

Simultaneous Crystallization of *in situ* Formed Conjugated Polymer and Inorganic Matrix for Structure Solving

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Materials and Methods

Experimental section: 4,4'-bipyridine, 4-bromopyridine hydrochloride, PbBr₂, HBr aqueous solution (HBr > 45%), Br₂, CH₃OH, CH₃CH₂OH and CH₃CH₂CH₂OH 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 PbBr₂ (3.84 mmol, 1.4 g) and 4,4'-bipyridine (0.64 mmol, 0.1 g) was heated with HBr aqueous solution (HBr > 45%, 2 ml), Br₂ (0.1 ml) and CH₃OH (CH₃CH₂OH or CH₃CH₂CH₂OH can also be used in this reaction) (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, light yellow needle crystals of **1** were obtained in ~ 50% yield (based on 4,4'-bipyridine). To synthesize compound **2**, a mixture of PbBr₂ (3.84 mmol, 1.4 g) and 4-bromopyridine hydrochloride (1.28 mmol, 0.25 g) was heated with HBr aqueous solution (HBr > 45%, 2 ml), Br₂ (0.1 ml) and CH₃CH₂CH₂OH (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, light yellow needle crystals of **2** were obtained in > 70% yield (based on 4-bromopyridine hydrochloride).

Single-crystal X-ray diffraction. Suitable single-crystals of compounds **1** and **2** were selected for single-crystal X-ray data collection with a Bruker SMART APEX-II CCD area detector on a D8 goniometer. Data were collected using graphite-monochromated and 0.5 mm-Mono Cap-collimated Mo-*K*α radiation ($\lambda = 0.71073 \text{ \AA}$) 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. For compound **2**, hydrogen atoms were placed in idealized positions and included as riding with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$. Crystallographic data and structural refinements are summarized in Table S1.

Powder x-ray diffraction. The phase identity and purity of crystalline samples **1** were verified by power X-ray diffraction (PXRD) on a Bruker-AXS D8 ADVANCE X-ray diffractometer equipped with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) in the 2θ range of $9\text{--}50^\circ$, with a step size of 0.02° and scan-speed of 0.2 s step^{-1} at room temperature.

UV–Vis spectrum. Absorption data were collected on a Hitachi U-4100 UV–vis–NIR spectrophotometer equipped with an integrating sphere operating in diffuse-reflectance mode at the ambient environment for crystalline sample **1**.

FT-IR spectroscopy. The attenuated total reflectance Fourier transform infrared spectra (ATR-FTIR) of crystalline **1** sample were recorded on a Thermo-Nicolet Nexus 670 spectrometer in the range of $650\text{--}4,000 \text{ cm}^{-1}$ at room temperature.

Thermal Measurement. Thermogravimetric test (TGA) for compound **1** is carried out on a TGA analyzer (Q500). The sample was placed in Pt crucible, and heated at a rate of $10 \text{ K} \cdot \text{min}^{-1}$ from room temperature to $690 \text{ }^\circ\text{C}$ under flowing nitrogen gas.

Elemental analysis. Elemental analysis was done by using a PerkinElmer 2400Series II CHNS/O elemental analyzer.

Photoelectron Chemical Measurements.

Electrode Preparation: To fabricate the photoelectrode, a well-dispersed 5 mg mL^{-1} suspension for compound **1** with pure ethanol as solvent was prepared by brief sonication in a water bath. Fluorine-doped tin oxide (FTO) coated glasses ($1.0 \times 2.0 \text{ cm}^2$) were used as the substrate. The substrates were cleaned thoroughly by sonication in 5% detergent (Decon $\text{\textcircled{R}}$ 90) for 30 minutes first and then rinsed with deionized water (DI water) for several times, which were followed by sonication in DI water,

