Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Morphology and Temperature Dependence of a Dual Excitonic Emissive 2D Bromoplumbate Hybrid Perovskite : the Key Role of Crystal Edges

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Table S1. Crystal data and structure refinement for $(C4\text{-}E)_2PbBr_4$

Empirical formula	C12 H28 Br4 N2 O4 Pb
Formula weight	791.19
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Ccm21
Unit cell dimensions	a = 8.2708(8) A alpha = 90 deg.
	b = 34.825(3) A beta = 90 deg.
	c = 8.2264(5) A gamma = 90 deg.
Volume	2369.5(3) A^3
Z, Calculated density	4, 2.218 Mg/m^3
Absorption coefficient	13.881 mm^-1
F(000)	1472
Crystal size	0.335 x 0.093 x 0.055 mm
Theta range for data collection	2.531 to 27.494 deg.
Limiting indices	-10<=h<=10, -36<=k<=45, -10<=l<=10
Reflections collected / unique	12795 / 2687 [R(int) = 0.0547]
Completeness to theta = 27.494	98.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.466 and 0.298
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2687 / 1 / 112
Goodness-of-fit on F^2	1.090
Final R indices [I>2sigma(I)]	R1 = 0.0379, wR2 = 0.0632
R indices (all data)	R1 = 0.0660, wR2 = 0.0705
Absolute structure parameter	0.041(17)
Extinction coefficient	n/a
Largest diff. peak and hole	0.890 and -0.893 e.A^-3

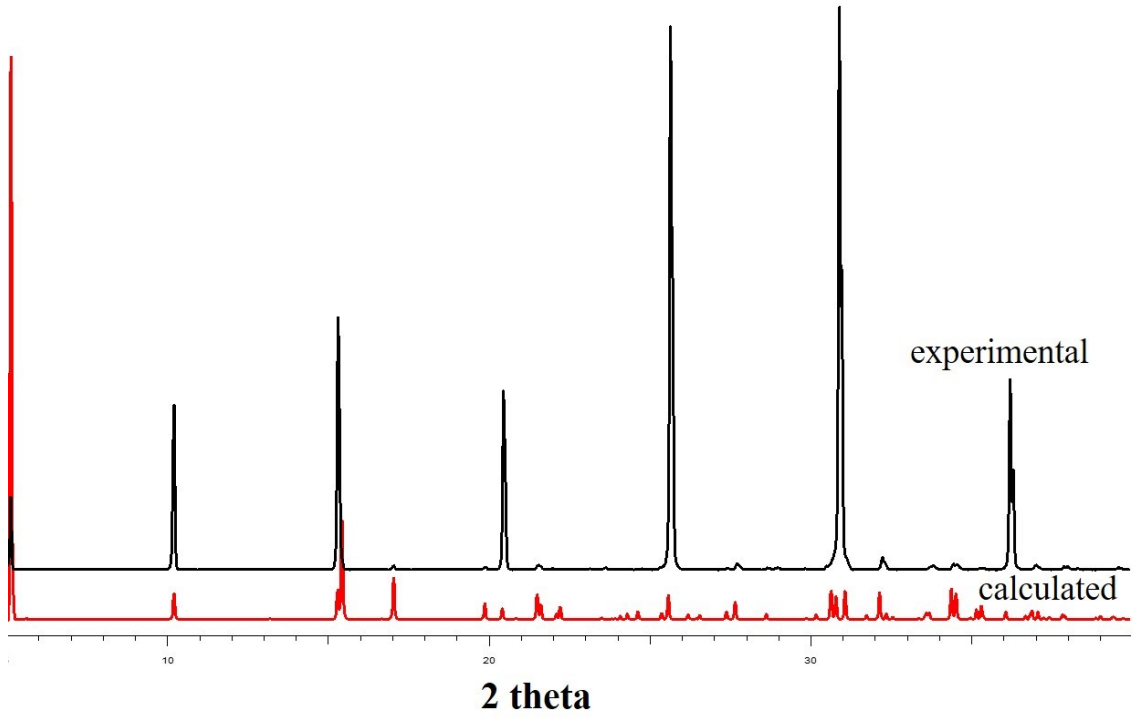


Figure S1. Experimental (crystallized powder) and calculated PXRD patterns of (C4-E)$_2$PbBr$_4$

