Supplementary Information for

Probing Lattice Vibrations of Stabilized CsPbl₃ Polymorphs via Low-Frequency Raman Spectroscopy

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Figure S1. XRD patterns of unconfined CsPbI₃ crystals at t = 0 and 6 min of exposure to air. Initially, the XRD pattern matched that of γ -CsPbI₃. After 6 minutes of exposure to air, peaks associated with δ -CsPbI₃ appeared. Reference powder patterns calculated from single crystal data are provided.¹



Figure S2. Room temperature low-frequency Raman (LFR) spectra of PbI_2 spin coated from a 30 wt% solution in dimethyl sulfoxide at 2000 rpm for 40 s onto an anodized aluminum oxide (AAO) template with average pore diameters of 100 nm in a nitrogen environment, and then dried at 453 K for 10 min before cooling to room temperature.



Figure S3. Scanning electron microscope (SEM) images collected in backscattering mode of γ -CsPbl₃ embedded in the cylindrical nanopores of anodized aluminum oxide templates with 100 nm pore diameters from a A) plan-view and B) cross-sectional view.



Figure S4. Temperature-dependent LFR spectra of γ -CsPbl₃ in the range of 77 – 300 K collected under vacuum.



Figure S5. LFR spectra for A) γ -CsPbl₃ and B) δ -CsPbl₃ nanoconfined in AAO templates at 0 days (solid line) and 120 days (dashed line) of storage in air. For nanoconfined γ -CsPbl₃, a peak at 109 cm⁻¹ appeared in the spectrum collected after 120 days of storage in air, indicating a small degree of transformation of γ -CsPbl₃ into δ -CsPbl₃. It is likely that this transformation occurred at the surfaces of the templates where the crystals are exposed to humidity.

Phase	γ-CsPbl ₃		δ-CsPbl₃	
Parameters	Experimental	Calculated	Experimental	Calculated
Equatorial Pb-I bond length (nm)	0.318, 0.318	0.318, 0.318	0.305,0.341	0.330, 0.320
Axial Pb-I bond length (nm)	0.317, 0.317	0.316, 0.316	0.327, 0.323	0.304, 0.335
Equatorial I-Pb-I bond angle (°)	90.9, 89.1	91.4, 88.6	84.6, 94.6, 95.9	94.9, 83.8, 97.3
Axial Pb-I-Pb bond angle (°)	159.8	161.4	174.7	174.8

Table S1. Bond lengths and angles for experimental and calculated structures.

Table S2. LFR peak locations of γ -CsPbI₃ and corresponding vibrational modes predicted by DFT calculations.

Experimental (cm ⁻¹)	Calculated (cm ⁻¹)	Mode	Supplementary Video
22	26	Skeletal I-Pb-I bending with octahedral tilting	1
37	35	Axial I-Pb-I bending with octahedral bending	2
61	53	Equatorial I-Pb-I bending with octahedral twisting	3

Table S3. LFR peak locations of δ -CsPbI₃ and corresponding vibrational modes predicted by DFT calculations.

Experimental (cm ⁻¹)	Calculated (cm ⁻¹)	Mode	Supplementary Video
21	22	Skeletal I-Pb-I bending with double octahedral tilting	4
36	37	Equatorial I-Pb-I bending with double octahedral axial stretching	5
57	59	I-Pb-I bending and stretching with double octahedral distortion	6
66	67	Axial double octahedral shearing	7
86	86	Equatorial double octahedral shearing	8
109	112	I-Pb-I stretching with double octahedral expansion	9

References

1 C. C. Stoumpos and M. G. Kanatzidis, *Acc. Chem. Res.*, 2015, **48**, 2791–2802.