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Electronic Supplementary Information

Design, synthesis and characterization of a new organic-inorganic hybrid perovskite with high-T_c dielectric transition

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^{1}H NMR measurement. All chemicals were purchased from commercial suppliers and were used without further purification. NMR spectra were measured on a Bruker AVANCE Ⅱ (MALDI-TOF) spectrometer (600 MHz for ^{1}H NMR) and DMSO was used as a solvent. ^{1}H NMR of **1** is shown in **Fig. S1**. ^{1}H NMR (600 MHz, DMSO) δ 5.38 (s, 1H), 3.38 (q, *J* = 7.3 Hz, 3H), 1.24 (t, *J* = 7.3 Hz, 5H).

Infrared measurement. Infrared measurement was carried on a Thermo-fisher Scientific Nicolet5700. Measurement range of wavelength is from 400 nm to 3800 nm (**Fig. S2**).

Powder X-ray diffraction (PXRD) measurements. Rigaku Ultima IV Powder X-Ray Diffractometer was used to check the phase purity of desired compound. The experimental PXRD patterns were recorded in the 2θ range of 5°-45° with a speed of 5°/min. As shown in **Fig. S3**, the consistency between the simulation and the actual measurement results confirmed the high purity of the sample.

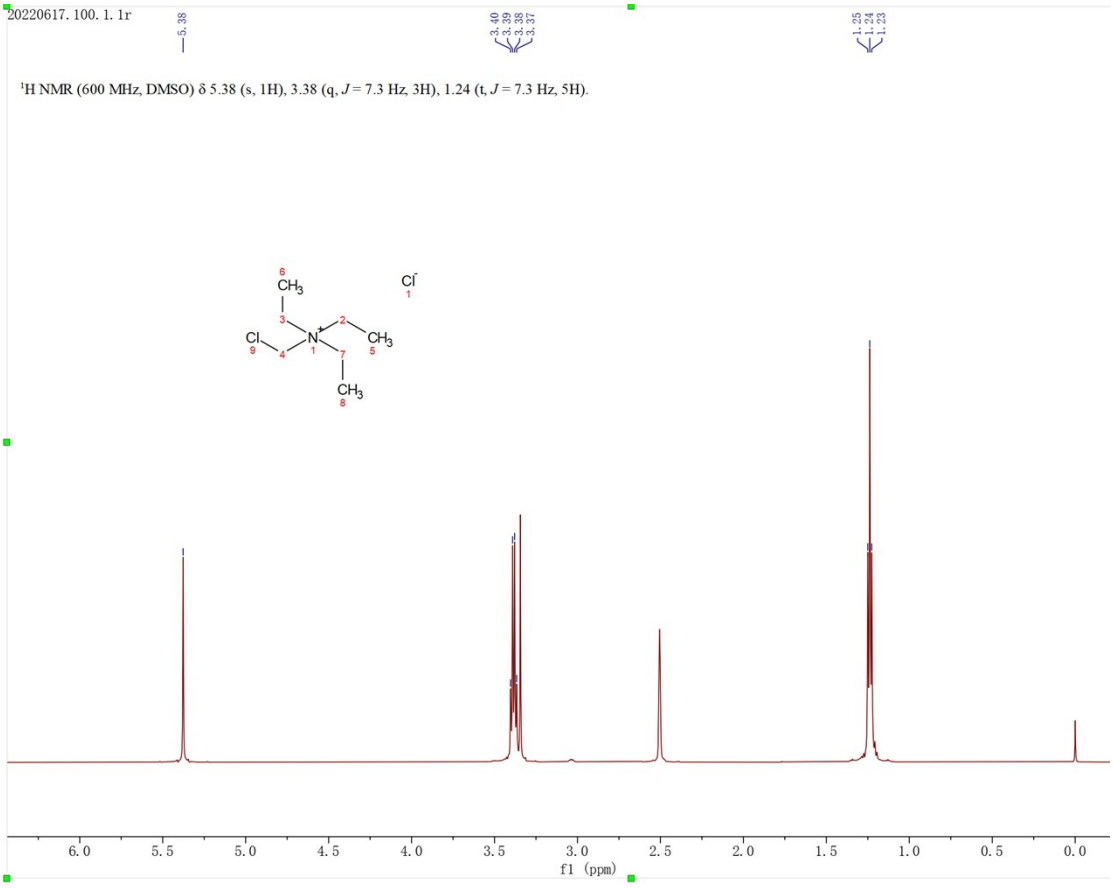

Fig. S1 ^{1}H-NMR of TEAClCl.