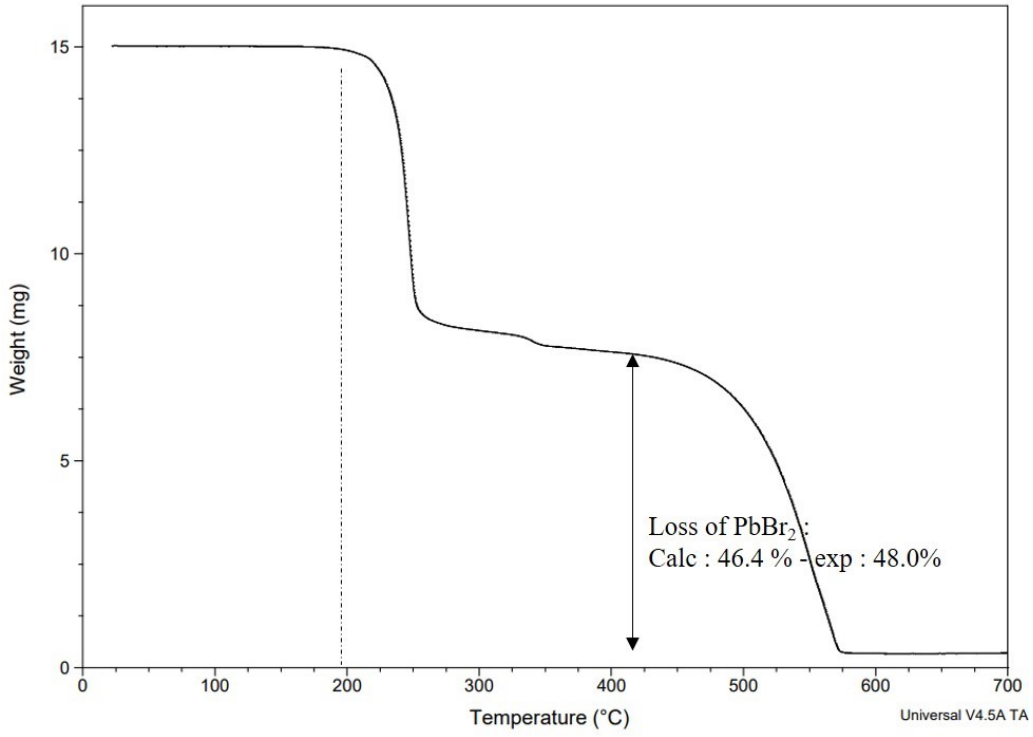


Figure S2. TGA of (C4-E)$_2$PbBr$_4$ showing the decomposition in two main steps: the first one corresponds to the departure of the organic component together with 2 HBr, the last one being the departure of PbBr$_2$ as shown by the 48% weight loss well corresponding to the calculated one.

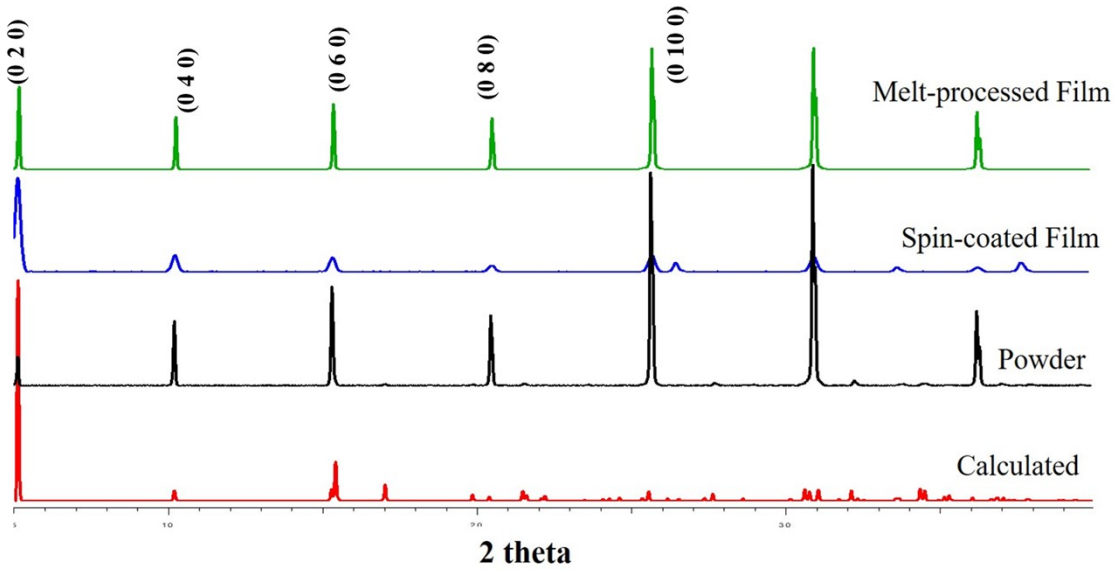
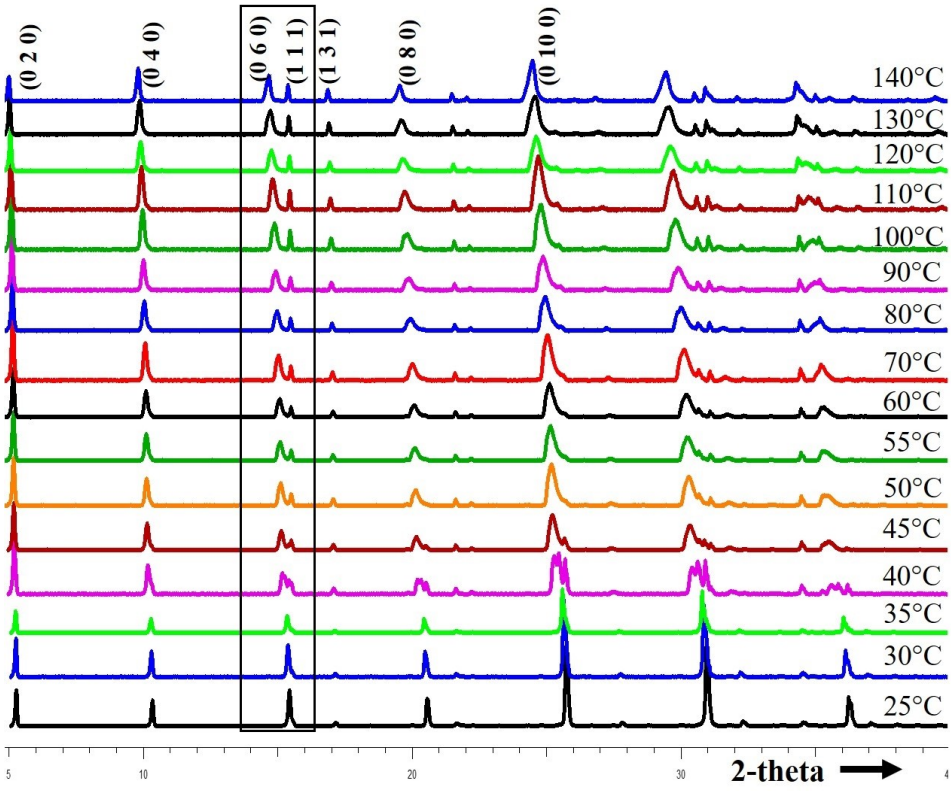


