

Interfacial alloying between lead halide perovskite crystals and hybrid glasses

Xuemei Li, Wengang Huang, Andraž Krajnc, Yuwei Yang, Atul Shukla, Jaeho Lee, Merhi Ghasemi, Isaac Martens, Bun Chan, Dominique Appadoo, Peng Chen, Xiaoming Weng, Julian A. Steele, Qiang Sun, Gregor Mali, Rijia Lin, Nicholas Bedford, Vicki Chen, Anthony K. Cheetham, Luiz H. G. Tizei, Sean M. Collins, Lianzhou Wang and Jingwei Hou

Methods

Preparation of crystal ZIF-62 and a_gZIF-62.

Crystalline ZIF-62 was synthesised by hydrothermal methods. For ZIF-62-bim_{0.05} solvothermal reactions, 1.2 g Zn(NO₃)₂, 891 mg imidazole and 12 mg benzimidazole were dissolved in 90 mL *N,N*-dimethylformamide (DMF), the whole solution was transferred in a 120 °C oven for 5 days. Off-stoichiometry ZIF-62 was used in this work to lower T_g. After cooling to room temperature, the solution was centrifugated to get crystal solid. To remove the unreacted precursors, a three-time washing-redispersion cycle in DMF was applied. After that, the product was dried in a 150 °C oven overnight¹.

ZIF-62 glass (a_gZIF-62) was obtained by heating crystal ZIF-62 in a tube furnace with a ramping rate of 20 °C/min. Once the temperature reached 450 °C, the whole tube was immediately removed from the furnace and quenched in liquid nitrogen. The whole process was under argon protection until the sample cooled down to room temperature.

Fabrication of CsPbI₃ perovskite

Inorganic lead halide perovskite (CsPbI₃) was prepared by a solvent-free mechanochemical process. A total amount of 400 mg stoichiometric mixture, which was composed of CsI (144.17 mg) and PbI₂ (255.83 mg), as well as zirconium oxide balls (16g) were added to a ball milling jar, then the ball milling was performed with a planetary ball milling machine at 800 RPM for 1 h. After that, the solid product was recovered, and then stored under ambient conditions prior to further testing.

Preparation of (CsPbI₃)_x(a_gZIF-62)_y

Powder (CsPbI₃)_x(a_gZIF-62)_y samples were prepared by mixing a total 200 mg of CsPbI₃ and a_gZIF-62 via ball milling (16 g balls) at 800RPM for 1h, here X and Y refer to mass ratios. For example, 20 mg CsPbI₃ perovskite mixed with 180 mg a_gZIF-62, the resultant mixtures were referred to as (CsPbI₃)_{0.1}(a_gZIF-62)_{0.9}, where 0.1 and 0.9 are the mass percentage of each component. For all samples in this search, X values changed from 0.01 to 0.85. The fabricated powder mixture samples were transferred to a tube furnace for thermal treatment and quenching process, which was similar to the ZIF glass preparation process. The thermal treatment temperature ranged from 150 °C to 350 °C.

Scanning electron microscopy (SEM)

The surface morphologies and atomic density information near the surface were investigated with a high-resolution scanning electron microscope, JEOL JSM-7100F, under both secondary electron and backscattering mode (15.0 kV acceleration voltage). All samples were

dried under an 80°C vacuum oven for eight hours, followed by a surface platinum coating. All samples were applied brief plasma surface cleaning before SEM analysis.

Powder X-ray diffraction (XRD) analysis

Room temperature powder XRD analysis was collected with a Bruker D8 Advance MKII diffractometer using Cu K α radiation with divergent (Bragg-Brentano) geometries. The 2 θ range was 5 to 50°, with a step size of 0.02° and a step rate of 10s. The temperature resolved *in-situ* powder XRD was performed by Rigaku Miniflex 600 Benchtop X-Ray Diffractometer equipped with Anton Paar XRD900 furnace with nitrogen protection. The ramping rate was 20°C/min, with the 2 θ range of 5 to 50°, a step size of 0.05° and a step rate of 10s. The measurement was performed under constant flow of nitrogen.

Thermogravimetric and calorimetric analysis

Thermogravimetric analysis (TGA) was conducted using a Mettler Toledo. The sample was placed in an alumina crucible and heated at a ramping rate of 20 °C/min under flowing (20 mL/min) Ar environment.

Mettler Toledo differential scanning calorimetry (DSC) 1 STARe system was used to determine the calorimetric features. For each measurement, *ca.* 10 mg sample was loaded into an aluminium crucible and heated under a flowing Ar (20 mL/min) environment. To determine the melting (T_m) and thermal decomposition (T_d) and crystal phase transition temperatures, samples were heated at a ramping rate of 20 °C/min to the targeted temperature. To determine the glass transition temperature (T_g), samples were heated above their melting temperature at 20 °C/min, and then cooled back to 40 °C at 10 °C/min, and then ramped up at a rate of 10 °C/min in the second upscan.

UV-Vis absorption

To determine the bandgap (E_g) changes of crystal ZIF-62, a_gZIF-62, powder mixture and (a_gZIF/perovskites) composite pellets, UV-Vis absorption spectroscopy was carried out using a Jasco V-650 UV-Vis spectrophotometer across a wavelength range of 400 nm to 800 nm. The bandgap was determined according to the equation of $E_g = 1240/\lambda_g$, where λ_g refers to the adsorption wavelength of different samples.

Photoluminescence measurements (PL)

Photoluminescence (PL) and time-resolved fluorescence emission spectra were collected at room temperature on an Edinburgh Instrument FLSP-900 fluorescence spectrophotometer. The steady PL spectra were measured with a monochromatized Xe lamp light source, while

the time-resolved PL (TRPL) decays were measured with a 375 nm pulsed diode laser excitation source. Photoluminescence quantum yield (PLQY) of the samples were measured using FS5 fluorescence spectrometer (Edinburgh Instruments). Absolute PLQY measurements were performed in a pre-calibrated integrating sphere. The samples were excited at 440 nm. The photostability was measured with constant laser excitation. The excitation spot was near-perfect circular (beam passed through the circular iris) with diameter ~ 0.8 mm. The excitation wavelength was 440 nm.

Synchrotron Tera-Hz Far-Infrared (THz/Far-IR) absorption spectroscopy

THz/Far-IR absorption spectra were acquired using a Bruker IFS 125/HR Fourier Transform (FT) spectrometer at the Australian Synchrotron's THz/Far-IR beamline. To increase the signal-to-noise ratio, the bolometer was kept in cryogenic mode with liquid helium, and a 6 m thick Multilayer Mylar beamsplitter was utilised.

Attenuated total reflection (ATR) was used for the measurement. Pressure was used to hold samples in place on the surface of the diamond crystal window. The ATR heating stage was used to capture temperature resolved *in-situ* spectra, and the sample was held under flowing Ar (about 20 mL/min). For data processing, the Extended ATR correction algorithms in the OPUS 8.0 programme were used, along with the NumPy module v1.15 and Python v3.5, for spectral data correction and peak fitting².

X-ray absorption spectroscopy and pair distribution function

XAS measurements at the Zn K-edge and Pb L-edge were performed at the 10-ID-B at APS beamline of Argonne National Laboratory. Data was collected from 100 eV below the Zn K-edge to ~ 600 eV above the edge, and 100 eV below the Pb L-edge to ~ 800 eV above the edge. Samples were loaded into 0.0395" inner diameter thin-walled Kapton X-ray capillaries and examined in fluorescence mode. Data processing and subsequent modeling was performed using the Demeter XAS software package. Zn K-edge and Pb L-edge EXAFS fitting was performed by background normalization, k^2 weighting, and Fourier transform. The Zn-N and Zn-C shells from the reported ZIF-62 structure were employed for the fitting of Zn K-edge. And the Pb-O, Pb-I, Pb-Zn shells were obtained from the DFT modelling of Pb_3O_4 , CsPbI_3 , and ZnPb_3 ³⁻⁵.

Diffraction patterns were collected at beamline ID31 at the European Synchrotron Radiation Facility. 1-2 mm thick pellets were measured in transmission geometry with a ~ 50 μm 65 keV (0.1907 $\text{\AA}$) beam, using a Pilatus 2M CdTe detector covering a range of 0.17 to 18.4 $\text{\AA}^{-1}$. The distance and peak broadening was calibrated using CeO_2 NIST SRM 674b. Data were radially integrated in pyFAI without absorption correction, while PDFs were calculated with GSAS-II, and fit using PDFgui. PDFs were fit from 1.5-50 $\text{\AA}$ using previously determined single crystal structures for the ZIF, γ -, and δ -phase CsPbI_3 . The refined lattice parameters of

the CsPbI₃ were a=8.832, b=12.485, c=8.651 and 10.457, b=4.795, c=17.773 for the γ and δ phases respectively.

For comparison, higher $Q_{\max}$ (25 Å⁻¹) data was obtained from beamline 11-ID-B at the Advanced Photon Source at 58.6 keV for sample containing 40 wt% CsPbI₃. While larger $Q_{\max}$ at shorter detector distances theoretically enhances the resolution of the PDF, in this case the sharp reflections of the crystalline CsPbI₃ phases become undersampled, leading to comparable PDF information. The beam sensitivity of the ZIF complicates the acquisition of high-resolution analyser crystal datasets.

Transmission electron microscopy (TEM)

Electron energy loss spectroscopy (EELS) was acquired using a Hitachi HF5000 scanning transmission electron microscope (STEM) at the University of Queensland equipped with a Quantum ER Gatan Imaging Filter (GIF) and operated at 200 kV. EELS data were acquired using a dispersion of 0.5 eV/channel in dualEELS mode to obtain zero loss peak and core loss edge information in tandem for each probe position. Collection and convergence semi-angles were recorded as 29 mrad and 32 mrad, respectively.

EELS data were processed using HyperSpy⁶, an open-source Python package for electron microscopy. First, the zero loss peak centring at 0 eV was checked. Background subtraction was carried out by power law fitting between 580 and 620 eV. Following background removal, spectra were cropped from 580 eV, the lowest energy used in the background fitting window before the I M_{45} edge with a first onset expected at 619 eV energy loss⁷. Spectra without background subtraction were normalised by dividing by each spectrum by the total integrated core loss intensity (to remove effects from differences in total inelastic scattering).

Cathodoluminescence (CL) in a STEM

Scanning transmission electron microscopy (STEM) imaging and CL spectroscopy were performed on a modified Nion Hermes200 operated with 100 keV kinetic energy electrons. With this microscope, a subnanometer electron beam can be generated for high spatial resolution imaging and spectroscopy⁸. High angle annular dark field (HAADF) images have an intensity which is proportional to the projected atomic number along the electron beam trajectory. Therefore, the heavier CsPbI₃ particles appear brighter in the lighter MOF. CL was performed with a Mönch system from Attolight fitted with a diffraction grating 150 grooves per millimeter (0.34 nm dispersion on the spectrometer used), which gives a wavelength resolution of about 1 nm at 600 nm⁹. The optical spectrometer was calibrated using an Ar-Hg lamp. The sample was kept at around 150 K using a liquid nitrogen cooled sample holder (HennyZ).

X-ray Photoelectron Spectroscopy (XPS)

XPS data was acquired at room temperature on a Kratos AXIS Supra Plus XPS system which uses a dual monochromated Al K α /Ag L α X-ray source. At pass energies of 160 and 20 eV, the survey and high-resolution spectra of vacuum-dried samples were recorded, respectively. During sample analysis, the chamber's basal pressure was between 10⁻⁹ and 10⁻⁸ Torr. Duplicate scans were processed, and a single area on each sample was analysed. The software CasaXPS was employed to execute peak fitting on the high-resolution data. Charge correction was performed on all high-resolution scans to the C-C peak at 284.6 eV.

Synchrotron X-ray small angle-angle scattering (SAXS)

Ex situ X-ray scattering data were gathered at the SAXS/WAXS beamline of the Australian Synchrotron. The detector was calibrated using silver behenate standards on the Dectris PILATUS3 X 2M. The intensity was normalised *via* an integrated diode beamstop. The X-ray beam energy was fixed at 11.001 keV. Using the in-house Scatterbrain programme, the obtained data were condensed to a single dimension. After fitting the SAXS data with the McSAS software using a basic Monte Carlo simulation, the size distribution profile was extracted¹⁰. A spherical model was fitted to the data.

Solid-state NMR

Solid-state NMR measurements were performed using a 1.6 mm HXY FastMAS probe on a 600 MHz Varian NMR system, with a sample spinning frequency set at 20 kHz. For the ¹³³Cs MAS NMR spectra, a 1 μ s excitation pulse, 1200 scans, and a repetition delay of 60 s were utilized, while the ¹H MAS NMR spectra were obtained using a 1.5 μ s excitation pulse, 8 scans, and a repetition delay of 5 s.

In the ¹H-¹³C CPMAS experiments, a cross-polarization (CP) block of 4 ms, and signal acquisition with high-power XiX proton decoupling were used, with a repetition delay of 1 s and a total of 6,000 scans collected. The length of the CP block in the ¹H-¹³³Cs CPMAS experiment was 4 ms, with a repetition delay of 0.6 s and 120,000 scans collected. The Larmor frequencies for ¹H, ¹³C, and ¹³³Cs were 599.36 MHz, 150.71 MHz, and 78.61 MHz, respectively. The ¹H and ¹³C spectral axes were referenced relative to the signals of tetramethylsilane, and the ¹³³Cs axis relative to the signal of caesium nitrate.

Computational Details

Standard computational chemistry calculations were carried out using the Gaussian 16¹¹ and AMS-DFTB¹². For the theoretical study of infrared spectroscopy, we use a model system of a tetrahedral complex between a Zn²⁺ cation surrounded by imidazole and iodide anions. Geometries and vibrational frequencies of these molecular models were obtained with the B3LYP method¹³ in conjunction with the 6-31+G(d,p)¹⁴ basis set. Modeling of bulk PbCsI₃ and the MOF materials, as well as the surface-cluster systems, were carried out using the XTB1 method¹⁵. For bulk materials, the geometries were taken from the crystal structures. For the cluster systems, we used constrained optimization with the PbCsI₃ component being fixed at crystal-structure geometries.

