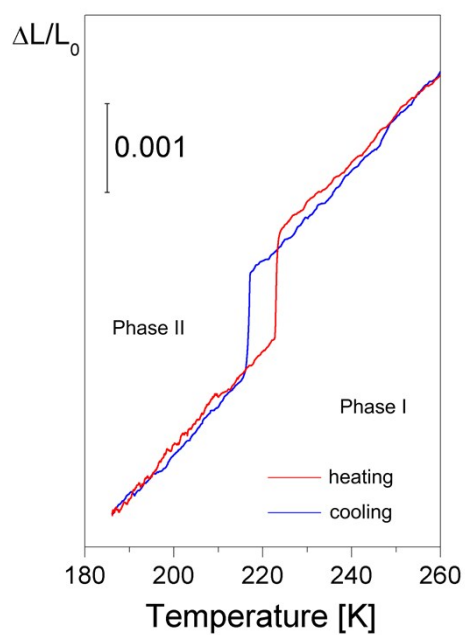


Figure S1. The linear thermal expansion along a-axis of **PBC**, upon cooling and heating.

2. Thermal properties:

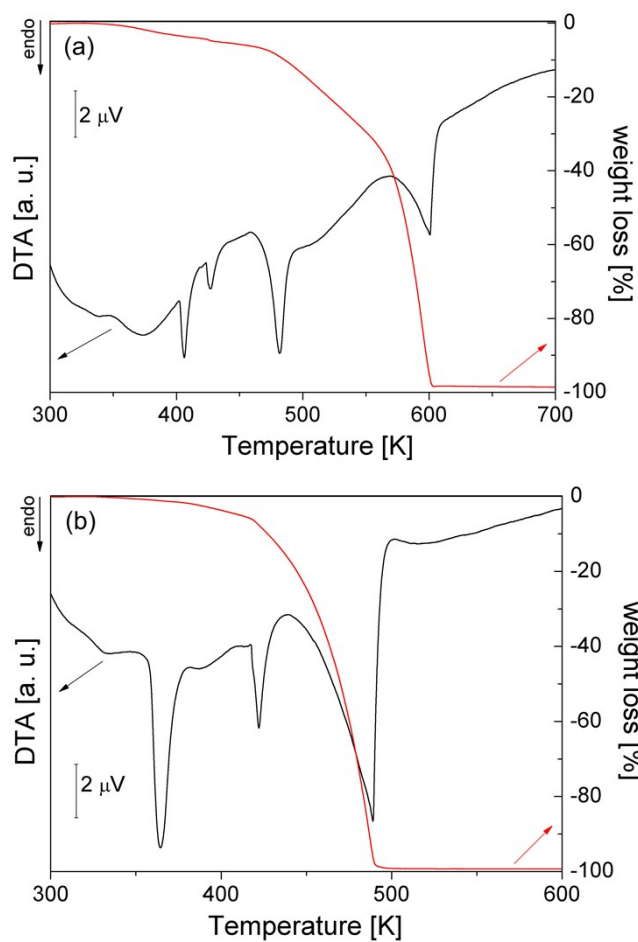


Figure S2. Simultaneous thermogravimetric analysis and differential thermal analysis scan for (a) **PBC** and (b) **PAC** (with the ramp rate of 2 K/min).

Table S1. Selected geometric parameters (Å, °)

