

**Table S1.** Crystal structure data and single-crystal X-ray diffraction refinement results for Cs<sub>4</sub>EuBr<sub>6</sub> and Cs<sub>4</sub>EuI<sub>6</sub>.

Formula	Cs <sub>4</sub> EuBr <sub>6</sub>	Cs <sub>4</sub> EuI <sub>6</sub>
fw (g)	1163.03	1445.01
<i>T</i> (K)	250(1)	250(1)
Crystal system	Trigonal	Trigonal
space group	$R\bar{3}c$	$R\bar{3}c$
<i>a</i> (Å)	13.7406(4)	14.5994(2)
<i>b</i> (Å)	13.7406(4)	14.5994(2)
<i>c</i> (Å)	17.3413(5)	18.3443(3)
$\alpha$ (°)	90	90
$\beta$ (°)	90	90
$\gamma$ (°)	120	120
<i>V</i> (Å <sup>3</sup> )	2835.4(13)	3386.1(10)
<i>Z</i>	6	6
<i>D</i> <sub>calc</sub> (mgm <sup>-3</sup> )	4.087	4.252
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	11.778	17.312
<i>F</i> (000)	2958	3606
Crystal size (mm)	0.2×0.1×0.05	0.2×0.15×0.05
$\theta$ range for data collection	3.52-32.59	3.41-32.00
Index ranges	-20 ≤ <i>h</i> ≤ 16 -19 ≤ <i>k</i> ≤ 20 -25 ≤ <i>l</i> ≤ 25	-21 ≤ <i>h</i> ≤ 21 -19 ≤ <i>k</i> ≤ 20 -26 ≤ <i>l</i> ≤ 25
No. reflections collected (equivalents agreement)	7379(0.025)	12517(0.053)
No. reflections collected with $ F_o  > 4\sigma F_o $	1002	1022
No. of variables	19	20
<i>R</i> <sub><i>F</i></sub>	0.021	0.028
<i>R</i> <sub>w<i>F</i></sub>	0.049	0.076
Goodness of fit	1.11	1.17
largest diff. peak and hole (eÅ <sup>-3</sup> )	0.95, -1.78	1.86, -1.84

**Table S2.** Fractional atomic coordinates and equivalent isotropic displacement parameters for Cs<sub>4</sub>EuBr<sub>6</sub>.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> (Å <sup>2</sup> )
Eu1	6b	0	0	0	0.01733(8)
Cs1	6a	0	0	-1/4	0.03699(14)
Cs2	18e	0.03875(2)	0.70542(2)	1/12	0.02798(8)
Br1	36f	0.02775(3)	0.83628(3)	0.101204(19)	0.02696(9)

**Table S3.** Fractional atomic coordinates and equivalent isotropic displacement parameters for Cs<sub>4</sub>EuI<sub>6</sub>.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> (Å <sup>2</sup> )
Eu1	6b	0	0	0	0.02062(16)
Cs1	6a	0	0	-1/4	0.0423(3)
Cs2	18e	0.04371(4)	0.71037(4)	1/12	0.03349(16)
I1	36f	0.03089(3)	0.83596(3)	0.10260(2)	0.03057(15)