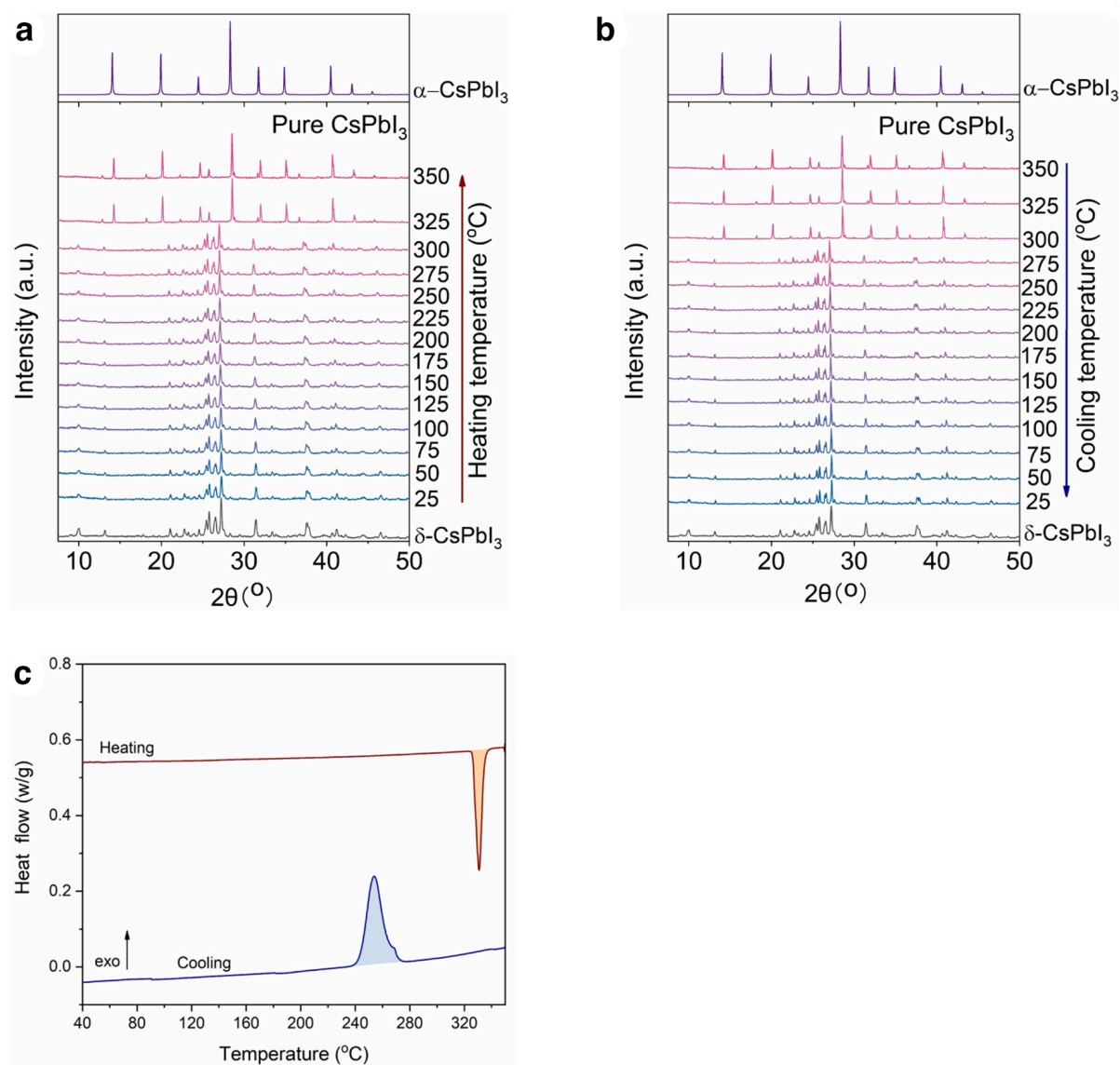


Figure S1. Phase transition of the pure CsPbI₃. (a) *In-situ* XRD pattern for pure CsPbI₃ during the heating process. (b) *In-situ* XRD pattern for pure CsPbI₃ during the cooling process. (c) DSC results for pure CsPbI₃ for heating and cooling ramps. Data was collected under constant flowing nitrogen protection (20 mL/min). The temperature ramping rates were 20 and 10 °C/min during the heating and cooling process, respectively.

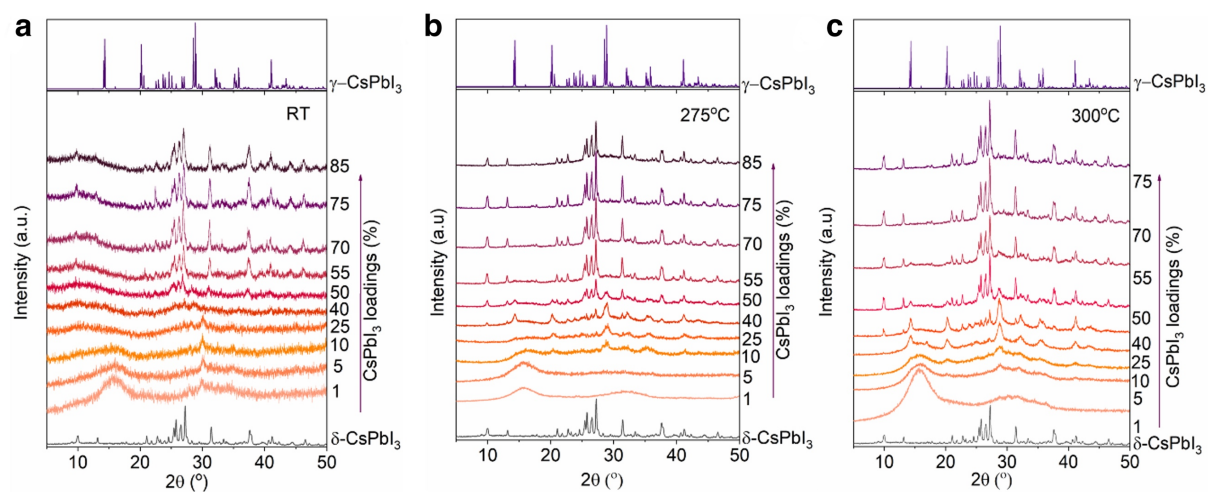
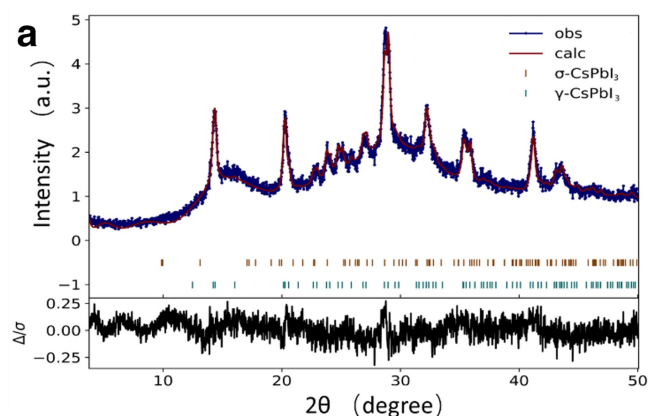
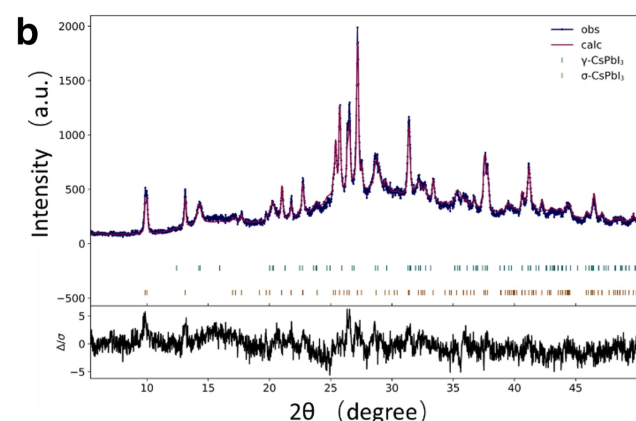


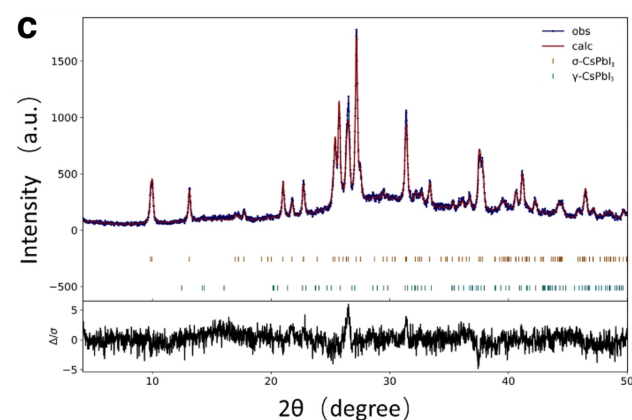
Figure S2. Crystal structures of the composites with different components and sintered under different temperatures. (a) *Ex-situ* XRD pattern of (CsPbI₃) (a_gZIF-62) (X/Y), and (CsPbI₃)_x(a_gZIF-62)_y composites prepared at (b) 275 $^{\circ}$ C and (c) 300 $^{\circ}$ C sintering.



Lattice parameters	Lattice parameters reported in ref.	Lattice parameters	Lattice parameters reported in ref.
a=10.3822 Å	a=10.4500(5) Å	a=8.6232 Å	a=8.6198(6) Å
b=4.8068 Å	b=4.7965(2) Å	b=8.8085 Å	b=8.8518(6) Å
c=17.7523 Å	c=17.7602(8) Å	c=12.4534 Å	c=12.5012(7) Å
α=90°	α=90°	α=90°	α=90°
β=90°	β=90°	β=90°	β=90°
γ=90°	γ=90°	γ=90°	γ=90°
V=885.929 Å³	V=890.20(7) Å³	V=945.920 Å³	V=953.852(11) Å³
Space group: <i>Pnma</i>		Space group: <i>Pbnm</i>	
Crystal system: Orthorhombic (σ)		Crystal system: orthorhombic (γ)	
Weight fraction: 0 (sig: 0.0078)		Weight fraction: 100% (sig: 0.0078)	
R _{wb} =8.074%			



Lattice parameters	Lattice parameters reported in ref.	Lattice parameters	Lattice parameters reported in ref.
a=10.4382 Å	a=10.4500(5) Å	a=8.7326 Å	a=8.6198(6) Å
b=4.7884 Å	b=4.7965(2) Å	b=8.8679 Å	b=8.8518(6) Å
c=17.7395 Å	c=17.7602(8) Å	c=12.3619 Å	c=12.5012(7) Å
$\alpha=90^\circ$	$\alpha=90^\circ$	$\alpha=90^\circ$	$\alpha=90^\circ$
$\beta=90^\circ$	$\beta=90^\circ$	$\beta=90^\circ$	$\beta=90^\circ$
$\gamma=90^\circ$	$\gamma=90^\circ$	$\gamma=90^\circ$	$\gamma=90^\circ$
V=888.665 Å ³	V=890.20(7) Å ³	V=957.306 Å ³	V=953.852(11) Å ³
Space group: <i>Pnma</i>		Space group: <i>Pbnm</i>	
Crystal system: Orthorhombic (σ)		Crystal system: orthorhombic (γ)	
Weight faction: 71.31% (sig: 0)		Weight faction: 28.69% (sig: 0)	
R _w =9.171%			



Lattice parameters	Lattice parameters reported in ref.	Lattice parameters	Lattice parameters reported in ref.
a=10.4493 Å	a=10.4500(5) Å	a=8.6447 Å	a=8.6198(6) Å
b=4.7966 Å	b=4.7965(2) Å	b=8.8178 Å	b=8.8518(6) Å
c=17.7603 Å	c=17.7602(8) Å	c=12.5002 Å	c=12.5012(7) Å
α=90°	α=90°	α=90°	α=90°
β=90°	β=90°	β=90°	β=90°
γ=90°	γ=90°	γ=90°	γ=90°
V=890.172 Å³	V=890.20(7) Å³	V=952.857 Å³	V=953.852(11) Å³
Space group: <i>Pnma</i>		Space group: <i>Pbnm</i>	
Crystal system: Orthorhombic (σ)		Crystal system: orthorhombic (γ)	
Weight faction: 97.63% (sig: 0)		Weight faction: 2.37% (sig: 0)	
R _w =8.612%			

Figure S3. Examples of identifying the proportions of various CsPbI₃ phases within composites using XRD refinement. (a) Rietveld refinement of powder XRD pattern of (CsPbI₃)_{0.25}(agZIF-62)_{0.75} composites sintering at 350 °C, (b) (CsPbI₃)_{0.5}(agZIF-62)_{0.5} composites prepared at 300 °C and (c) (CsPbI₃)_{0.70}(agZIF-62)_{0.30} composites sintering at 275°C.

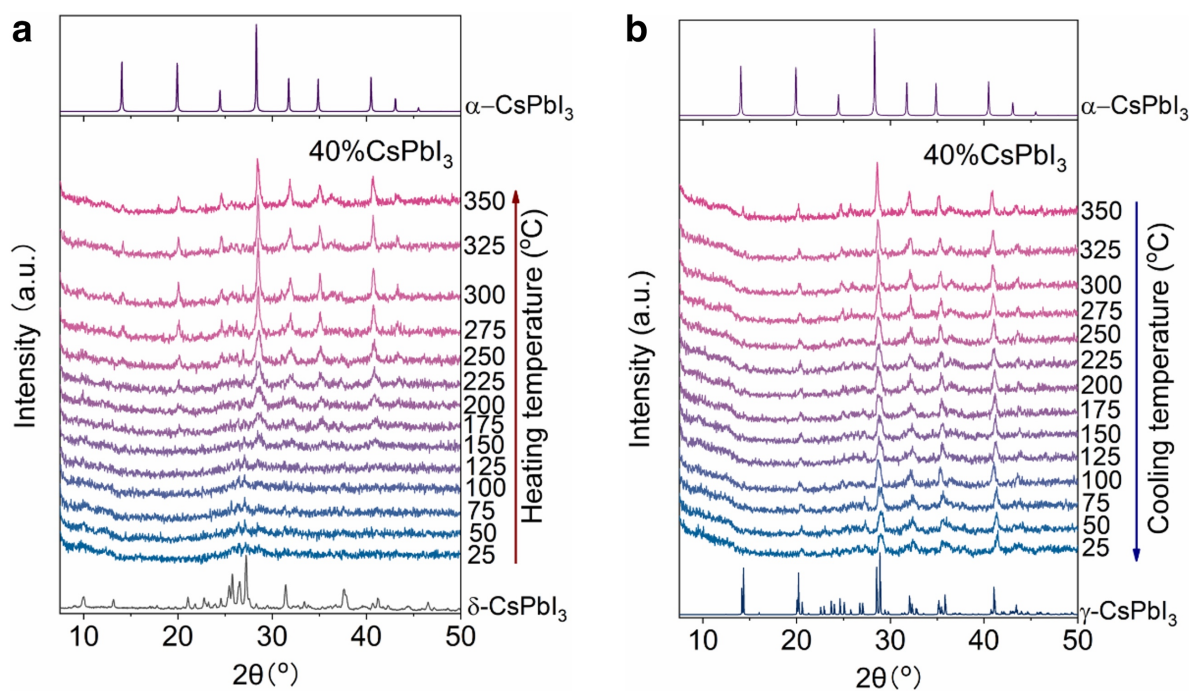


Figure S4. (a) *In-situ* XRD pattern of (CsPbI₃)_{0.4}(agZIF-62)_{0.6} heated from 25 °C to 350 °C and (b) corresponding cooling down process. The temperature ramp is 20 °C/min under the protection of N₂. The reference XRD patterns of α -, γ - and δ -CsPbI₃ are retrieved from ref¹⁶. The intermediate β -phase was not resolved using our benchtop XRD instrument, due to resolution limits. During the cooling ramp, the perovskite gradually lowered its symmetry, resulting in the formation of the orthorhombic γ -phase upon returning to room temperature.

