

## Supporting Information

### **HgBr<sub>2</sub>: An Easily Growing Wide-Spectrum Birefringent Crystal**

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## 1. Experimental section

### 1.1 Reagents.

The reagents utilized in this work were sourced exclusively from commercial suppliers and used without undergoing any additional purification steps. The reagents required for the growth of HgBr<sub>2</sub> crystals were as follows: mercuric bromide powder (99.5%), anhydrous ethanol (99.7%).

### 1.2 Properties Characterization.

The crystallographic data for HgBr<sub>2</sub> were acquired at 297 K using a Rigaku FR-X Microfocus diffractometer equipped with a graphite monochromator Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Data collection and reduction were executed using CrystalClear software, followed by refinement through full-matrix least-squares on  $F^2$  with the SHELXTL program package.<sup>1-2</sup> Structure determinations relied upon the direct methods, while the face-indexed absorption correction based on utilized XPREP program. The final structure was verified via PLATON analysis to confirm absence of higher symmetries.<sup>3</sup> The powder X-ray diffraction patterns (PXRD) of HgBr<sub>2</sub> were analyzed using a Rigaku MiniFlex 600 diffractometer with Cu-K $\alpha$  radiation at room temperature, scanning the  $2\theta$  range from 5 to 65° with a step size of 0.02°. The experimental PXRD patterns closely matched the calculated patterns generated from CIF data using Mercury software. As depicted in **Fig. S1**, the experimental PXRD pattern of HgBr<sub>2</sub> was basically consistent with the simulated one. Notably, due to the preferred orientation, the diffraction peak intensity of the (002) crystallographic plane at low angle ( $\sim 14^\circ$ ) was significantly higher compared to other planes. Consequently, the diffraction peaks within the  $2\theta$  range from 20° to 65° appeared less prominent; however, their positions align precisely with those predicted by simulation. This observation served as evidence for confirming the purity of our sample. Elemental analysis of HgBr<sub>2</sub> crystal was detected by an energy dispersive X-ray spectroscopy (EDS)-equipped Hitachi S-3500 scanning electron microscope. The EDS results indicated that the average molar ratio of elements was consistent with its chemical formula (Hg : Br = 1 : 1.95, **Fig. S2**). The diffuse-reflectance spectrum of HgBr<sub>2</sub> was acquired at 297 K using a Perkin-Elmer Lambda 900 spectrophotometer with BaSO<sub>4</sub> served as the reference. And such a date was collected within the wavelength range spanning from 200 to 2500 nm. The infrared (IR) spectroscopy data of single-crystal HgBr<sub>2</sub> was carried out within the range of 4000–400 cm<sup>-1</sup> by a Nicolet Magana 750 FT-IR spectrometer. The Raman spectrum of HgBr<sub>2</sub> in the range of 4000–100 cm<sup>-1</sup> was measured using the LABRAM HR Evolution spectrometer with a 532 nm laser as the excitation source. The birefringence of HgBr<sub>2</sub> was performed using a ZEISS Axio Scope. A1 polarizing microscope equipped with a tilting compensator and the light source possessed the 546 nm wavelength. To calculate the birefringence  $\Delta n$ , we utilized the formula  $R = \Delta n \times T$ , where  $R$  represents the optical path difference and  $T$  is the thickness of the crystal.

### 1.3. Computational Method.

The polarizability anisotropy and HOMO-LUMO gap of five linear units ([HgCl<sub>2</sub>] in HgCl<sub>2</sub>, [HgBr<sub>2</sub>] in HgBr<sub>2</sub>, [Hgl<sub>2</sub>] in Hgl<sub>2</sub>, [HgS<sub>2</sub>] in BaHgS<sub>2</sub>, [HgSe<sub>2</sub>] in BaHgSe<sub>2</sub>) were calculated using the Gaussian 09 with def2-QZVPD basis set.<sup>4-6</sup> The aforementioned relevant data of [BS<sub>3</sub>] are cited from the research findings conducted by Prof. Pan et al. on HgB<sub>2</sub>S<sub>4</sub>. The electronic structure of HgBr<sub>2</sub> was computed using ABINIT software based on density functional theory (DFT).<sup>7-8</sup> The exchange correlation functional used in the theoretical calculation was the Perdew-Burke-Ernzerhof (PBE) form of the generalized gradient approximation (GGA).<sup>9</sup> The following orbital electrons were considered as valence electrons: Hg-6s<sup>2</sup>5d<sup>10</sup>, Br-4s<sup>2</sup>4p<sup>5</sup>. The calculation for HgBr<sub>2</sub> was performed using a plane-wave cutoff energy of 18 Hartree (about 500 eV), ensuring convergence in all computations through the implementation of an 8 × 8 × 3 *k*-points sampling. The linear optical properties were assessed through the computation of the complex dielectric function  $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ . The real component of the dielectric function  $\varepsilon_1$  can be determined via the Kramers-Kronig transform, enabling derivation of the refractive index and calculation of birefringence.

