Supporting Information

A Nanowire Array with Two Types of Bromoplumbate Chains and High Anisotropic Conductance

Cai Sun,[ab] Ming-Xiu Du,[a] Jian-Gang Xu,[ab] Fei-Fei Mao,[ab] Ming-Sheng Wang,*[a] and Guo-Cong Guo[a]

[a.] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China*

[b.] *University of Chinese Academy of Sciences, Beijing 100039, People's Republic of China*

E–mails: mswang@fjirsm.ac.cn

Index

1. Experimental section

Materials. All chemicals were used as purchased without further purification. Water was deionized and distilled before use.

Measurements. The elemental analyses of C, H, and N were measured on an Elementar Vario EL III microanalyzer. The FT-IR spectrum was measured on a PerkinElmer Spectrum One FT-IR spectrometer using a KBr pellet. The electronic absorption spectra were measured in the diffuse reflectance mode on a PerkinElmer Lambda 900 UV/vis/near-IR spectrophotometer equipped with an integrating sphere, and a $BaSO_4$ plate was used as the reference. Powder X-ray diffraction (PXRD) patterns were measured on a Rigaku Desktop MiniFlexII diffractometer using Cu K_α radiation (λ = 1.54056 Å) powered at 30 kV and 15 mA. The simulated PXRD pattern was derived from the Mercury Version 3.5.1 software. A Mettler TOLECO simultaneous TGA/DSC apparatus was used to obtain the TGA curve under N_2 atmosphere in the range of 30–800 °C with a heating rate of 10 °C/min. The ESI-MS was measured using a ThermoFinnigan LCQ Deca XP MAX LC/MS system. The temperature-dependent electrical conductivities and *I–V* curves were measured in a Keithley 4200-SCS semiconductor parameter analyzer using pellet sample by the two probe method using silver paste.

Temperature and vacuum control for electric tests. We placed the single-crystal sample onto a piece of sapphire, and put the lateral device architecture onto the sample stage of a probe station (Lake Shore CRX-VF) with thermally conductive and electrically insulating grease (DuPont Krytox). The temperature of the sample was monitored by a GaAs diode (Lake Shore, top model 336) and was kept constant to within 0.01 °C. Moreover, the pressure of vacuum chamber was kept at ~ 1.4×10^{-6} torr to ensure the reliability and quality of data during the electric measurements.

Synthesis of $\{(EV)_{12}[Pb_{18}Br_{54}][Pb_{6.5}Br_{19}]\}_n$ (EVPbBr, EV = 1,1'-diethyl-4,4'-bipyridimium-1,1'-diium). **EVPbBr** was prepared by the solvothermal reaction of $PbBr_2$ (110 mg, 0.3 mmol), 4,4'-bipyridine (47 mg,0.3 mmol), concentrated HBr (1.0 mL, 40% v/v), saturated KBr (aq., 5 ml) and ethanol (5ml) at 150 °C for 3 days. Upon cooling to room temperature, yellow needle-like crystals of **1** were obtained. Yield: 82% (based on $PbBr_2$). Elem anal. Calcd for $C_{336}H_{432}N_{48}Pb_{49}Br_{146}$: H, 1.61; C, 14.97; N, 2.49. Found: H, 1.80; C, 15.20; N, 2.51. IR (KBr, 4000–400 cm–1): 3443(s), 3115(m), 3052(m), 1636(s,) 1558(m), 1503(w), 1443(m), 1344(w), 1233(w), 1178(w), 1083(w), 968(w), 869(w), 828(m), 715(w), 561(w).

X-ray crystallographic study. The single-crystal X-ray diffraction measurements of **EVPbBr** was performed on a Rigaku SuperNova diffractometer, using graphite monochromated Cu *Kα* radiation (λ = 1.54178 Å). Intensity data sets were collected using ω scan techniques, and corrected for *Lp* effects. The

structures were solved and refined by full-matrix least squares on F^2 using the Siemens SHELXTL^{TM} Version 5 package of crystallographic software,[1] with anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms were added geometrically and refined using the riding model. Crystal data and structure refinement results for the compounds are summarized in **Table S1**.

