Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Regulating the microscopic structure of solutions to synthesize centimeter-sized low-dimensional $Cs_mSb_nCl_{m+3n}$ perovskite single crystals for visible-blind ultraviolet photodetectors

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Table S1. Solubilities of CsCl, $SbCl_3$, CsCl and $SbCl_3$ mixed powders, and ground powder from as-grown $Cs_3Sb_2Cl_9$ single crystals in different solvents at 60 °C.

Solvent	**CsCl**	**$SbCl_3$**	**CsCl+$SbCl_3$**	**$Cs_3Sb_2Cl_9$**
DI Water	Highly Soluble	Hydrolysis Reaction	Insoluble	Insoluble
Hydrochloric Acid (37 wt.%)	Highly Soluble	Soluble	Slightly Soluble	Slightly Soluble
Hydrochloric Acid (8 wt.%)	Highly Soluble	Highly Soluble	Soluble	Soluble
Ethyl Alcohol	Slightly soluble	Highly Soluble	Insoluble	Insoluble
Isopropanol	Slightly soluble	Soluble	Insoluble	Insoluble
DMSO	Slightly soluble	Highly Soluble	Slightly Soluble	Slightly Soluble
NMP	Slightly soluble	Highly Soluble	Slightly Soluble	Insoluble
DMF	Insoluble	Soluble	Insoluble	Insoluble
GBL	Insoluble	Soluble	Insoluble	Insoluble
DMSO+DMF	Slightly soluble	Highly Soluble	Slightly Soluble	Slightly Soluble
DMSO+NMP	Slightly soluble	Highly Soluble	Slightly Soluble	Slightly Soluble
DMSO+GBL	Slightly soluble	Highly Soluble	Slightly Soluble	Slightly Soluble
DMSO+ Hydrochloric Acid (8 wt.%)	Soluble	Highly Soluble	Highly Soluble	Highly Soluble

Notes: Highly Soluble: > 10 g/100 g (solvent); Soluble: 1 g/100 g (solvent) ~ 10 g/100 g (solvent); Slightly soluble: 0.01 g/100 g (solvent) ~ 1 g/100 g (solvent); Insoluble: < 0.01 g/100 g (solvent).

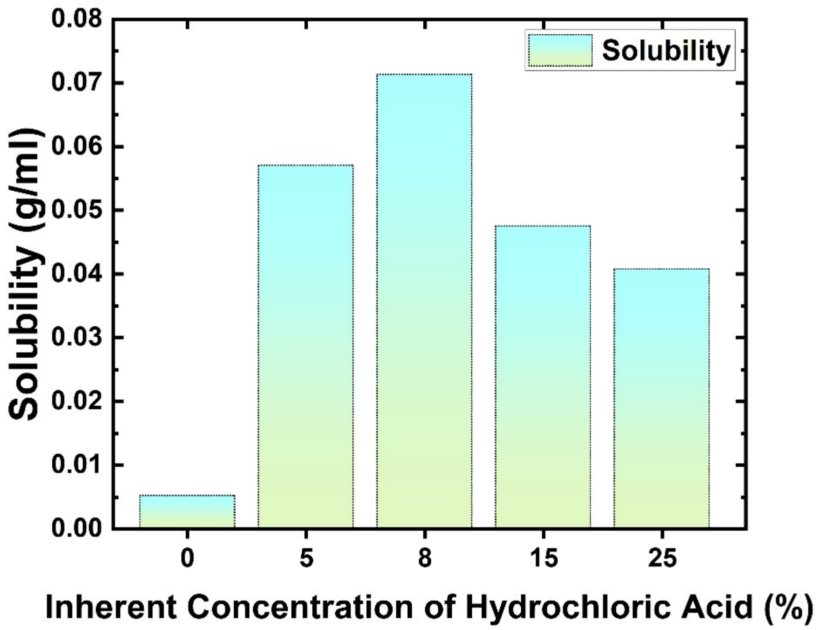

Figure S1. Solubilities of CsCl and $SbCl_3$ mixed powders in the hybrid solvent of DMSO and the dilute hydrochloric acid in different concentrations with the fixed volume ratio of 4:1.