acetone, 2-propanol for each 15 minutes. After that, 50 μL of different sample suspensions were dropped onto the surface of FTO substrates, which were masked using Ti foil with an effective area of 0.283 cm^2 . The samples were dried under vacuum at 80 $^\circ\text{C}$ for 6 hrs. Photoelectrochemical Measurements: the photoelectrochemical tests were performed using an electrochemical workstation (CHI760E). The PEC property of compound **1** was measured in a three-electrode electrochemical system with Ag/AgCl electrode in a saturated KCl solution, Pt plate, thin film of **1**, and 0.5 M Na_2SO_4 as reference, counter, working electrodes, and electrolyte under a 300 W xenon lamp (Newport) coupled to an AM 1.5G filter. To convert the measured voltage into the voltage vs. the reversible hydrogen electrode (RHE), the following calculation was performed: $V_{\text{RHE}} = V_{\text{Ag/AgCl}} + 0.197 + 0.059 \times \text{pH}$.

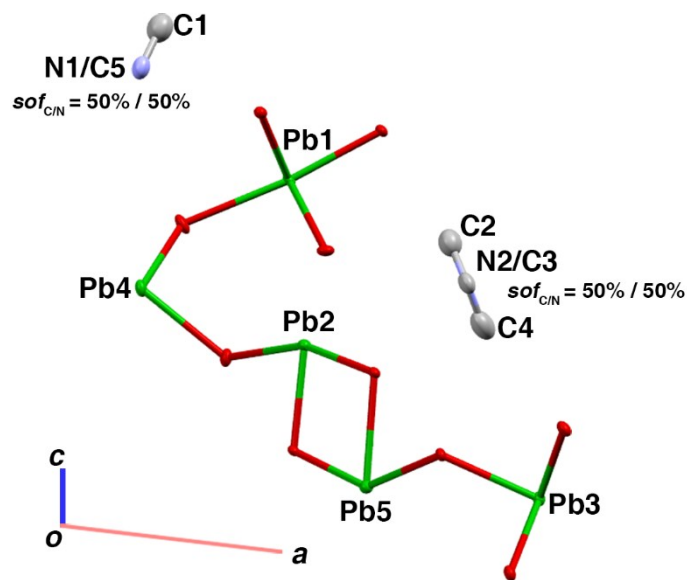


Figure S1. The asymmetric unit of compound **1** with 50% probability ellipsoids. Color scheme: Pb(II), green; Br, red; C, grey; N, blue.

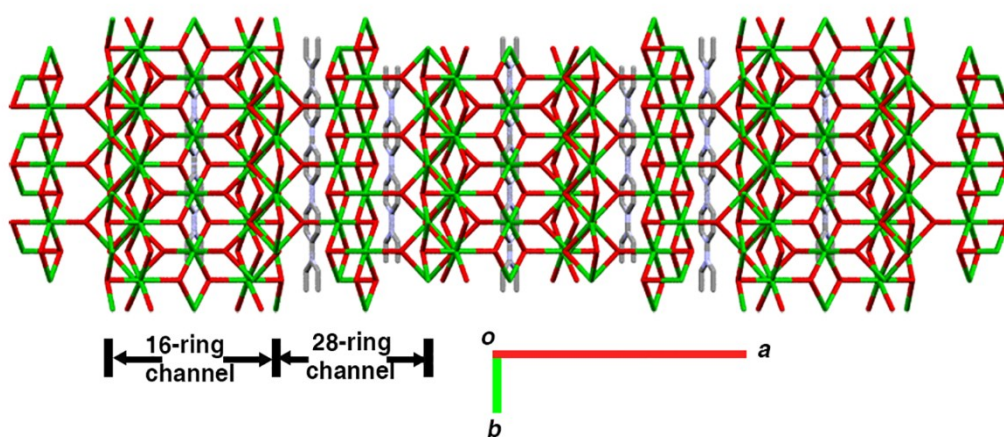


Figure S2. The poly(1,4-pyridinium) polycationic chains are encapsulated in the bromoplumbate 3D open frameworks (viewed along the c axis). Color scheme: Pb(II), green; Br, red; C, grey; N, blue.

