

# SUPPLEMENTARY INFORMATION

## Chiral 2D organic-inorganic hybrid perovskites based upon L-histidine

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## Measurement Methods.

**Elemental analyses** were performed with Vario Micro Cube (Elemental) CHNOS elemental analyzer.

**X-ray powder diffraction.** Powder patterns of **Br<sub>3</sub>I**, **Br<sub>3</sub>I** were acquired on Bruker D8 diffractometer using Cu-K $\alpha$  radiation (4 – 50 ° range, 0.01605 ° step). Powder patterns of **Br<sub>2</sub>I<sub>2</sub>** was acquired on Benchtop Rigaku Miniflex 600 diffractometer using Cu-K $\alpha$  radiation (2 – 50 ° range, 0.025 ° step).

**Rietveld refinement.** Crystal structure of compound **Br<sub>0.4</sub>I<sub>3.6</sub>** was chosen as an initial model. Chebyshev function with 13 terms was used to fit the background. Gaussian function was used to model the peak shape. The  $R_{wp}$  and  $R_p$  values are listed in Table 5.

**Thermogravimetric analysis (TGA).** TGA were carried out on a Setsys TG-DTA 16 analyzer (Setaram Inc.). The sample was placed in Al crucible, and heated at the rate 10 K min<sup>-1</sup> from 295 K to 620 K, under flowing nitrogen gas.

**UV-vis measurements.** The optical absorbance was recorded on a Varian Cary 50 UV-vis spectrophotometer instrument within a 200 – 800 nm range.

**Photoluminescence (PL).** The PL spectra were recorded using Shimadzu RF-6000 Fluorescence Spectrometer.

**X-ray structure determination.** Intensity data were collected on an Xcalibur, Eos diffractometer with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$ ). The crystals were kept at 293 K during data collection. The structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimization.<sup>71</sup> Hydrogen atoms were placed geometrically on idealized positions. Low values of Flack parameters ascertained the homochirality of studied compounds. Therefore, absolute configuration of chiral cation was chosen according to known absolute configuration of starting reagent. Figures were generated using Olex2.<sup>72</sup> The crystallographic data of the structures described in this paper were deposited to the Cambridge crystallographic Data Center (CCDC 2207739 - 2207741).

**Table S1.** Selected bond lengths (Å) for **I<sub>4</sub>**, **Br<sub>0.4</sub>I<sub>3.6</sub>** and **Br<sub>4</sub>**