PAC		PBC (Phase I)		PBC (Phase II)	
Sb1—Cl1	2.3987 (8)	Bi1—Cl1	2.5113 (18)	Bi2—Cl4	2.7728 (16)
Sb1—Cl2	2.4162 (8)	Bi1—Cl2	2.5285 (17)	Bi2—Cl5	2.7264 (16)
Sb1—Cl3	2.4584 (9)	Bi1—Cl3	2.5188 (17)	Bi2—Cl6	2.6413 (15)
Sb1—Cl5 ⁱ	2.8606 (8)	Bi1—Cl4	2.9406 (16)	Bi2—Cl7	2.6920 (16)
Sb2—Cl4	2.7323 (8)	Bi1—Cl5 ⁱⁱ	2.9611 (17)	Bi2—Cl8	2.5398 (19)
Sb2—Cl5	2.8785 (8)	Bi2—Cl4	2.7546 (19)	Bi1—Cl1	2.5261 (16)
Sb2—Cl6	2.5335 (9)	Bi2—Cl5	2.7486 (17)	Bi1—Cl2	2.5323 (16)
Sb2—Cl7	2.4616 (8)	Bi2—Cl6	2.6570 (18)	Bi1—Cl3	2.5076 (16)
Sb2—Cl8	2.4001 (8)	Bi2—Cl7	2.6751 (16)	Bi1—Cl4	2.9413 (17)
N1—N2	1.340 (3)	Bi2—Cl8	2.5082 (16)	Bi1—Cl5 ⁱⁱⁱ	2.9850 (17)
Cl1—Sb1—Cl2	90.67 (3)	Cl1—Bi1—Cl2	88.21 (6)	Cl5—Bi2—Cl4	81.51 (5)
Cl1—Sb1—Cl3	87.92 (2)	Cl1—Bi1—Cl3	88.94 (6)	Cl6—Bi2—Cl4	167.59 (5)
Cl1—Sb1—Cl5 ⁱ	81.48 (2)	Cl1—Bi1—Cl4	79.83 (6)	Cl6—Bi2—Cl5	92.81 (5)
Cl2—Sb1—Cl3	92.74 (4)	Cl1—Bi1—Cl5 ⁱⁱ	80.20 (5)	Cl6—Bi2—Cl7	86.33 (5)
Cl2—Sb1—Cl5 ⁱ	92.34 (3)	Cl2—Bi1—Cl4	166.90 (5)	Cl7—Bi2—Cl4	96.36 (5)
Cl3—Sb1—Cl5 ⁱ	168.288 (19)	Cl2—Bi1—Cl5 ⁱⁱ	95.15 (6)	Cl7—Bi2—Cl5	165.29 (5)
Cl4—Sb2—Cl5	82.89 (3)	Cl3—Bi1—Cl2	91.81 (6)	Cl8—Bi2—Cl4	82.14 (5)
Cl6—Sb2—Cl4	167.505 (18)	Cl3—Bi1—Cl4	93.28 (6)	Cl8—Bi2—Cl5	81.92 (5)
Cl6—Sb2—Cl5	92.46 (3)	Cl3—Bi1—Cl5 ⁱⁱ	166.88 (5)	Cl8—Bi2—Cl6	86.16 (5)
Cl7—Sb2—Cl4	91.42 (3)	Cl4—Bi1—Cl5 ⁱⁱ	77.66 (5)	Cl8—Bi2—Cl7	83.37 (5)
Cl7—Sb2—Cl5	169.325 (19)	Cl5—Bi2—Cl4	82.00 (6)	Cl1—Bi1—Cl2	87.12 (5)
Cl7—Sb2—Cl6	91.24 (3)	Cl6—Bi2—Cl4	167.85 (4)	Cl1—Bi1—Cl4	79.17 (5)
Cl8—Sb2—Cl4	82.43 (2)	Cl6—Bi2—Cl5	93.92 (6)	Cl1—Bi1—Cl5 ⁱⁱⁱ	79.44 (5)
Cl8—Sb2—Cl5	81.72 (2)	Cl6—Bi2—Cl7	86.74 (6)	Cl2—Bi1—Cl4	164.96 (5)
Cl8—Sb2—Cl6	85.43 (2)	Cl7—Bi2—Cl4	94.71 (6)	Cl2—Bi1—Cl5 ⁱⁱⁱ	95.62 (6)
Cl8—Sb2—Cl7	88.60 (2)	Cl7—Bi2—Cl5	167.16 (4)	Cl3—Bi1—Cl1	89.24 (5)
Sb1 ⁱⁱ —Cl5—Sb2	125.89 (3)	Cl8—Bi2—Cl4	82.47 (6)	Cl3—Bi1—Cl2	91.66 (6)
		Cl8—Bi2—Cl5	82.19 (5)	Cl3—Bi1—Cl4	94.28 (6)
		Cl8—Bi2—Cl6	85.64 (6)	Cl3—Bi1—Cl5 ⁱⁱⁱ	166.18 (5)
		Cl8—Bi2—Cl7	85.07 (5)	Cl4—Bi1—Cl5 ⁱⁱⁱ	75.94 (5)
		Bi2—Cl4—Bi1	120.94 (6)	Bi2—Cl4—Bi1	120.16 (6)
		Bi2—Cl5—Bi1 ⁱ	120.78 (6)	Bi2—Cl5—Bi1 ^{iv}	117.24 (6)

Symmetry code(s): (i) $x+1, y, z$; (ii) $x-1, y, z$; (iii) $x, y-1, z$; (iv) $x, y+1, z$.