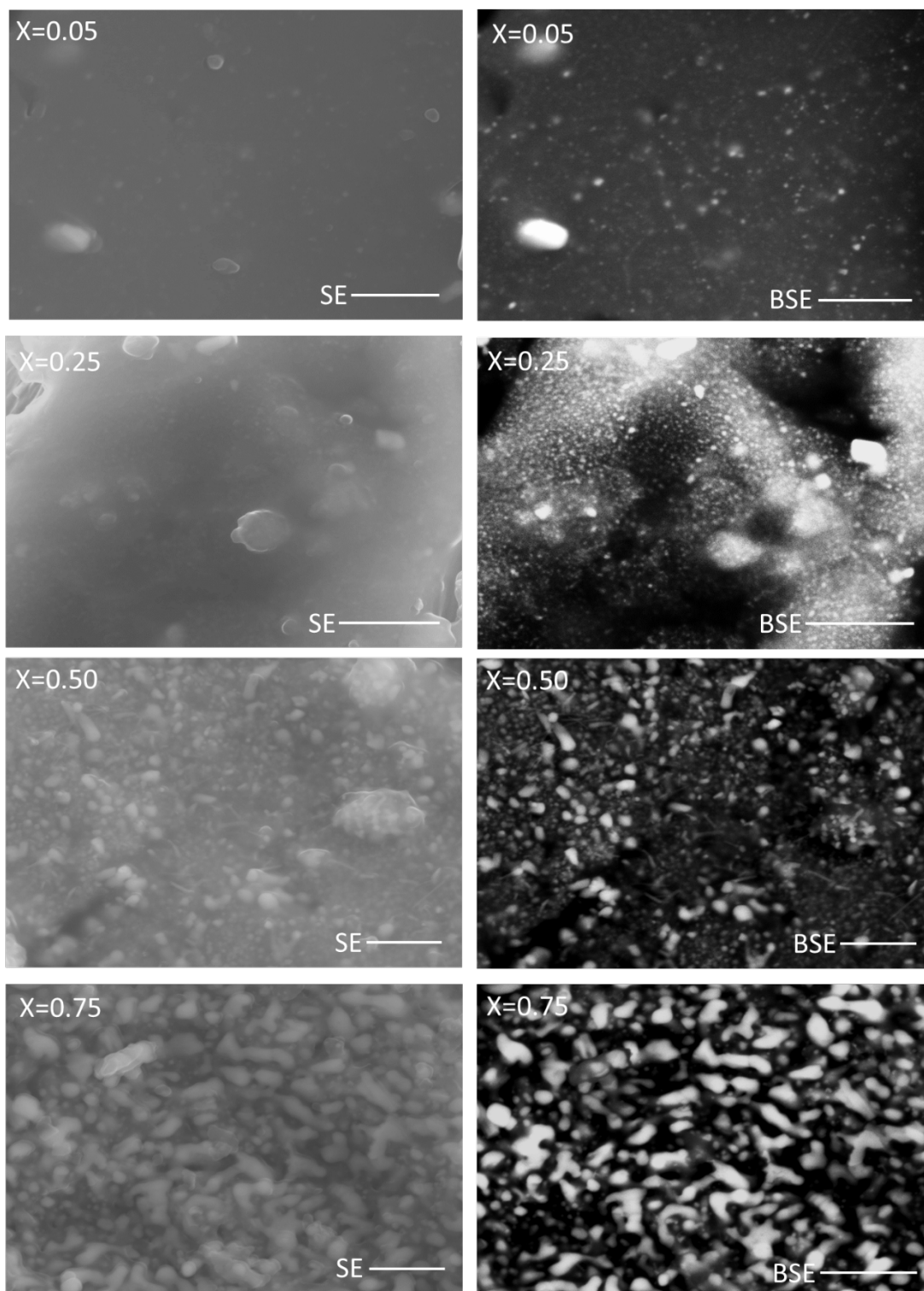


Figure S5. SEM secondary electron image (SE, left) and backscattering image (BSE, right) of $(\text{CsPbI}_3)_x(\text{aZIF-62})_y$ composites sintered at 350 °C. The scale bar is 1 μm .

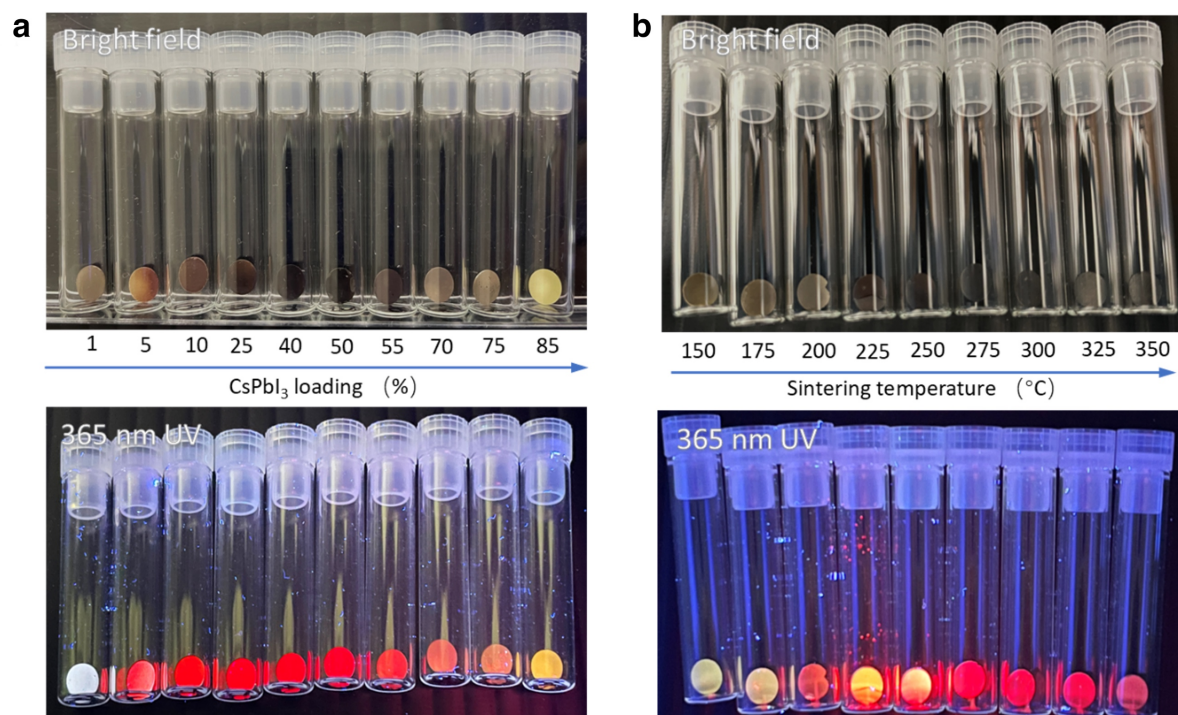


Figure S6. PL emission of the composites. (A) Optical images of the $(\text{CsPbI}_3)_x(\text{agZIF-62})_y$ composites sintering at 275 °C with different CsPbI_3 components and (B) $(\text{CsPbI}_3)_{0.25}(\text{agZIF-62})_{0.75}$ composites with various sintering temperatures.

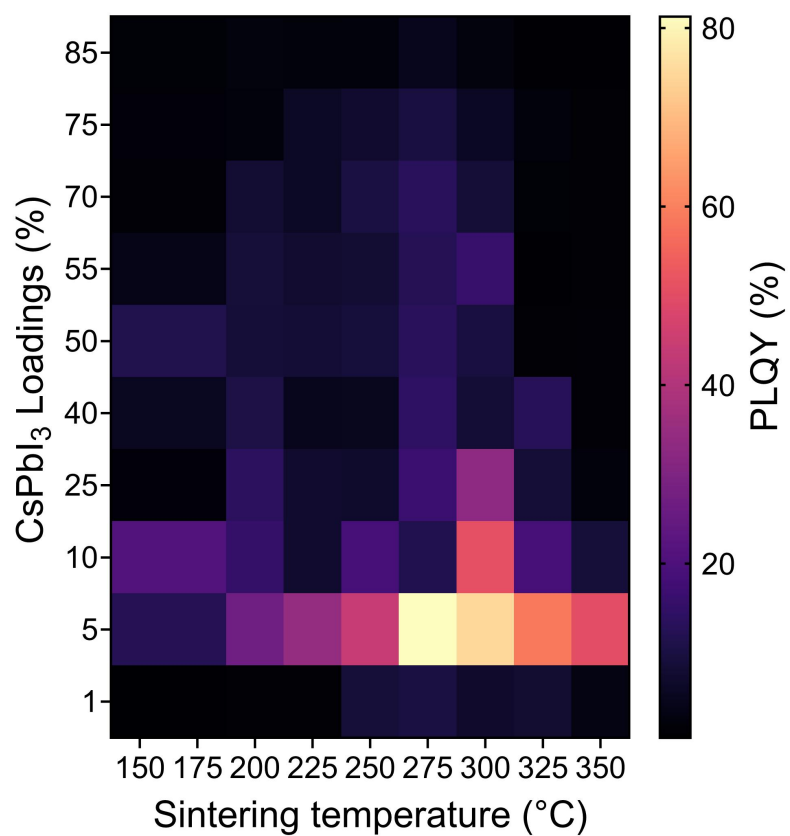


Figure S7. PLQY of different (CsPbI₃)_x(agZIF-62)_y composites.

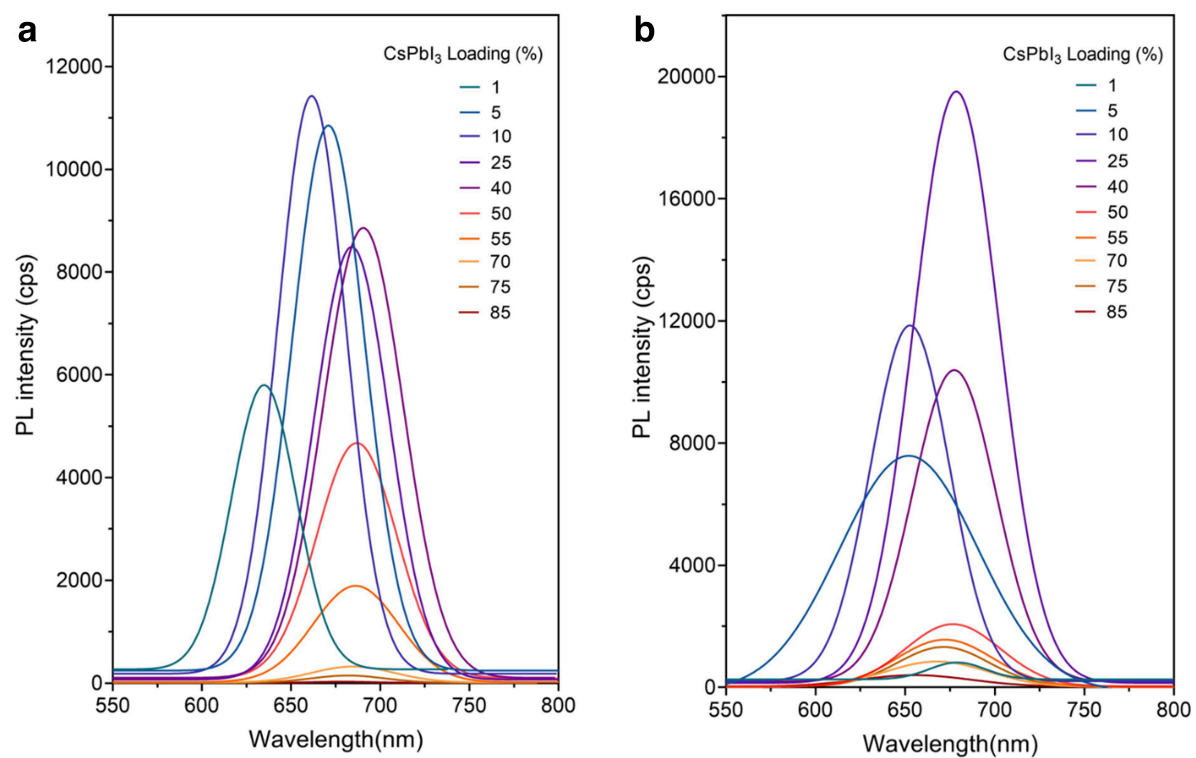


Figure S8. PL profiles of different CsPbI₃ loading samples sintered at (A) 300°C and (B) 275°C.

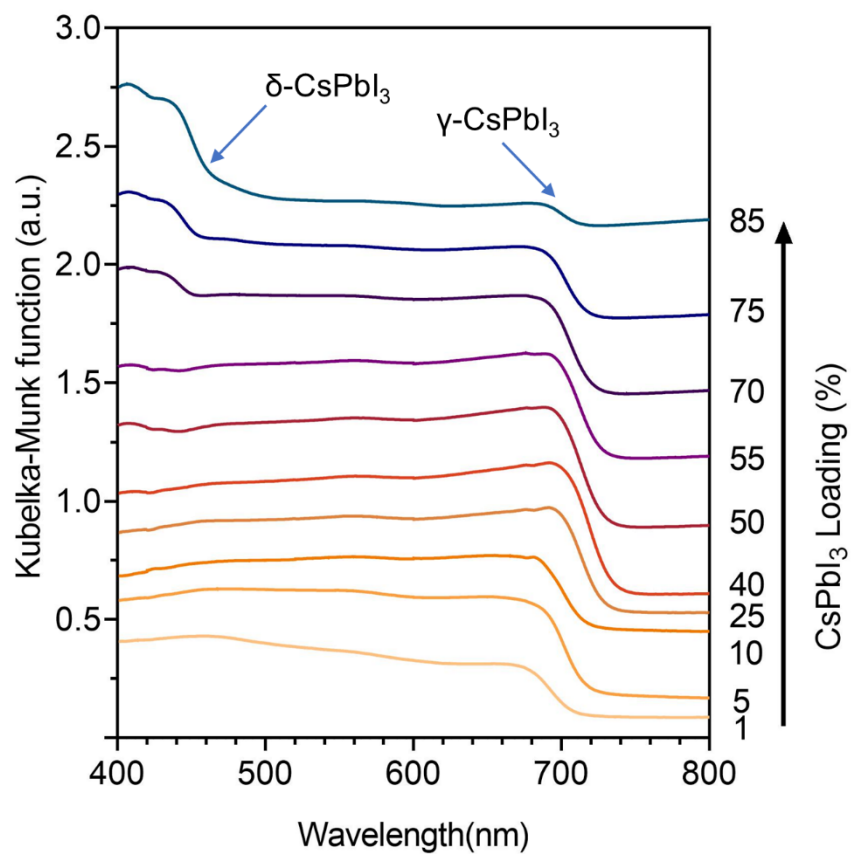


Figure S9. UV-Vis absorption spectra for different CsPbI₃ percentages composites sintered at 300 °C.

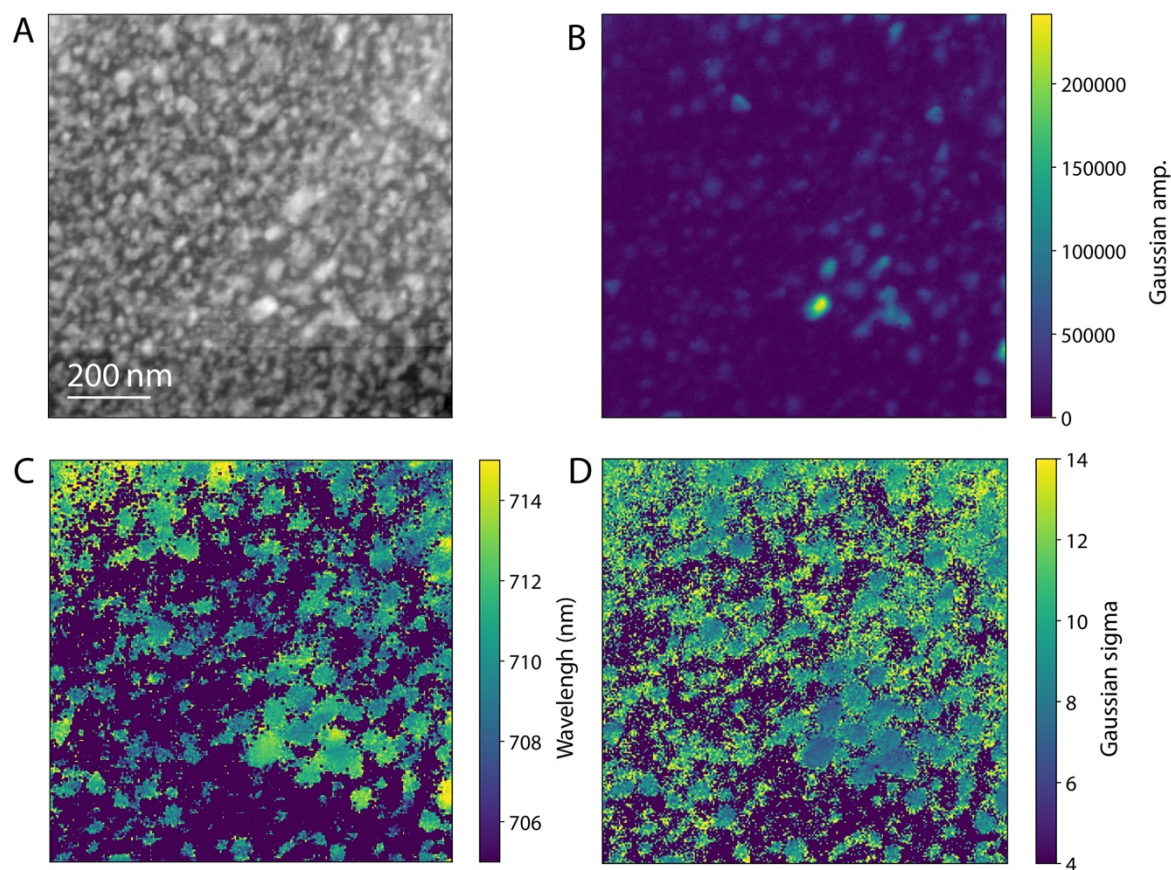


Figure S10 Catholuminescence (CL)-STEM characterisation of the $(\text{CsPbI}_3)_{0.1}(\text{agZIF-62})_{0.9}$ composites sintered at 350 °C, and thinned with FIB-SEM. (A) ADF-STEM image. (B) Mapping of the Gaussian fitted CL peak intensity. (C) Mapping of the Gaussian fitted CL peak position values.

