Extra thermostable one-dimensional organic-inorganic hybrid perovskite [N-methyldabconium]PbI_3 showing switchable dielectrics, conductivity and bright yellow-green emission

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Part One: Experimental

Chemical and Materials

All of the solvents and chemicals are of analysis pure grade supplied by Sinopharm Chemical Reagent Co. Ltd. Of China, and were used without further purification.

Synthesis of 1

The [N-methyldabconium]PbI_3 was prepared by dissolving PbI_2 and [N-methyldabconium]I with a molar ratio of 1:1 in the minimum amount of DMF. Light-yellow rod-like crystals were harvested after two weeks via solvent evaporation at 333 K. Yields: 81% based on the reactant PbI_2. Elemental analysis calcd (%) for $C_7H_{15}I_3N_2Pb$ (719.12): C, 11.76; H, 2.11; N, 3.92; found: C, 12.19; H, 2.36; N, 3.68.

Physical measurement

Elemental analyses for C, H and N were performed with an Elementar Vario EL III analytic instrument. Thermogravimetric analysis (TG) was performed using a TA2000/2960 thermogravimatric analyzer in the temperature range of 293-1073 K (20-800 °C) under nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements were carried out on a NETZSCH DSC 204F1 Phoenix calorimeter for powdered samples between 193 and 593 K, with a temperature scanning rate of 10 $K \cdot min^{-1}$. Fourier transform infrared (FT-IR) spectroscopy in the wavenumber range of 400−4000 cm^{-1} was collected on a Bruker VERTEX80 V Fourier transform infrared spectrometer (KBr disk) at room temperature. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance powder diffractometer operating at 40 kV and 40 mA using Cu Kα radiation with λ = 1.5418XXX Å. The 2θ angle spans from 5 to 50° with a rate of 0.01° $step^{-1}$. The measurements of dielectric permittivity and impedance spectra were performed for the powdered sample, which is prepared into a disk form with a diameter of 7 mm and a thickness of 0.8 mm and sandwiched between two parallel platinum electrodes, using a Concept 80 system (Novocontrol, Germany), the measurement was performed under N_2 atmosphere in the temperature range of 143-453 K and the frequency ranges of 1-10^7 Hz. Optical diffuse reflectance measurements were performed using a Shimadzu UV-3010 UV-vis-NIR spectrometer operating in the 200-1000 nm region using $BaSO_4$ as the reference of 100% reflectance. Photoluminescence spectra were acquired using a Fluorolog Tau-3 fluorometer at ambient temperature.

X-ray single Crystallography

Single-crystal X-ray diffraction data were collected for **1** at 298 and 373 K using the

graphite-monochromated Mo Ka (λ = 0.71073 Å) radiation on a CCD area detector (Bruker SMART). Data reduction and absorption corrections were performed using the SAINT and SADABS software packages,[1] respectively. Structures were solved by direct methods using the SHELXL-2014 software package.[2] The non-hydrogen atoms were anisotropically refined using a full-matrix least-squares method on F^2. All hydrogen atoms were placed at the calculated positions and refined as riding mode with isotropic temperature factors on the parent atoms. The details of data collection, structure refinement and crystallography are summarized in Table S1.

1. Software Packages SMART and SAINT; Siemens Analytical X-ray Instrument Inc.: Madison, WI, 1996.
2. G. M. Sheldrick, SHELX-97, Program for the refinement of crystal structure; University of Göttingen: Göttingen, Germany, 1997.

Part two

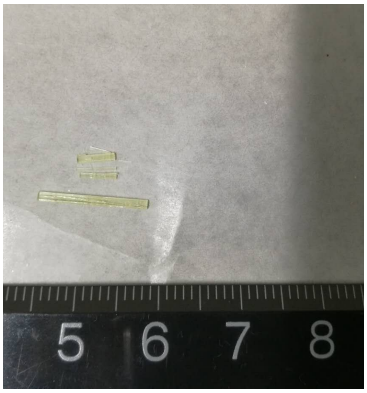


Fig. S1 Optical images of yellowish crystals of [N-methyldabconium]PbI_3 (**1**) at ambient temperature.

