Supplementary information for

Abnormal bandgap enlargement made promising mid-infrared nonlinear optical material Rb_2CdBrI_3 with ultrahigh laser damage threshold

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Abstract: Low laser damage threshold of commercial infrared nonlinear optical materials is the main bottleneck to hinder their high-power coherent source applications. Here, a new compound Rb_2CdBrI_3 was successfully synthesized in a controlled manner by rational halogen substitution. It features zero-dimensional $[CdBrI_3]^{2-}$ tetrahedra and inserted Rb^+ cations as the counter cations. Contrast to isomorphic $Rb_2CdBr_2I_2$, Rb_2CdBrI_3 exhibits an anomalously enlarged bandgap of 4.01 eV and unprecedented high laser damage threshold up to 46 times that of $AgGaS_2$. Theoretical calculations elaborate that the abnormal bandgap attributes to weak conduction band dispersion from reduced net dipole moment and enhanced halogen s-p orbital mixing when Br is replaced by I. This work not only promotes Rb_2CdBrI_3 as a promising infrared nonlinear converter, but also supplies new modulating viewpoints for band-sensitive optoelectronic devices, such as hybrid perovskite solar cells with mixed halogen.

Contents

Table S1. Selected bond lengths (Å) for Rb_2CdBrI_3

bond	lengths (Å)	bond	lengths (Å)
Cd1-I1	2.741(3)	Cd1[1]-I2	2.768(15)
Cd1[1]-I1	2.741(3)	Cd1-Br1	2.667(3)
Cd1-I2	2.768(15)		

[1]3/2-X,+Y,+Z; [2]+X,-1/2+Y,-1/2+Z; [3]1/2+X,1/2-Y,1/2+Z; [4]+X,-1/2+Y,1/2+Z; [5]+X,+Y,-1+Z; [6]3/2-X,+Y,-1+Z; [7]2-X,1/2-Y,-1/2+Z; [8]1/2+X,1-Y,+Z; [9]1/2+X,1/2-Y,-1/2+Z; [10]1-X,1-Y,+Z

Table S2. Selected bond angles (°) for Rb_2CdBrI_3

bond	angles (°)	bond	angles (°)

I1-Cd1-I2	111.93(6)	Br1-Cd1--I1	106.73(12)
I1-Cd1--I2[1]	111.93(6)	Br1-Cd1--I2[1]	108.03(6)
I2[1]-Cd1--I2	109.99(8)	Br1-Cd1--I2	108.03(6)

Table S3. The proportion of element in Rb_2CdBrI_3 by EDS

Element	Experimental values	
	Weight/%	Atomic weight/%
Rb	22.10	27.26
Cd	17.88	16.77
Br	12.51	16.50
I	47.51	39.47

Table S4. Dipole moment calculation of Rb_2CdBrI_3 and $Rb_2CdBr_2I_2$

	vectors (x) (Debye)	vectors (y) (Debye)	vectors (z) (Debye)	Vectors (total) (Debye)
Rb_2CdBrI_3	0	-0.0004	0.559	0.559
$Rb_2CdBr_2I_2$	0	-0.09	-1.532	1.535