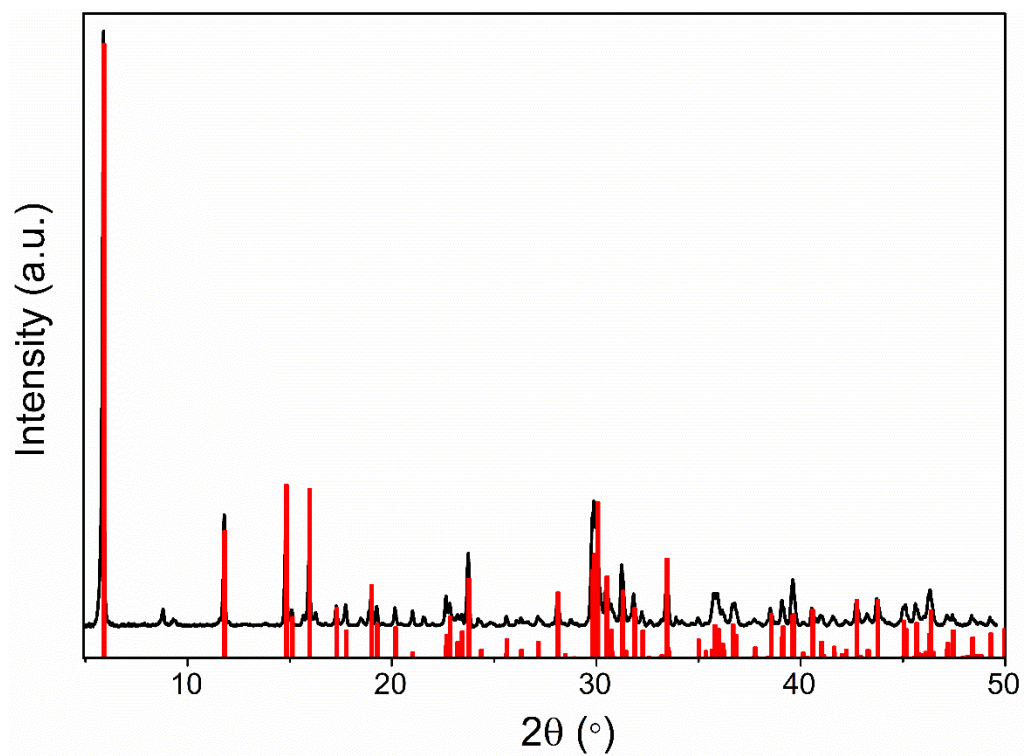
<b>I<sub>4</sub></b>			
Pb1–I2 <sup>1</sup>	3.1496(13)	Pb1–I2 <sup>3</sup>	3.1752(12)
Pb1–I2	3.1496(12)	Pb1–I1 <sup>1</sup>	3.2133(11)
Pb1–I2 <sup>2</sup>	3.1752(12)	Pb1–I1	3.2134(11)
<sup>1)</sup> +x, 1 – y, 1 – z; <sup>2)</sup> –1/2 + x, 1/2 – y, 1 – z; <sup>3)</sup> –1/2 + x, 1/2 + y, +z			
<b>Br<sub>0.4</sub>I<sub>3.6</sub></b>			
Pb1–I2 Br2	3.1872(14)	Pb1–I1 Br1 <sup>2</sup>	3.094(6)
Pb1–I2 <sup>1</sup>  Br2 <sup>1</sup>	3.1872(14)	Pb1–I1 Br1 <sup>1</sup>	3.145(6)
Pb1–I1 Br1 <sup>3</sup>	3.094(6)	Pb1–I2 Br2	3.1872(14)
Pb1–I1 Br1	3.145(6)	Pb1–I1 Br1	3.145(6)
<sup>1)</sup> 1 – x, +y, –z; <sup>2)</sup> –1/2 + x, –1/2 + y, +z; <sup>3)</sup> 3/2 – x, –1/2 + y, –z			
<b>Br<sub>4</sub></b>			
Pb1–Br2 <sup>1</sup>	2.953(3)	Pb1–Br2	3.100(3)
Pb1–Br2 <sup>2</sup>	3.100(3)	Pb1–Br1	3.002(3)
Pb1–Br2 <sup>3</sup>	2.953(3)	Pb1–Br1 <sup>2</sup>	3.002(3)
<sup>1)</sup> 3/2 – x, 1/2 + y, 1/2 – z; <sup>2)</sup> 1 – x, +y, 1/2 – z; <sup>3)</sup> –1/2 + x, 1/2 + y, +z			