Table S2. Selected hydrogen-bond parameters.

<i>D</i> —H... <i>A</i>	<i>D</i> —H (Å)	H... <i>A</i> (Å)	<i>D</i> ... <i>A</i> (Å)	<i>D</i> —H... <i>A</i> (°)
PAC				
O1—H1A...Cl1	0.847 (13)	2.85 (3)	3.473 (3)	131 (3)
O1—H1A...Cl3	0.847 (13)	2.78 (3)	3.424 (2)	134 (4)
O1—H1A...Cl4	0.847 (13)	2.72 (4)	3.292 (2)	126 (3)
O1—H1B...Cl5	0.852 (13)	2.30 (2)	3.131 (2)	164 (5)
O2—H2A...Cl4 ⁱ	0.846 (13)	2.35 (2)	3.137 (2)	155 (4)
O2—H2B...Cl5	0.849 (13)	2.81 (5)	3.288 (2)	118 (4)
O2—H2B...Cl6	0.849 (13)	2.62 (3)	3.377 (2)	148 (5)
O2—H2B...Cl8	0.849 (13)	2.90 (4)	3.424 (2)	121 (4)
N1—H1...Cl4	0.88	2.91	3.418 (3)	118.8
N1—H1...O1	0.88	2.04	2.879 (3)	159.8
N2—H2...O2 ⁱⁱ	0.88	1.90	2.746 (3)	161.7
N6—H6...Cl5	0.88	2.96	3.444 (3)	116.5
N6—H6...O2	0.88	1.99	2.840 (3)	162.8
N7—H7...O1 ⁱⁱⁱ	0.88	1.91	2.754 (3)	159.1
PBC (RT)				
O1—H1A...Cl3	0.855 (10)	2.97 (5)	3.653 (5)	138 (6)
O1—H1A...Cl4	0.855 (10)	2.74 (5)	3.375 (5)	133 (6)
O1—H1B...Cl1 ^{iv}	0.850 (10)	2.79 (2)	3.582 (5)	156 (5)
O1—H1B...Cl5	0.850 (10)	2.86 (6)	3.358 (5)	120 (5)
O2—H2A...Cl4 ^{iv}	0.851 (10)	2.87 (5)	3.316 (4)	115 (5)
O2—H2A...Cl8 ^{iv}	0.851 (10)	2.80 (3)	3.598 (5)	157 (7)
O2—H2B...Cl5	0.851 (10)	2.54 (4)	3.311 (5)	151 (6)
N1—H1...O1	0.87	2.03	2.866 (7)	160.8
N2—H2...O1 ^v	0.87	1.95	2.769 (7)	156.4
N6—H6...O2	0.87	2.15	2.998 (9)	163.6
N7—H7...O2 ^{vi}	0.87	1.97	2.763 (7)	151.8
PBC (LT)				
O1—H1A...Cl4	0.854 (10)	2.55 (5)	3.212 (5)	135 (6)
O1—H1A...Cl5	0.854 (10)	2.97 (6)	3.382 (4)	112 (4)
O1—H1B...Cl1 ^{vii}	0.854 (10)	2.56 (2)	3.395 (5)	167 (7)
O2—H2A...Cl8 ^{vii}	0.850 (10)	2.507 (12)	3.351 (5)	172 (5)
O2—H2B...Cl5	0.852 (10)	2.43 (3)	3.197 (5)	149 (6)
N1—H1...O1	0.88	1.96	2.822 (7)	166.2
N2—H2...Cl3 ^{viii}	0.88	2.98	3.400 (6)	111.7
N2—H2...O1 ^{viii}	0.88	2.02	2.802 (7)	148.2
N6—H6...O2	0.88	1.97	2.838 (7)	167.6
N7—H7...O2	0.88	2.00	2.792 (8)	149.9

Symmetry code(s): (i) $x-1, y, z$; (ii) $-x+1, y-1/2, -z+1/2$; (iii) $-x+1, y+1/2, -z+1/2$; (iv) $x+1, y, z$; (v) $-x+1, -y+1, -z$; (vi) $-x+2, -y+1, -z+1$; (vii) $x, y+1, z$; (viii) $-x, -y+1$.