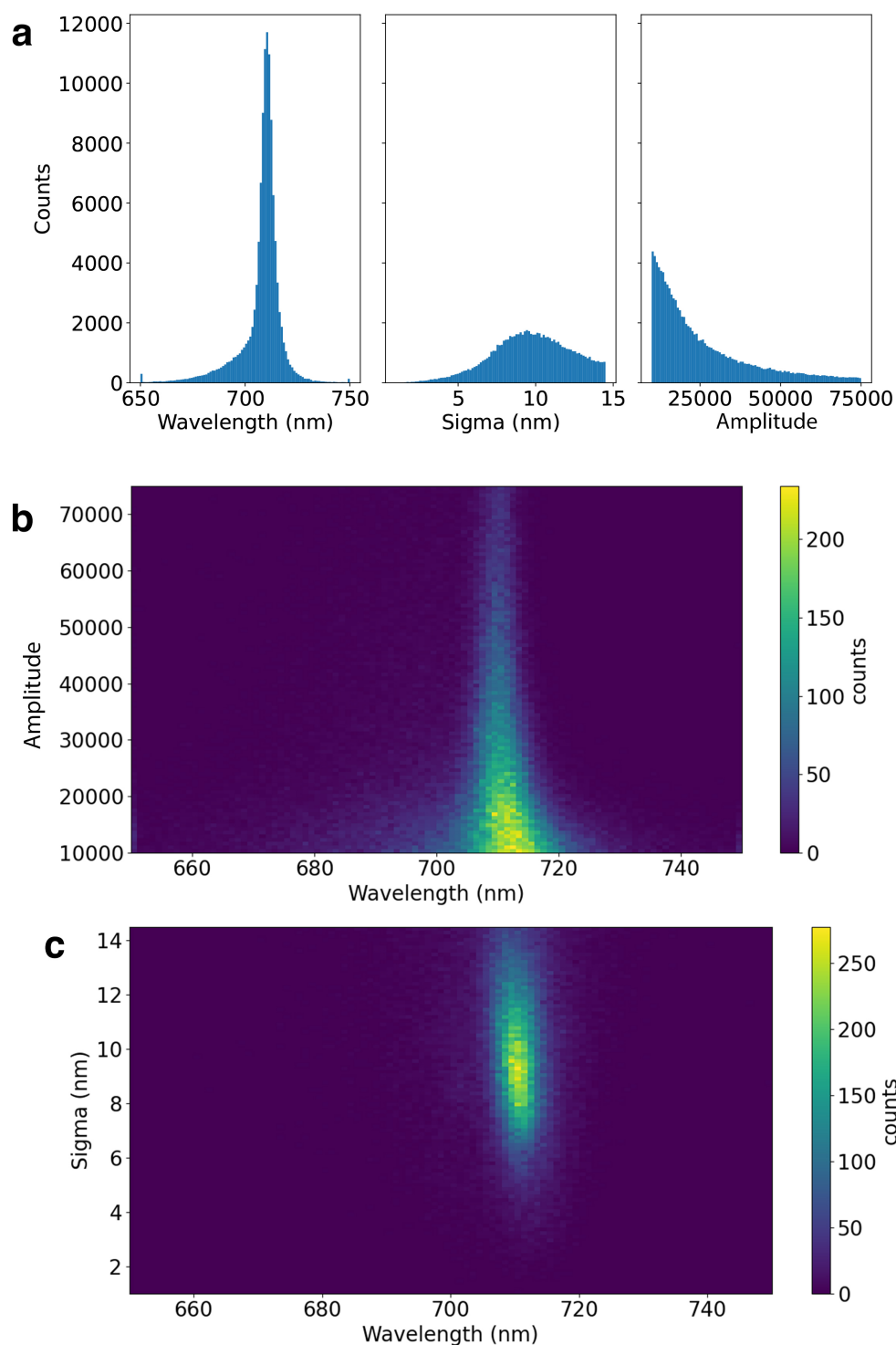


Figure S11 CL-STEM characterisation of the $(\text{CsPbI}_3)_{0.1}(\text{agZIF-62})_{0.9}$ composites sintered at 350 °C. CL data cubes have been acquired from a total project area of $6.9 \mu\text{m}^2$. A one Gaussian model was fitted to each spectrum. (A) Histograms of the fitted coefficients across the whole measured area: Gaussian peak center, sigma and amplitude. (B-C) 2D histogram of the amplitude versus wavelength and sigma versus wavelength shows that correlations exist. Lower wavelength peaks are associated to higher intensities.

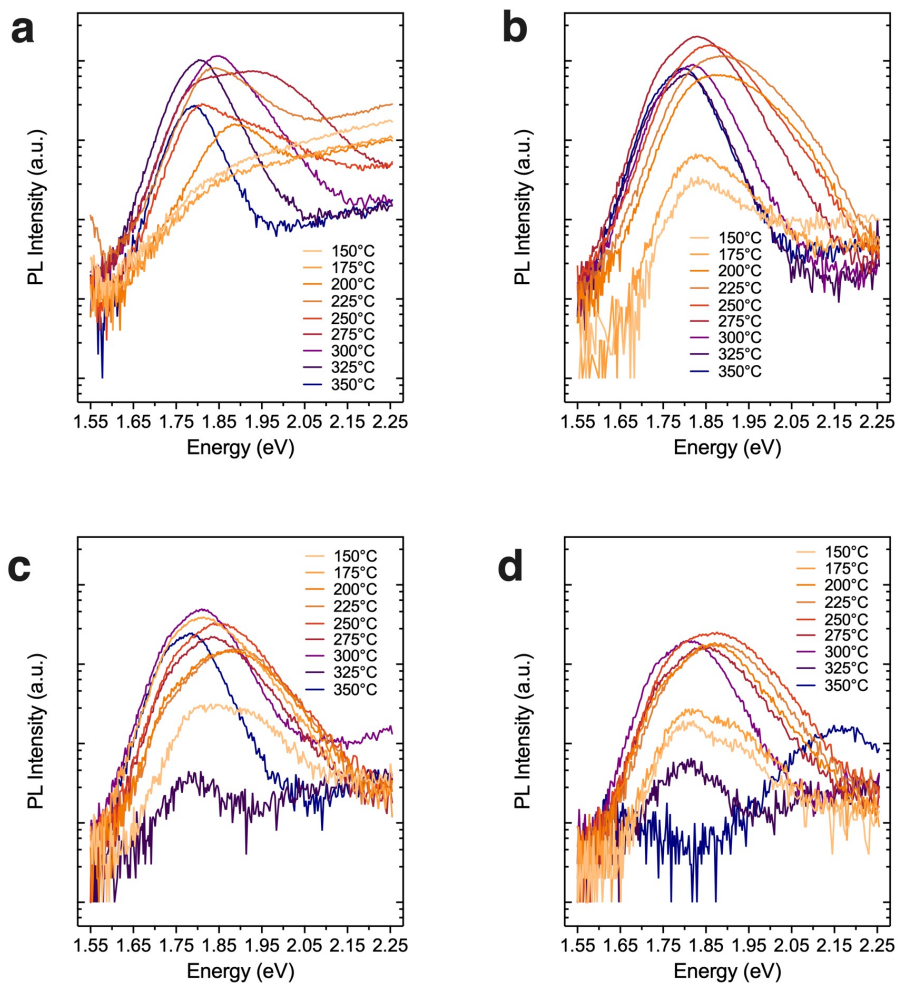
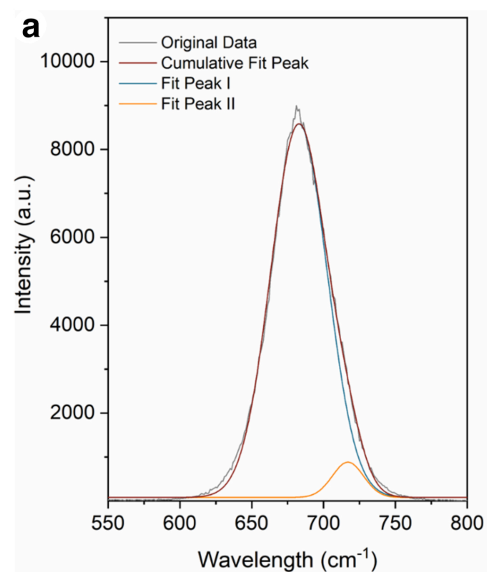


Figure S12. PL spectra shown in log scale for (a) $(\text{CsPbI}_3)_{0.05}(\text{agZIF-62})_{0.95}$ composite, (b) $(\text{CsPbI}_3)_{0.25}(\text{agZIF-62})_{0.75}$ composite, (c) $(\text{CsPbI}_3)_{0.50}(\text{agZIF-62})_{0.50}$ composite, (d) $(\text{CsPbI}_3)_{0.45}(\text{agZIF-62})_{0.55}$ composite and (f) $(\text{CsPbI}_3)_{0.55}(\text{agZIF-62})_{0.45}$ composite.



b

Model	Gauss	
Equation	$y=y_0 + (A/(w*\sqrt{\pi/2}))*\exp(-2*((x-x_c)/w)^2)$	
Plot	Peak I	Peak II
y_0	81.13 ± 9.77	81.13 ± 9.77
x_c	682.82 ± 0.20	716.94 ± 0.97
w	39.27 ± 0.33	21.78 ± 1.75
A	418305.79 ± 3918.98	21896.09 ± 3476.46
Reduced Chi-Sqr	13025.42	
R-Square (COD)	0.998	
Adj. R-Square	0.998	

Figure S13. Representative PL fitting with two-Gaussian function. (a) PL curve of (CsPbI₃)_{0.25}(agZIF-62)_{0.75} composite sintering at 300 °C fitted by two peaks Gaussian fits, the peaks were noted as Peak I and Peak II. (b) The summary of fitting results and peak parameters. Peak I represents the high energy peak and the Peak II represents the low energy peak.

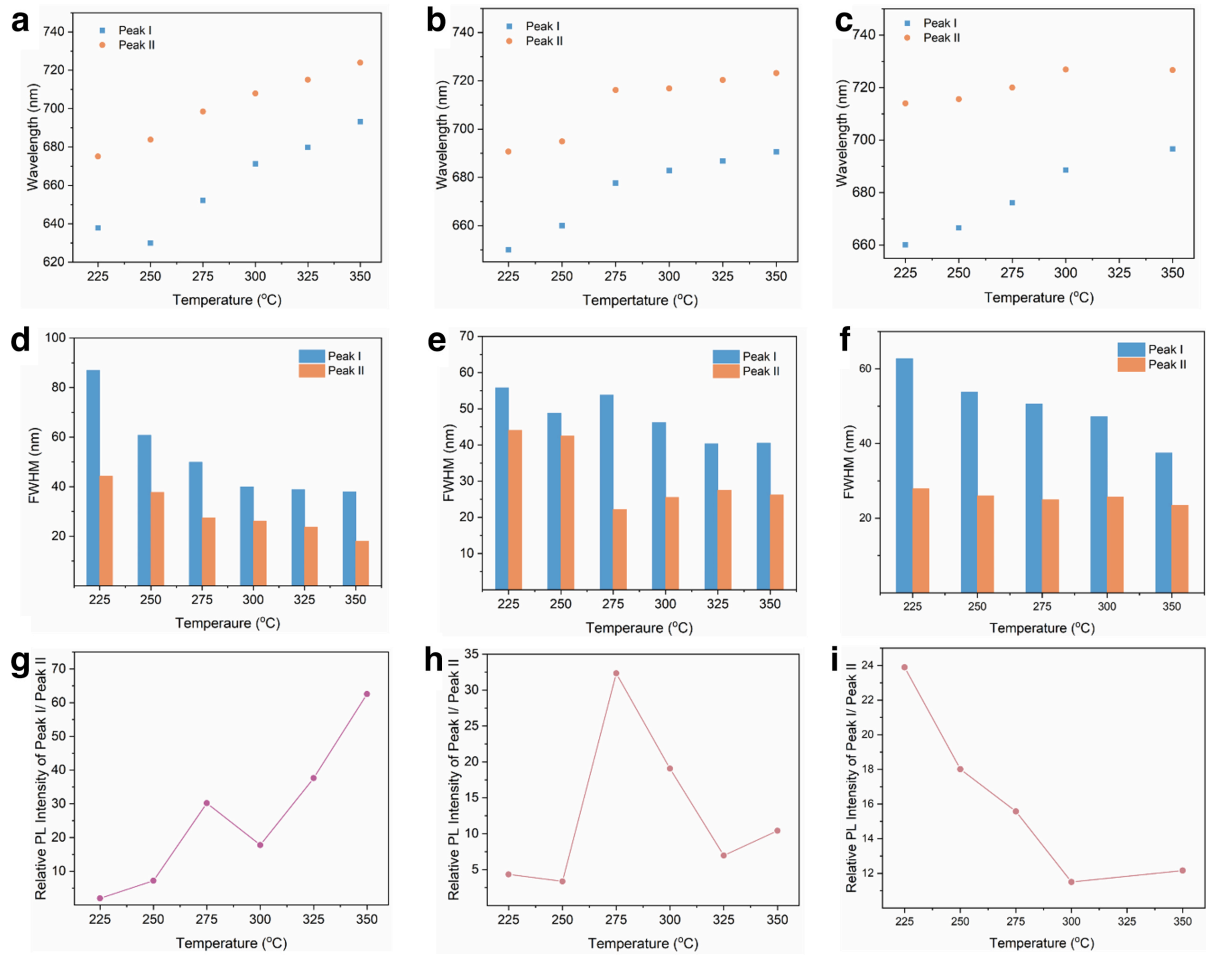


Figure S14. Summary of the two-Gaussian fitting of PL, where Peak I represents the high energy peak and the Peak II represents the low energy peak. The extracted peak positions for (a) $(\text{CsPbI}_3)_{0.1}(\text{agZIF-62})_{0.9}$, (b) $(\text{CsPbI}_3)_{0.25}(\text{agZIF-62})_{0.75}$ and (c) $(\text{CsPbI}_3)_{0.40}(\text{agZIF-62})_{0.60}$ composites. The summary of peak bandwidths from (d) $(\text{CsPbI}_3)_{0.1}(\text{agZIF-62})_{0.9}$, (e) $(\text{CsPbI}_3)_{0.25}(\text{agZIF-62})_{0.75}$ and (f) $(\text{CsPbI}_3)_{0.40}(\text{agZIF-62})_{0.60}$ composites. The relative intensity of Peak I and Peak II from (g) $(\text{CsPbI}_3)_{0.1}(\text{agZIF-62})_{0.9}$, (h) $(\text{CsPbI}_3)_{0.25}(\text{agZIF-62})_{0.75}$ and (i) $(\text{CsPbI}_3)_{0.40}(\text{agZIF-62})_{0.60}$ composites.