Figure S3. PXRD patterns of crystallized powder, spin-coated thin films and melt processed thin film of of $(C4\text{-}E)_2PbBr_4$ (indexation of some (h k l) lines in the orthorhombic unit cell a= 8.271 Å, b= 34.825 Å, c= 8.2264 Å)



T°C	*b*
25	34.32
30	34.44
35	34.56
40	34.69
45	34.85
50	34.97
60	35.20
70	35.30
80	35.40
90	35.49
100	35.60
110	35.75
120	35.88
130	36.02
140	36.21

Figure S4. PXRD Thermodiffractometry of $(C4\text{-}E)_2PbBr_4$ in the 25-140°C range. The black rectangle shows the splitting of (0 6 0) and (1 1 1) lines along with the temperature (indexation of some (h k l) lines in the RT orthorhombic unit cell a= 8.271 Å, b= 34.825 Å, c= 8.2264 Å). Right part : b unit cell parameter calculated from the position of (0k0) lines in the temperature range 25-140°C.

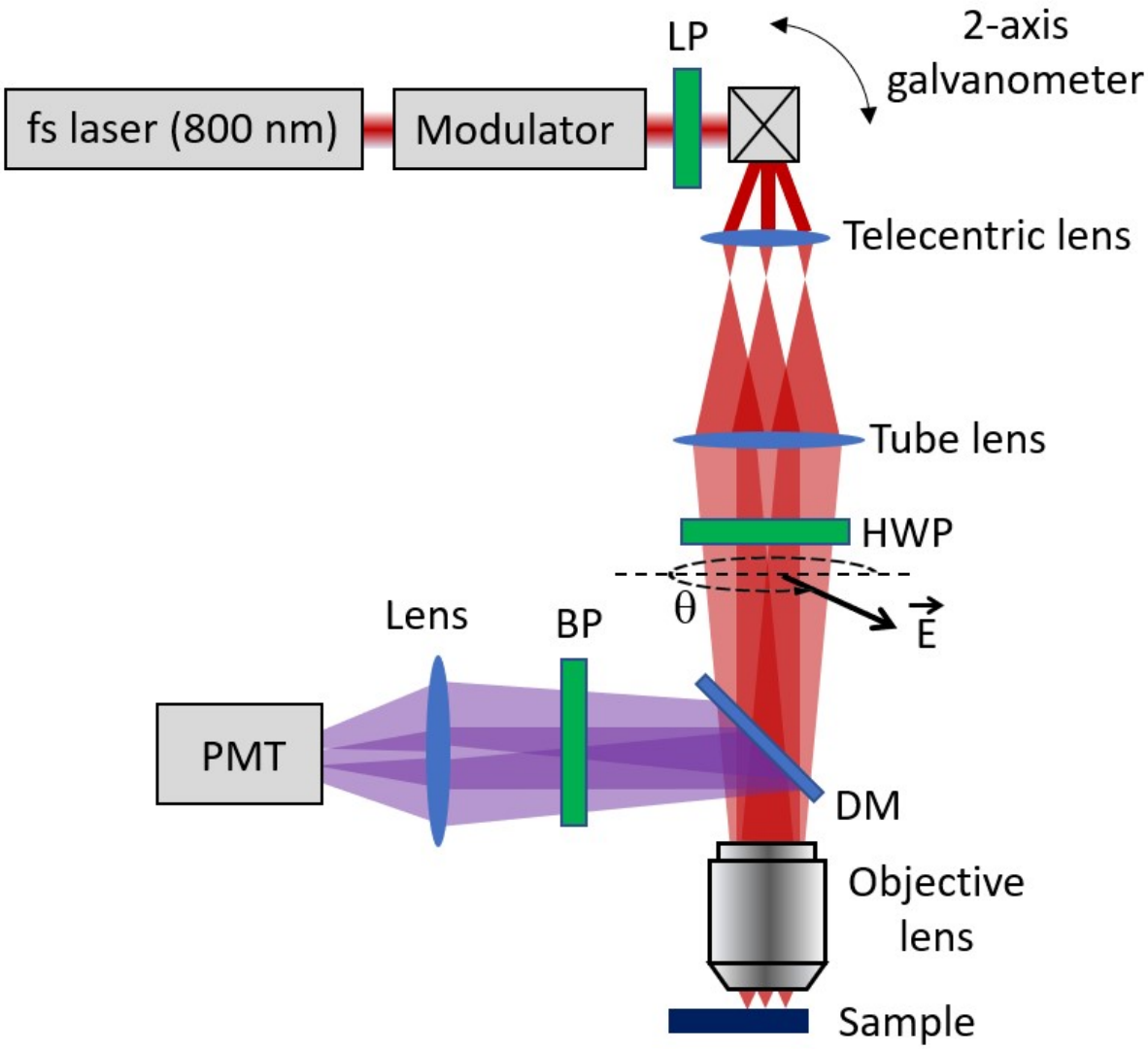


