Supporting Information

Surfactants As Additives Make the Structures of Organic–Inorganic Hybrid Bromoplumbates Diverse

Guangfeng Liu,[†,§] Jie Liu,[‡,§] Xutang Tao[‡], Dong-sheng Li,[*,⊥] and Qichun Zhang[*,†,#]

[†]School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore. Email: qczhang@ntu.edu.sg

[‡]State Key Laboratory of Crystal Materials, Shandong University, Jinan, Shandong 250100, China

[⊥]College of Materials and Chemical Engineering, Hubei Provincial Collaborative Innovation Center for New Energy Microgrid, China Three Gorges University, Yichang 443002, P. R. China. Email:lidongsheng1@126.com

[#]Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore

[§]These two authors have equal contribution to this paper.

Contents:

Materials and Methods

Figures S1 to S4

Table S1 and S2

Materials and Methods:
4,4'-bipyridine, $PbBr_2$, HBr aqueous solution (> 45%), CH_3OH, PVP (average molecular weight 10000), SDS and PEG-400 were purchased from Sigma-Aldrich Company. All starting materials are analytical-grade and were used as received without further purification.

To synthesize compound **1**, a mixture of $PbBr_2$ (0.54 mmol, 200 mg) and 4,4'-bipyridine (0.64 mmol, 100mg) was heated with HBr (> 45%, 1.5 ml) and CH_3OH (5 ml) in 25 ml Teflon-lined stainless-steel autoclaves at 120 °C for 5 days. Upon cooling to room temperature at 10 K h^{-1}, red prismatic crystals of **1** were obtained in 61% yield (based on $PbBr_2$). To synthesize the compound **2**, **3**, and **4**, all of the synthetic conditions (including raw materials qualities, reaction temperatures, reaction times, cooling rate and Teflon tank volume) are kept consistent with the reaction route for preparation **1,** only except that different surfactants (PVP, SDS and PEG-400) were chosen as additives to induce crystal growth. The addition amounts of surfactants PVP, SDS and PEG-400 for the preparation of compounds **2-4** (also see Table S1) are 1g, 1g and 1ml respectively, respectively. The yields for **2-4** are 52%, 51% and 10%, respectively (based on $PbBr_2$).
For comparison, we chose 100 °C and 80 °C as the reaction temperatures next for all routes and kept raw materials, surfactants and other crystallization parameters as same with the 120 °C experiments. At the 100 °C experiments, the results shown that the yields for **1** and **2** are dramatically decreased (about 15% for **1** and about 20% for **2**) and the yield for **4** is about 15%; we didn't obtain the compound **3** at this temperature. At the 80 °C experiments, all routes didn't produce any crystals of **1-4**.

Single-crystal X-ray diffraction. Suitable **1-4** single-crystals were selected for single-crystal X-ray data collection with a Bruker SMART APEX-II CCD area detector on a D8 goniometer. All data were collected using graphite-monochromated and 0.5 mm-Mono Cap-collimated Mo-$K\alpha$ radiation (λ = 0.71073 Å) with the ω scan method.[1] Data were processed with the SAINT program of the APEX2 software for reduction and cell refinement. Multi-scan absorption corrections were applied by using the SADABS program for area detector. All structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 (SHELX-97).[2] All non-H atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and included as riding with U_{iso} (H) = 1.2 U_{eq} (C). Crystallographic data and structural refinements are summarized in Table S2. Additional information in the form of CIF has also been supplied as Supporting Information.

Powder x-ray diffraction. The phase identity and purity of crystalline samples **1-4** were verified by power X-ray diffraction (PXRD) on a Bruker-AXS D8 ADVANCE X-ray diffractometer equipped with Cu $K\alpha$ radiation (λ = 1.54056 Å) in the 2θ range of 9–50°, with a step size of 0.02° and scan-speed of 0.2 sec/step at room temperature.

UV−Vis spectra. Absorption data were collected on a Hitachi U-4100 UV−vis−NIR

spectrophotometer equipped with an integrating sphere operating in di□use-reflectance mode at 298 K For crystalline samples **1-4**.

FT-IR spectroscopy. The attenuated total reflectance Fourier transform infrared spectra (ATR-FTIR) of crystalline **1-4** samples were recorded on a Thermo-Nicolet Nexus 670 spectrometer in the range of 700-4,000 cm^{-1} at room temperature.