The entry of CCDC-1577216 contains the supplementary crystallographic data for **EVPbBr**. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallograp hic Dat a Centre, 12, Uni on Road, Cambridge CB2 1EZ, U.K. Fax: (Internet) +44-1223/336-033. E-mail: deposit@ccdc.cam.ac.uk.

Computational approaches. All calculations were based on the density functional theory (DFT) level using the b3lyp functional and 6-31G* basis set by Gaussian 09 D01 version software.[2] The calculation model of a EV^{2+} dimer was token from the single crystal structures of **EVPbBr**.

The reduced density gradient RDG (s) is a fundamental dimensionless quantity in DFT used to describe the deviation from a homogeneous electron distribution. It was defined as

$$s = \frac{|\nabla\rho|}{2(3\pi^2)^{1/3}\rho^{4/3}},$$

where ρ is the electronic density and $\nabla\rho$ is the first derivative of ρ.[3] The results were analysed by the Multiwfn software.[4]

2. Supporting data.

1) Crystal and Structure Refinement Data.

Table S1. Crystal and Structure Refinement Data for **EVPbBr.**

Formula	$C_{168}H_{216}N_{24}Pb_{24.5}Br_{73}$
Mr	13481.22
Cryst size (mm^3)	0.03 × 0.04 × 0.12
Cryst syst	trigonal
Space group	$R\bar{3}$
a (Å)	47.1755(5)
b (Å)	47.1755(5)
c (Å)	11.6900(2)
α (deg)	90
β (deg)	90
γ (deg)	120
V (Å^3)	22530.9(6)
D_{calcd} (g/cm^3)	2.981
Z	3
F(000)	17868.0
Abs coeff (mm^{-1})	37.760
Reflns collcd/unique (R_{int})	49280/10136 (0.0440)
Data/params/restraints	10136/437/0
R_1[a]	0.0501
ωR_2[b]	0.1287
GOF on F^2	1.129
$\Delta\rho_{max}$ and $\Delta\rho_{min}$ (e/Å^3)	6.75 and –2.23

[a]$R_1 = \sum||F_o|-|F_c||/\sum|F_o|$, [b]$\omega R_2 = \{\sum\omega[(F_o)^2-(F_c)^2]^2/\sum\omega[(F_o)_2]^2\}^{1/2}$

Table S2. Bond lengths for **EVPbBr**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pb11	Br11	2.9368(11)	N12	C8	1.343(16)
Pb11	Br12	2.9845(12)	N12	C9	1.345(15)
Pb11	Br13[1]	3.0854(11)	N12	C13	1.505(18)
Pb11	Br13	3.1170(12)	N21	C22	1.329(16)
Pb11	Br14	3.1219(10)	N21	C23	1.329(16)
Pb11	Br15	3.0243(11)	N21	C33	1.483(16)
Pb12	Br12[2]	3.0609(12)	N22	C28	1.343(16)
Pb12	Br14	3.1995(11)	N22	C29	1.314(16)
Pb12	Br15	3.0989(11)	N22	C31	1.493(16)
Pb12	Br16	2.7969(13)	C1	C2	1.36(2)
Pb12	Br17	2.8978(12)	C1	C5	1.397(16)
Pb13	Br11[3]	3.1473(13)	C3	C4	1.358(19)
Pb13	Br17	3.0590(12)	C4	C5	1.409(15)
Pb13	Br18	2.7966(14)	C5	C6	1.459(16)
Pb13	Br19	2.7652(13)	C6	C7	1.379(14)
Br11	Pb13[4]	3.1473(13)	C6	C10	1.393(15)
Br12	Pb12[2]	3.0609(12)	C7	C8	1.373(18)
Br13	Pb11[1]	3.0854(11)	C9	C10	1.347(18)
Pb21	Br21	2.7893(14)	C11	C12	1.47(2)
Pb21	Br22[5]	3.0593(13)	C13	C14	1.48(2)
Pb21	Br22	2.9351(13)	C21	C22	1.367(18)
Pb21	Br23	3.0867(13)	C21	C25	1.374(15)
Pb22	Br23[6]	3.1967(13)	C23	C24	1.372(18)
Pb22	Br23[7]	3.1967(13)	C24	C25	1.379(14)
Pb22	Br23	3.1967(13)	C25	C26	1.497(16)
Pb22	Br23[8]	3.1967(13)	C26	C27	1.379(16)
Pb22	Br23[9]	3.1967(13)	C26	C30	1.397(14)
Pb22	Br23[10]	3.1967(13)	C27	C28	1.378(19)
Br22	Pb21[11]	3.0593(13)	C29	C30	1.366(17)
N11	C2	1.321(16)	C31	C32	1.50(2)
N11	C3	1.342(17)	C33	C34	1.53(2)
N11	C11	1.468(18)			