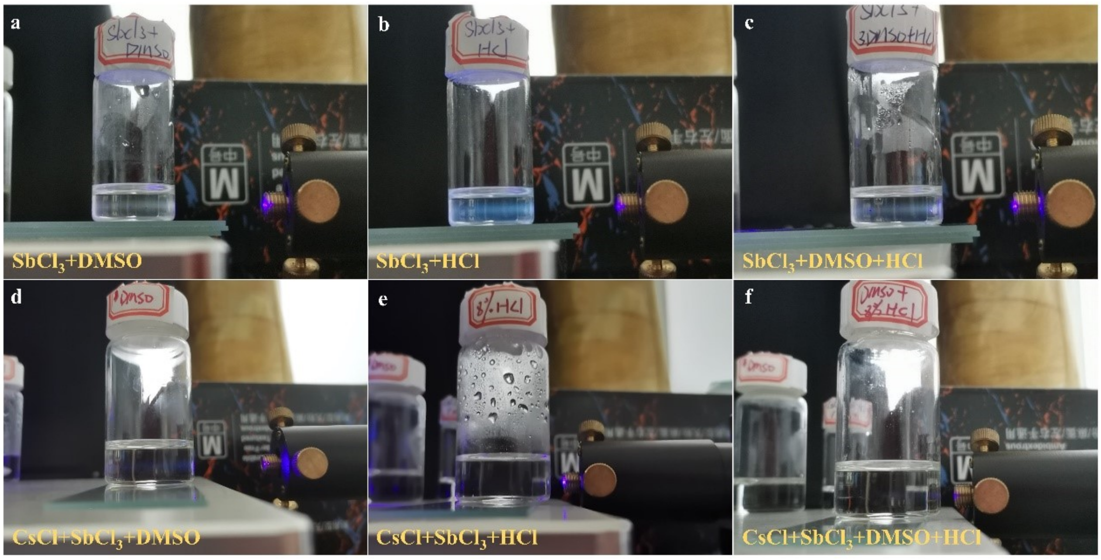

Figure S2. The typical Tyndall effect of the colloidal solution.

Table S2. Atomic parameters of trigonal α-$Cs_3Sb_2Cl_9$ obtained from the Rietveld refinement of PXRD data.

	x/a	**y/b**	**z/c**	**U(eq)**	**Wyck.**
Cs1	0.33333	0.66667	0.32567	0.000	2d
Cs2	0.00000	0.00000	0.00000	0.000	1a
Sb	0.33333	0.66667	0.82006	0.000	2d
Cl1	0.53012	0.53012	0.00000	0.000	3e
Cl2	0.35597	0.20333	0.32530	0.000	6g
Bond lengths (Å)	Sb–Cl1		2.8470(0)		
	Sb–Cl2		2.5280(0)		
Bond angles (°)	Cl1-Sb-Cl1		87.1780		
	Cl2-Sb-Cl2		92.6074		
	Cl1-Sb-Cl2		90.3757		
a (Å)		7.8093			
c (Å)		9.5738			
α (°)		90			
γ (°)		120			

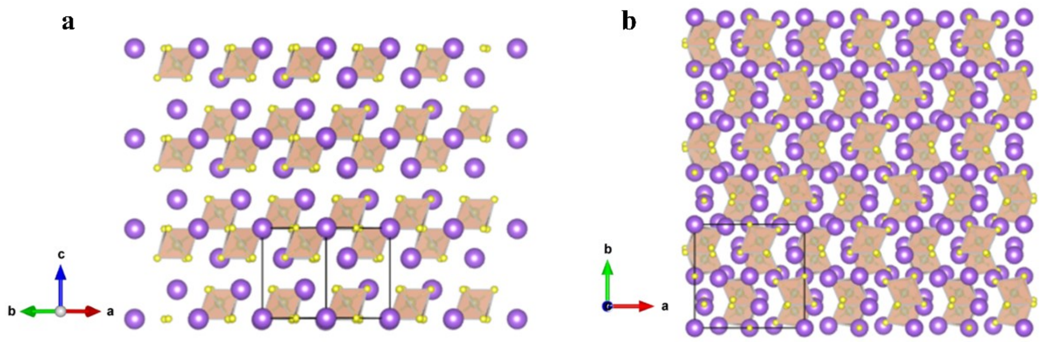

Figure S3. Schematic illustration of the crystal structures of CSC. a) 2D α-$Cs_3Sb_2Cl_9$, b) 0D $Cs_5Sb_2Cl_{11}$.