Thermal Measurement. Thermogravimetric and differential scanning calorimetry synergetic tests (TGA-DSC) for **1-4** is carried out on a TGA/DSC/1600HT analyzer (METTLER TOLEDO Instruments). The samples were placed in Al_2O_3 crucible, and heated at a rate of 10 K· min^{-1} from room temperature to 490 °C under flowing nitrogen gas.

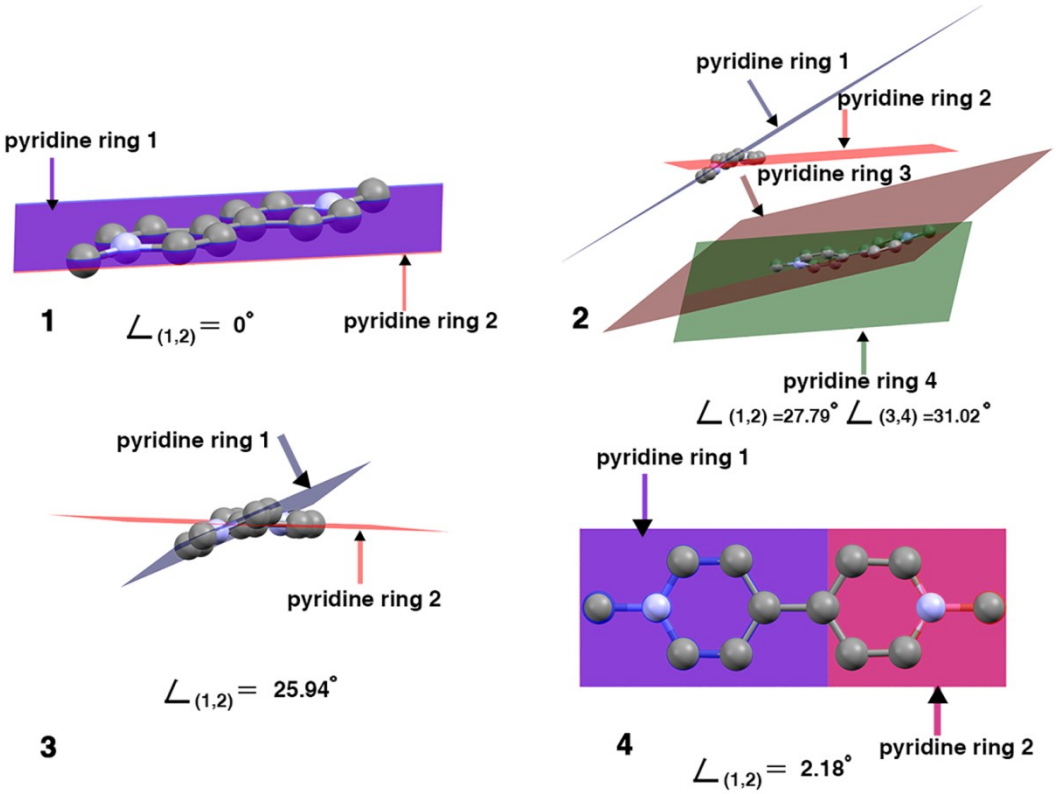

Fig S1. The dihedral angles between two N-methylate pyridine rings for 1-4 are as following: **1**: 0°; **2**: 27.79 and 31.02°; **3**: 25.94°; **4**: 2.18°.