Figure S5 Schematic of the second harmonic generation (SHG) measurements. The experiments were carried out by a commercial microscope (IX-71, Olympus). A linear polarized (LP) beam from a Ti-sapphire femtosecond oscillator system (Tsunami, Spectra-Physics, 800 nm, 10 fs and 80 MHz) was focused by a 20X objective. The reflected SHG signal is collected with the same objective and directed to a fast photomultiplier (PMT). A Dichroic Mirror (DM) is used to reflect short wavelength and a bandpass filter (BP) was placed in front of the PMT to keep only the SHG spectrum. A half-wave plate (HWP) was used to control the polarization direction of the laser. The sample were scanned by a fast 2-axis galvanometer system.

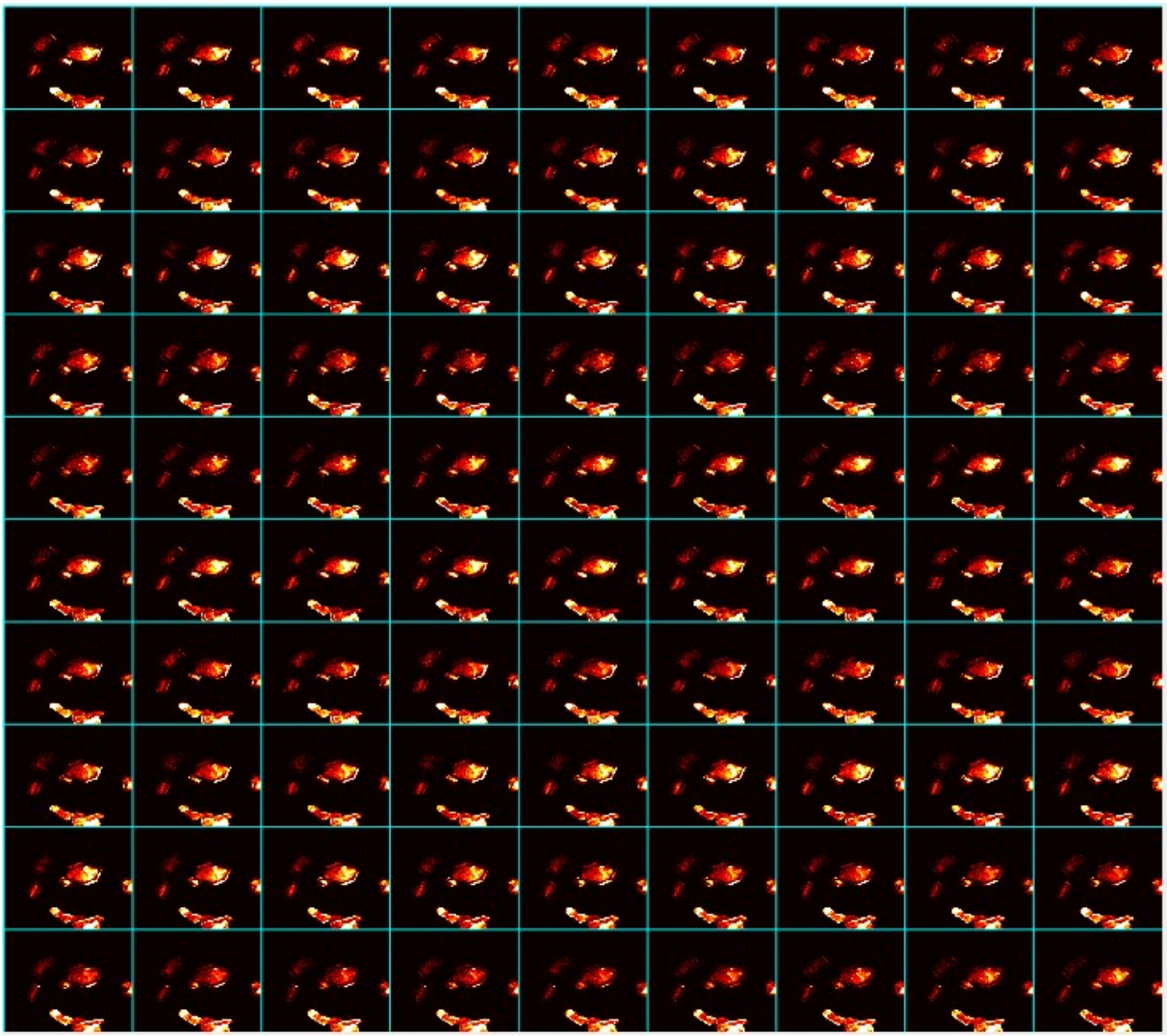


Figure S6 90 SHG images obtained by 360° rotation of laser polarization angle with a step of 4°. The peak intensity SHG image is obtained by taking the maximum value for each pixel for all images.