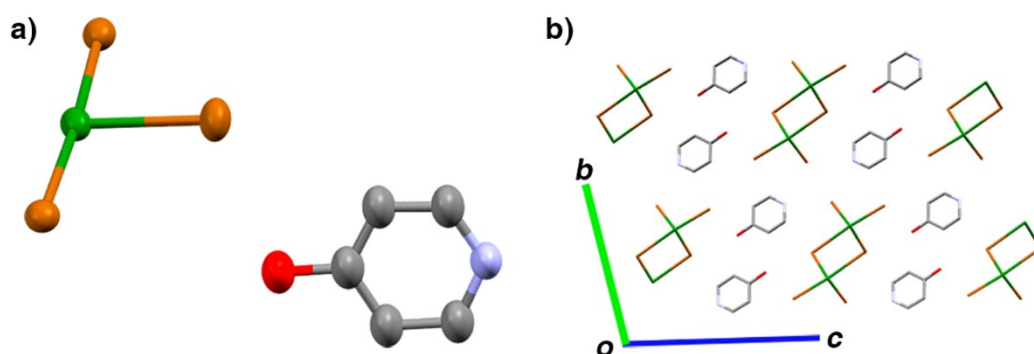


Figure S3. a) The asymmetric unit of compound **2** with 50% probability ellipsoids. Color scheme: Pb(II), green; Br, brown; O, red; C, grey; N, blue. The hydrogen atoms are omitted for clarity. b) The packing pattern of compound **2** viewed along the a -axis, showing 1D $[\text{PbBr}_3]_n^-$ chains.

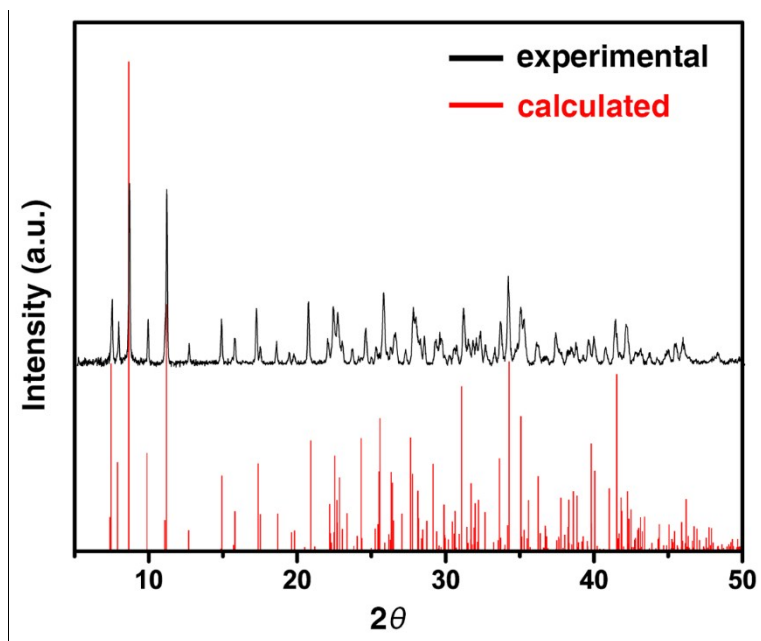


Figure S4. Simulated and experimental XRD powder patterns of compound **1**.

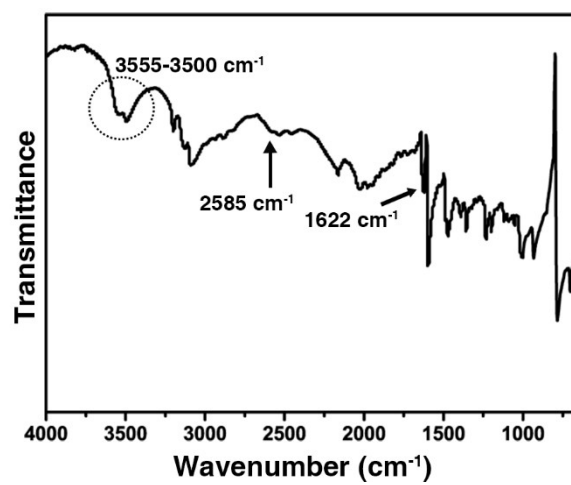


Figure S5. The FT-IR spectrum of compound **1**.