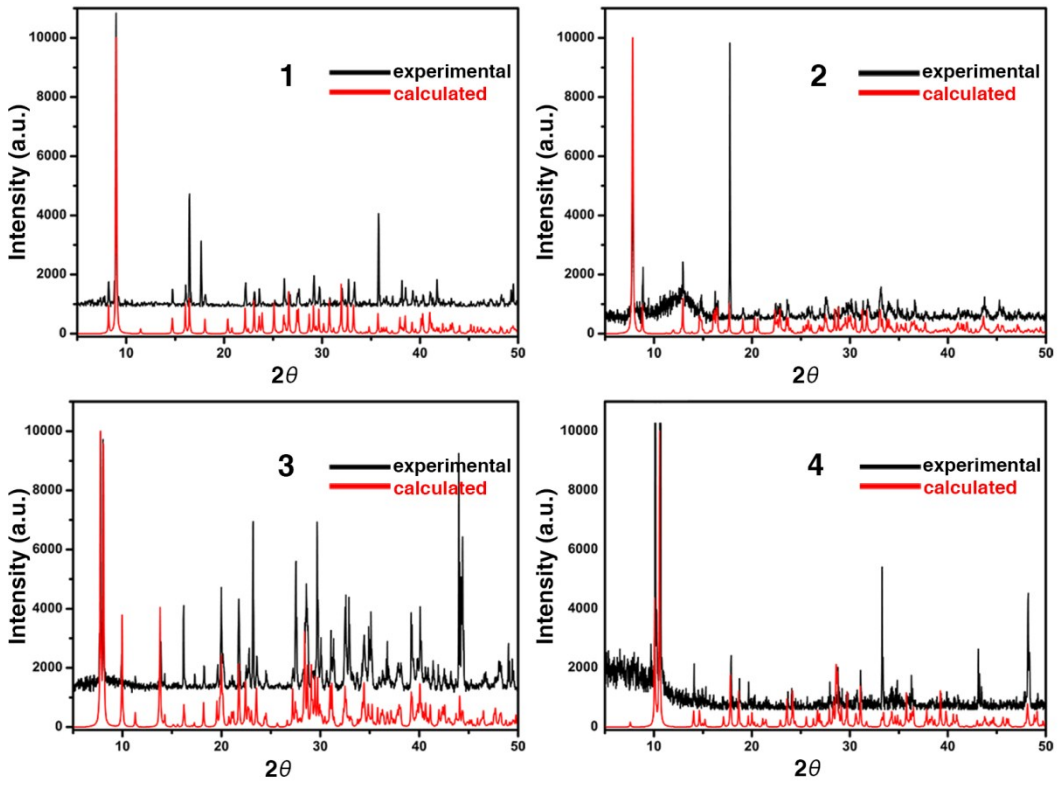

Fig S2. Simulated and experimental XRD powder patterns for **1-4**.