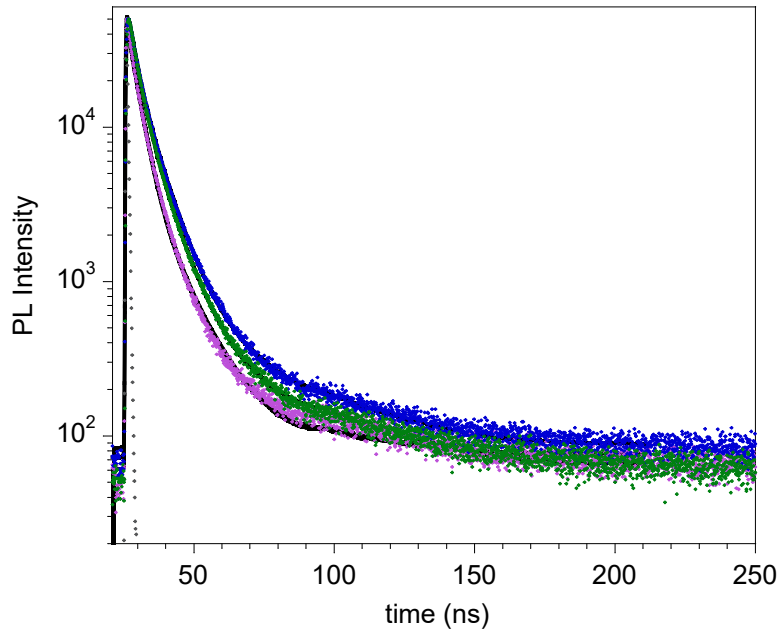


Figure S7 PL decay of $(C4\text{-}E)_2PbBr_4$ crystalline powders. Excitation at 300 nm, emission at 388nm (pink diamonds), 410nm (blue diamonds) and 540nm (green diamonds). Prompt (black squares). Solid lines are three exponential fits (388nm: τ_{av}=4.90ns t_1= 8.225438E-11 sec (0.92); t_2= 3.626906E-09 sec (0.07); t_3= 1.169675E-08 sec (0.01) χ^2= 3.173268. 410nm: τ_{av}=7.43ns t_1= 2.554528E-09 sec (0.54); t_2= 6.946813E-09 sec (0.44); t_3= 2.390131E-08 sec (0.02) χ^2= 1.767013. 540nm: τ_{av}=6.82ns t_1= 2.900886E-09 sec (0.66); t_2= 7.364486E-09 sec (0.33); t_3= 2.557564E-08 sec (0.01) χ^2= 1.325964.

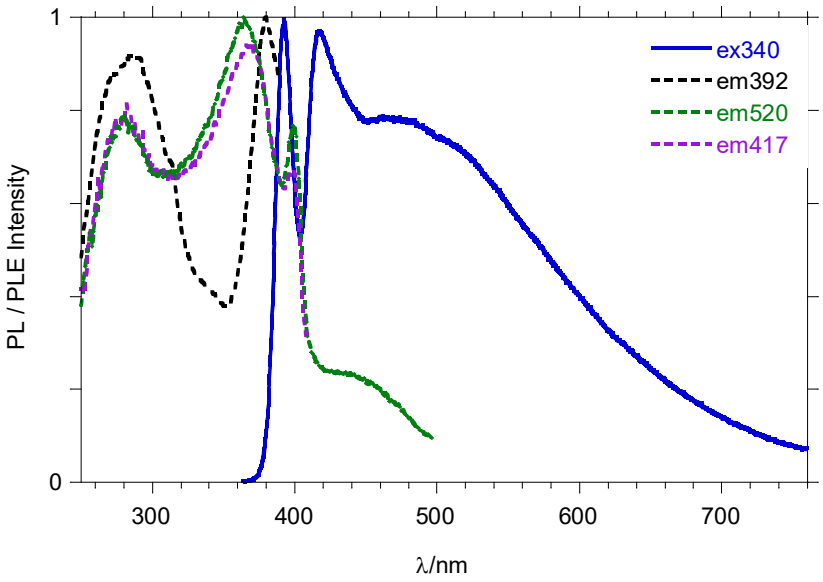


Figure S8. PL and PLE of spectra of $(C4\text{-}E)_2PbBr_4$ film from melt. Excitation 370nm (blue solid line), emissions at 392 nm (black dashed line), 417nm (pink dashed line), 520nm (green dashed line). The PL excitation profile of the BB emission is similar to that of the LE peak.