Table S3. Positional parameters of $Cs_5Sb_2Cl_{11}$ obtained from the Rietveld refinement of XRD data.

	x/a	**y/b**	**z/c**	**U(eq)**
Cs1	0.58913(2)	0.29623(2)	0.35755(2)	0.02030(7)
Cs2	0.71850(2)	0.02074(2)	0.14475(2)	0.02073(7)
Cs3	0.5	0.5	0.0	0.01673(7)
Sb1	0.59006(2)	0.66240(2)	0.38202(2)	0.01097(6)
Cl1	0.5	0.5	0.5	0.01822(18)
Cl2	0.76046(5)	0.55251(5)	0.39049(5)	0.02110(14)
Cl3	0.65128(5)	0.77309(5)	0.52129(5)	0.02301(14)
Cl4	0.66432(5)	0.78799(6)	0.26887(5)	0.02351(14)
Cl5	0.41422(4)	0.76951(5)	0.38693(5)	0.01893(13)
Cl6	0.52496(5)	0.54427(5)	0.23593(4)	0.01913(13)

Table S4. Bond lengths of $Cs_5Sb_2Cl_{11}$ obtained from the Rietveld refinement of XRD data.

Bond	**Bond lengths (Å)**
Sb1-Cl1	2.8920(17)
Sb1-Cl2	2.6277(6)
Sb1-Cl3	2.5629(7)
Sb1-Cl4	2.4592(7)
Sb1-Cl5	2.6698(6)
Sb1-Cl6	2.7057(6)

Table S5. Bond angles of $Cs_5Sb_2Cl_{11}$ obtained from the Rietveld refinement of XRD data.

Bond	**Bond angles (°)**
Cl4-Sb1-Cl3	93.12(2)
Cl3-Sb1-Cl2	88.51(2)
Cl3-Sb1-Cl5	89.11(2)
Cl4-Sb1-Cl6	87.33(2)
Cl2-Sb1-Cl6	91.42(2)
Cl4-Sb1-Cl1	174.327(19)
Cl2-Sb1-Cl1	87.718(16)
Cl6-Sb1-Cl1	87.125(15)
Cl4-Sb1-Cl2	91.21(2)
Cl4-Sb1-Cl5	92.63(2)
Cl2-Sb1-Cl5	175.58(2)
Cl3-Sb1-Cl6	179.54(2)
Cl5-Sb1-Cl6	90.94(2)
Cl3-Sb1-Cl1	92.419(17)
Cl5-Sb1-Cl1	88.667(15)
Sb1-Cl1-Sb1#10	180.0