**Table S2.** Selected bond angles (°) for **I<sub>4</sub>**, **Br<sub>0.4</sub>I<sub>3.6</sub>** and **Br<sub>4</sub>**

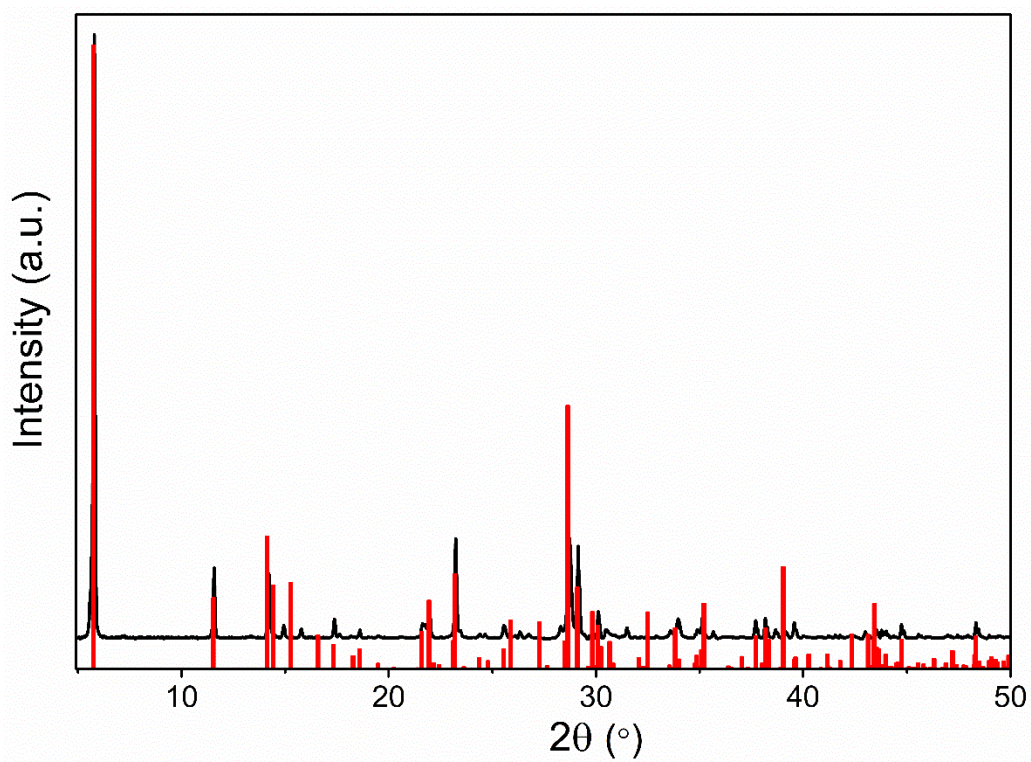
<b>I<sub>4</sub></b>			
I2 <sup>1</sup> –Pb1–I2	94.43(5)	I2–Pb1–I1 <sup>1</sup>	88.70(6)
I2 <sup>1</sup> –Pb1–I2 <sup>2</sup>	176.42(5)	I2 <sup>2</sup> –Pb1–I1 <sup>1</sup>	91.03(6)
I2–Pb1–I2 <sup>2</sup>	82.144(15)	I2 <sup>3</sup> –Pb1–I1 <sup>1</sup>	90.27(6)
I2 <sup>1</sup> –Pb1–I2 <sup>3</sup>	82.145(15)	I2 <sup>1</sup> –Pb1–I1	88.70(6)
I2–Pb1–I2 <sup>3</sup>	176.42(5)	I2–Pb1–I1	89.91(6)
I2 <sup>2</sup> –Pb1–I2 <sup>3</sup>	101.30(5)	I2 <sup>2</sup> –Pb1–I1	90.27(6)
I2 <sup>1</sup> –Pb1–I1 <sup>1</sup>	89.91(6)	I1 <sup>1</sup> –Pb1–I1	177.95(5)
I2 <sup>3</sup> –Pb1–I1	91.03(6)	Pb1–I2–Pb1 <sup>4</sup>	176.42(5)
<sup>1)</sup> +x, 1 – y, 1 – z; <sup>2)</sup> –1/2 + x, 1/2 – y, 1 – z; <sup>3)</sup> –1/2 + x, 1/2 + y, +z; <sup>4)</sup> 1/2 + x, –1/2 + y, +z			
<b>Br<sub>0.4</sub>I<sub>3.6</sub></b>			
I2 Br2 <sup>1</sup> –Pb1–I2 Br2	178.6(2)	I1 Br1 <sup>2</sup> –Pb1–I1 Br1 <sup>3</sup>	82.4(3)
I1 Br1 <sup>2</sup> –Pb1–I2 Br2	91.76(11)	I1 Br1 <sup>2</sup> –Pb1–I1 Br1	178.3(2)
I2 Br1 <sup>1</sup> –Pb1–I2 Br2	89.41(11)	I1 Br1–Pb1–I2 Br2 <sup>1</sup>	89.41(11)
I2 Br1–Pb1–I2 Br2	89.53(14)	I1 Br1–Pb1–I1 Br1 <sup>1</sup>	80.2(3)
I2 Br1 <sup>3</sup> –Pb1–I2 Br2	89.29(13)	I1 Br1–Pb1–I2 Br2	89.53(14)
I1 Br1 <sup>3</sup> –Pb1–I1 Br1	98.741(8)		
<sup>1)</sup> 1 – x, +y, –z; <sup>2)</sup> –1/2 + x, –1/2 + y, +z; <sup>3)</sup> –3/2 + x, –1/2 + y, –z; <sup>4)</sup> 1/2 + x, 1/2 + y, +z			
<b>Br<sub>4</sub></b>			
Br2 <sup>1</sup> –Pb1–Br2 <sup>2</sup>	93.07(12)	Br2 <sup>1</sup> –Pb1–Br1 <sup>3</sup>	89.8(2)
Br2 <sup>2</sup> –Pb1–Br2	174.08(12)	Br2 <sup>1</sup> –Pb1–Br1	88.66(19)
Br2 <sup>1</sup> –Pb1–Br2	81.039(8)	Br1–Pb1–Br2 <sup>3</sup>	90.7(2)
Br2 <sup>1</sup> –Pb1–Br2 <sup>3</sup>	174.07(12)	Br1 <sup>3</sup> –Pb1–Br2 <sup>3</sup>	90.7(2)
Br2 <sup>3</sup> –Pb1–Br2	104.86(11)	Br1–Pb1–Br2	90.7(2)
Br2 <sup>2</sup> –Pb1–Br2 <sup>3</sup>	81.039(8)	Br1 <sup>3</sup> –Pb1–Br2	90.7(2)
Br2 <sup>2</sup> –Pb1–Br1 <sup>3</sup>	88.66(19)	Br1 <sup>3</sup> –Pb1–Br1	177.83(14)
Br2 <sup>2</sup> –Pb1–Br1	89.8(2)	Pb1 <sup>4</sup> –Br2–Pb1	174.08(12)
<sup>1)</sup> 3/2 – x, 1/2 + y, 1/2 – z; <sup>2)</sup> –1/2 + x, 1/2 + y, +z; <sup>3)</sup> 1 – x, +y, 1/2 – z; <sup>4)</sup> 1/2 + x, –1/2 + y, +z			