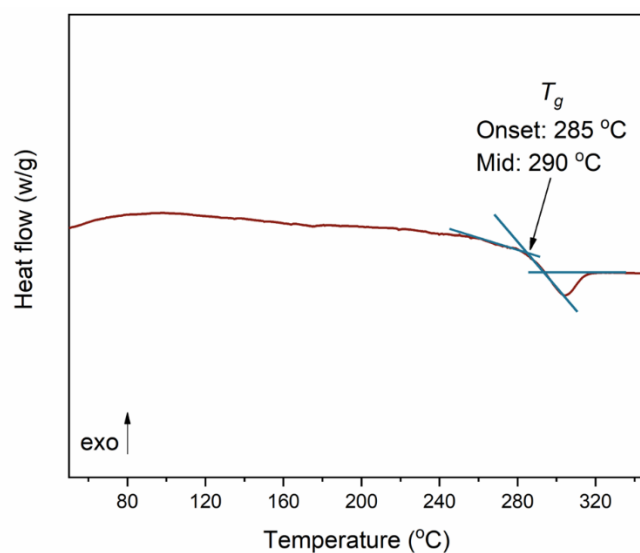


Figure S15. Differential scanning calorimetry (DSC) results for melt-quenched a_gZIF-62 under constant flowing nitrogen (20 mL/min). The temperature ramp rate was 20 °C/min.

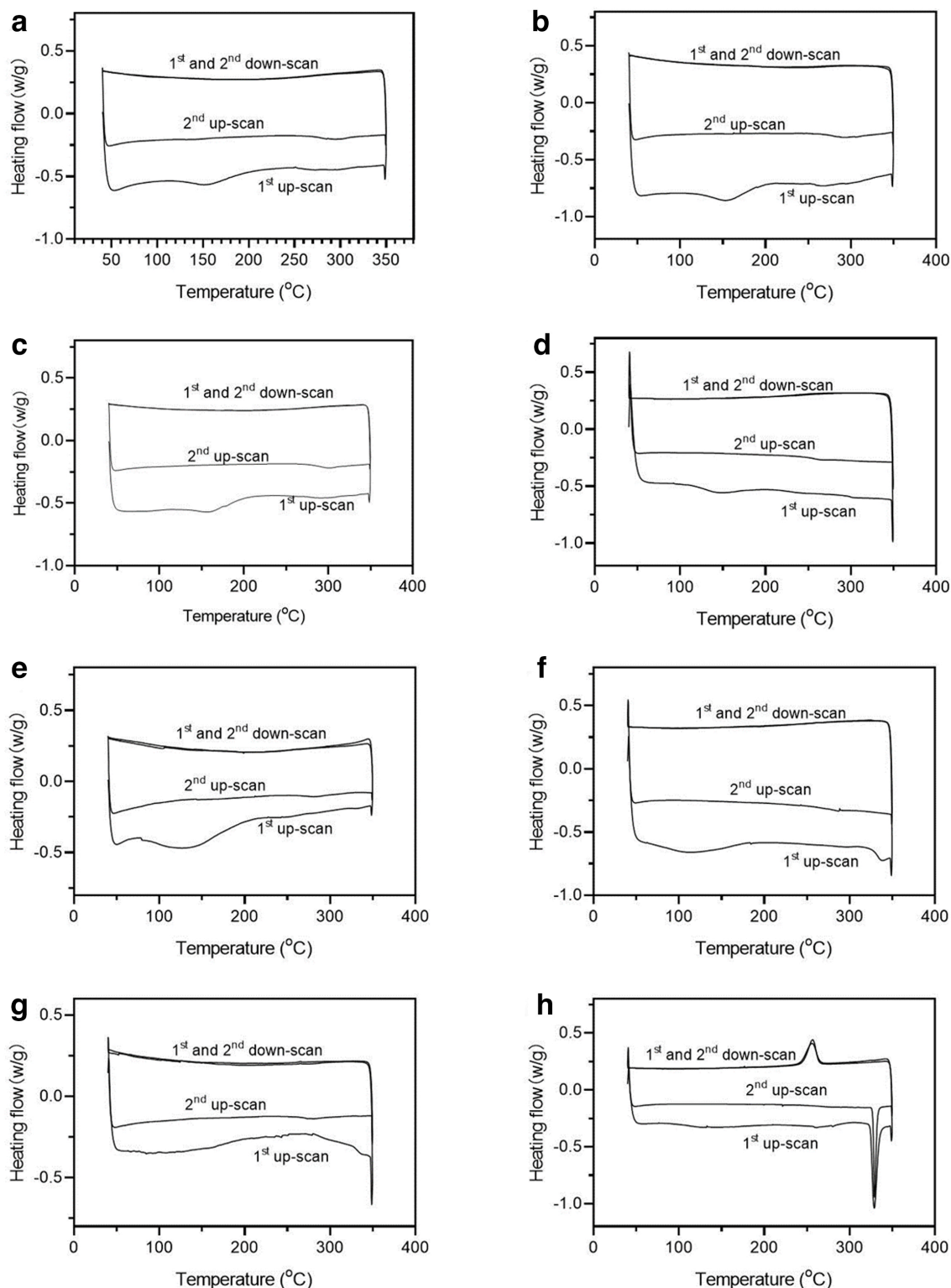


Figure S16. DSC data of $(\text{CsPbI}_3)_x(\text{agZIF-62})_y$ composites with different CsPbI_3 loadings. (a) $\text{CsPbI}_3_{0.01}(\text{agZIF-62})_{0.99}$, (b) $(\text{CsPbI}_3)_{0.05}(\text{agZIF-62})_{0.95}$, (c) $(\text{CsPbI}_3)_{0.10}(\text{agZIF-62})_{0.90}$, (d) $(\text{CsPbI}_3)_{0.25}(\text{agZIF-62})_{0.75}$, (e) $\text{CsPbI}_3_{0.40}(\text{agZIF-62})_{0.60}$, (f) $\text{CsPbI}_3_{0.50}(\text{agZIF-62})_{0.50}$, (g) $\text{CsPbI}_3_{0.55}(\text{agZIF-62})_{0.45}$ and (h) $\text{CsPbI}_3_{0.75}(\text{agZIF-62})_{0.25}$ composites. The temperature ramping rate for the first up-scan was 20 °C/min, and the ramping rate was 10 °C/min during the DSC cooling and second up-scan.

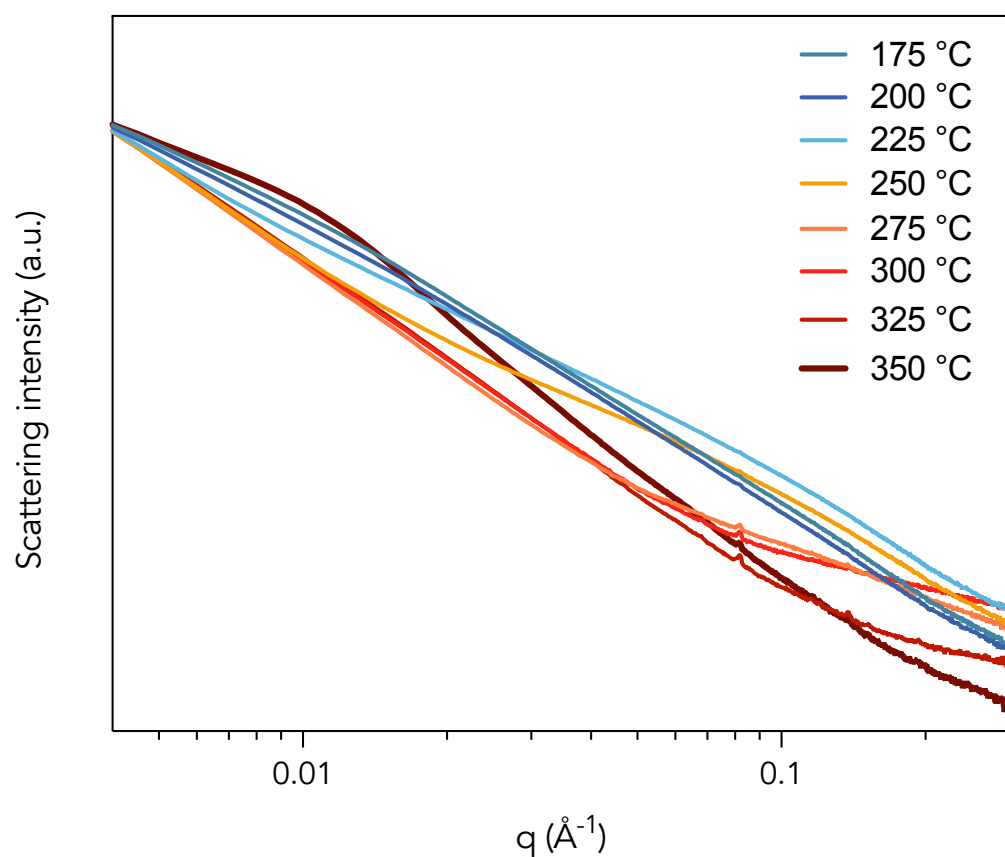


Figure S17 *Ex-situ* synchrotron small angle scattering (SAXS) of $(\text{CsPbI}_3)_{0.1}(\text{agZIF-62})_{0.9}$ fabricated with different sintering temperatures. The spike at *ca.* $0.08 \text{ \AA}^{-1}$ is attributed to the detector configuration.

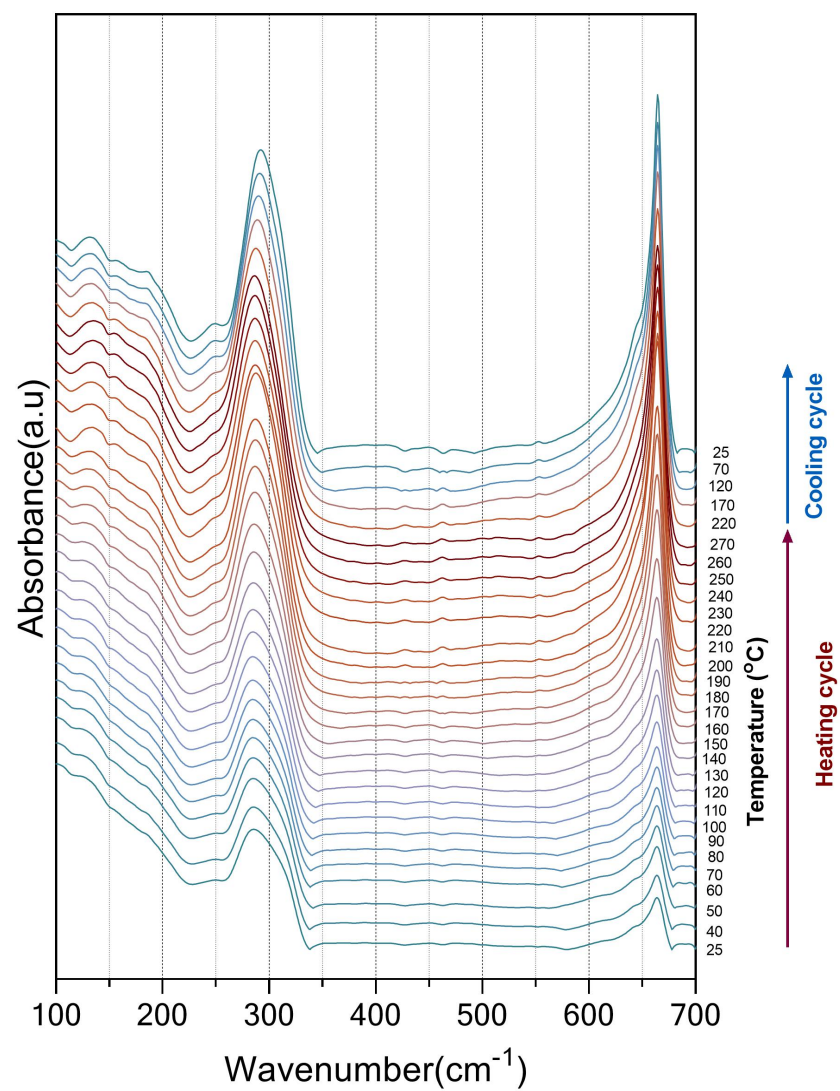


Figure S18 Temperature-resolved *in-situ* THz FarIR spectra for (CsPbI₃)(agZIF-62)(10/90) composites during heating and cooling ramps. Ramp rate was 10°C/min.

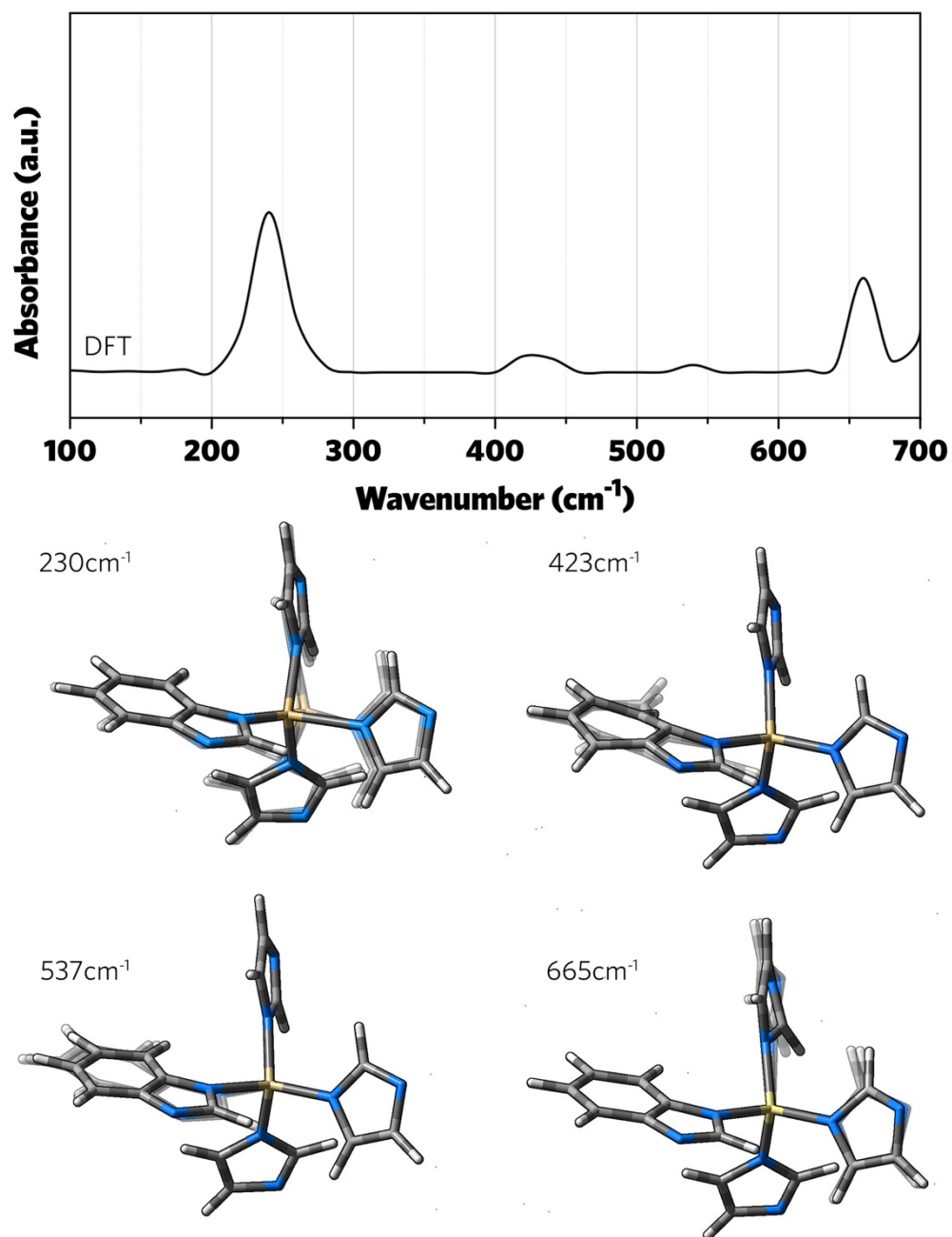


Figure S19. DFT calculations of the ZIF-62 THz absorbance spectrum. The scheme represent the vibration and deformation movement of the corresponding features. More detailed DFT calculation procedures can be found in our previous publication¹⁷.