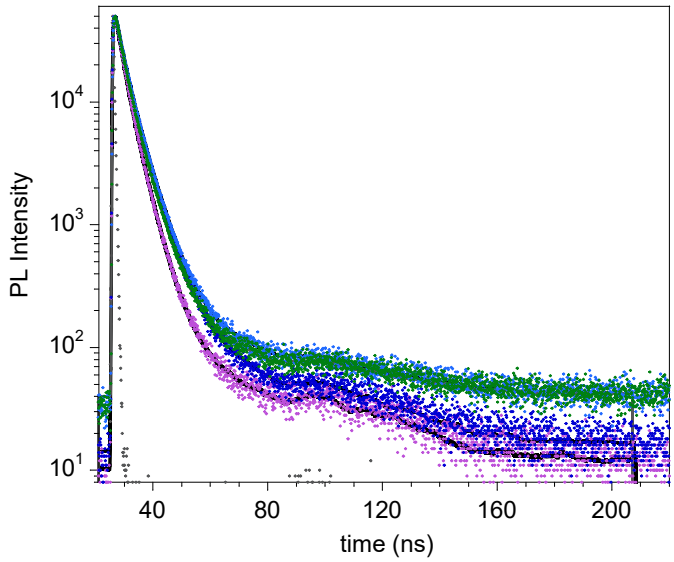


Figure S9 PL decay of $(C4\text{-}E)_2PbBr_4$ film from melt. Excitation at 300 nm. Thin area of the film, emission at 388nm (pink diamonds); Thick area of the film, emission at 388nm (blue diamonds), 415nm (light blue diamonds) and 540nm (green diamonds). Prompt (black squares). Solid lines are three exponential fits. (thin area, 388nm: τ_{av}=3.95ns; t_1= 2.010228E-09 sec (0.51); t_2= 4.255784E-09 sec (0.48); t_3= 1.618456E-08 sec (0.01) χ^2= 1.318454. thick area, 388nm: τ_{av}=4.78ns; t_1= 2.077758E-09 sec (0.44); t_2= 4.911436E-09 sec (0.55); t_3= 1.684682E-08 sec (0.01) χ^2= 1.344408; τ_{av}=5.00ns; 415nm: t_1= 2.420755E-09 sec (0.52); t_2= 5.292044E-09 sec (0.48); t_3= 2.115704E-08 sec (0.01) χ^2= 1.220066. 540nm: τ_{av}=4.59ns; t_1= 1.357982E-09 sec (0.56); t_2= 5.042091E-09 sec (0.43); t_3= 1.926709E-08 sec (0.01) χ^2= 1.178522

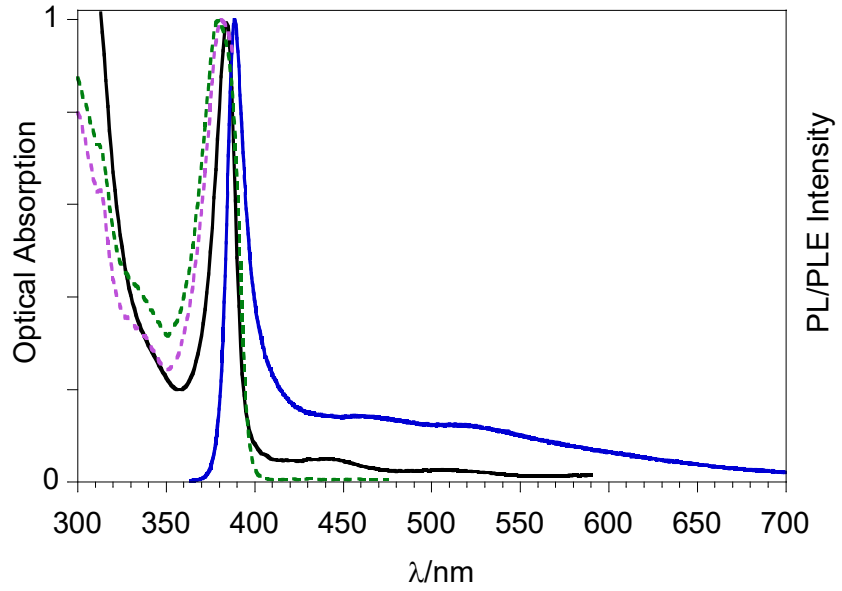


Figure S10. Normalized absorption (black solid line) and PL spectra of $(C4\text{-}E)_2PbBr_4$ film obtained by spin-coating. Excitation at 340 nm (blue solid line), emission at 389nm (dashed pink line) and 540nm (dashed green line). Thin spincoated films display mirror-image absorption-emission spectral profiles. The excitation profiles of BB and HE are similar.

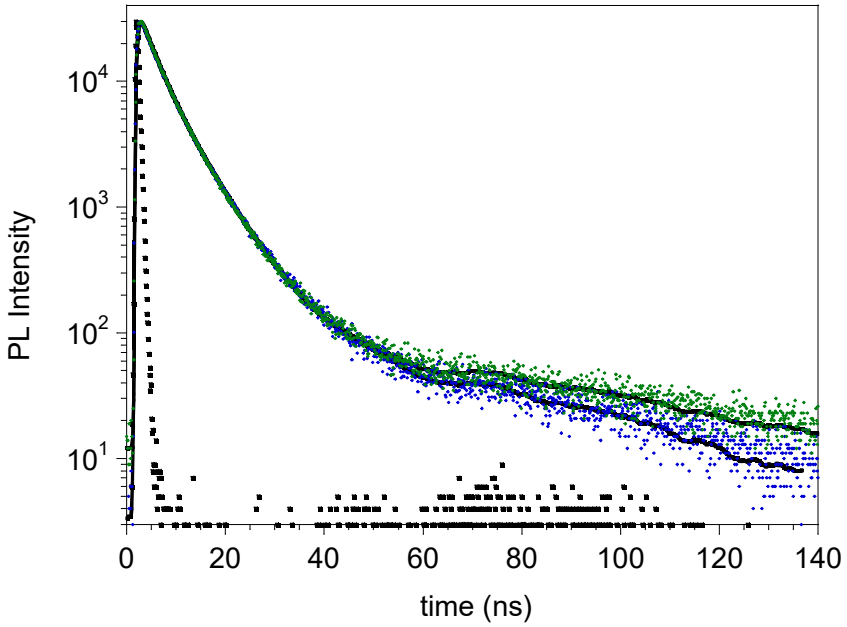


Figure S11. PL decay of $(C4\text{-}E)_2PbBr_4$ spincoated film. Excitation at 300 nm, emission at 388nm (blue diamonds) and 520nm (green diamonds). Prompt (black squares). Solid lines are three exponential fits (388nm: τ_{av}=6.01ns; t_1= 2.800739E-09 sec (0.51); t_2= 6.260507E-09 sec (0.47); t_3= 2.010148E-08 sec (0.01) χ^2= 1.295091. 520nm: τ_{av}=5.95ns; t_1= 3.057265E-09 sec (0.58); t_2= 6.557337E-09 sec (0.42); t_3= 2.351801E-08 sec (0.01) χ^2= 1.175781

