

Supporting Information For: Enhanced Amplified Spontaneous Emission in Perovskites using a Flexible Cholesteric Liquid Crystal Reflector

Samuel D. Stranks^{1†}, Simon M. Wood², Konrad Wojciechowski¹, Felix Deschler³, Michael Saliba¹, Hitesh Khandelwal⁴, Jay B. Patel¹, Steve J. Elston², Laura M. Herz¹, Michael B. Johnston¹, Albertus P.H. J. Schenning⁴, Michael G. Debije⁴, Moritz K. Riede¹, Stephen M. Morris^{2*}, Henry J. Snaith^{1*}*

¹Clarendon Laboratory, University of Oxford, Parks Road, Oxford, OX1 3PU, U. K.

²Department of Engineering Science, University of Oxford, Parks Road, Oxford, OX1 3PJ, U.K.

³Cavendish Laboratory, University of Cambridge, J J Thomson Avenue, Cambridge CB3 0HE, U. K.

⁴Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, Netherlands

AUTHOR INFORMATION

Corresponding Author

*stranks@mit.edu, *stephen.morris@eng.ox.ac.uk, *h.snaith1@physics.ox.ac.uk

Present Addresses

†Research Laboratory of Electronics, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA, 02139, U.S.A.

S1. Materials and Methods

Device Stack Fabrication.

Preparation of CLC reflectors: First, polyimide glass substrates were prepared as follows. Glass substrates were cleaned by sonication in ethanol for 30 minutes. Substrates were treated with UV-ozone (Ultra Violet Products, PR-100) for 20 minutes. The polyimide solution was spin-coated on the clean glass plates at 5000 rpm for 30 seconds. After curing at 180°C for 45 min, the polyimide plates were rubbed on velvet cloth to obtain the alignment layer.

For the 50% reflectors, liquid crystal RM-257 (94.8 wt%, Merck), chiral dopant LC-765 (3.2 wt%, BASF), photoinitiator Irgacure 651 (1 wt%, Ciba Specialty Chemicals Ltd) and surfactant 2-(n-ethylperfluoro-octanesulfonamido)-ethyl methacrylate (1 wt%, Acrose Organics) were dissolved in 1.1 wt% of xylene and stirred for one hour at 40°C. The mixture was spin-coated on the rubbed polyimide glass plates at 1000 rpm for 30 seconds. Thereafter, it was polymerised by illuminating with UV light (7.5 mW/cm²) for 5 minutes. The thickness of the polymer CLC layer was found to be $\sim 7 \pm 1$ μm using interferometry measurements.

For the 80% reflectors, liquid crystal LC-242 (94.8 wt%, BASF), chiral dopant LC-756 (3.2 wt%, BASF), photoinitiator Irgacure 651 (1 wt%, Ciba Specialty Chemicals Ltd) and surfactant 2-(n-ethylperfluoro-octanesulfonamido)-ethyl methacrylate (1 wt%, Acrose Organics) were dissolved in 0.75 wt% of xylene and stirred for one hour at 40°C. The mixture was spin-coated on the rubbed (on velvet cloth) half-wave film at 1000 rpm for 25 seconds. Thereafter, it was polymerised by illuminating with UV light (7.5 mW/cm²) for 5 minutes at 60°C. A similar procedure was followed to spin coat the CLC on the other side of the half-wave film.

Atomic Layer Deposition of Alumina: A compact layer of Al₂O₃ was deposited in a home-made Atomic Layer Deposition (ALD) system. High purity trimethylaluminium (Me₃Al) and water

were used as alumina precursors.¹ Nitrogen was used as a carrier and purging gas, with the flow rate set to 20 sccm and controlled by a mass flow controller. The deposition was carried out at 102 °C, base pressure of 0.3 mbar and growth rate of 1.07 Å per cycle. Each cycle consisted of 5 seconds of precursor dose and 20 seconds of purging, with Me₃Al dosed first, followed by H₂O.