Symmetry codes: [1]5/3-X, 4/3-Y, 1/3-Z; [2]5/3-X, 4/3-Y, 4/3-Z; [3]+X, +Y, 1+Z; [4]+X, +Y, -1+Z; [5]+Y, 1-X+Y, 1-Z; [6]1-Y+X, +X, -Z; [7]2-Y, 1+X-Y, +Z; [8]1+Y-X, 2-X, +Z; [9]2-X, 2-Y, -Z; [10]+Y, 1-X+Y, -Z; [11]1-Y+X, +X, 1-Z.

Table S3. Bond angles for **EVPbBr**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Br11	Pb11	Br12	96.84(3)	Br23^{10}	Pb22	Br23^{7}	180.00(3)
Br11	Pb11	Br13^{1}	91.00(3)	Br23^{10}	Pb22	Br23^{9}	96.23(3)
Br11	Pb11	Br13	89.18(3)	Br23	Pb22	Br23^{8}	96.23(3)
Br11	Pb11	Br14	173.55(3)	Br23^{8}	Pb22	Br23^{9}	180
Br11	Pb11	Br15	90.52(3)	Br23^{6}	Pb22	Br23^{8}	83.77(3)
Br12	Pb11	Br13^{1}	84.93(3)	Br23	Pb22	Br23^{10}	96.23(3)
Br12	Pb11	Br13	166.23(4)	Pb21	Br22	Pb21^{11}	102.36(4)
Br12	Pb11	Br14	83.50(3)	Pb21	Br23	Pb22	97.66(3)
Br12	Pb11	Br15	93.11(4)	C2	N11	C3	120.0(12)
Br13^{1}	Pb11	Br13	82.59(3)	C2	N11	C11	120.1(12)
Br13	Pb11	Br14	91.91(3)	C3	N11	C11	119.9(12)
Br13^{1}	Pb11	Br14	95.44(3)	C8	N12	C9	121.0(11)
Br15	Pb11	Br13^{1}	177.65(3)	C8	N12	C13	119.8(11)
Br15	Pb11	Br13	99.23(3)	C9	N12	C13	119.2(11)
Br15	Pb11	Br14	83.03(3)	C22	N21	C33	118.3(11)
Br12^{2}	Pb12	Br14	99.91(3)	C23	N21	C22	119.8(11)
Br12^{2}	Pb12	Br15	174.35(3)	C23	N21	C33	121.9(11)
Br15	Pb12	Br14	80.60(3)	C28	N22	C31	117.8(11)
Br16	Pb12	Br12^{2}	88.98(4)	C29	N22	C28	120.8(11)
Br16	Pb12	Br14	92.44(4)	C29	N22	C31	121.4(11)
Br16	Pb12	Br15	96.63(4)	C2	C1	C5	121.6(12)
Br16	Pb12	Br17	93.60(4)	N11	C2	C1	120.8(12)
Br17	Pb12	Br12^{2}	92.04(4)	N11	C3	C4	122.2(11)
Br17	Pb12	Br14	166.70(3)	C3	C4	C5	119.6(11)
Br17	Pb12	Br15	86.94(3)	C1	C5	C4	115.8(11)
Br17	Pb13	Br11^{3}	177.04(3)	C1	C5	C6	124.0(10)
Br18	Pb13	Br11^{3}	93.92(4)	C4	C5	C6	120.2(10)
Br18	Pb13	Br17	83.49(4)	C7	C6	C5	121.4(10)
Br19	Pb13	Br11^{3}	88.11(4)	C7	C6	C10	117.6(11)
Br19	Pb13	Br17	90.72(4)	C10	C6	C5	121.1(9)
Br19	Pb13	Br18	95.53(5)	C8	C7	C6	120.4(11)
Pb11	Br11	Pb13^{4}	98.97(3)	N12	C8	C7	119.9(11)
Pb11	Br12	Pb12^{2}	101.77(3)	N12	C9	C10	120.3(11)
Pb11^{1}	Br13	Pb11	97.41(3)	C9	C10	C6	120.8(10)
Pb11	Br14	Pb12	96.08(3)	N11	C11	C12	111.6(14)
Pb11	Br15	Pb12	100.29(3)	C14	C13	N12	110.7(11)
Pb12	Br17	Pb13	101.26(3)	C22	C21	C25	121.2(11)
Br21	Pb21	Br22	94.37(4)	N21	C22	C21	120.4(12)