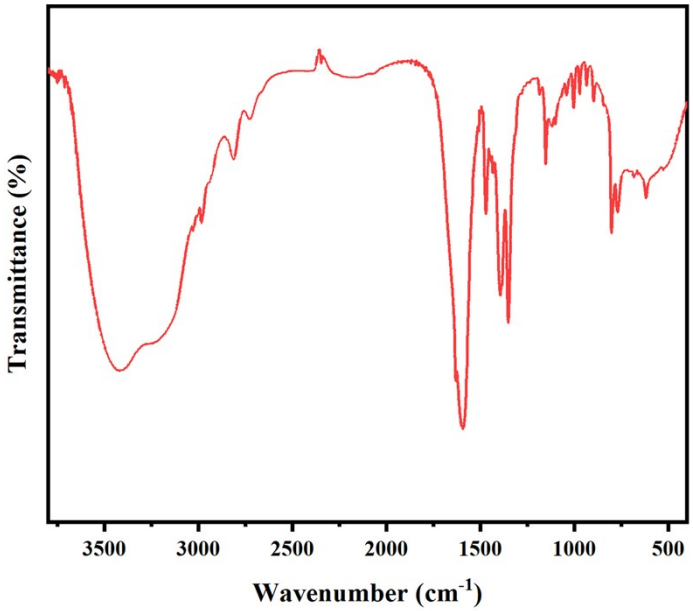

Figure. S2 Infrared spectrum of **1** at room temperature.

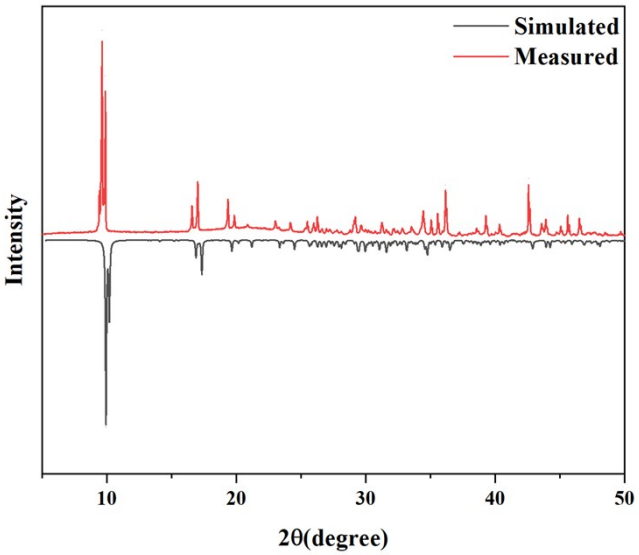

Figure. S3 Measured and simulated powder X-ray diffraction patterns of **1**.

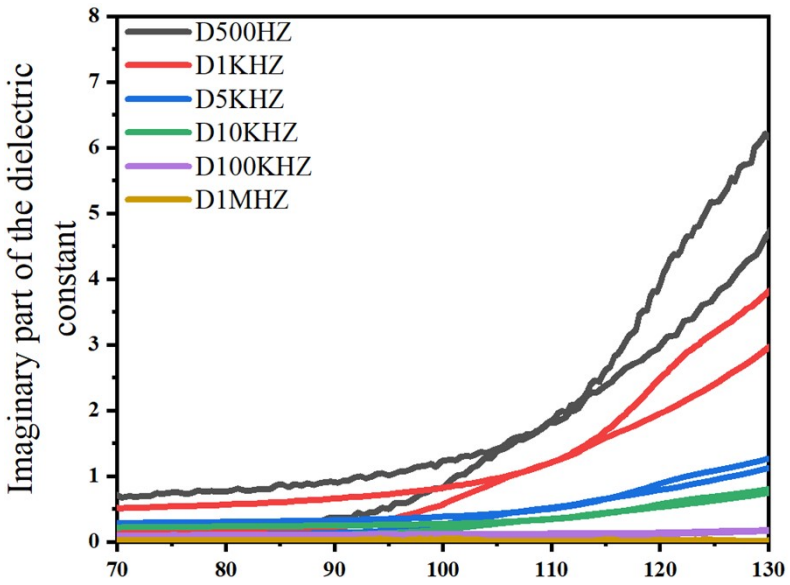

Fig. S4 Imaginary part of the dielectric permittivity of **1**.