Preparation of Perovskite Layer: The perovskite was fabricated using the vapor-assisted solution processing (VASP) technique reported elsewhere.² 50 nm PbI₂ were first thermally evaporated at a base pressure of 3x10⁻⁶ bar onto the substrate using an Edwards 306 evaporator. The substrates were then heated to 100°C for 10 minutes under ambient conditions to remove any residual moisture, and transferred to a nitrogen-filled glovebox where they were heated to 155°C in a small closed dish containing methylammonium iodide (MAI) powder for 3 hours to convert the PbI₂ into perovskite. The substrates were then washed with isopropanol and heated at 100°C for a further 30 minutes in the glovebox. PMMA (10 mg/ml in chlorobenzene) was then spin-coated on top of the perovskite under ambient conditions at 700 rpm to achieve a ~200 nm thin layer. Finally, the gold back reflector (~75 nm) was evaporated at ~10⁻⁶ bar using a Nano36 evaporator.

For the flexible substrates, the device stack was manufactured as follows, where the flexible substrates was attached to a glass slide for processing. First, PMMA (10 mg/ml in chlorobenzene) was spin-coated on the flexible CLC substrate by spin-coating under ambient conditions at 2000 rpm. The perovskite was then deposited by dual-source co-evaporation, whereby lead chloride (PbCl₂) and MAI were deposited simultaneously onto the CLC/PMMA substrates under high vacuum.^{3,4} 500 mg of MAI and 100 mg of PbCl₂ were loaded into separate crucibles and the substrate was mounted on a holder above the sources. The volatile impurities were then removed by heating the two crucibles above the desired deposition temperatures under high vacuum (10⁻⁵ mbar) for 5 minutes. Key deposition parameters such as the deposition rates

and duration for the two sources were set in guidance with the previously optimized conditions for best performance of the material in solar cells.³ This includes using a MAI:PbCl₂ molar ratio of 4:1 and deposition rates of 8 Å/s for MAI (crucible temperature of ~116°C) and 1.3 Å/s for PbCl₂ (crucible temperature of ~320°C), maintained for 87 minutes. The substrate holder was kept at 21°C and was rotated to ensure a uniform coating while the film was deposited on the substrate. The perovskite films were then fully crystallized in a nitrogen-filled glove box by annealing at 100°C for 60 min, with a final film thickness of ~300 nm. The device stack was finished with a spin-coated layer of PMMA (10mg/ml in chlorobenzene; 2000 rpm under ambient conditions) on top of the perovskite and a gold back reflector deposited by evaporation as described above.

Characterization

Characterization was carried out under ambient conditions unless specified otherwise. Steady-state transmission spectra were acquired with a Varian Cary 300 UV/Vis spectrophotometer. Scanning electron microscope (SEM) images were acquired using a field emission SEM (Hitachi S-4300). Sample thicknesses were measured using a combination of SEM images and a Veeco Dektak 150 surface profilometer.

Photoluminescence quantum efficiency (PLQE) values were determined using a 532 nm CW laser excitation source (Suwtech LDC-800, ~200 mW/cm² excitation intensity) to illuminate a sample in an integrating sphere (Oriel Instruments 70682NS), and the laser scatter and PL collected using a fiber-coupled spectrometer (Ocean Optics MayaPro). The spectral response of the fiber-coupled spectrometer was calibrated using a spectral irradiance standard (Oriel Instruments 63358). PLQE calculations were carried out using established techniques.⁵

Time-resolved PL decays and steady-state spectra were acquired using a time-correlated single photon counting (TCSPC) setup (FluoTime 300, PicoQuant GmbH). Samples were photoexcited using a 507 nm laser head (LDH-P-C-510, PicoQuant GmbH) with pulse duration of 117 ps, a fluence of $\sim 0.03 \mu\text{J}/\text{cm}^2/\text{pulse}$, and a repetition rate of 1MHz. Samples were illuminated with the pulsed light until emission stabilised and steady-state was reached.