Br21	Pb21	Br22[5]	89.59(5)	N21	C23	C24	122.0(10)
Br21	Pb21	Br23	97.39(5)	C23	C24	C25	119.3(11)
Br22	Pb21	Br22[5]	88.331(13)	C21	C25	C24	117.3(11)
Br22	Pb21	Br23	86.71(4)	C21	C25	C26	123.4(10)
Br22[5]	Pb21	Br23	171.72(4)	C24	C25	C26	119.3(10)
Br23	Pb22	Br23[6]	180	C27	C26	C25	122.9(10)
Br23[7]	Pb22	Br23[8]	96.23(3)	C27	C26	C30	116.3(11)
Br23[7]	Pb22	Br23[9]	83.77(3)	C30	C26	C25	120.7(9)
Br23[6]	Pb22	Br23[10]	83.77(3)	C28	C27	C26	120.5(11)
Br23[6]	Pb22	Br23[9]	96.23(3)	N22	C28	C27	120.4(11)
Br23	Pb22	Br23[7]	83.77(3)	N22	C29	C30	120.8(11)
Br23[10]	Pb22	Br23[8]	83.77(3)	C29	C30	C26	121.1(11)
Br23[6]	Pb22	Br23[7]	96.23(3)	C32	C31	N22	111.6(12)
Br23	Pb22	Br23[9]	83.77(3)	N21	C33	C34	112.2(11)

Symmetry codes: [1]5/3-X, 4/3-Y, 1/3-Z; [2]5/3-X, 4/3-Y, 4/3-Z; [3]+X, +Y, 1+Z; [4]+X, +Y, -1+Z; [5]+Y, 1-X+Y, 1-Z; [6]1-Y+X, +X, -Z; [7]2-Y, 1+X-Y, +Z; [8]1+Y-X, 2-X, +Z; [9]2-X, 2-Y, -Z; [10]+Y, 1-X+Y, -Z; [11]1-Y+X, +X, 1-Z.

2) PXRD patterns.