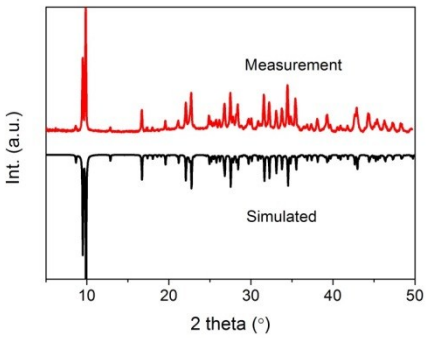


Fig. S2 Profile of powder X-ray diffraction (PXRD) of **1** at ambient temperature (low-temperature phase), which shows in agreement well with the simulated PXRD pattern obtained from the single crystal X-ray diffraction data of **1** at 298 K.

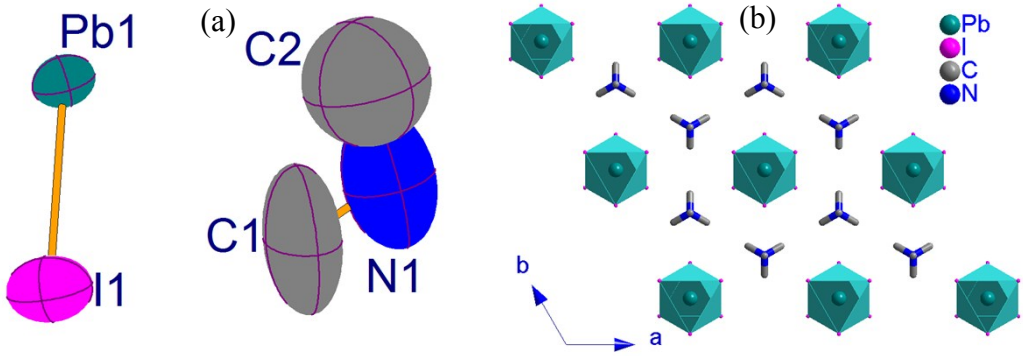


Fig. S3 (a) ORTEP view of **1**, which thermal ellipsoids are drawn at 50% probability scale (b) packing diagram of **1** viewed along c-axis direction at 473 K.

