



STRUCTURAL
CHEMISTRY

Volume 75 (2019)

Supporting information for article:

A two-dimensional organic–inorganic hybrid perovskite-type semiconductor: poly[(2-azaniumylethyl)trimethylphosphonium [tetra- μ -bromido-plumbate(II)]]

Ling Cheng and Yingjie Cao

Ultraviolet–Visible (UV–Vis) Absorption Spectrum.

UV-vis diffuse-reflectance spectra measurements was measured at room temperature by using a Shimadzu UV- 2600 spectrophotometer mounted with ISR-2600 integrating sphere operating in the range of 200-900 nm. BaSO₄ was used as a 100% reflectance reference. The band gap (Eg) of 1 was estimated by the Kubelka–Munk equation: $F(R_\infty)=(1-R_\infty)^2/2R_\infty$. The E_g was determined by the variant of the Tauc equation:

$$(h\nu F(R_\infty))^{1/n} = A(h\nu - E_g)$$

Where:

h: Planck's constant, *F(R_∞)*: the Kubelka–Munk function, *v*: frequency of vibration, *A*: proportional constant. The exponent *n* denotes the nature of the sample transition. For indirect allowed transition, *n* = 2. The optical band gap *Eg* can be obtained from a Tauc plot by plotting $(hv \cdot F(R_\infty))^{1/n}$ against the energy in eV and extrapolation of the linear region to the X-axis intercept.

The phase purity of **1** was confirmed by powder X-ray diffraction (PXRD) pattern (**Figure S1**) and IR spectroscopy (**Figure S2**), using a Shimadzu model IR-60 spectrometer and Rigaku company D/Max-2000 X-ray powder diffractometer. Besides, the PXRD pattern matches very well with the simulated pattern based on the crystal structures of **1** for the room temperature phase, confirming the phase purity of the as-grown crystals.

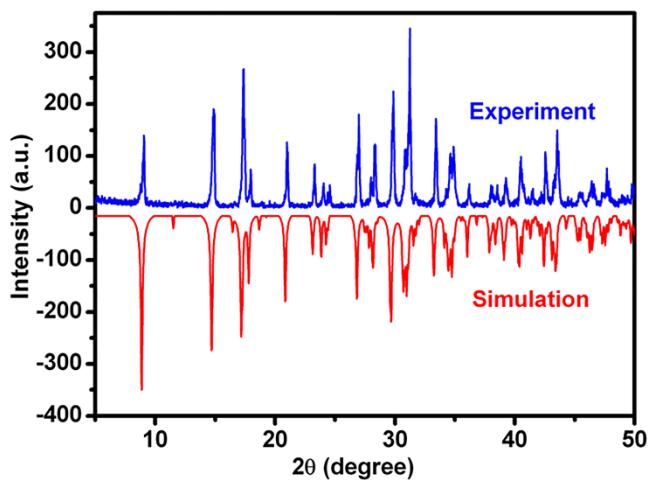


Figure S1 Powder XRD patterns of (**1**) at 293 K

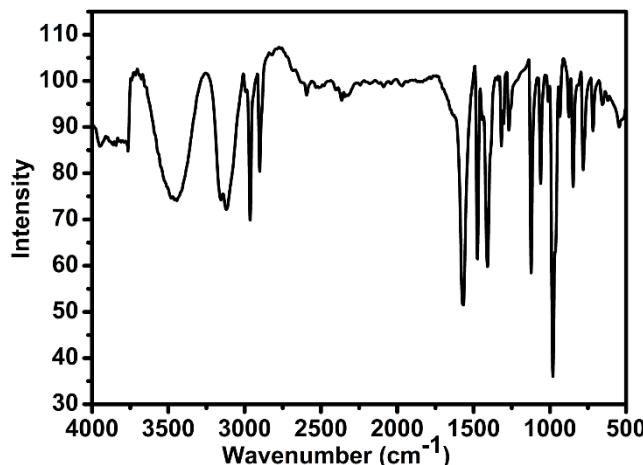


Figure S2 IR spectrum of (**1**) measured on a KBr-diluted pellet at room temperature

Special details

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	Uiso*/Ueq
Pb1	0.99441 (8)	0.47547 (5)	1.01083 (5)	0.01630 (18)
Br2	0.9858 (3)	0.22134 (17)	1.04342 (17)	0.0348 (4)
Br3	0.9976 (3)	0.40750 (16)	0.72279 (16)	0.0314 (4)
Br4	0.9586 (3)	0.50865 (16)	1.30396 (17)	0.0406 (6)
P1	0.5945 (6)	0.2047 (4)	0.4259 (4)	0.0216 (9)
Br1	0.5008 (2)	0.4928 (3)	0.99230 (18)	0.0355 (7)
C3	0.490 (3)	0.2820 (19)	0.289 (2)	0.046 (6)
H3A	0.5859	0.3441	0.2725	0.070*
H3B	0.3433	0.3081	0.3091	0.070*
H3C	0.4844	0.2357	0.2105	0.070*
C4	0.504 (3)	0.2613 (12)	0.5792 (17)	0.025 (4)
H4A	0.5755	0.3327	0.5922	0.030*
H4B	0.3450	0.2743	0.5731	0.030*
C1	0.506 (3)	0.0669 (16)	0.407 (2)	0.048 (6)
H1A	0.3563	0.0598	0.4385	0.073*
H1B	0.6020	0.0189	0.4574	0.073*