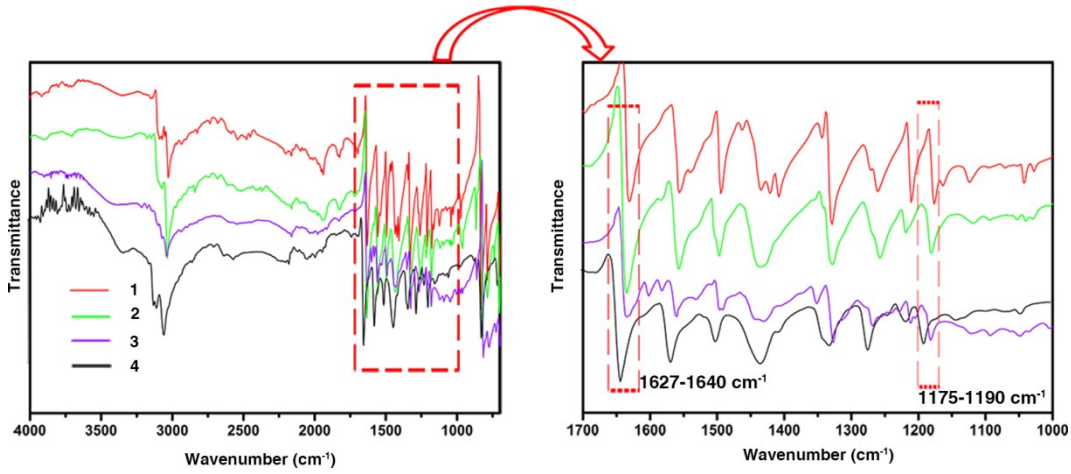

Fig S3 The FT-IR spectra and partial enlarged details for **1-4.**

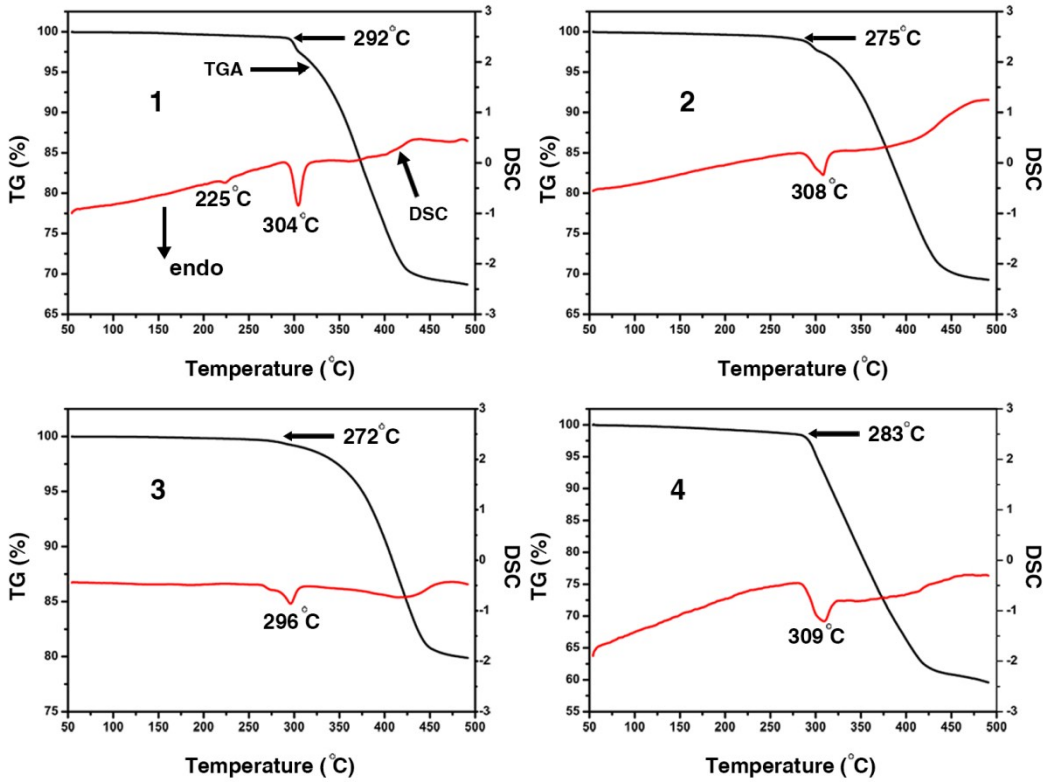

Fig S4. The TGA-DSC curves for the compounds **1-4**

Table S1. Crystallization parameters in the routes **1-4**

	1	**2**	**3**	**4**
4,4'-bpy	0.1 g (0.64 mmol)	0.1 g (0.64 mmol)	0.1 g (0.64 mmol)	0.1 g (0.64 mmol)
$PbBr_2$	0.2 g (0.54 mmol)	0.2 g (0.54 mmol)	0.2 g (0.54 mmol)	0.2 g (0.54 mmol)
HBr	1.5 ml (> 45%)	1.5 ml (> 45%)	1.5 ml (> 45%)	1.5 ml (> 45%)
CH_3OH	5 ML	5 ML	5 ML	5 ML
Surfactant	None	PVP (average molecular weight: 10000) 1g	SDS 1g	PEG-400 (1ML)
Reaction temperature	120 °C 100 °C 80 °C	120 °C 100 °C 80 °C	120 °C 100 °C 80 °C	120 °C 100 °C 80 °C
Reaction time	5 days	5 days	5 days	5 days
Cooling rate	10 °C/h	10 °C/h	10 °C/h	10 °C/h
Teflon tank volume	25 ML	25 ML	25 ML	25 ML

Table S2. Crystallographic data and structure refinement parameters of **1-4**

	1	**2**	**3**	**4**
T (K)	296	296	296	296
Formula	$C_6NH_7PbBr_3$	$C_6NH_7PbBr_3$	$(C_{12}N_2H_{14})_2Pb_7Br_{18}$	$(C_{12}N_2H_{14})_2Pb_3Br_{10}$
Formula weight	540.05	540.05	3261.21	1793.17
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	*P*	*P*	*C*2/m
Z	4	4	1	2
a (Å)	4.3566 (7)	8.0898(6)	9.7421(6)	18.748(3)
b (Å)	21.531(3)	12.4533(9)	12.9277(8)	9.5035(16)
c (Å)	11.0429(17)	22.9102(16)	13.2958(8)	12.453(2)
α (deg)	90	82.1090(10)	116.0700(10)	90.00
β (deg)	91.093(2)	89.5550(10)	110.7090(10)	110.850(2)
γ (deg)	90	76.3130(10)	90.9180(10)	90.00
V (Å^3)	1035.7(3)	2220.6(3)	1377.36(15)	2073.5(6)
ρ calcd (g/cm^3)	3.463	3.231	3.932	2.872
λ (Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073
Collected reflns	11594	25698	15048	5952
Unique reflns	2383	9710	5612	2243
Parameters	101	401	243	111
R (int)	0.0411	0.0463	0.0525	0.0699
R_1 [$I > 2\sigma(I)$]	0.0273	0.0331	0.0365	0.0490
wR_2 [$I > 2\sigma(I)$]	0.0669	0.0667	0.0874	0.1153
GOF	1.099	0.995	1.009	0.996

References:

1. APEX2 (version 2009.9); Bruker AXS Inc., (Madison, WI, 2009).
2. G. M. Sheldrick, *A short history of SHELX. Acta.crystallogr.* **A64**, 112 (2008).