The emission properties of the 50% reflector devices (on glass) were tested by pumping with a Nd:YAG laser (EKSPLA, NT340) operating at 530 nm with 4-ns pulses at a repetition rate of 10 Hz. Optimal pumping occurs perpendicular to the sample and this is also the direction of emission (parallel to the PBG), so a dichroic mirror was used to allow pumping and collection in the same direction. The emission was measured with an Ocean Optics MayaPro spectrometer (1.8 nm FWHM resolution) coupled with a 50 μm fiber and a 0.16 numerical aperture collection lens. Low temperature measurements were carried by holding the sample *in vacuo* in an Oxford Instruments OptistatDN cryostat. The flexible 80% reflector substrates were measured by pumping with a laser (CryLaS GmbH 6FTSS355-Q4-S) operating at 532 nm with 5-ns pulses at a repetition rate of 100 Hz and the emission measured using a 600 μm fiber with achromatic collimating lens coupled to a spectrometer (Ocean Optics USB2000+, 1.5 nm FWHM resolution).

The photoluminescence temporal evolution was monitored using a gated intensified CCD camera system (Andor iStar DH740 CCI-010) connected to a grating spectrometer (Andor SR303i). Excitation was performed with femtosecond laser pulses which were generated by a homebuilt setup by second harmonic generation (SHG) in a BBO crystal from the fundamental output (pulse energy 1.55 eV, pulse length 50 fs) of a Ti:Sapphire laser system (Spectra Physics Solstice). The laser pulses generated from the SHG had a photon energy of 2.3 eV, pulse length

~100 fs and fluence as indicated. PL spectra were obtained by measuring the emission from the sample with a constant gate window from zero to 30 ns time delay with respect to the excitation pulse. Temporal evolution of the emission was monitored by acquiring spectra with 6 Hz in free-running mode of the iCCD. For all measurements, the sample was kept in a holder under nitrogen.

Optical Modelling: The data shown in Figure 2b of the main text was obtained by using Berreman's 4x4 Matrix method⁶ to solve Maxwell's equations for anisotropic media for light propagating parallel to the helical axis of the chiral nematic liquid crystal (CLC) so as to determine the transmission spectrum for the following stack:

- CLC (7 microns-thick, pitch, 486 nm, refractive indices of 1.53 and 1.68)
- Al₂O₃ (170 nm-thick, refractive index of 1.75)
- Perovskite (50 nm-thick, refractive index of 2.3)⁷
- PMMA (170 nm-thick, refractive index of 1.5)

We note that we do not include the absorption in the perovskite layer in these calculations.