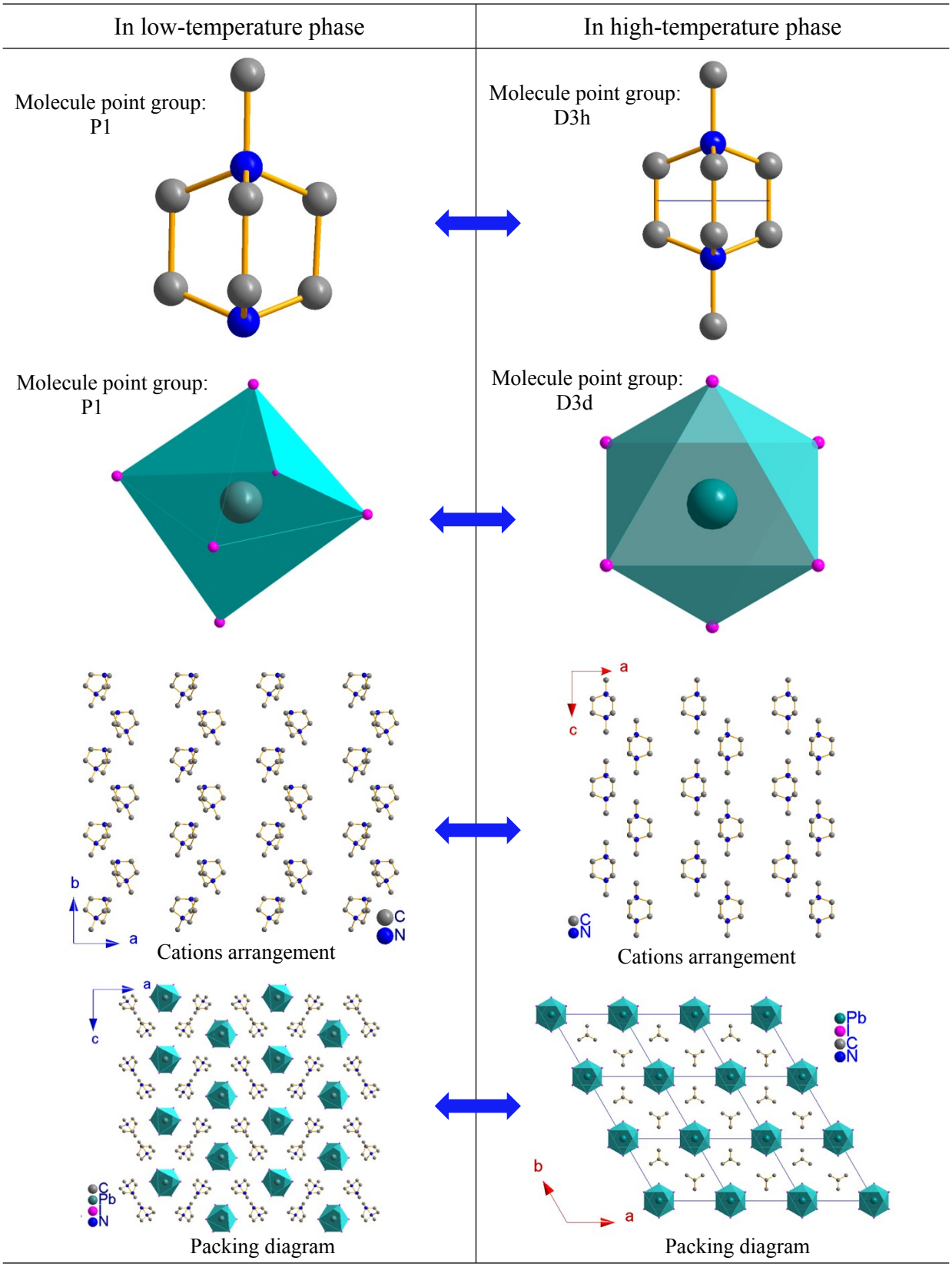


Fig. S4 Comparison of molecule and packing structure between low- and high-temperature phases for **1**.