**Table S3.** H-bonds parameters in the crystal structure of **I<sub>4</sub>**, **Br<sub>0.4</sub>I<sub>3.6</sub>** and **Br<sub>4</sub>**

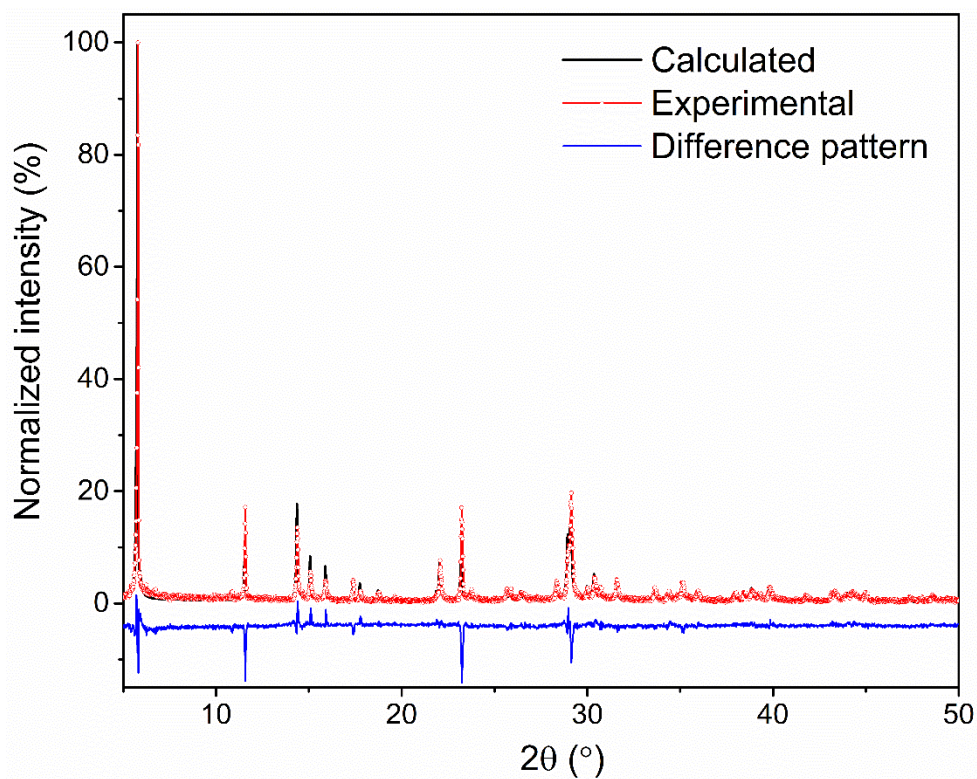
D-H...A	D-H, Å	H...A, Å	D...A, Å	∠DHA, °	Symmetry codes for A
<b>I<sub>4</sub></b>					
C5-H5...I1 <sup>1</sup>	0.93	2.71	3.591(19)	158	<sup>1</sup> ) $-1/2 + x, 1/2 + y, +z$
C6-H6...I1 <sup>2</sup>	0.93	2.94	3.748(19)	146	<sup>2</sup> ) $-1/2 + x, -1/2 + y, +z$
N3-H3...O3	0.86	1.99	2.71(2)	141	–
O3-H3C...I2 <sup>3</sup>	0.85	1.94	2.75(3)	159	<sup>3</sup> ) $-1/2 + x, 1/2 - y, 1 - z$
O1-H1...N2 <sup>4</sup>	0.81	2.05	2.81(2)	156	<sup>4</sup> ) $3/2 - x, -1/2 + y, 1/2 - z$
N1-H1A...O2 <sup>4</sup>	0.89	1.83	2.718(19)	176	<sup>4</sup> ) $3/2 - x, -1/2 + y, 1/2 - z$
N1-H1B...O1 <sup>5</sup>	0.89	1.91	2.79(2)	171	<sup>5</sup> ) $2 - x, +y, 1/2 - z$
N1-H1C...I1	0.89	2.79	3.612(13)	154	–
<b>Br<sub>0.4</sub>I<sub>3.6</sub></b>					
C6-H6...(Br2/I2) <sup>2</sup>	0.93	2.91	3.70(5)	144	<sup>2</sup> ) $-1/2 + x, -1/2 + y, +z$