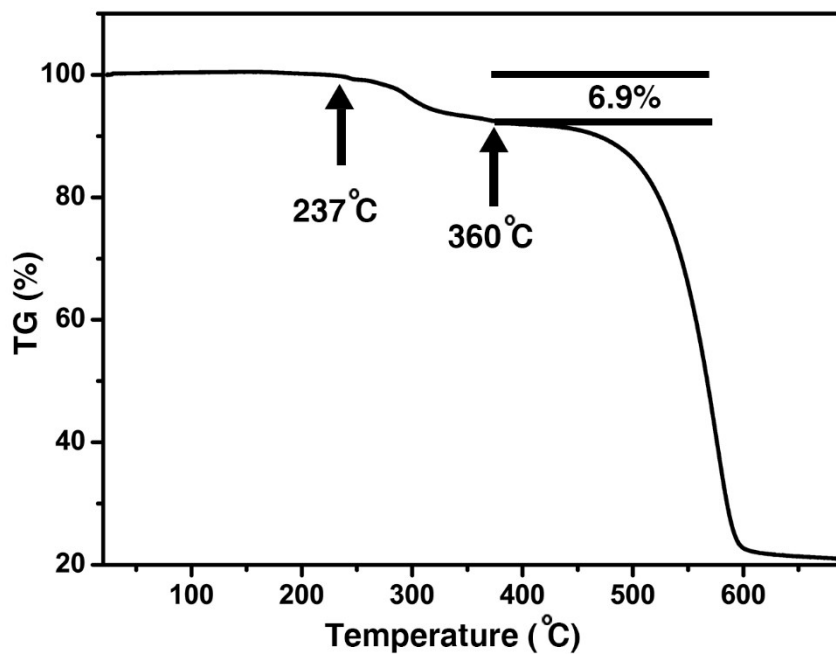


Figure S6. TGA curve of compound 1.

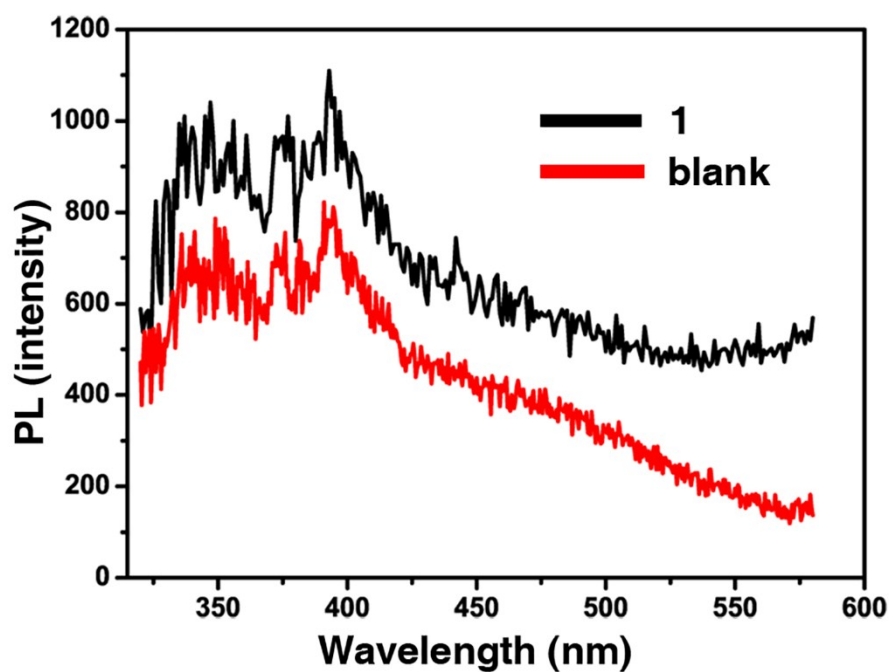


Figure S7. The PL spectrum of compound 1 with the excitation wavelength as 300 nm.