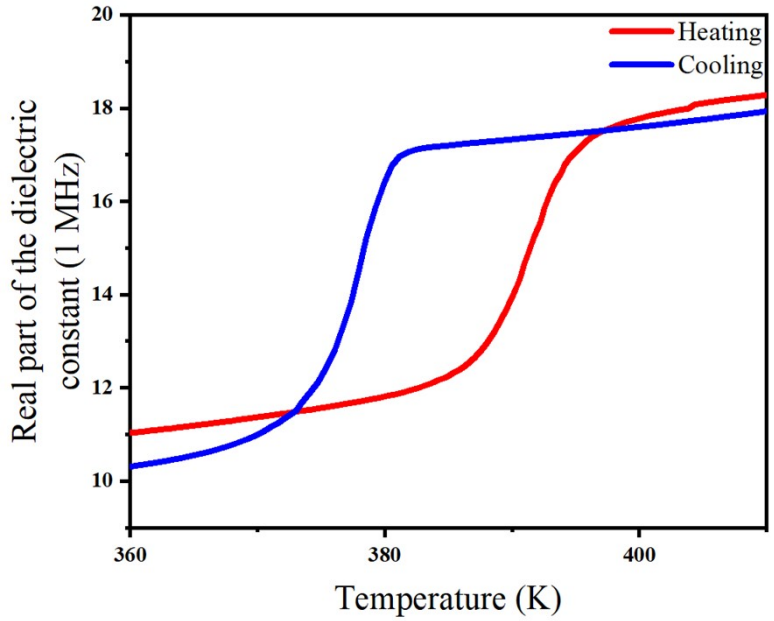

Fig. S5 Real part of the dielectric permittivity of **1** using silver paste.

Table. S1 The Values of the T_c, $\Delta\varepsilon'$, ε', excitonic absorption, bandgap and photoluminescence for Selected Hybrid organic-inorganic.

Material	T_c (K)	ε'**(LT)**	ε'**(HT)**	**Excitonic absorption (nm, eV)**	**Band gap (eV)**	**emission (nm)**	**Stokes shift (nm)**	**Ref**
$(FTEA)PbBr_3$	378	9.9	18.3	311 (3.99)	3.48	670	390	1
$(Et_4N)PbBr_3$	367	10.0	16.1	-	-	-	373	2
$PyrPbI_3$	262.2	10	14	-	2.62	680	305	3
$IMPbBr_3$	200	10	14	388 (3.20)	3.34	688	194	4

$CEPbBr_3$	300.06	7.5	11.0	-	3.33	385	133	5
$BEPbBr_3$	286.08	3.4	6.0	-	3.24	391	138	6
$Pyr_2KCr(CN)_6$	234.1	38.5	67.5	-	3.85	804	538	7
$(TEACCl)PbBr_3$	359	11.2	15.3	314 (3.94)	3.57	715		**This work**

Table. S2 Crystal structure of **1** at 296 K and 410 K.

Temperature (K)	296	410
Crystal system	Monoclinic	Hexagonal
CCDC Number	2212352	2212353
Space group	$P2_1/c$	$P6_3/mmc$
a / Å	10.8678(4)	10.570(2)
b / Å	35.6850(15)	10.570(2)
c / Å	7.7853(3)	7.9754(16)
α / °	90	90
β / °	100.9530(10)	90
γ / °	90	120
Volume /(Å^3)	2964.3(2)	771.673
Z	8	2
Radiation	Mo-Kα (λ = 0.71073)	Mo-Kα (λ = 0.71073)
ρ_{calc} / g cm^{-3}	2.678	2.572
F(000)	2160.0	540.0
Goodness-of-fit on F^2	1.018	1.034
R_1[I>2sigma(I)]	0.0409	0.0893
wR_2[I>2sigma(I)]	0.0782	0.2454
R_{int}	0.0562	0.078

Table. S3 Selected bond lengths for **1** at 296 K.

Atom1	Atom2	Length	Atom1	Atom2	Length
Pb1	Br1	2.998	C7	Cl1	1.70(1)
Pb1	Br2	3.061	C7	N1	1.51(1)
Pb1	Br3	3.041	C8	C9	1.56(2)
Pb2	Br1	2.984	C8	N2	1.51(1)
Pb2	Br2	3.058	C10	C11	1.61(2)
Pb2	Br3	3.047	C10	N2	1.50(2)
Pb3	Br4	3.067(1)	C12	C13	1.58(2)
Pb3	Br5	3.029(1)	C12	N2	1.51(1)
Pb3	Br6	2.947(1)	C14	Cl2	1.72(1)
C1	C2	1.54(1)	C14	N2	1.51(1)
C2	N1	1.53(1)	C5	C6	1.60(1)
C3	C4	1.53(2)	C5	N1	1.50(1)
C3	N1	1.52(1)			

Table. S4 Selected angles [°] for **1** at 296 K.