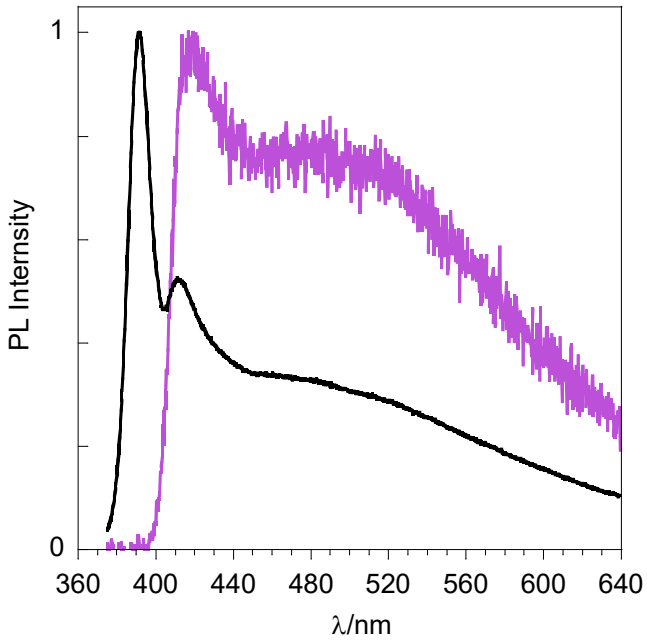


Figure S12 Normalized PL spectra of a $(C4\text{-}E)_2PbBr_4$ film from melt measured in different experimental conditions: by excitation from the back (transmission, pink solid line) or front side (backscattering, black solid line). Excitation at 340nm. The HE peak is completely quenched when the sample is excited from the back, due to re-absorption

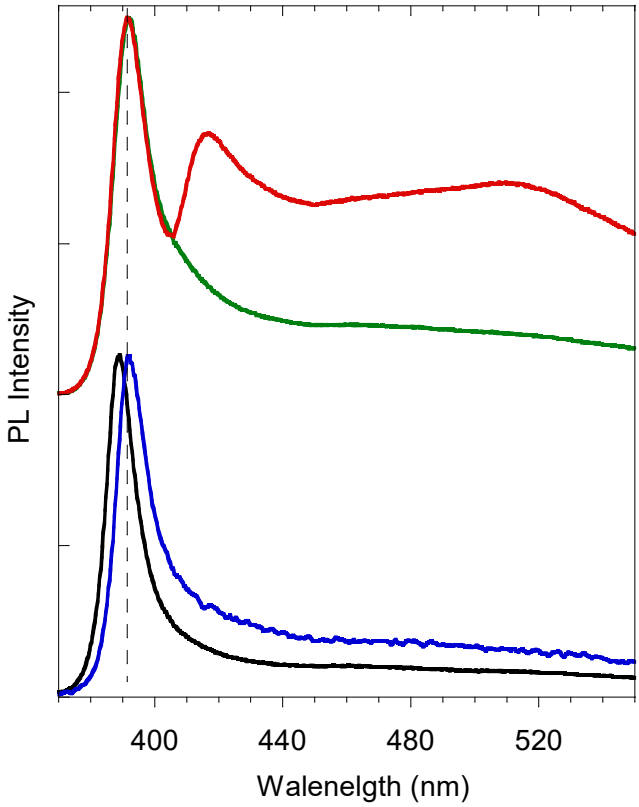


Figure S13 Normalized PL spectra of $(C4\text{-}E)_2PbBr_4$ films obtained from melt (top spectra) and by spincoating from solution (bottom spectra). Film from melt is analysed in transparent homogeneous (green line) region (thickness 3-5μm) and opaque thicker (red line) region (thickness 30-50 μm) . Spincoated film (thickness 30-40nm) is analysed in the surface (black line) and edge (blue line) regions. All the measurements have been obtained in the backscattering geometry, by exciting at 340nm.

The slight red-shift of the emission observed for the spincoated film by exciting at the edge of the films might be due to the higher thickness of the sample (not homogeneous at the substrate edges) that induces a stronger self-absorption, as occurs in thin regions of the film from melt. Differently thick regions of the latter film display the additional LE and a stronger BB emissions.