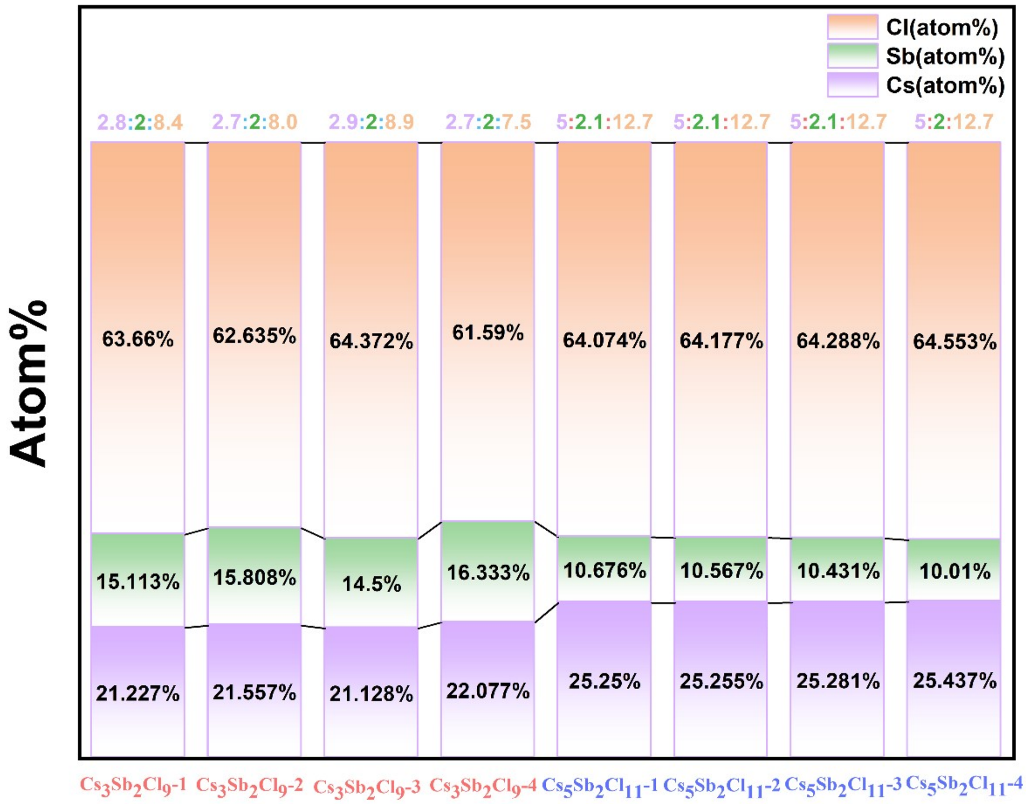

Figure S4. Summary of X-ray fluorescence results for multiple CSC single crystal samples.

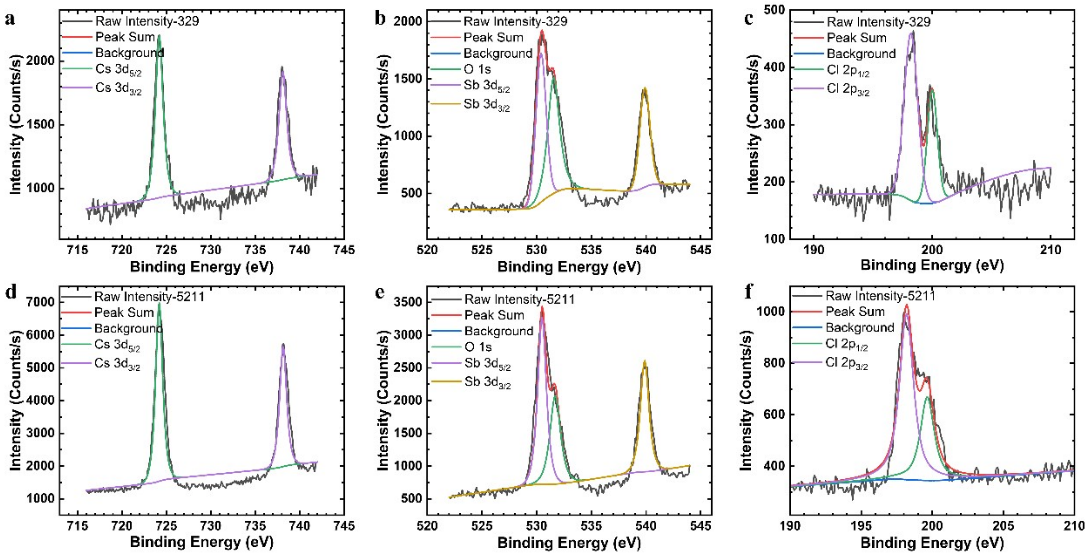

Figure S5. X-ray photoelectron spectroscopy spectra of CSC single crystals. a, d) Cs 3d. b, e) Sb 3d. c, f) Cl 2p. a, b, and c) $Cs_3Sb_2Cl_9$. d, e, and f) $Cs_5Sb_2Cl_{11}$.