S2. Low Temperature Emission Measurements

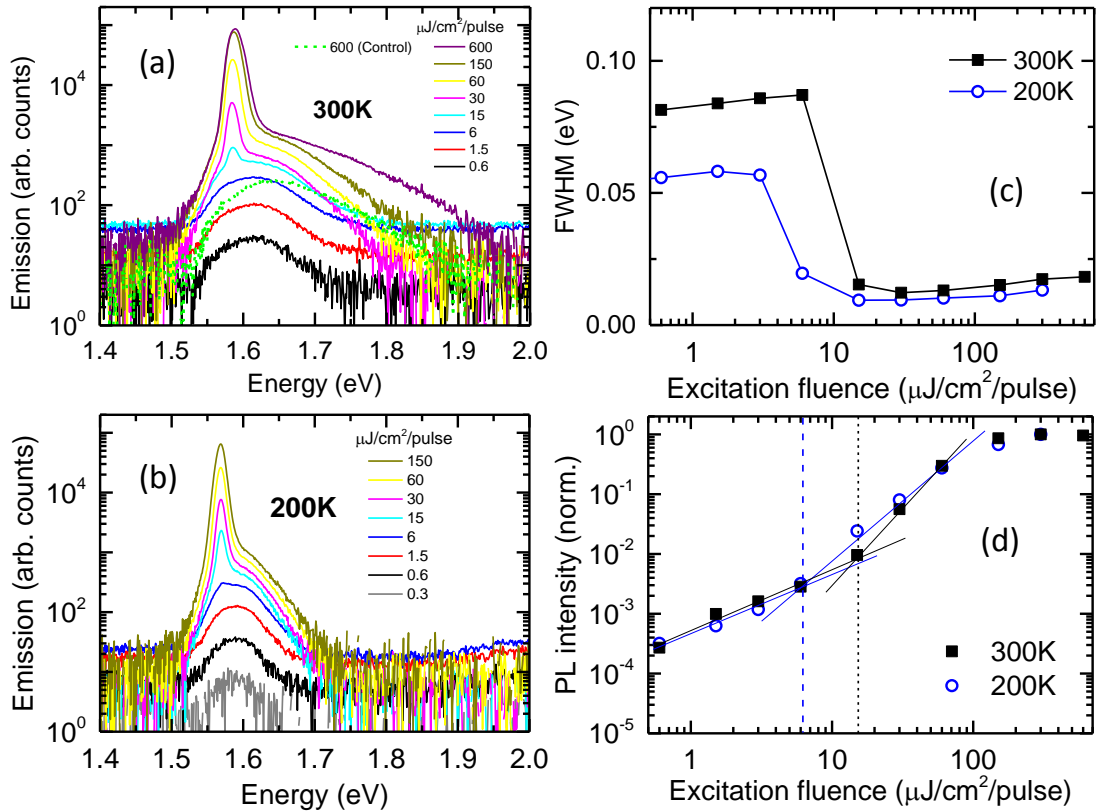


Figure S1. Emission from the device stack using 50% CLC reflectors (glass/CLC/ $\text{Al}_2\text{O}_3/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PMMA}/\text{Au}$) following photo-excitation (530 nm, 4-ns pulses, 10-Hz repetition rate) at a range of excitation fluences at (a) 300 K and (b) 200 K. Emission from the control without the CLC (glass/ $\text{Al}_2\text{O}_3/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PMMA}/\text{Au}$) is also shown for the highest fluence (600 $\mu\text{J}/\text{cm}^2/\text{pulse}$) in (a). Emission (c) FWHM and (d) intensity at each temperature. The extracted ASE threshold fluences are denoted by the blue dashed line for 200 K (6.2 $\mu\text{J}/\text{cm}^2/\text{pulse}$) and the black short-dashed line for 300 K (15.3 $\mu\text{J}/\text{cm}^2/\text{pulse}$). The spectral resolution of the detector setup at the relevant wavelength range was ~ 6 meV (~ 1.8 nm). We note that the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite undergoes a transition from its room temperature tetragonal phase to an orthorhombic phase below at $T \sim 160$ K,⁸⁻¹⁰ so temperatures lower than 160 K may not be useful for comparison.

S3. Preparation and Characterization of the 80% Reflector

The 80% reflector was prepared by spin-coating the CLCs on both sides of a half-wave film. A phase shift of π is introduced by the half wave film between two plane polarized electric field vectors that represent the circularly polarized light. As a result right/left handed circularly polarized light is converted into left/right handed circularly polarized light. On shining unpolarized light, light of the same handedness will be reflected whereas light of the opposite handedness will be transmitted through the CLC layer on top of the half-wave film. The transmitted light from the top CLC layer will change its handedness while passing through the half-wave film and will be further reflected by CLC on the bottom side of the film. Thus the reflection of CLC is enhanced and results in up to ~80% reflection of unpolarized light.^{11, 12}