H1C	0.5109	0.0468	0.3135	0.073*
C5	0.551 (3)	0.1901 (15)	0.7009 (16)	0.033 (4)
H5A	0.4845	0.1175	0.6874	0.039*
H5B	0.7099	0.1802	0.7109	0.039*
N1	0.463 (3)	0.2386 (14)	0.8236 (14)	0.047 (5)
H1D	0.5500	0.2941	0.8502	0.071*
H1E	0.4580	0.1871	0.8876	0.071*
H1F	0.3260	0.2642	0.8081	0.071*
C2	0.888 (2)	0.2065 (16)	0.4267 (16)	0.031 (4)
H2A	0.9430	0.1617	0.4994	0.046*
H2B	0.9397	0.2814	0.4379	0.046*
H2C	0.9417	0.1776	0.3432	0.046*

Atomic displacement parameters (\AA^2)

	U ¹¹	U ²²	U ³³	U ¹²	U ¹³	U ²³
Pb1	0.0116 (3)	0.0198 (3)	0.0176 (3)	-0.0001 (2)	0.00187 (18)	-0.0012 (3)
Br2	0.0516 (11)	0.0196 (7)	0.0332 (9)	0.0005 (9)	0.0074 (8)	0.0007 (9)
Br3	0.0330 (10)	0.0420 (9)	0.0192 (8)	0.0051 (8)	-0.0024 (7)	-0.0049 (7)
Br4	0.0507 (12)	0.0502 (12)	0.0211 (9)	-0.0198 (9)	0.0067 (8)	-0.0090 (7)
P1	0.0174 (19)	0.025 (2)	0.022 (2)	0.0001 (18)	0.0033 (16)	-0.0007 (16)
Br1	0.0111 (7)	0.0474 (19)	0.0480 (10)	0.0018 (8)	-0.0007 (7)	-0.0085 (9)
C3	0.019 (9)	0.083 (15)	0.037 (12)	0.006 (10)	-0.001 (9)	0.030 (11)

C4	0.025 (9)	0.024 (8)	0.025 (9)	-0.004 (7)	0.009 (8)	-0.003 (6)
C1	0.045 (13)	0.040 (10)	0.060 (14)	-0.016 (10)	0.019 (11)	-0.026 (11)
C5	0.028 (9)	0.044 (11)	0.027 (10)	0.008 (9)	0.012 (8)	-0.010 (8)
N1	0.069 (12)	0.049 (10)	0.023 (8)	0.030 (9)	-0.006 (8)	-0.002 (7)
C2	0.017 (7)	0.048 (10)	0.027 (9)	-0.010 (8)	0.008 (7)	0.004 (8)

Geometric parameters (\AA , $^{\circ}$)

Pb1—Br4	2.9568 (18)	P1—C1	1.754 (18)
Pb1—Br1	2.9798 (15)	P1—C4	1.763 (16)
Pb1—Br3	2.9844 (17)	P1—C3	1.764 (17)
Pb1—Br2 ⁱ	3.016 (2)	P1—C2	1.766 (14)
Pb1—Br1 ⁱⁱ	3.0587 (16)	Br1—Pb1 ^{iv}	3.0587 (15)
Pb1—Br2	3.082 (2)	C4—C5	1.510 (17)
Br2—Pb1 ⁱⁱⁱ	3.016 (2)	C5—N1	1.46 (2)
Br4—Pb1—Br1	88.39 (6)	Br2 ⁱ —Pb1—Br2	175.51 (2)
Br4—Pb1—Br3	171.02 (6)	Br1 ⁱⁱ —Pb1—Br2	95.26 (7)
Br1—Pb1—Br3	88.47 (6)	Pb1 ⁱⁱⁱ —Br2—Pb1	163.28 (6)
Br4—Pb1—Br2 ⁱ	92.71 (5)	C1—P1—C4	111.5 (9)
Br1—Pb1—Br2 ⁱ	87.76 (7)	C1—P1—C3	108.0 (12)
Br3—Pb1—Br2 ⁱ	95.57 (5)	C4—P1—C3	110.9 (9)
Br4—Pb1—Br1 ⁱⁱ	97.48 (6)	C1—P1—C2	108.3 (9)
Br1—Pb1—Br1 ⁱⁱ	169.41 (10)	C4—P1—C2	107.9 (8)

Br3—Pb1—Br1 ⁱⁱ	86.96 (6)	C3—Pb1—C2	110.3 (8)
Br2 ⁱ —Pb1—Br1 ⁱⁱ	83.19 (7)	Pb1—Br1—Pb1 ^{iv}	169.41 (10)
Br4—Pb1—Br2	91.67 (5)	C5—C4—P1	114.8 (11)
Br1—Pb1—Br2	93.35 (7)	N1—C5—C4	112.2 (14)
Br3—Pb1—Br2	80.13 (5)		

Symmetry codes: (i) $-x+2, y+1/2, -z+2$; (ii) $x+1, y, z$; (iii) $-x+2, y-1/2, -z+2$; (iv) $x-1, y, z$.