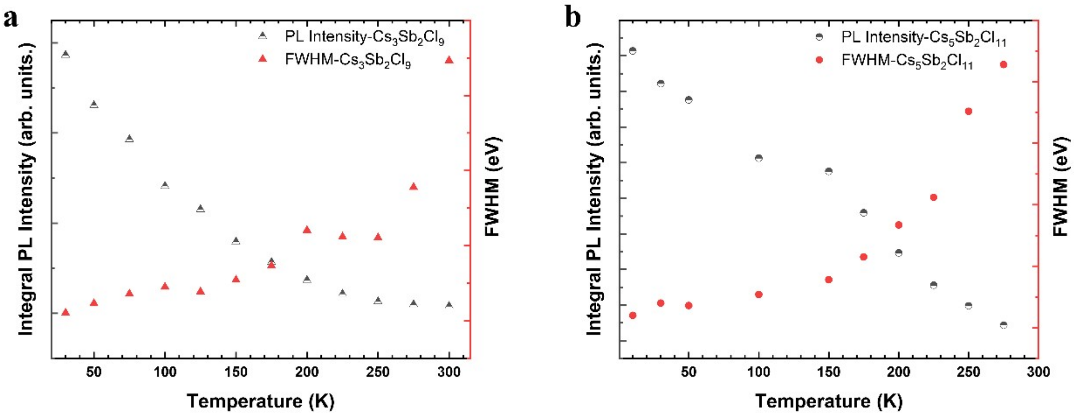

Figure S6. PL intensity and FWHM of CSC crystals as a function of temperature. a) $Cs_3Sb_2Cl_9$. b) $Cs_5Sb_2Cl_{11}$.

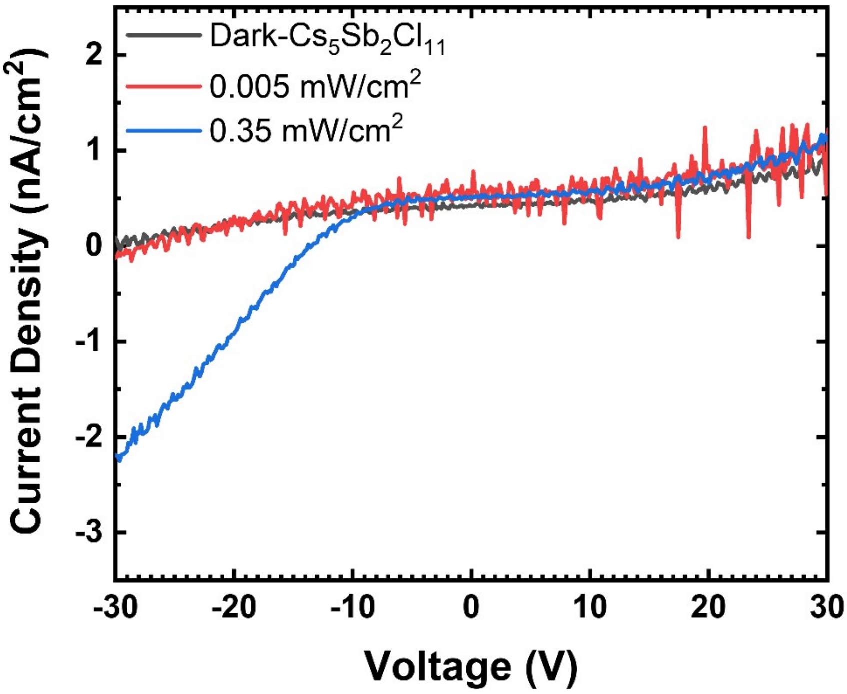

Figure S7. I-V curves of the $Cs_5Sb_2Cl_{11}$ single-crystal photodetector in the dark and under different irradiations at 266 nm for bias voltage in the range from -30 V to 30 V.