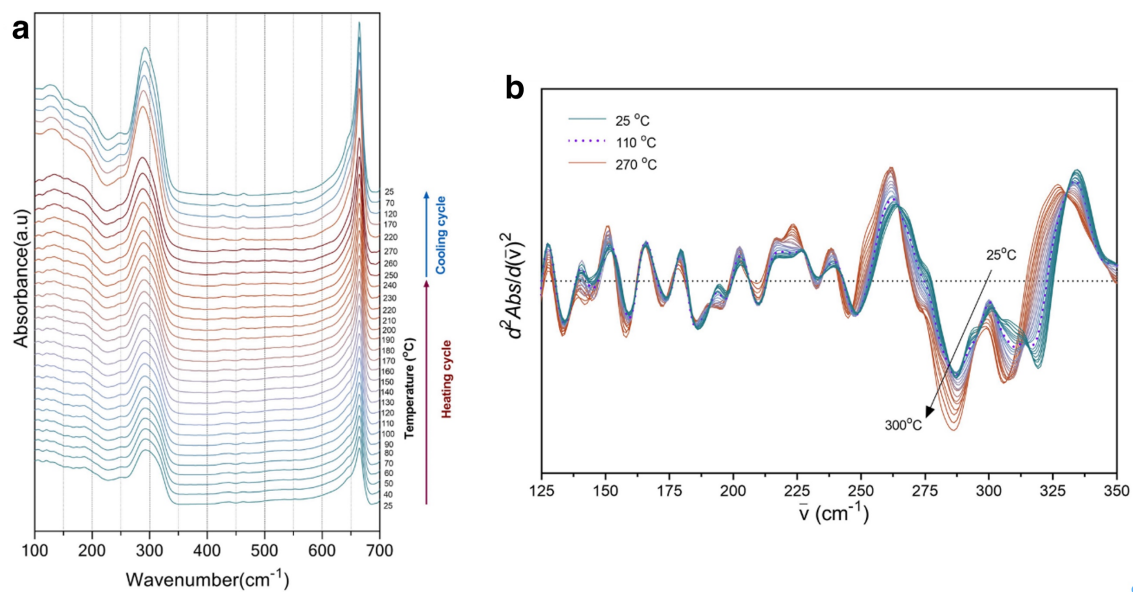


Figure S20. (a) Temperature-resolved *in-situ* THz FarIR spectra for $(\text{CsPbI}_3)_3(\text{agZIF-62})_{1/99}$ composites and (b) corresponding second derivative spectra. The sample were heated to 270 °C and cooling back to room temperature under Ar protections.

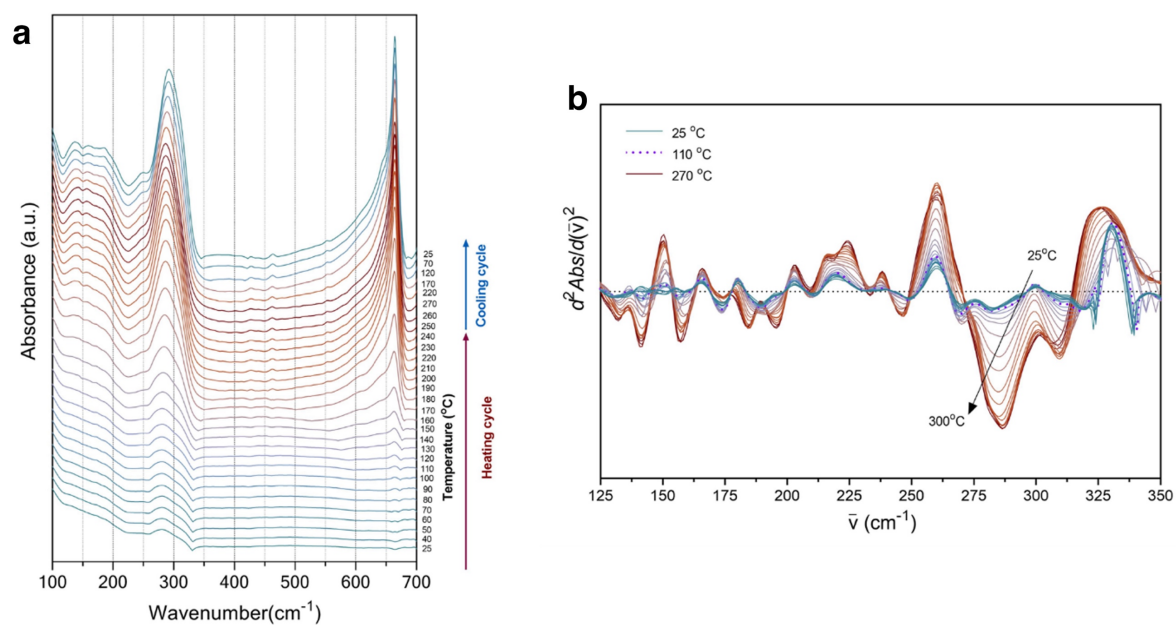


Figure S21. (a) Temperature-resolved *in-situ* THz FarIR spectra for $(\text{CsPbI}_3)(\text{agZIF-62})(25/75)$ composites and (b) corresponding second derivative spectra. The sample were heated to 270 °C and cooling back to room temperature under Ar protections.

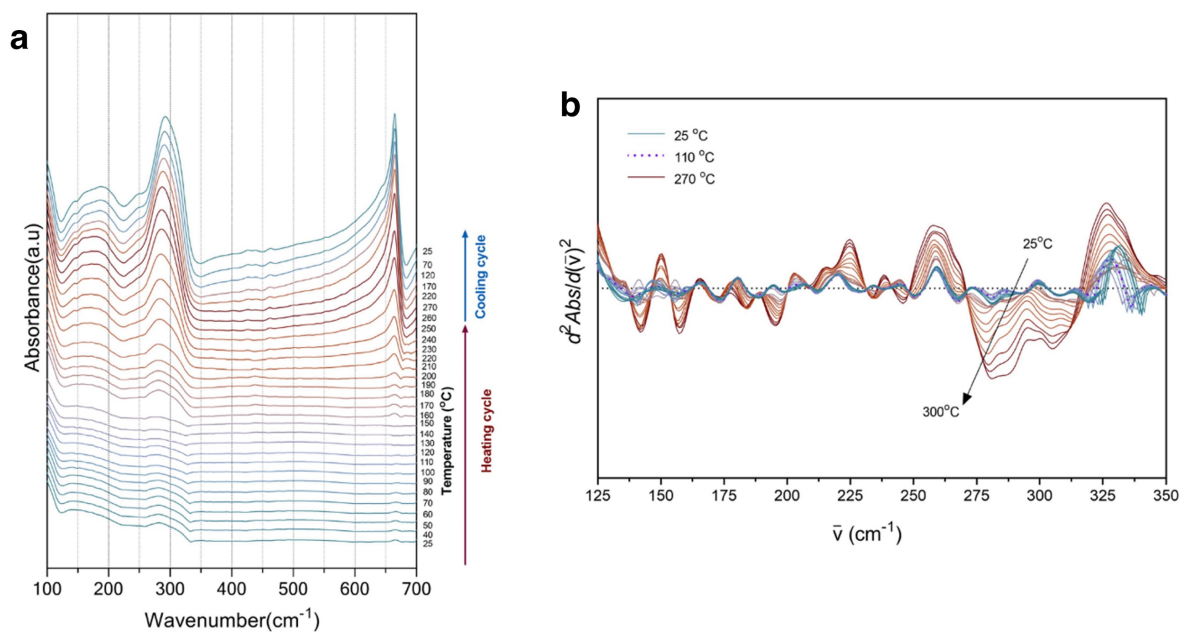


Figure S22. (a) Temperature-resolved *in-situ* THz FarIR spectra for $(\text{CsPbI}_3)(\text{agZIF-62})(55/45)$ composites and (b) corresponding second derivative spectra. The sample were heated to 270 °C and cooling back to room temperature under Ar protections.

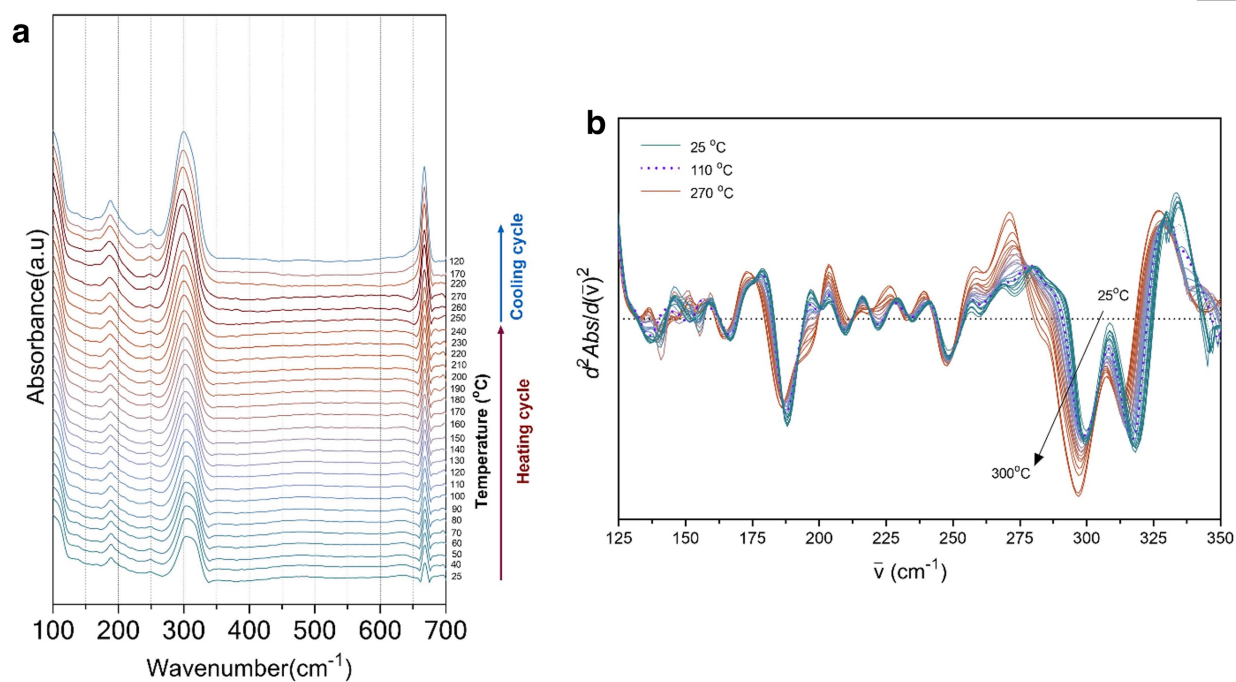


Figure S23. (a) Temperature-resolved *in-situ* THz FarIR spectra for $(\text{CsPbI}_3)_3(\text{agZIF-62})(85/15)$ composites and (b) corresponding second derivative spectra. The sample were heated to 270 $^{\circ}\text{C}$ and cooling back to room temperature under Ar protections.

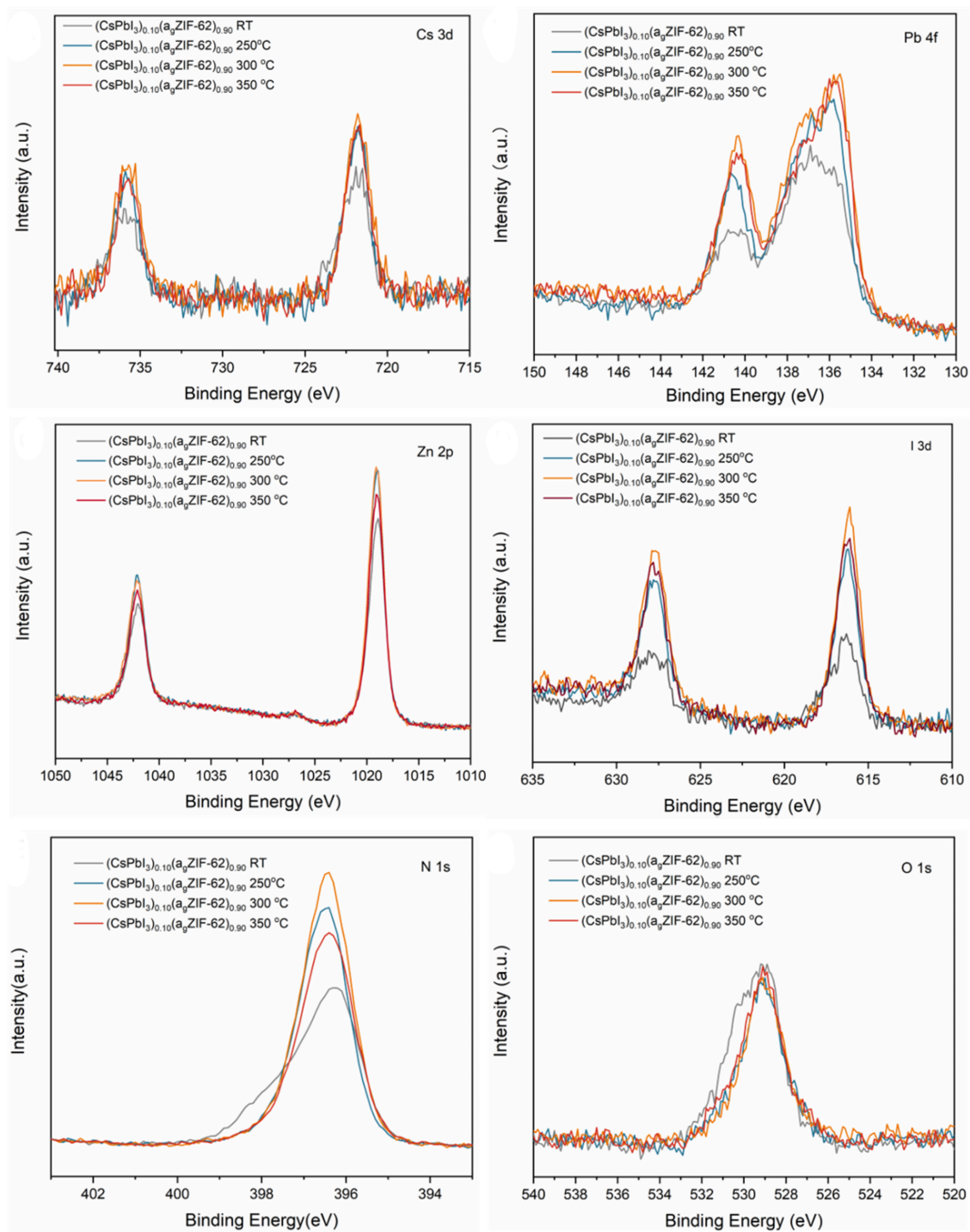


Figure S24. X-ray photoelectron spectroscopy (XPS) of $(\text{CsPbI}_3)_{0.1}(\text{a}_9\text{ZIF-62})_{0.9}$ composites at different sintering temperatures.