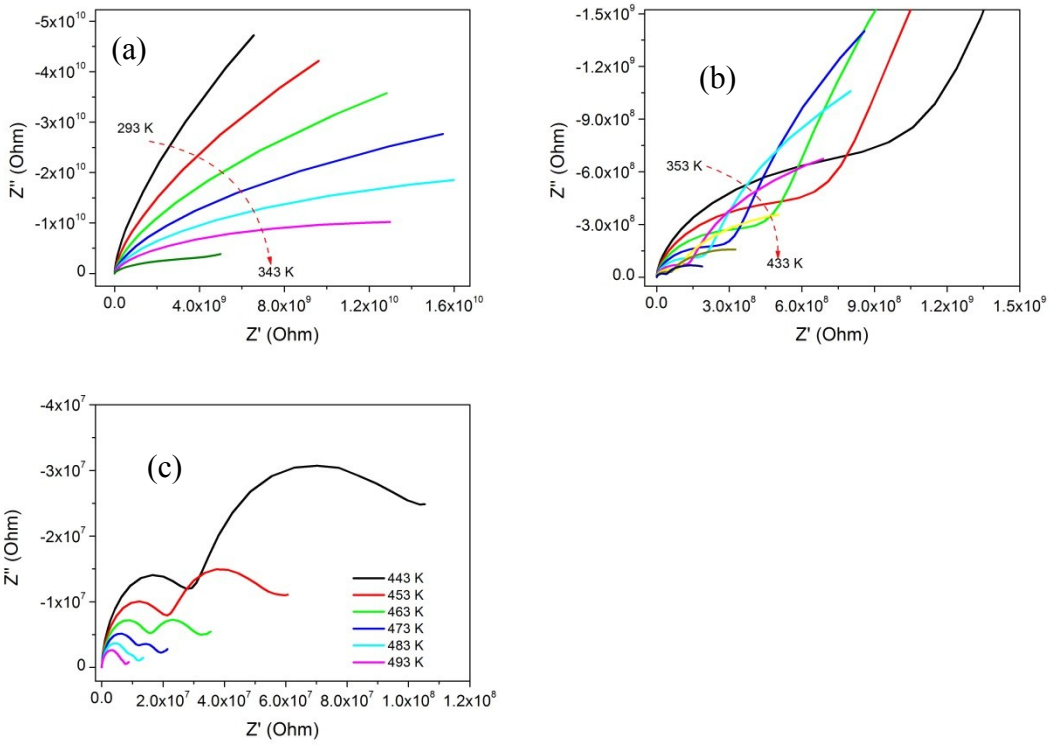


Fig. S5 (a-c) Impedance plots at selected temperatures in the range of 293-493 K.

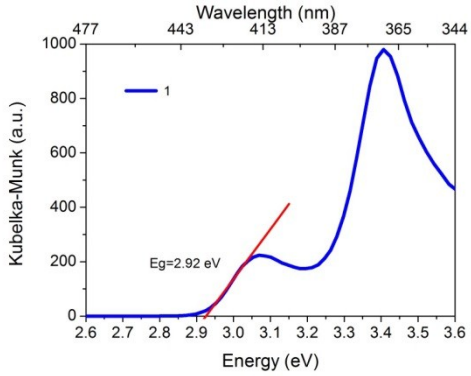


Fig. S6 Tauc plot ranges from 2.6 to 3.6 eV for **1** obtained by the Kubelka-Munk function transformation.

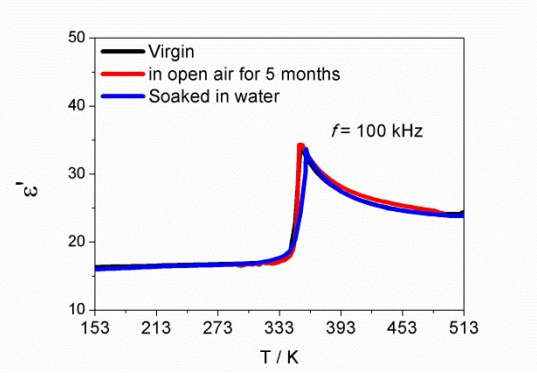


Fig. S7 dielectric permittivity of the virgin sample, the samples storaged in open air for 5 months and soaked in water for 1 month, respectively.

Table S1: Crystallographic Data and Refinement Parameter for **1** at 298 and 373 K

Temperature (K)	293	373
Formula	$C_7H_{15}N_2PbI_3$	$C_7H_{15}N_2PbI_3$
FW	715.11	715.10
Cryst syst	orthorhombic	hexagonal
Space group	*Pbca* (No. 61)	*P6₃/mmc* (No.194)
a (Å)	18.6221(7)	10.4821(3)
b (Å)	8.0211(3)	10.4821(3)
c (Å)	20.4046(7)	8.1053(5)
V (Å^3)	3047.83(19)	771.25(7)
Dcalcd (g/cm^3)	3.117	3.079
Z	8	2
F(000)	2496	624
abs coeff (mm^{-1})	17.119	16.913
R_{int}	0.047	0.037
indep reflns / restraints / param	3524 / 0 / 120	371/ 0 / 25
Refinement method	full-matrix least squares on F^2	
GOF on F^2	1.02	1.07
R_1/wR_2 (obsd dat[a])	0.0275 / 0.0472	0.0323 / 0.0792
Residual (eÅ^{-3})	-0.80, 0.71	-0.56, 0.46

[a] $R_1 = \sum||Fo| - |Fc||/|Fo|$, $wR_2 = [\sum w(\sum Fo^2 - Fc^2)^2/\sum w(Fo^2)^2]^{1/2}$

Table S2: The angles (α) between the lines passing through two N atoms in N-methyldabconium and the Pb^{2+} ions in $\{PbI_3\}_\infty$ chain