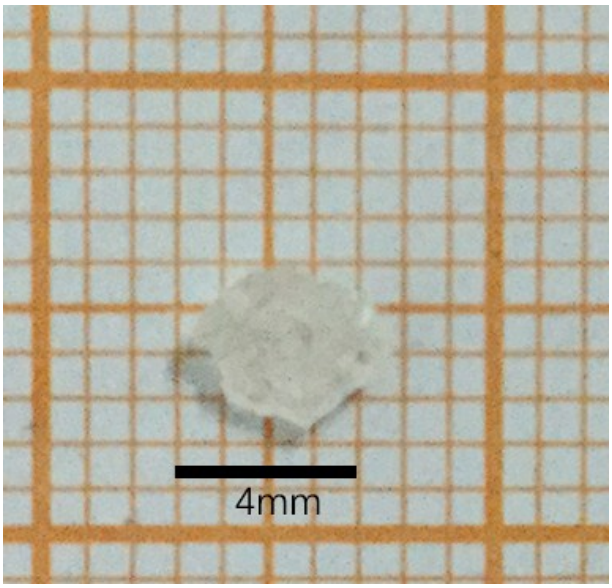

Figure S1. Photograph of Rb_2CdBrI_3 crystal

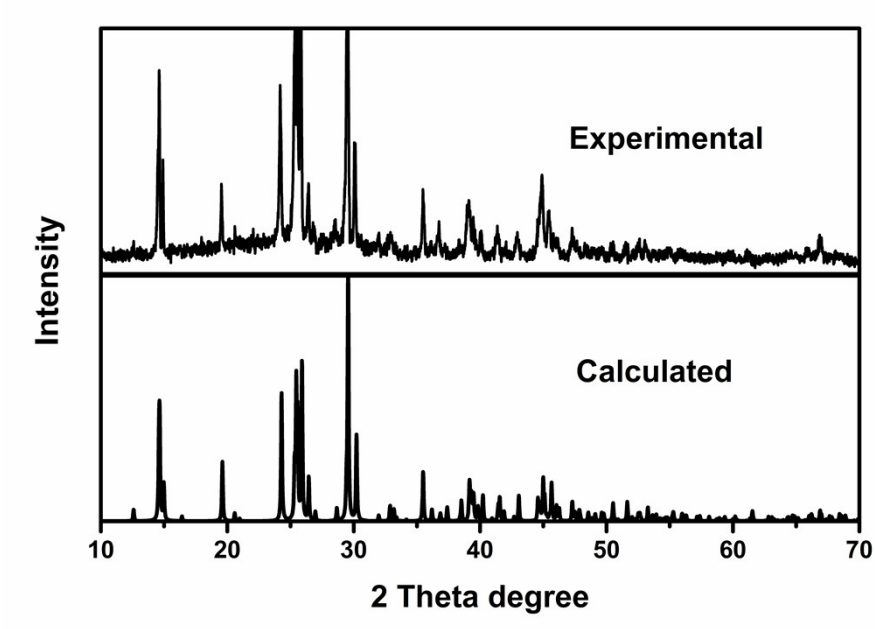

Figure S2. Simulated and measured powder X-ray diffraction patterns of

Rb_2CdBrI_3

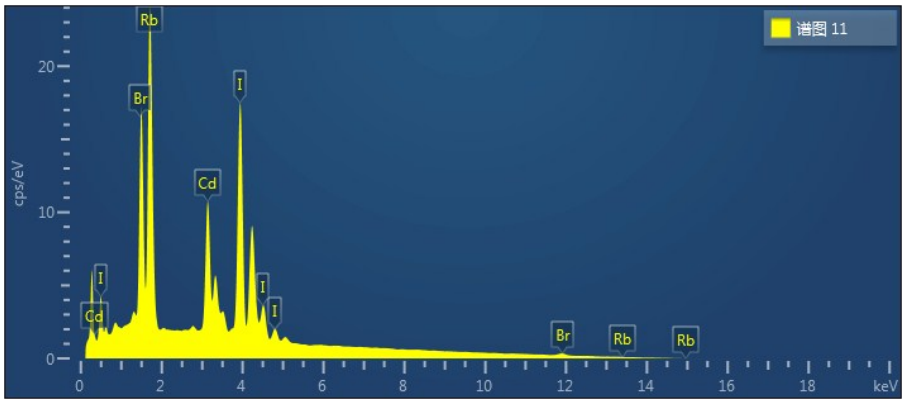

Figure S3. The EDS spectrum of Rb_2CdBrI_3

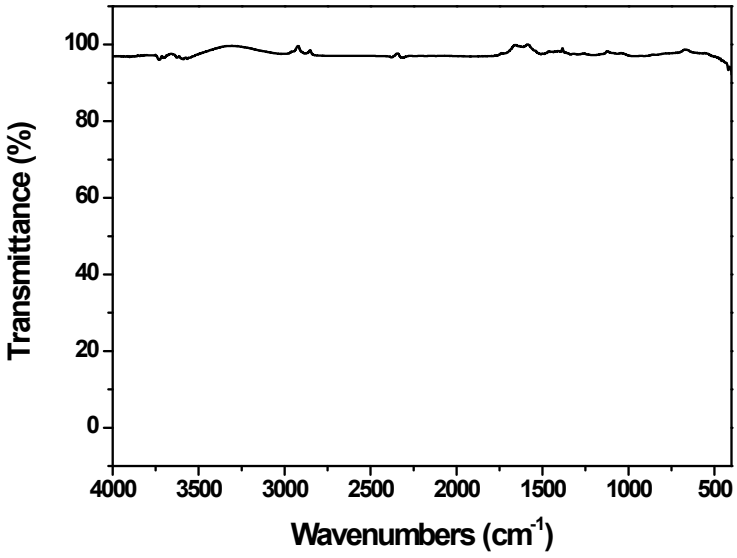

Figure S4. The infrared spectrum of Rb_2CdBrI_3

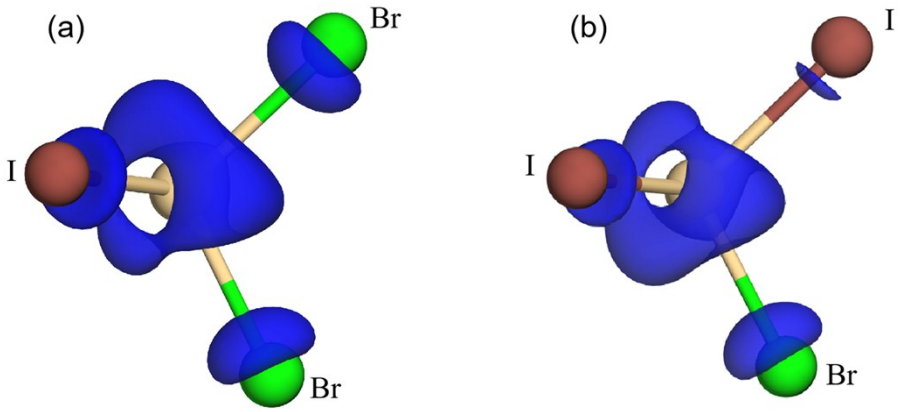

Figure S5. The simulated lowest unoccupied molecular orbitals (LUMO) of (a) $Rb_2CdBr_2I_2$ and (b) Rb_2CdBrI_3