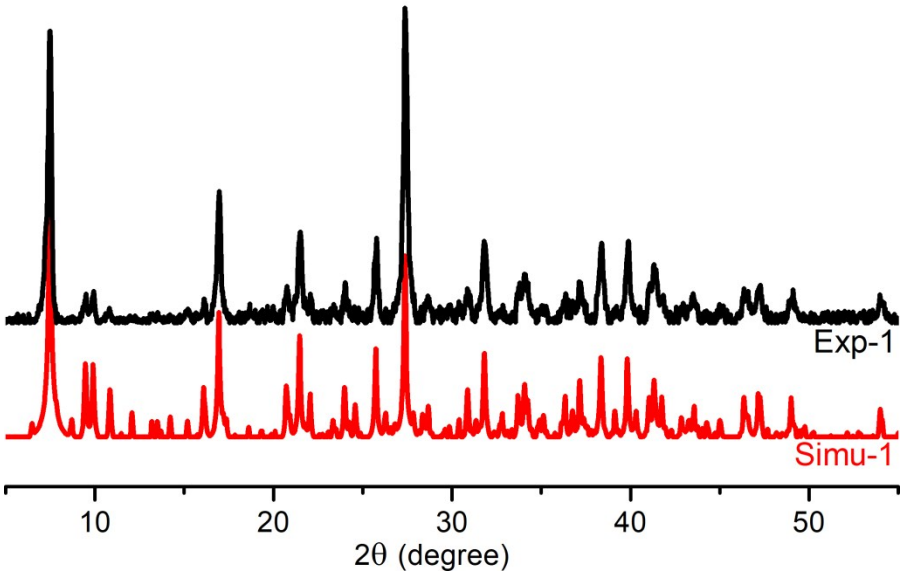

Figure S1. Experimental (Exp) and simulated (Simu) PXRD patterns of **EVPbBr**.

3) Thermogravimetric analysis.