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Br1	Pb1	Br2	84.45	C6	C5	N1	115.4(8)
Br1	Pb1	Br3	84.17	Cl1	C7	N1	114.0(7)
Br1	Pb1	Br1	180	C2	N1	C3	110.3(7)
Br1	Pb1	Br2	95.55	C2	N1	C5	107.6(7)
Br1	Pb1	Br3	95.83	C2	N1	C7	111.4(7)
Br2	Pb1	Br3	80.6	C3	N1	C5	111.8(7)
Br2	Pb1	Br1	95.55	C3	N1	C7	104.7(7)
Br2	Pb1	Br2	180	C5	N1	C7	111.0(7)
Br2	Pb1	Br3	99.4	C9	C8	N2	116.3(9)
Br3	Pb1	Br1	95.83	C11	C10	N2	115(1)
Br3	Pb1	Br2	99.4	C13	C12	N2	116.2(9)
Br3	Pb1	Br3	180	Cl2	C14	N2	112.8(7)
Br1	Pb1	Br2	84.45	C8	N2	C10	111.4(8)
Br1	Pb1	Br3	84.17	C8	N2	C12	107.6(8)
Br2	Pb1	Br3	80.6	C8	N2	C14	110.8(8)
Br1	Pb2	Br2	84.76	C10	N2	C12	111.2(8)
Br1	Pb2	Br3	84.3	C10	N2	C14	105.7(8)
Br1	Pb2	Br1	180	C12	N2	C14	110.1(8)
Br1	Pb2	Br2	95.24	Br5	Pb3	Br5	98.03(3)
Br1	Pb2	Br3	95.7	Br5	Pb3	Br6	99.90(3)
Br2	Pb2	Br3	80.55	Br6	Pb3	Br4	94.27(3)
Br2	Pb2	Br1	95.24	Br6	Pb3	Br5	94.51(3)
Br2	Pb2	Br2	180	Br6	Pb3	Br6	175.10(3)
Br2	Pb2	Br3	99.45	Br4	Pb3	Br5	84.14(4)
Br3	Pb2	Br1	95.7	Br4	Pb3	Br6	81.64(3)
Br3	Pb2	Br2	99.45	Br5	Pb3	Br6	82.42(3)
Br3	Pb2	Br3	180	Pb3	Br4	Pb3	79.71(3)
Br1	Pb2	Br2	84.76	Pb3	Br5	Pb3	80.93(3)
Br1	Pb2	Br3	84.3	Pb3	Br6	Pb3	79.84(3)
Br2	Pb2	Br3	80.55	C1	C2	N1	117.0(8)
Pb1	Br1	Pb2	81.19	C4	C3	N1	115.2(8)
Pb1	Br2	Pb2	79	Br4	Pb3	Br5	84.14(4)
Pb1	Br3	Pb2	79.49	Br4	Pb3	Br6	81.64(3)
Pb1	Br1	Pb2	81.19	Br5	Pb3	Br6	82.42(3)
Pb1	Br2	Pb2	79	Br4	Pb3	Br6	83.45(3)
Pb1	Br3	Pb2	79.49	Br4	Pb3	Br4	95.69(4)
Br1	Pb2	Br2	84.76	Br4	Pb3	Br5	177.94(4)
Br1	Pb2	Br3	84.3	Br4	Pb3	Br6	99.60(3)
Br2	Pb2	Br3	80.55	Br5	Pb3	Br6	84.28(3)
Br4	Pb3	Br5	82.10(3)	Br5	Pb3	Br4	177.47(4)

Symmetry codes:

#1 = -x+1, -y+1, -z+1;

#2 = -x+1, -y+1, -z+2;

#3 = x, -y+1/2, z+1/2;

#4 = x, -y+1/2, z-1/2.

Table. S5 Selected bond lengths for **1** at 410 K.

Atom1	Atom2	Length	Atom1	Atom2	Length
Pb1	Br1	3.026	C5	Cl1	1.7(1)
C2	N9	1.5(1)	C2	C1	1.5(3)
C3	N9	1.5(1)	C6	C7	1.5(1)
C5	N9	1.4(9)	C3	C4	1.4(1)
C6	N9	1.5(1)			

Table. S6 Selected angles [°] for **1** at 410 K.

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Br1	Pb1	Br2	81.3(0)	C3	N1	C6	110.1(4)
C2	N1	C3	109.3(2)	N1	C5	Cl1	114.4(9)
C2	N1	C5	109.1(3)	N1	C6	C7	118.5(5)
C2	N1	C6	109.4(2)	N1	C2	C1	117.5(6)
C3	N1	C5	109.2(9)	N1	C3	C4	120.8(6)

Symmetry codes:

#1 = x, -y, 2-z;

#2 = +y-x, -x, +z;

#3 = -y, +x-y, +z;

#4 = +y, -x+y, 2-z;

#5 = -y+x, +x, 2-z;

#6 = -x, -y, 1/2+z.

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