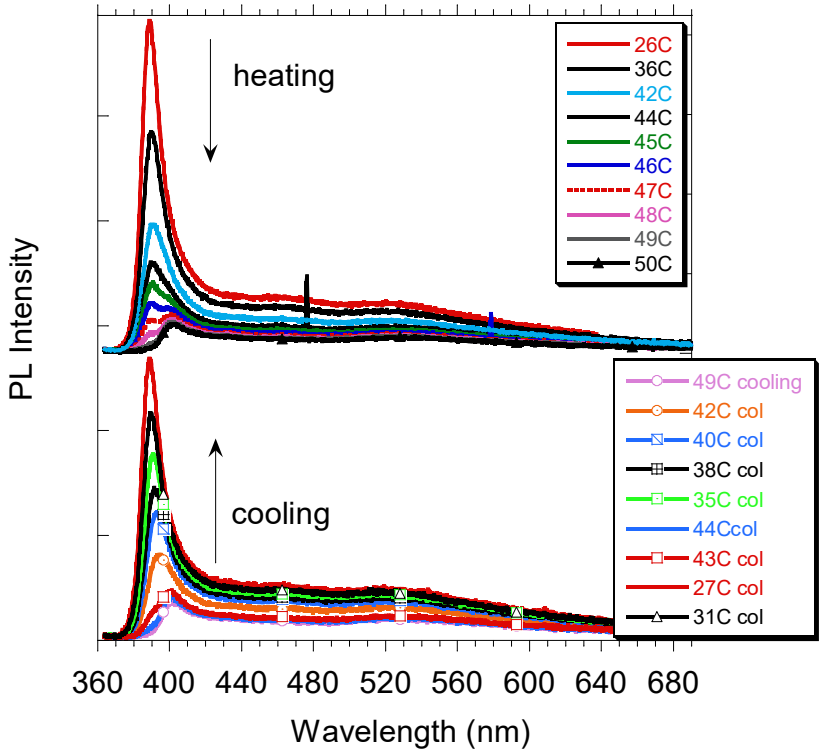


Figure S14 PL spectra of $(C4\text{-}E)_2PbBr_4$ film obtained by spincoating at different temperatures, by heating (upper spectra) or cooling (bottom spectra), excitation at 350nm from the back.

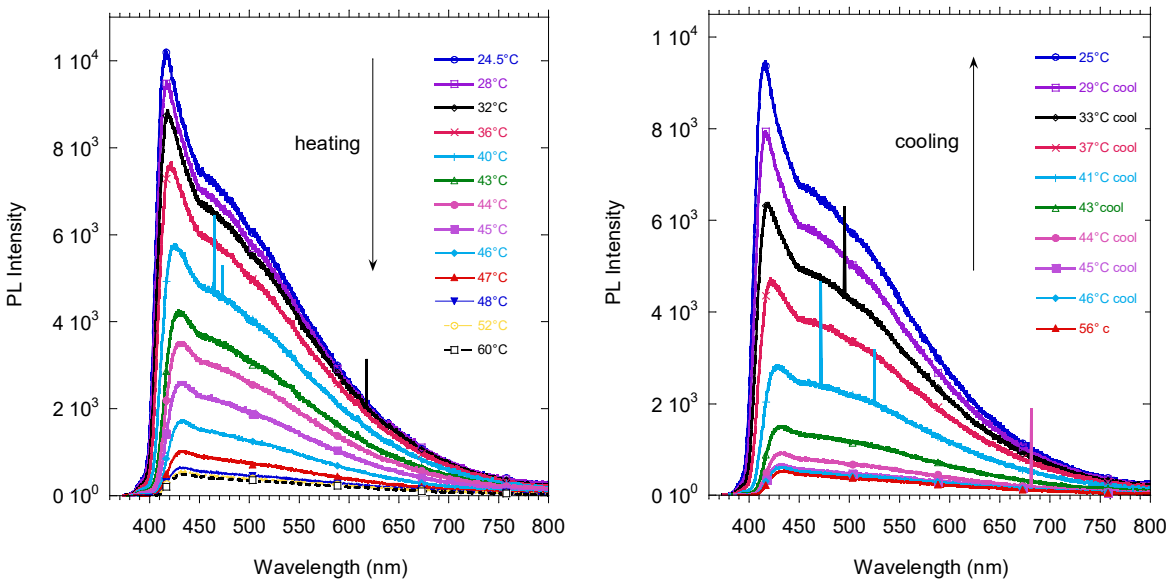


Figure S15 PL spectra of $(C4\text{-}E)_2PbBr_4$ crystalline powders at different temperatures, by heating (left) or cooling (right), excitation at 350nm from the back.

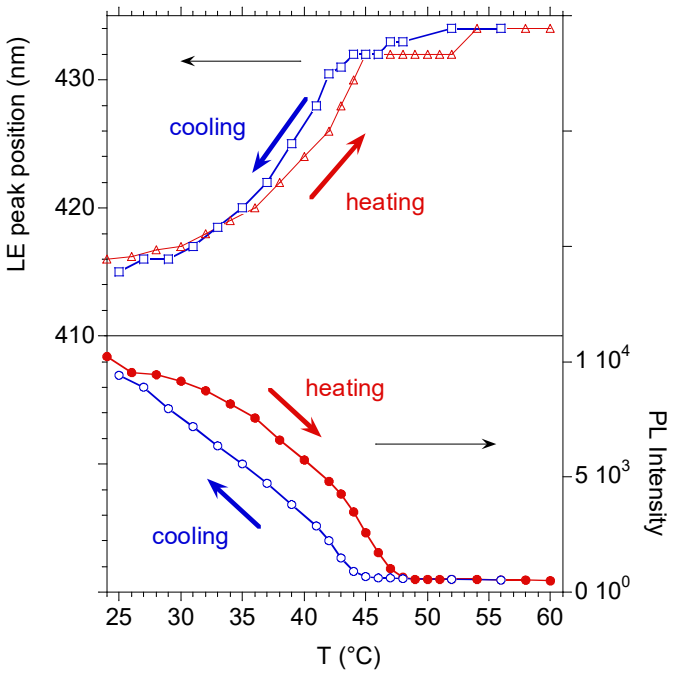


Figure S16 PL LE peak position (top) and LE maximum intensity (bottom) of $(C4\text{-}E)_2PbBr_4$ crystalline powders at different temperatures, by heating (red points) or cooling (blue points), by excitation at 350nm from the back.