C5-H5...(Br2/I2) <sup>1</sup>	0.94	2.78	3.67(4)	158	<sup>1</sup> ) $-1/2 + x, 1/2 + y, +z$
O1-H1...N3 <sup>6</sup>	0.83	2.26	2.94(4)	139	<sup>6</sup> ) $1/2 - x, 1/2 + y, 1 - z$
N1-H1B...O2 <sup>7</sup>	0.90	1.85	2.74(3)	173	<sup>7</sup> ) $1/2 - x, -1/2 + y, 1 - z$
N1-H1C...O1 <sup>8</sup>	0.90	1.81	2.71(3)	171	<sup>8</sup> ) $1 - x, +y, 1 - z$
N1-H1C...Br2/I2	0.90	2.74	3.55(2)	151	–
<b>Br<sub>4</sub></b>					
C5-H5...Br1 <sup>9</sup>	0.93	2.64	3.464(19)	148	<sup>9</sup> ) $1/2 + x, -1/2 + y, +z$
C6-H6...Br1 <sup>2</sup>	0.93	2.69	3.516(19)	148	<sup>2</sup> ) $-1/2 + x, -1/2 + y, +z$
O1-H1...N2 <sup>10</sup>	0.83	2.10	2.83(3)	148	<sup>10</sup> ) $-1/2 + x, 3/2 - y, 1 - z$
N1-H1A...O2 <sup>11</sup>	0.89	1.83	2.71(4)	169	<sup>11</sup> ) $1/2 + x, 3/2 - y, 1 - z$
N1-H1B...O1 <sup>12</sup>	0.89	1.86	2.74(3)	171	<sup>12</sup> ) $+x, 2 - y, 1 - z$
N1-H1C...Br1	0.89	2.60	3.46(2)	163	–



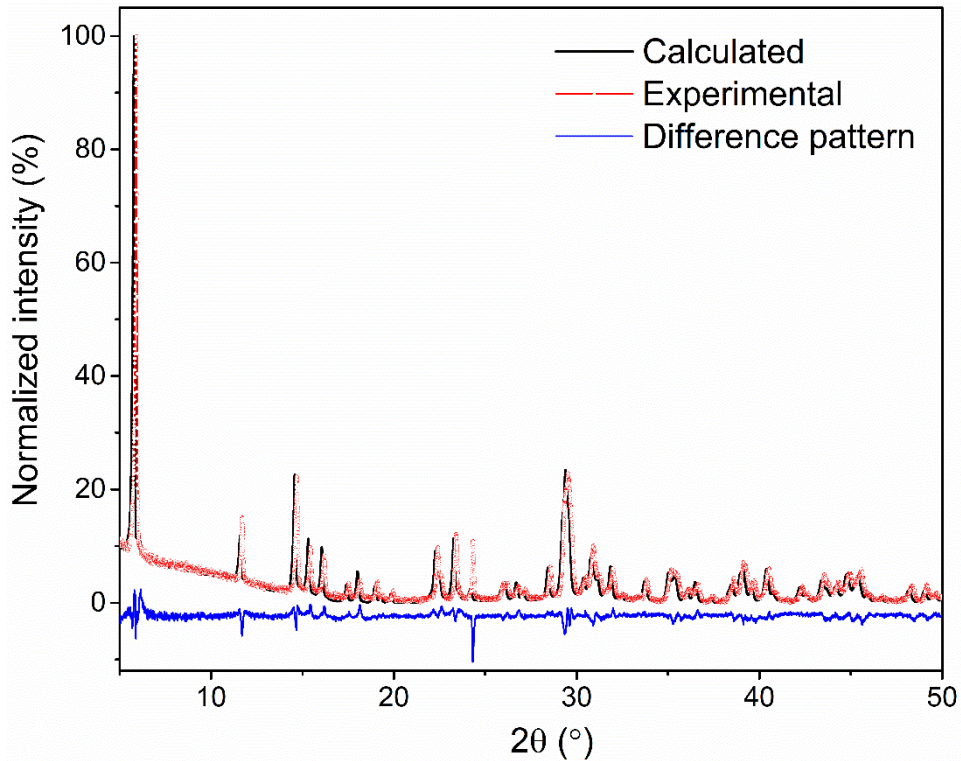
**Figure S1.** Powder X-ray diffraction pattern of **Br<sub>4</sub>**