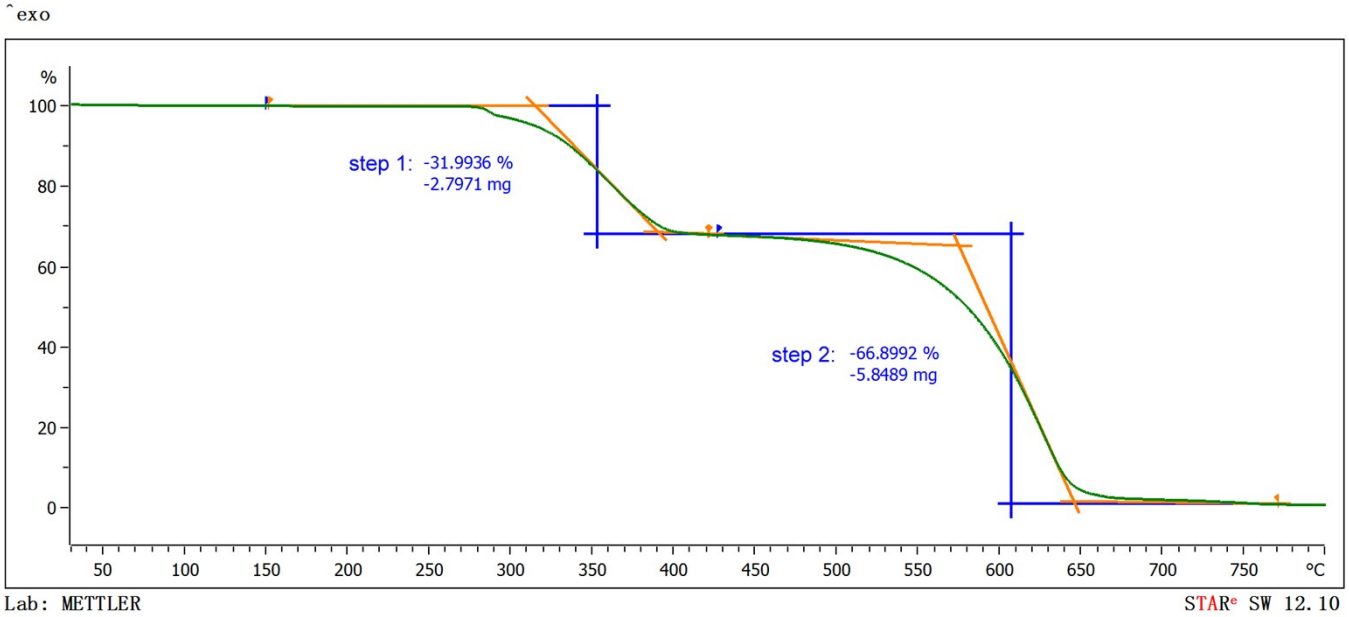

Figure S2. Thermogravimetric analysis of **EVPbBr** at nitrogen atmosphere. The ramp rate was 10 °C/min.

4) Optical absorption spectra of EVPbBr.

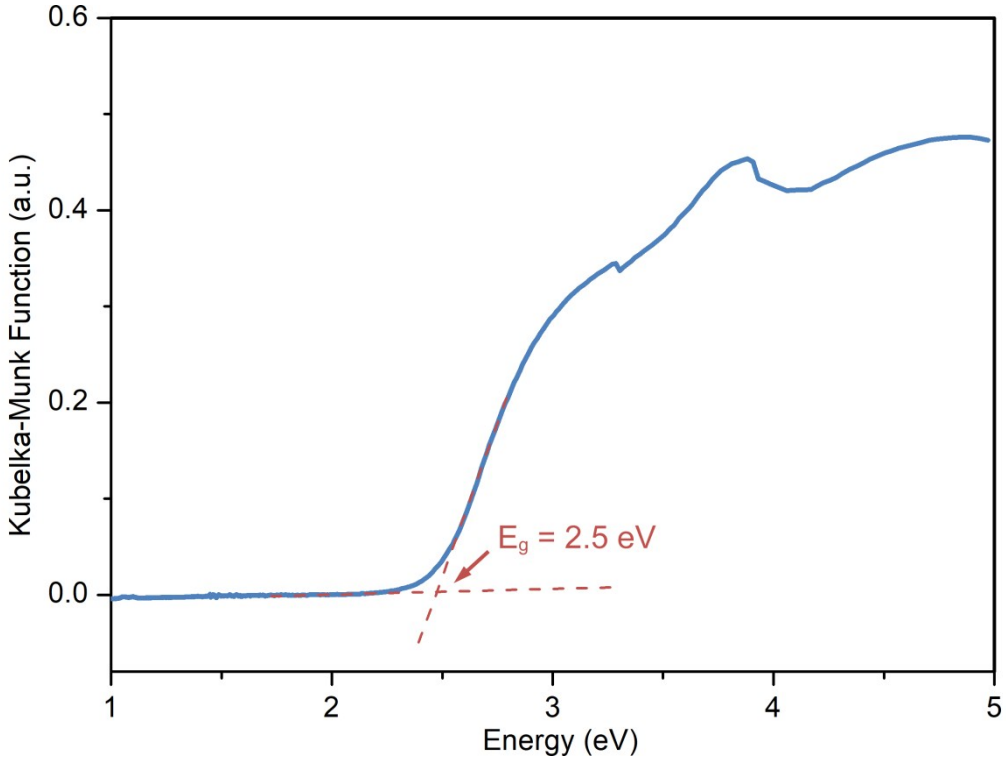

Figure S3. Optical absorption spectra of **EVPbBr**.

References:

(1) Siemens; Inc., S. E. A., Ed. Madison, Wisconsin, USA, 1994.

(2) Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox Gaussian, Inc., Wallingford CT, **2009**.

(3) E. R. Johnson, et al. *J. Am. Chem. Soc.* **2010**, *132*, 6498-6506.

(4) T. Lu and F. W. Chen, *J. Comput. Chem.* **2012**, *33*, 580–592.