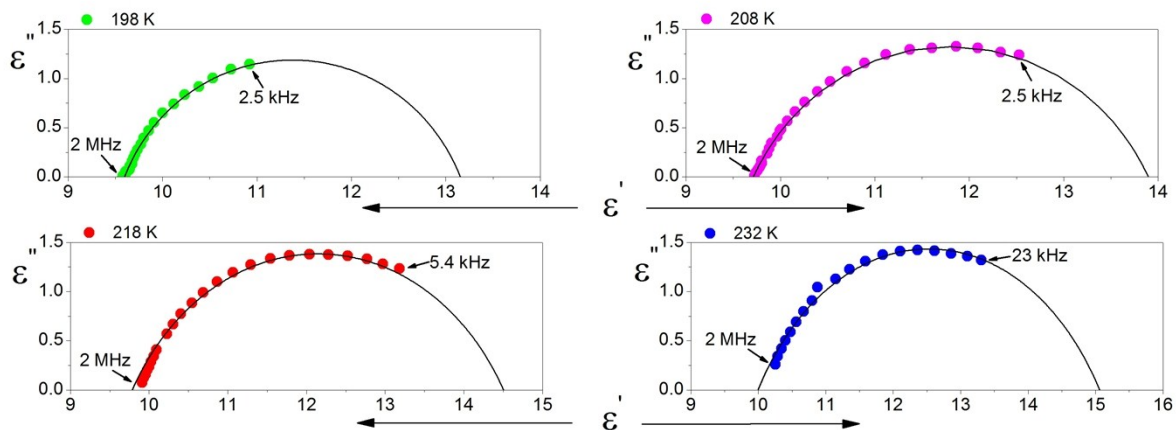


Figure S3. Cole–Cole plots of ϵ'' versus ϵ' at selected temperatures showing the relaxation nature of the dielectric dispersion for PAC.