## 2. Figures and tables.

### 2.1. Figures.

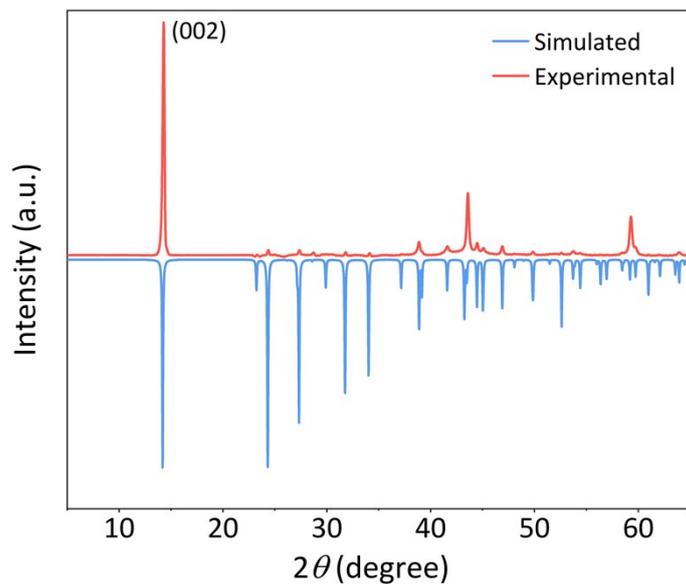


Fig. S1 PXRD patterns of the simulated and experimental for  $\text{HgBr}_2$ .

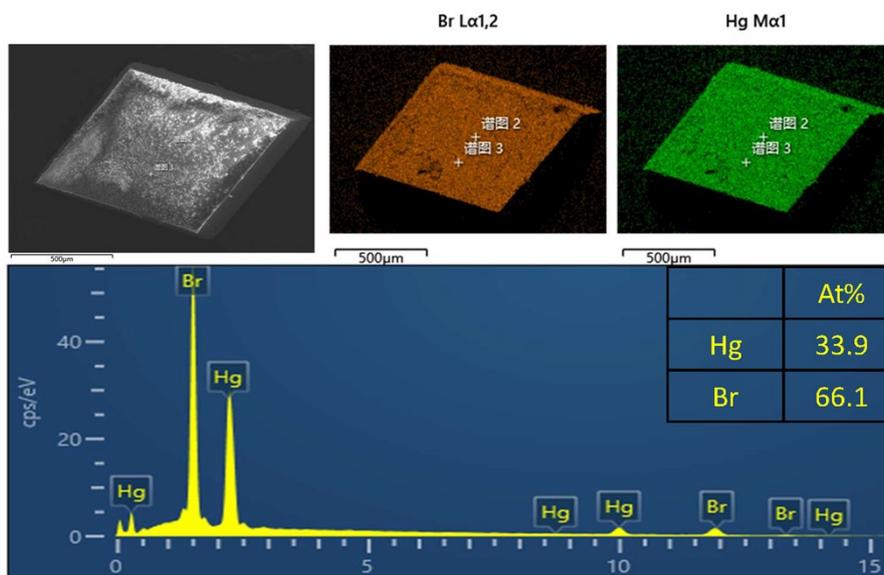


Fig. S2 EDS of single crystal  $\text{HgBr}_2$ .

## 2.2. Tables.

**Table S1.** Crystal data and structure refinement results for HgBr<sub>2</sub>.

| Empirical formula  | HgBr <sub>2</sub>         |
|--|---------------------------|
| Fw   | 360.41                    |
| Temperature (K)  | 293(2)                    |
| Space group  | <i>Cmc</i> 2 <sub>1</sub> |
| <i>a</i> (Å)   | 4.6215(6)                 |
| <i>b</i> (Å)   | 6.7794(7)                 |
| <i>c</i> (Å)   | 12.4277(19)               |
| Volume (Å <sup>3</sup> )   | 389.37(9)                 |
| Z  | 4                         |
| <i>D</i> <sub>calcd</sub> (g·cm <sup>-3</sup> )                            | 6.148                     |
| $\mu$ (mm <sup>-1</sup> )  | 59.789                    |
| GOF on <i>F</i> <sup>2</sup>   | 1.004                     |
| <i>R</i> <sub>1</sub> <sup>a</sup> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))   | 0.0650                    |
| w <i>R</i> <sub>2</sub> <sup>b</sup> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> )) | 0.1596                    |
| <i>R</i> <sub>1</sub> <sup>a</sup> (all data)                              | 0.0675                    |
| w <i>R</i> <sub>2</sub> <sup>b</sup> (all data)                            | 0.1621                    |
| Flack  | 0.19(17)                  |
| $\Delta\rho_{\max}/\Delta\rho_{\min}$ (e Å <sup>-3</sup> )                 | 7.90/−2.06                |

<sup>a</sup> $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ , <sup>b</sup> $wR = (\sum(w(F_o^2 - F_c^2)^2) / \sum(w(F_o^2)^2))^{1/2}$ .

**Table S2.** Fractional atomic coordinates and equivalent isotropic displacement parameters for HgBr<sub>2</sub>.

| Atom | x      | y         | z         | U(eq)      | Wyck. |
|------|--------|-----------|-----------|------------|-------|
| Hg1  | 1.0000 | 0.8307(3) | 0.6310(5) | 0.0449(9)  | 4a    |
| Br1  | 1.0000 | 0.5619(8) | 0.7600(4) | 0.0415(15) | 4a    |
| Br2  | 1.0000 | 0.9003(9) | 1.0000(4) | 0.0412(15) | 4a    |

**Table S3.** Selected distances (Å) for HgBr<sub>2</sub>.

| Bond    | Distances | Bond    | Distances |
|---------|-----------|---------|-----------|
| Hg1-Br1 | 2.427(6)  | Hg1-Br2 | 2.445(7)  |

**Table S4.** Selected angles (°) for HgBr<sub>2</sub>.

| Atom-Atom-Atom | Angles    |
|----------------|-----------|
| Br1-Hg1-Br2    | 179.58(3) |

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