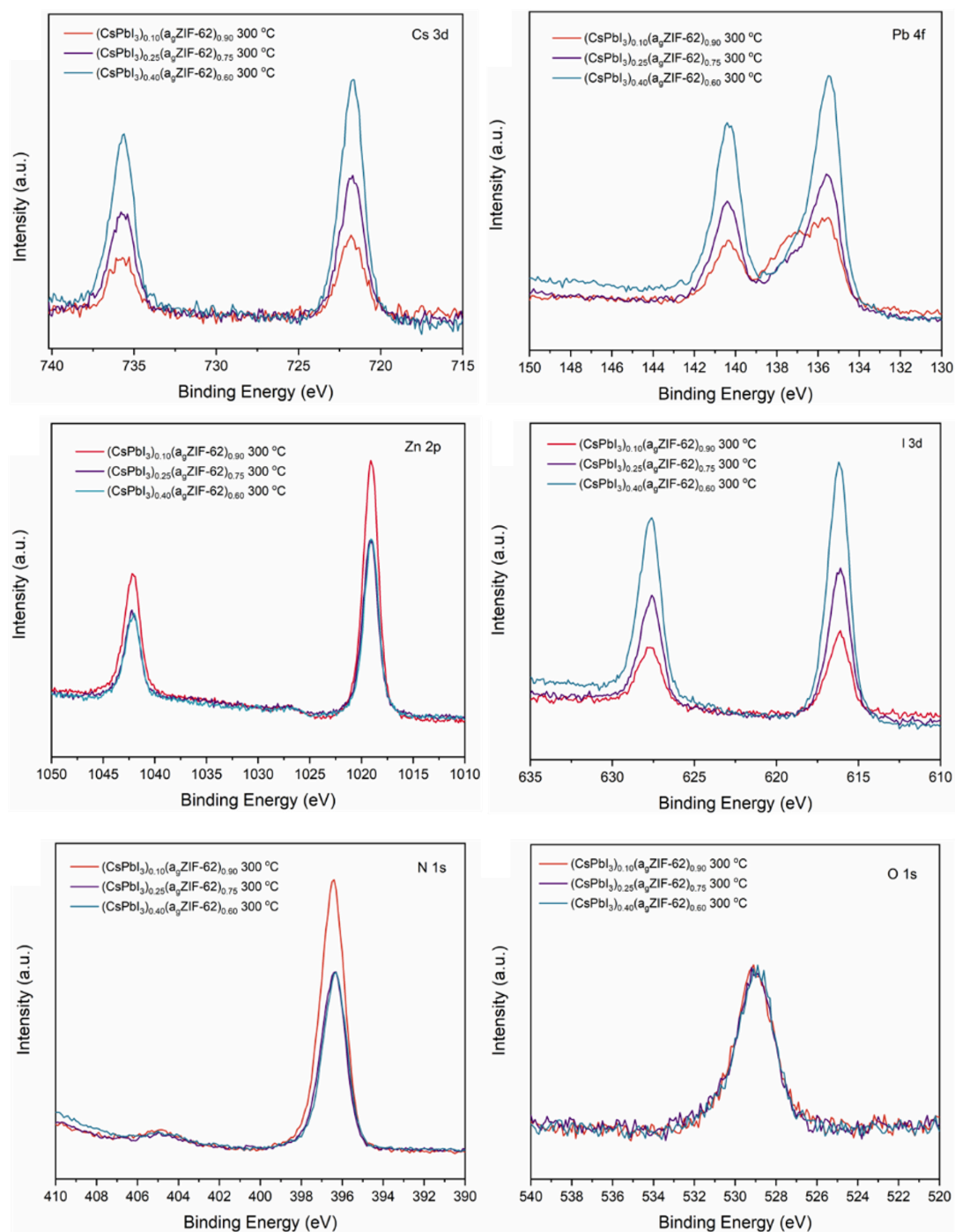


Figure S25. X-ray photoelectron spectroscopy (XPS) of $(\text{CsPbI}_3)_x(\text{a}_9\text{ZIF-62})_y$ composites sintering at $300\text{ }^\circ\text{C}$ with different components.

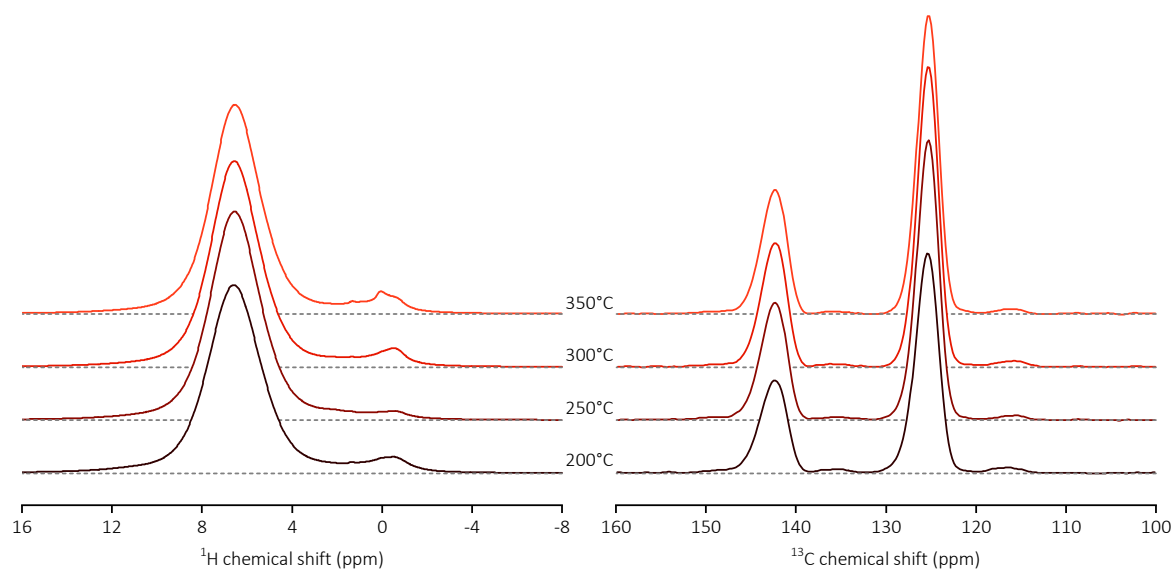


Figure S26. ^1H and ^{13}C MAS NMR spectra of $(\text{CsPbI}_3)_{0.25}(\text{agZIF-62})_{0.75}$ composites sintered at 200, 250, 300, and 350 $^{\circ}\text{C}$.

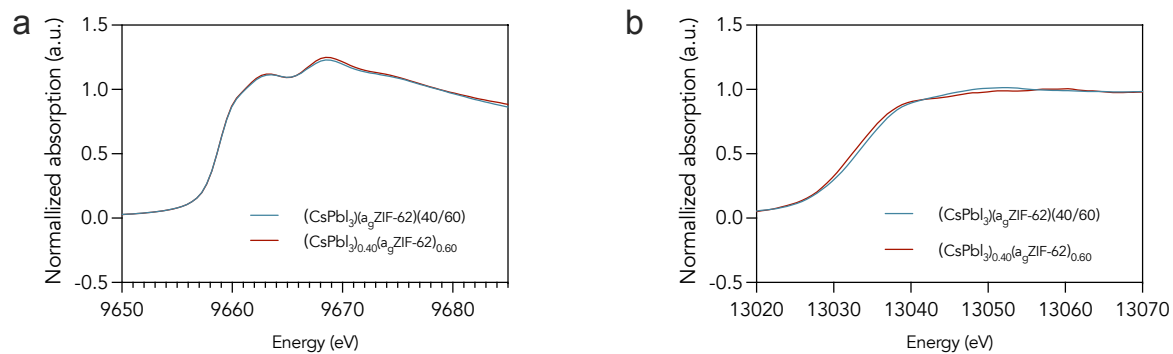


Figure S27. X-ray absorption of 40 wt% CsPbI₃ / agZIF-62 composites prior and after 350 °C sintering.
 (a) Zn K edge X-ray absorption spectrum near edge structure (XANES) and (b) Pb L₃-edge XANES.

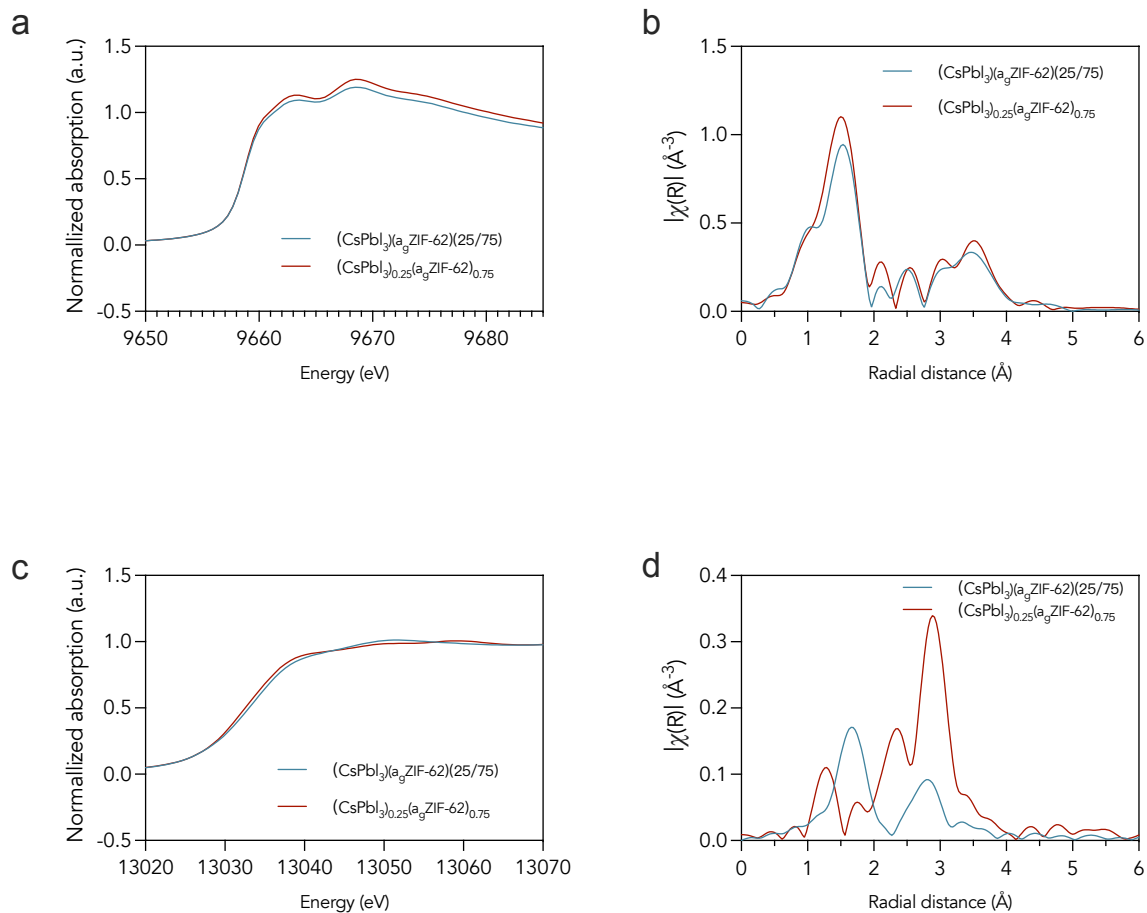


Figure S28. X-ray absorption of 25 wt% CsPbI_3 / ag-ZIF-62 composites prior and after 350 °C sintering. (a) Zn edge X-ray absorption spectrum near edge structure (XANES) and (b) correspondent phase-uncorrected moduli of the Fourier transform results. (c) Pb edge X-ray absorption spectrum near edge structure (XANES) and (d) correspondent phase-uncorrected moduli of the Fourier transform results.

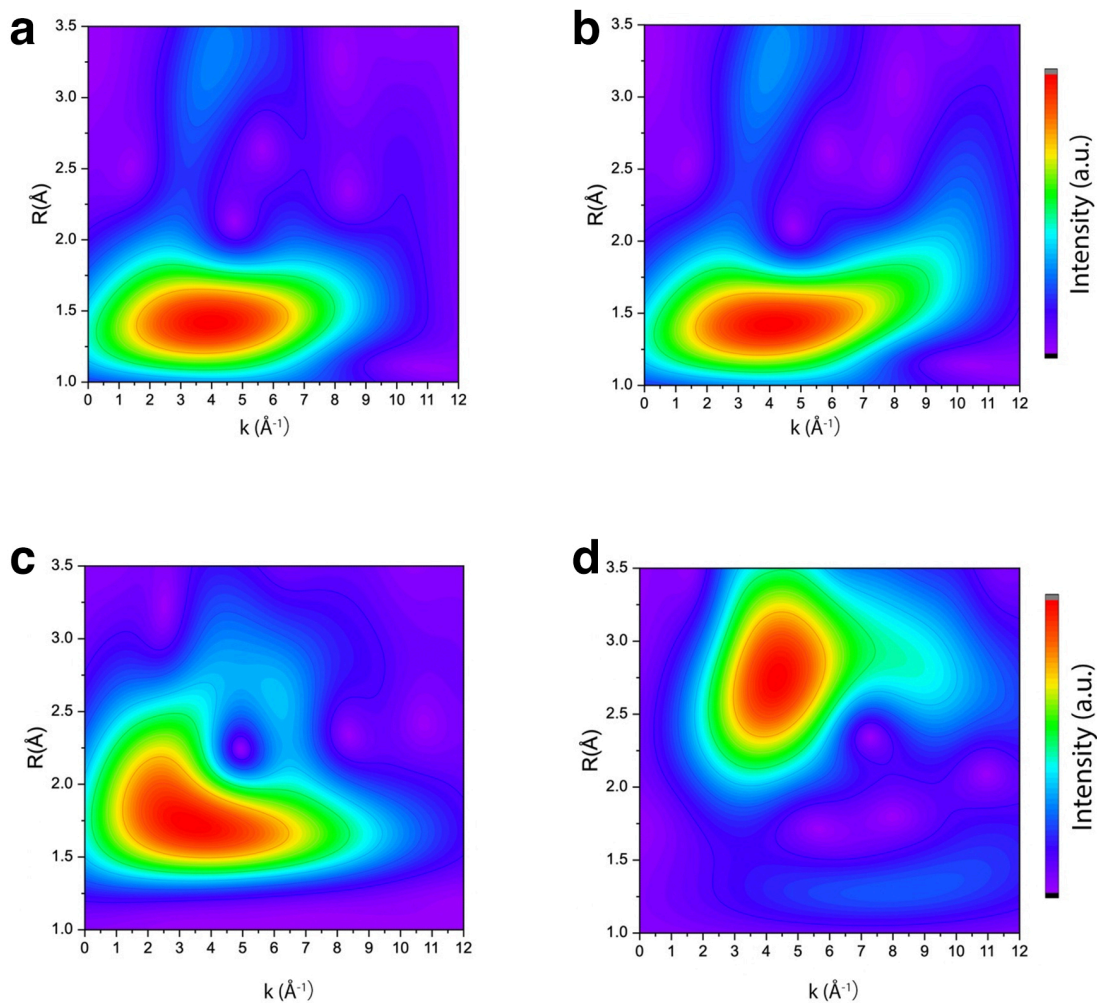


Figure S29. Full-range wavelet transform representation of the EXAFS signal for the $(\text{CsPbI}_3)_{0.25}(\text{agZIF-62})_{0.75}$ composites. (a) Zn and (c) Pb represent the sample prior to sintering, and (b) Zn and (d) Pb represent the sample after 350 °C sintering.

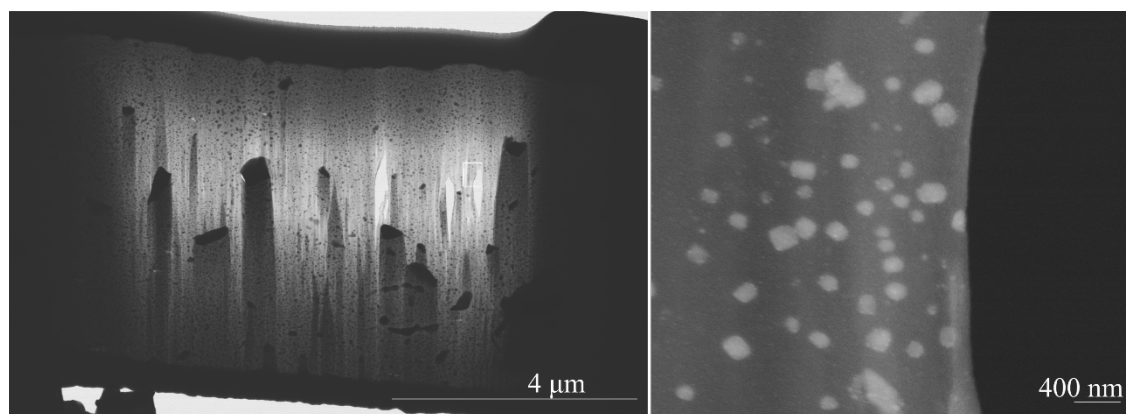


Figure S30. FIB-SEM images for $(\text{CsPbI}_3)_{0.25}(\text{agZIF-62})_{0.75}$ composites sintering 350 °C.