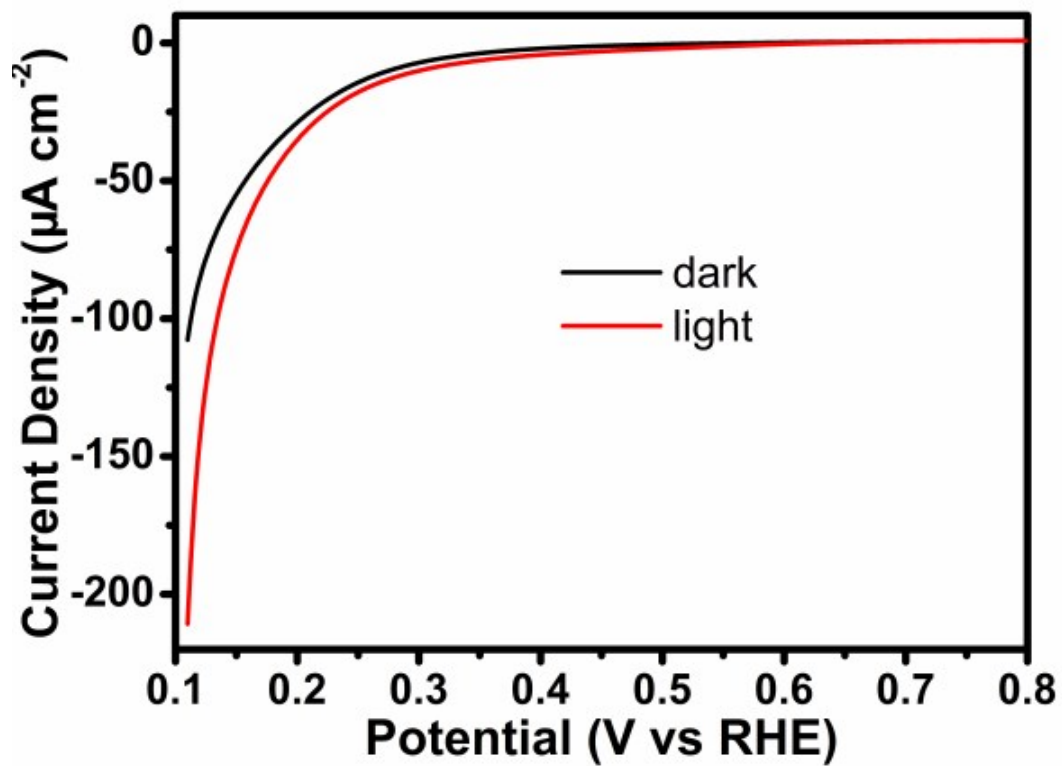


Figure S8. LSV of film of **1** under dark (black line) and under simulated solar light irradiation (red line) in 0.5 M Na_2SO_4 aqueous solution.

Table S1. Crystallographic data and structure refinement parameters of compound **1** and **2**.

Compound	1	2
Crystal system	Monoclinic	triclinic
Space group	<i>C</i> ₂ / <i>m</i>	P-1
Z	2	2
color	faint yellow	faint yellow
a (Å)	47.7482 (16)	4.3093 (8)
b (Å)	4.34560 (10)	10.586 (2)
c (Å)	12.0277 (4)	12.335 (2)
α (deg)	90	103.012 (2)
β (deg)	96.628 (3)	97.348 (2)
γ (deg)	90	94.651 (2)
V (Å ³)	2479.00 (13)	540.23 (18)
λ (Mo K α) (Å)	0.71073	0.70173
Collected	26766	2481
reflns	3203	2481
Unique reflns	130	102
Parameters	0.0335	0.0421
R (int)	0.0204	0.0368
R ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0455	0.1044
wR ₂ [<i>I</i> > 2 σ (<i>I</i>)]	1.178	1.081
GOF		

[S1] APEX2 (version 2009.9-0); Bruker AXS Inc., Madison, WI, **2009**.

[S2] Sheldrick, G. M., *Acta. Crystallogr.* **2008**, *A64*, 112.