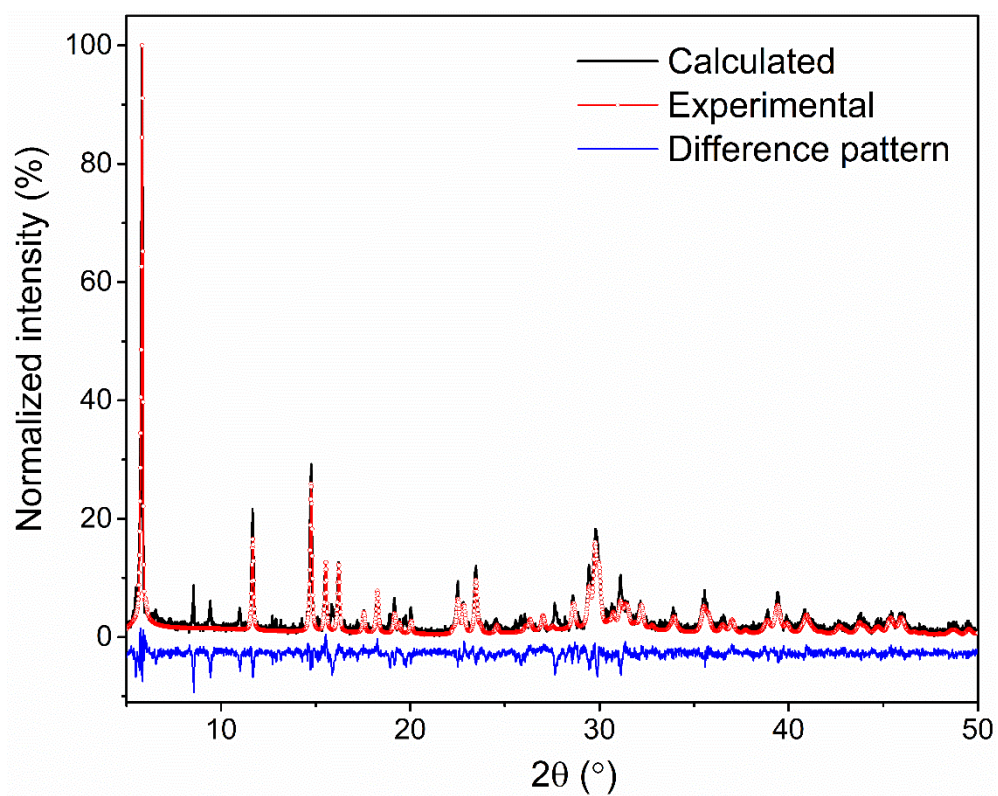
**Figure S2.** Powder X-ray diffraction pattern of **I<sub>4</sub>**



**Figure S3.** Experimental (red line) and calculated (black circles) PXR D patterns of  $\text{BrI}_3$ . The difference pattern is shown as a blue line



**Figure S4.** Experimental (red line) and calculated (black circles) PXR D patterns of  $\text{Br}_2\text{I}_2$ . The difference pattern is shown as a blue line.



**Figure S5.** Experimental (red line) and calculated (black circles) PXRD patterns of  $\text{Br}_3\text{I}$ . The difference pattern is shown as a blue line.