Supporting Information

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

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Table S1 and S2
Materials and Methods:
4,4'-bipyridine, PbBr$_2$, HBr aqueous solution (> 45%), CH$_3$OH, 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$_3$OH (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-Kα radiation ($\lambda = 0.71073$ Å) with the $\omega$ scan method. 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). All non-H atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and included as riding with $U_{	ext{iso}}$ (H) = 1.2 $U_{	ext{eq}}$ (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 ($\lambda = 1.54056$ 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 diffuse-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\(_2\)O\(_3\) crucible, and heated at a rate of 10 K·min\(^{-1}\) from room temperature to 490 °C under flowing nitrogen gas.

![Diagrams](image)

**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

<table>
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<tr>
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<th>2</th>
<th>3</th>
<th>4</th>
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<tr>
<td>4,4’-bpy</td>
<td>0.1 g (0.64 mmol)</td>
<td>0.1 g (0.64 mmol)</td>
<td>0.1 g (0.64 mmol)</td>
<td>0.1 g (0.64 mmol)</td>
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<tr>
<td>PbBr₂</td>
<td>0.2 g (0.54 mmol)</td>
<td>0.2 g (0.54 mmol)</td>
<td>0.2 g (0.54 mmol)</td>
<td>0.2 g (0.54 mmol)</td>
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<tr>
<td>HBr</td>
<td>1.5 ml (&gt; 45%)</td>
<td>1.5 ml (&gt; 45%)</td>
<td>1.5 ml (&gt; 45%)</td>
<td>1.5 ml (&gt; 45%)</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>5 ML</td>
<td>5 ML</td>
<td>5 ML</td>
<td>5 ML</td>
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<tr>
<td>Surfactant</td>
<td>None</td>
<td>PVP (average molecular weight: 10000)</td>
<td>SDS 1g</td>
<td>PEG-400 (1ML)</td>
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<tr>
<td>Reaction temperature</td>
<td>120 °C</td>
<td>120 °C</td>
<td>120 °C</td>
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<tr>
<td></td>
<td>100 °C</td>
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<td>100 °C</td>
<td>100 °C</td>
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<tr>
<td></td>
<td>80 °C</td>
<td>80 °C</td>
<td>80 °C</td>
<td>80 °C</td>
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<td>Reaction time</td>
<td>5 days</td>
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<td>5 days</td>
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<td>Cooling rate</td>
<td>10 °C/h</td>
<td>10 °C/h</td>
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<td>Teflon tank volume</td>
<td>25 ML</td>
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### Table S2. Crystallographic data and structure refinement parameters of 1-4

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<td><strong>T (K)</strong></td>
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<td>296</td>
<td>296</td>
<td>296</td>
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<tr>
<td><strong>Formula</strong></td>
<td>C₆NH₂PbBr₃</td>
<td>C₆NH₂PbBr₃</td>
<td>(C₁₂N₂H₁₄)₂Pb₂Br₁₈</td>
<td>(C₁₂N₂H₁₄)₂Pb₃Br₁₀</td>
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<tr>
<td><strong>Formula weight</strong></td>
<td>540.05</td>
<td>540.05</td>
<td>3261.21</td>
<td>1793.17</td>
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<tr>
<td><strong>Crystal system</strong></td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
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<tr>
<td><strong>Space group</strong></td>
<td>P₂₁/c</td>
<td>P</td>
<td>P</td>
<td>C2/m</td>
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<td><strong>Z</strong></td>
<td>4</td>
<td>4</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td><strong>a (Å)</strong></td>
<td>4.3566 (7)</td>
<td>8.0898 (6)</td>
<td>9.7421 (6)</td>
<td>18.748 (3)</td>
</tr>
<tr>
<td><strong>b (Å)</strong></td>
<td>21.531 (3)</td>
<td>12.4533 (9)</td>
<td>12.9277 (8)</td>
<td>9.5035 (16)</td>
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<tr>
<td><strong>c (Å)</strong></td>
<td>11.0429 (17)</td>
<td>22.9102 (16)</td>
<td>13.2958 (8)</td>
<td>12.453 (2)</td>
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<tr>
<td><strong>α (deg)</strong></td>
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<td>82.1090 (10)</td>
<td>116.0700 (10)</td>
<td>90.00</td>
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<td><strong>β (deg)</strong></td>
<td>91.093 (2)</td>
<td>89.5550 (10)</td>
<td>110.7090 (10)</td>
<td>110.850 (2)</td>
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<td><strong>γ (deg)</strong></td>
<td>90</td>
<td>76.3130 (10)</td>
<td>90.9180 (10)</td>
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<td><strong>V (Å³)</strong></td>
<td>1035.7 (3)</td>
<td>2220.6 (3)</td>
<td>1377.36 (15)</td>
<td>2073.5 (6)</td>
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<td><strong>ρ calcd (g/cm³)</strong></td>
<td>3.463</td>
<td>3.231</td>
<td>3.932</td>
<td>2.872</td>
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<tr>
<td><strong>λ (Mo Kα) (Å)</strong></td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
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<td>15048</td>
<td>5952</td>
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<td><strong>Unique reflns</strong></td>
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<tr>
<td><strong>Parameters</strong></td>
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<td>401</td>
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<td>111</td>
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<td><strong>R (int)</strong></td>
<td>0.0411</td>
<td>0.0463</td>
<td>0.0525</td>
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<tr>
<td><strong>R₁ [I &gt; 2σ(I)]</strong></td>
<td>0.0273</td>
<td>0.0331</td>
<td>0.0365</td>
<td>0.0490</td>
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<tr>
<td><strong>wR₂ [I &gt; 2σ(I)]</strong></td>
<td>0.0669</td>
<td>0.0667</td>
<td>0.0874</td>
<td>0.1153</td>
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<td><strong>GOF</strong></td>
<td>1.099</td>
<td>0.995</td>
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<td>0.996</td>
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**References:**

1. APEX2 (version 2009.9); Bruker AXS Inc., (Madison, WI, 2009).