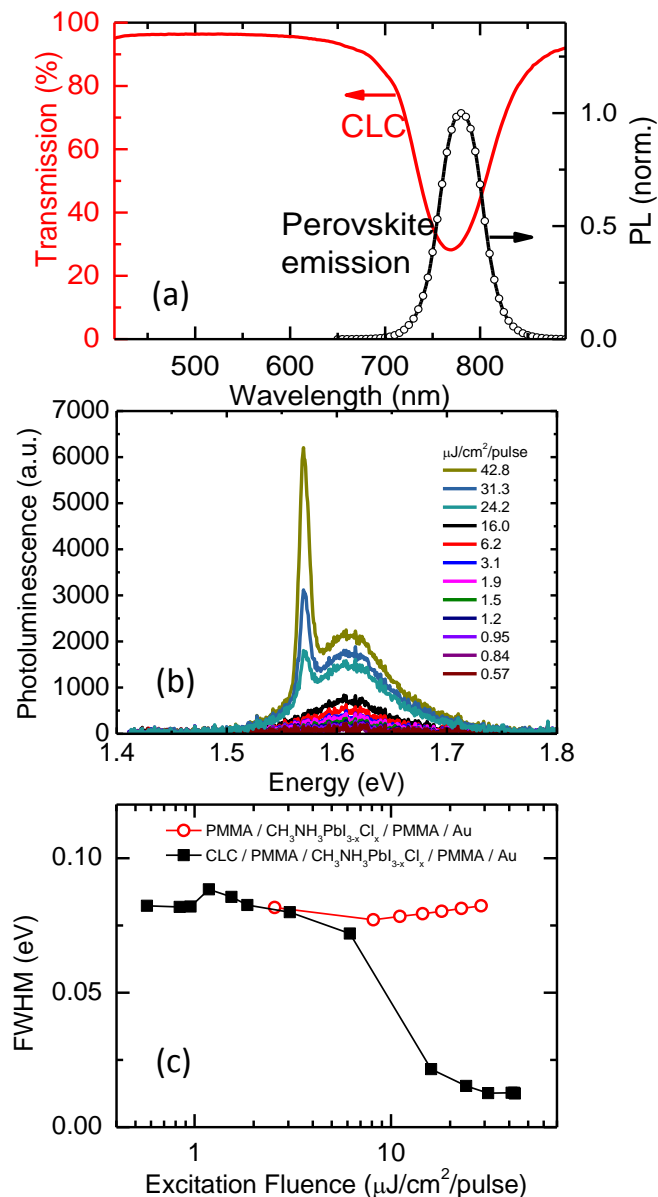


Figure S2. (a) Transmission spectrum of the 80% CLC flexible reflector (red line, left axis) with PL spectrum from the perovskite thin film overlaid (black circles, right axis). (b) Emission from the flexible device stack (flexible wave-plate / CLC / $\text{CH}_3\text{NH}_3\text{PbI}_3$ / PMMA / Au) following photo-excitation (532 nm, 5-ns pulses, 100-Hz repetition rate) at a range of fluences at 300K. (c) Emission FWHM for the perovskite in the device stack with the CLC on the wave-plate (black squares) and without the CLC but on glass (red open circles).