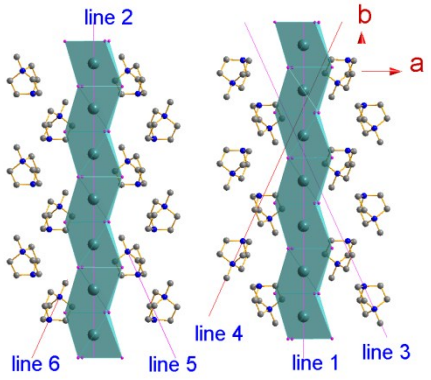
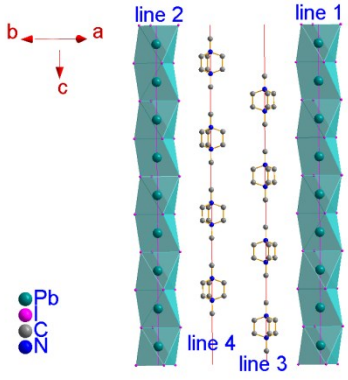
Angle/°	Low-temperature phase	high-temperature phase
		
$\alpha_{line\ 1\ldots line\ 2}$	0	0
$\alpha_{line\ 1\ldots line\ 3}$	36.6(1)°	0
$\alpha_{line\ 1\ldots line\ 4}$	36.6(1)°	0
$\alpha_{line\ 1\ldots line\ 5}$	36.6(1)°	
$\alpha_{line\ 1\ldots line\ 6}$	36.6(1)°	

Table S3 Onset of decompressed temperature for serious low dimensional perovskites.

Compound / Organic part	Dimensional	Decomposition Temperature (K)	Reference (DOI)
[2-methylpiperidine]$PbBr_3$	1 D	533 K	10.1021/acs.inorgchem.7b00521
[1,5-bis(1-methylimidazolium)-pentane]$PbBr_3$	1D	566 K	10.1039/c5dt02739j
[N,N'-dimethylethylenediamine]$PbBr_4$	1D	498 K	10.1038/ncomms14051
[2-Methylpiperidine]PbI_3	1 D	ca. 610 K	10.1039/c7tc03844e
$[(CH_3)_2NH_2]PbI_3$	1D	ca. 595 K	10.1021/acs.inorgchem.6b03095
[N-methyldabconium]PbI_3	**1D**	**653 K**	**This work**
[Triethylpropylammonium]PbI_3	1D	524 K	10.1021/acs.inorgchem.7b00881
[Tetrabutylammonium]PbI_3	1D	573 K	10.1016/j.inoche.2014.04.030
[4′-methyl-1-aminopyridinium]PbI_3	1D	573 K	10.1016/j.inoche.2013.03.017
[1-propyl-4-aminopyridinium]PbI_3	1D	593 K	10.1039/c7ra03524a
[N-(3-aminopropyl)imidazolete]$PbCl_4$	2D	ca. 530 K	10.1039/c7tc04868h
$(Benzylammonium)_2PbCl_4$	2D	480 K	10.1038/ncomms8338
$[(CH_3)_2NH_2]_7Pb_4Cl_{15}$	2D	ca. 450 K	10.1021/acs.inorgchem.7b03217
$[(CH_3)_2NH_2]_7Pb_4Br_{15}$	2D	ca. 470 K	10.1021/acs.inorgchem.7b03217

(cis-1,3-bis(methylamino-hydrobromide)cyclohexane)$PbBr_4$	2D	592 K	10.1002/cssc.201701227
(3- (aminomethyl)piperidinium)$(MA)_{n-1}Pb_nI_{3n+1}$ (n=1,2,3,4)	2D	608 K (n=1), ca. 590 K (n=2,3,4)	10.1021/jacs.8b00542
(4- (aminomethyl)piperidinium)$(MA)_{n-1}Pb_nI_{3n+1}$ (n=1,2,3,4)	2D	613 K (n=1), ca. 593 K (n=2,3,4)	10.1021/jacs.8b00542