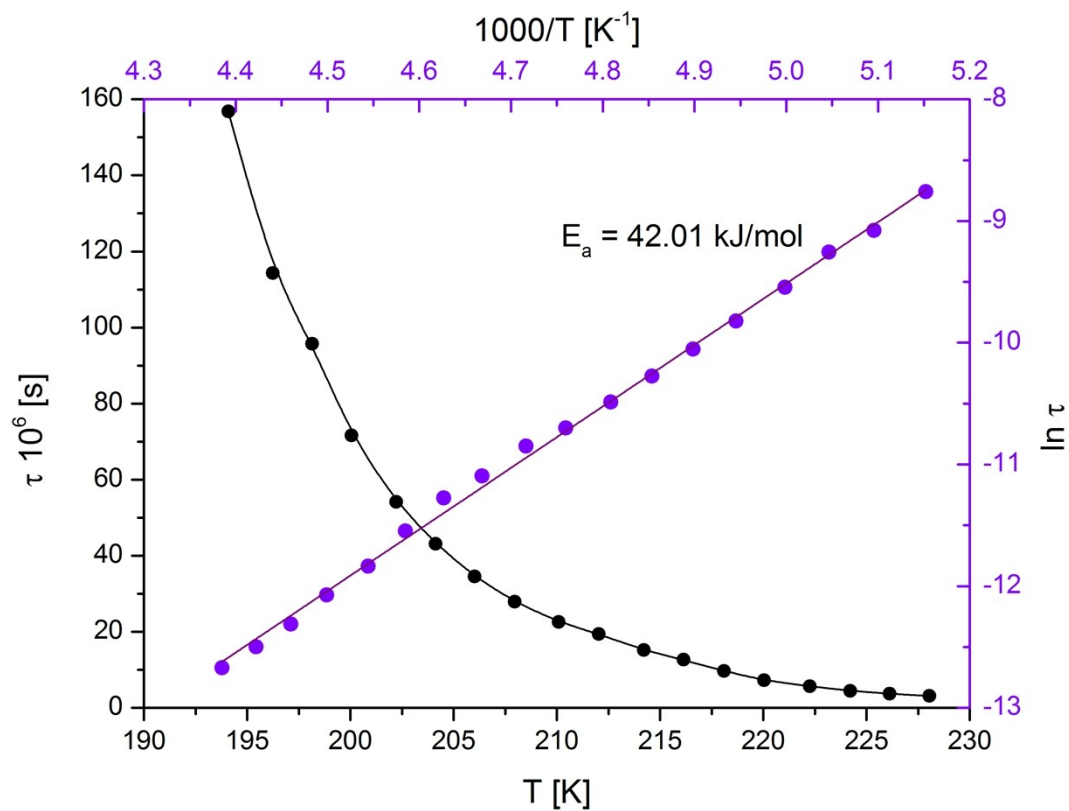


Figure S4. Temperature dependence of the macroscopic relaxation time (s) and its inverse (s^{-1}) of the PAC.

Table S3. Selected parameters fitted to the experimental data

T_1		
parameter	PAC	PBC
E_a [kcal/mol]	5.86	1.7
τ_0 [s]	$7.4 \cdot 10^{-14}$	$8.8 \cdot 10^{-12}$
C [s^{-2}]	$2.8 \cdot 10^8(15\text{MHz})$	$9.4 \cdot 10^7(15\text{MHz})$
E_a [kcal/mol]	-	4.4
τ_0 [s]	-	$4.23 \cdot 10^{-13}$
C [s^{-2}]	-	$1.6 \cdot 10^9$
R_Q [s^{-1}]		$1.1 \cdot 10^8(15\text{MHz})$

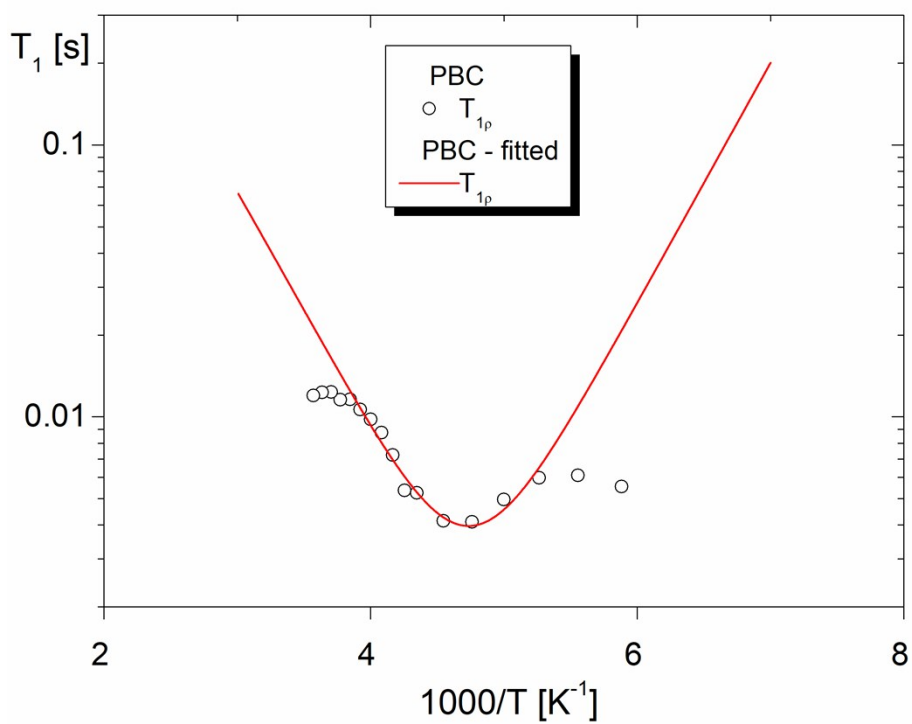


Figure S5. Temperature dependence of ^1H T_1 observed for PBC.