S4. Checking polarization of the output from the stack

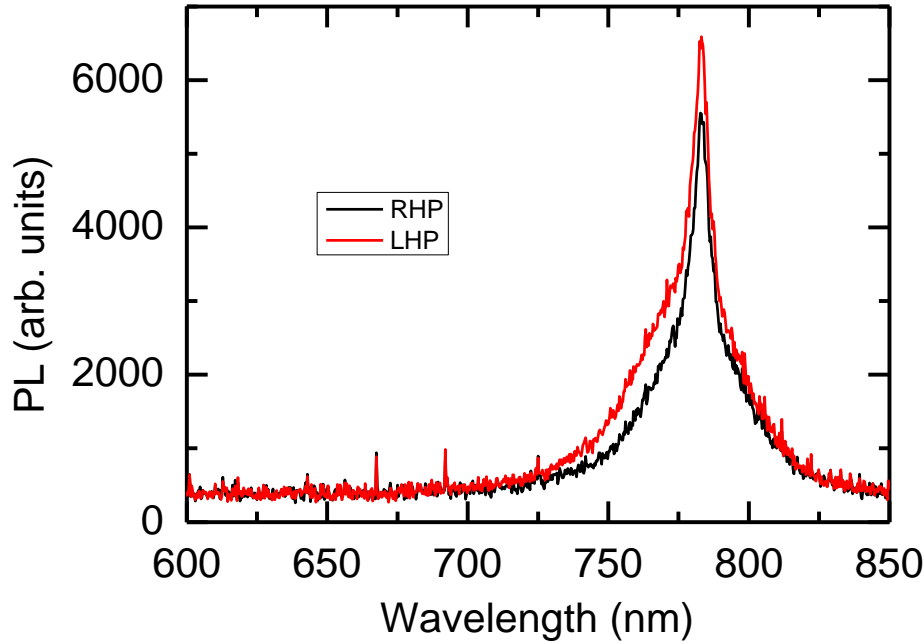


Figure S3. Polarization of the output emission from a CLC stack (CLC / Al₂O₃ 95nm / 200nm perovskite / Al₂O₃ 95nm / Au) as measured using right- (RHP) or left-handed polarizers (LHP). There is only a very small difference in polarization, and we note that the emission is clearly not circularly polarized. The samples were photo-excited at 532 nm with 5-ns pulses, 100-Hz repetition rate and a fluence of 43 $\mu\text{J}/\text{cm}^2/\text{pulse}$.

REFERENCES

1. Ylivaara, O. M. E.; Liu, X. W.; Kilpi, L.; Lyytinen, J.; Schneider, D.; Laitinen, M.; Julin, J.; Ali, S.; Sintonen, S.; Berdova, M.; Haimi, E.; Sajavaara, T.; Ronkainen, H.; Lipsanen, H.; Koskinen, J.; Hannula, S. P.; Puurunen, R. L. *Thin Solid Films* **2014**, 552, 124-135.
2. Chen, Q.; Zhou, H.; Hong, Z.; Luo, S.; Duan, H. S.; Wang, H. H.; Liu, Y.; Li, G.; Yang, Y. *J. Am. Chem. Soc.* **2014**, 136, 622-625.
3. Liu, M.; Johnston, M. B.; Snaith, H. J. *Nature* **2013**, 501, 395-398.
4. Wehrenfennig, C.; Liu, M.; Snaith, H. J.; Johnston, M. B.; Herz, L. M. *Energy & Environmental Science* **2014**, 7, 2269.
5. de Mello, J. C.; Wittmann, H. F.; Friend, R. H. *Adv. Mater.* **1997**, 9, 230-232.
6. Berreman, D. W. *J. Opt. Soc. Am.* **1972**, 62, 502-510.
7. Ball, J. M.; Stranks, S. D.; Hörantner, M. T.; Hüttner, S.; Zhang, W.; Crossland, E. J. W.; Ramirez, I.; Riede, M.; Johnston, M. B.; Friend, R. H.; Snaith, H. J. *Energy Environ. Sci.* **2015**, 8, 602-609.
8. Ishihara, T.; Takahashi, J.; Goto, T. *Phys. Rev. B* **1990**, 42, 11099-11107.
9. Baikie, T.; Fang, Y. N.; Kadro, J. M.; Schreyer, M.; Wei, F. X.; Mhaisalkar, S. G.; Graetzel, M.; White, T. J. *J. Mater. Chem. A* **2013**, 1, 5628-5641.
10. D'Innocenzo, V.; Grancini, G.; Alcocer, M. J.; Kandada, A. R.; Stranks, S. D.; Lee, M. M.; Lanzani, G.; Snaith, H. J.; Petrozza, A. *Nat. Commun.* **2014**, 5, 3586.
11. Makow, D. M. *Appl. Opt.* **1980**, 19, 1274-1277.
12. Khandelwal, H.; Loonen, R. C. G. M.; Hensen, J. L. M.; Schenning, A. P. H. J.; Debije, M. G. *J. Mater. Chem. A* **2014**, 2, 14622-14627.