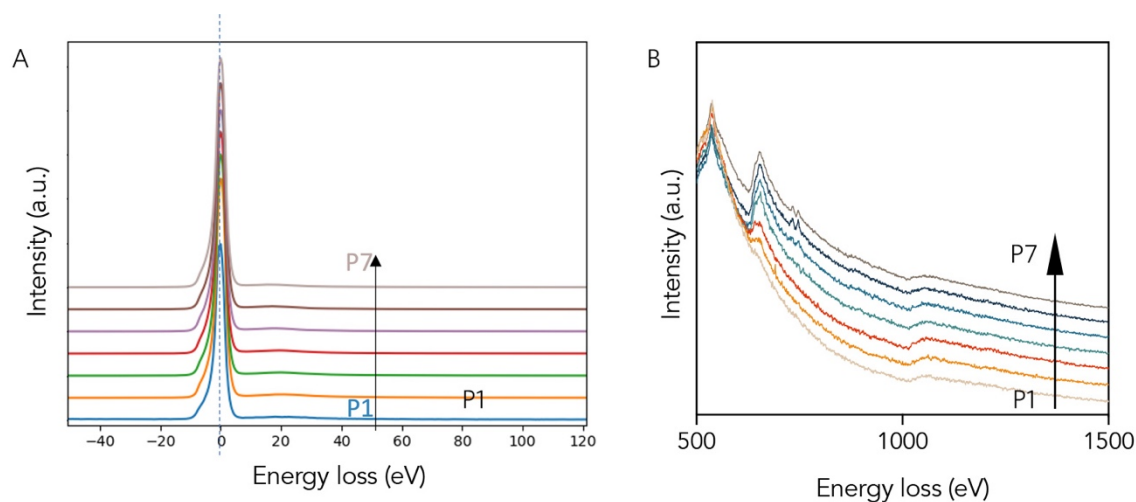


Figure S31. Data processing to for the TEM-EELS results of $(\text{CsPbI}_3)_{0.1}(\text{agZIF-62})_{0.9}$ composites sintered at 350 °C. (A) Zero loss peak: normalised to total low loss scattering (plot with Y-offsets) and (B) Core loss: Normalised to total core loss scattering (plot with Y-offsets)

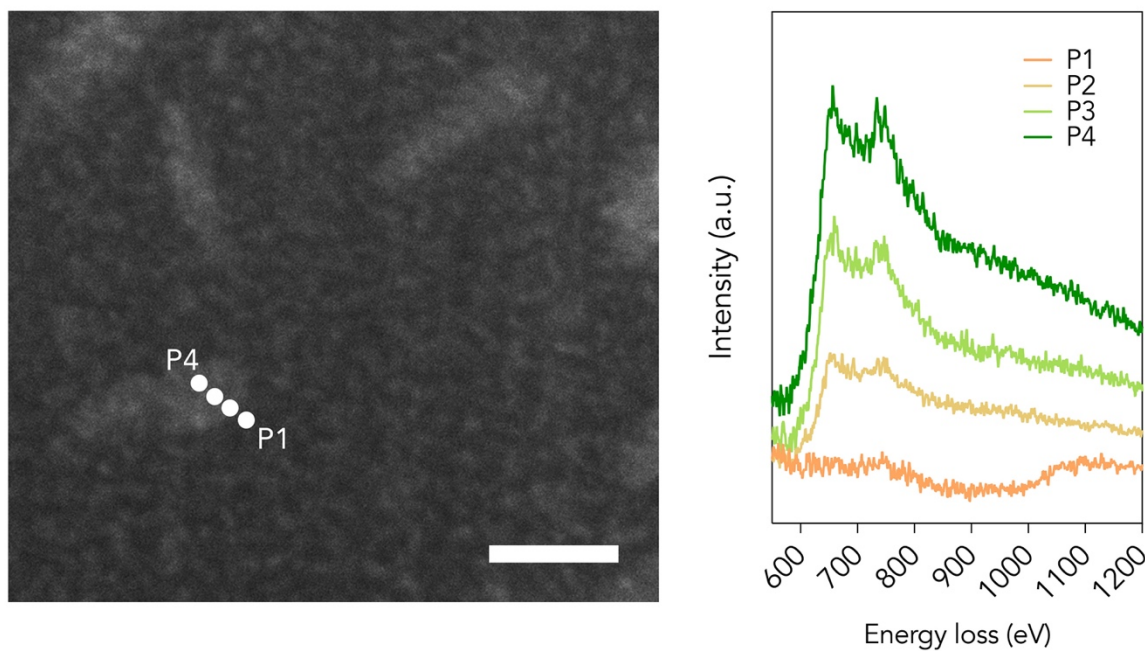


Figure S32. (A) Bright field STEM image of $(\text{CsPbI}_3)_{0.1}(\text{agZIF-62})_{0.9}$ composites sintered at 275 °C. Scale bar, 50 nm. (B) EELS spectrum acquired from the marked points shown in TEM image.

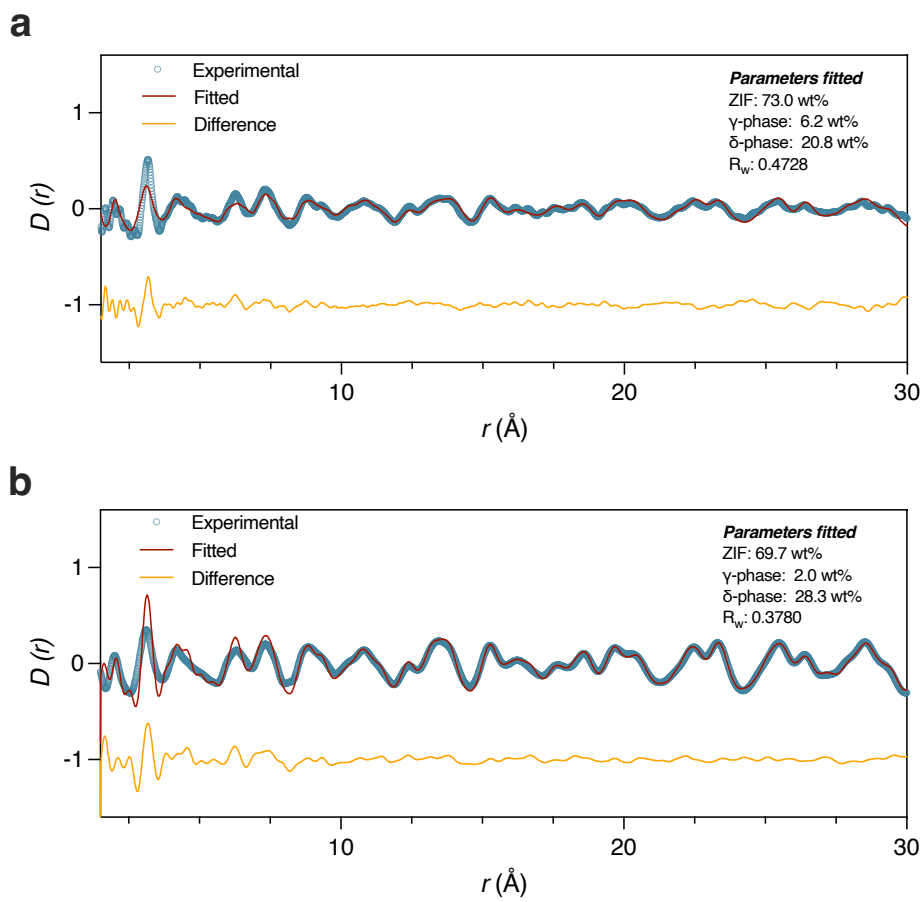


Figure S33. Atomic pair distribution functions for $(\text{CsPbI}_3)_{0.40}(\text{a}_g\text{ZIF-62})_{0.60}$ composites sintered at (a) 325 and (b) 350 °C. Pair distribution function $D(r)$ calculated *via* Fourier transform of the X-ray total scattering function.

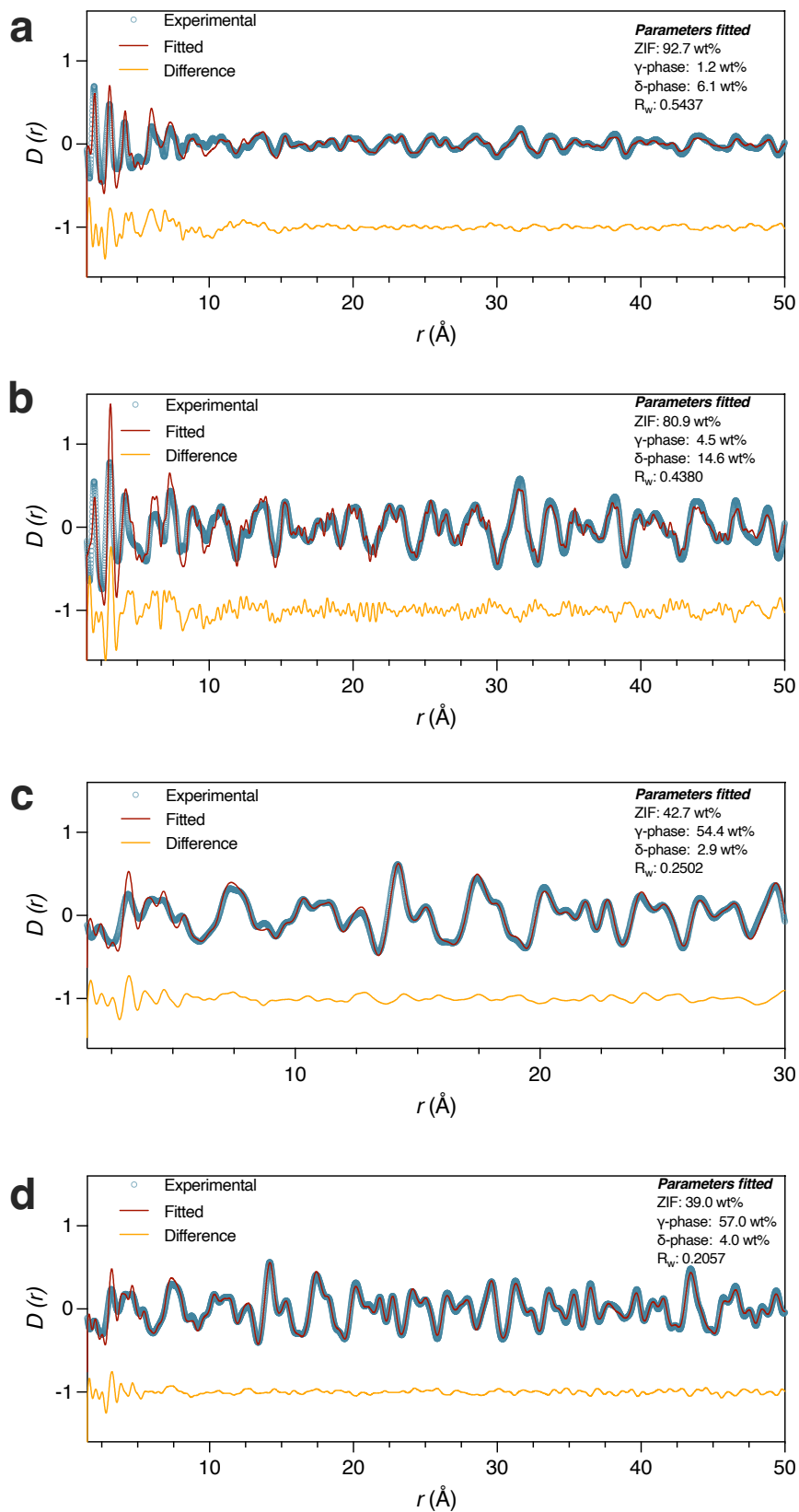


Figure S34. Atomic pair distribution functions for composite sintered at 350 °C with different CsPbI₃ loadings. (a) 10 wt%, (b) 25 wt%, (c) 70 wt% and (d) 85 wt%.

References

- 1 Frentzel-Beyme, L., Kloss, M., Kolodzeiski, P., Pallach, R. & Henke, S. Melttable Mixed-Linker Zeolitic Imidazolate Frameworks and Their Microporous Glasses: From Melting Point Engineering to Selective Hydrocarbon Sorption. *J Am Chem Soc* **141**, 12362-12371 (2019).
- 2 Stéfan van der Walt, S. Chris Colbert & Gael Varoquaux. The NumPy array: a structure for efficient numerical computation.pdf. *Computing in Science and Engineering* **13**, 22-30 (2011).
- 3 Ravel, B. & Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *Journal of synchrotron radiation* **12**, 537-541 (2005).
- 4 Gandara-Loe, J., Bueno-Perez, R., Missyul, A., Fairen-Jimenez, D. & Silvestre-Albero, J. Molecular Sieving Properties of Nanoporous Mixed-Linker ZIF-62: Associated Structural Changes upon Gas Adsorption Application. *ACS Applied Nano Materials* **4**, 3519-3528 (2021).
- 5 Jain, A. *et al.* Commentary: The Materials Project: A materials genome approach to accelerating materials innovation. *APL materials* **1**, 011002 (2013).
- 6 F. de la Peña, E. P., V.T. Fauske, P. Burdet, P. Jokubauskas, M. Nord, T. Ostasevicius, K.E. MacArthur, M. Sarahan, D.N. Johnstone, J. Taillon, J. Lähnemann, V. Migunov, A. Eljarrat, J. Caron, T. Aarholt, S. Mazzucco, M. Walls, T. Slater, F. Winkler, pquinn-dls, B. Martineau, G. Donval, R. McLeod, E.R. Hoglund, I. Alxneit, D. Lundebj, T. Henninen, L.F. Zagonel, A. Garmannslund, hyperspy/hyperspy: HyperSpy v1.5.2,. (2019).
- 7 Ahn, C. C. & Krivanek, O. L. *EELS Atlas: A Reference Guide of Electron Energy Loss Spectra Covering All Stable Elements*. (Gatan, 1983).
- 8 Bonnet, N. *et al.* Nanoscale modification of WS₂ trion emission by its local electromagnetic environment. *Nano Letters* **21**, 10178-10185 (2021).
- 9 Kociak, M. & Zagonel, L. Cathodoluminescence in the scanning transmission electron microscope. *Ultramicroscopy* **176**, 112-131 (2017).
- 10 I. Bressler, B. R. P., A. F. Thünemann. McSAS : software for the retrieval of model parameter distributions from scattering patterns. *Journal of Applied Crystallography* **48**, 962-969 (2015).
- 11 Frisch, M. J. T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; et al. . Gaussian 16, Revision A.03; Gaussian Inc.: Wallingford CT. (2016).
- 12 Rüger, R. F., M.; Trnka, T.; Yakovlev, A.; van Lenthe, E.; Philipsen, P.; van Vuren, T.; Klumpers, B.; Soini, T. AMS 2022.1; SCM, Theoretical Chemistry, Vrije Universiteit: Amsterdam. (2022).
- 13 Stephens, P. J. D., F. J.; Chabalowski, C. F.; Frisch, M. J. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. Phys. Chem.* **98**, 11623–11627 (1994).
- 14 Clark, T. C., J.; Spitznagel, G. W.; Schleyer, P. V. R. Efficient Diffuse Function-Augmented Basis Sets for Anion Calculations. III. The 3-21+G Basis Set for First-Row Elements, Li-F. *J. Comput. Chem.* **4**, 294–301 (1983).
- 15 Grimme, S. B., C.; Shushkov, P. A Robust and Accurate Tight-Binding Quantum Chemical Method for Structures, Vibrational Frequencies, and Noncovalent Interactions of Large Molecular Systems Parametrized for All spd-Block Elements (Z = 1–86). *J. Chem. Theory Comput.* **13**, 1989–2009 (2017).
- 16 Marronnier, A. *et al.* Anharmonicity and Disorder in the Black Phases of Cesium Lead Iodide Used for Stable Inorganic Perovskite Solar Cells. *ACS Nano* **12**, 3477-3486 (2018).
- 17 Hou, J. *et al.* Halogenated Metal-Organic Framework Glasses and Liquids. *J. Am. Chem. Soc.* **142**, 3880-3890 (2020).