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# **Circularly Polarized Photoluminescence from** Chiral Perovskite Thin Films at Room Temperature

Daniele Di Nuzzo,\* Linsong Cui, Jake L. Greenfield, Baodan Zhao, Richard H. Friend, and Stefan C. J. Meskers



via easily accessible solution-based techniques. This has allowed tremendous development in optoelectronic applications, primarily solar cells and light-emitting diodes. Allowed by the ease of access to nanostructure, chirality has recently been introduced in semiconducting perovskites as a promising way to obtain advanced control of charge and spin and for developing circularly polarized light sources. Circular polarization of photoluminescence (CPL) is a powerful tool to probe the electronic structure of materials. However, CPL in chiral perovskites has been



scarcely investigated, and a study in bulk thin films and at room temperature is still missing. In this work, we fabricate bromine-based chiral perovskites by using a bulky chiral organic cation mixed with CsBr, resulting in Ruddlesden-Popper perovskite thin films. We measure CPL on these films at room temperature and, by using unpolarized photoexcitation, we record a degree of circular polarization of photoluminescence in the order of  $10^{-3}$  and provide a full spectral characterization of CPL. Our results show that chirality is imparted on the electronic structure of the semiconductor; we hypothesize that the excess in polarization of emitted light originates from the charge in the photogenerated Wannier exciton describing an orbit in a symmetry-broken environment. Furthermore, our experiments allow the direct measurement of the magnetic dipole moment of the optical transition, which we estimate to be  $\geq 0.1 \ \mu_{B}$ . Finally, we discuss the implications of our findings on the development of chiral semiconducting perovskites as sources of circularly polarized light.

**KEYWORDS:** hybrid perovskites, chirality, chiral semiconductors, circularly polarized luminescence, chiroptical spectroscopy, magnetic dipole moment, excitons

ybrid organic-inorganic perovskites allow for easily accessible, yet complex nanoscale design of semiconducting thin films, offering synthesis via solutionprocessing and a vast choice of organic and inorganic precursors. High crystallinity and low density of deep electronic traps<sup>1</sup> result in high charge-carrier mobility and photoluminescence quantum efficiency; these properties have contributed to spur a large amount of research toward application in photovoltaics, light-emitting sources, and transistors.<sup>2,3</sup>

At the same time, the ease and freedom of nanostructural design open future possibilities for semiconductor science. Inversion-symmetry breaking has recently attracted interest for the control of charge and spin in condensed matter systems, with relevance to future energy-saving information technology and for enabling quantum-computing in the solid state at room temperature.4-7 Structurally chiral materials are a possible approach to exploit inversion-symmetry breaking; however, only a limited number of these materials are available, and they are not easily tailored.<sup>8,9</sup>

Owing to the large variety of chiral organic ligands easily accessible via organic chemistry, organic-inorganic perovskites may represent a promising and largely unexplored playground for realizing structurally chiral materials and for exploring chirality in semiconductors. Inversion-symmetry breaking and Rashba spin-orbit coupling have been recently studied in

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Figure 1. (a) Chemical structure of the chiral organic ligand NEA, showing the (S) and (R) enantiomers. (b) UV-vis absorbance spectrum of a perovskite film in its (R)-version ("(R)-film") on a glass substrate, fabricated using the precursors PbBr<sub>2</sub>:CsBr:(R)-NEABr in a 1:1:2 molar ratio. (c) SEM image of a (R)-film sample deposited on ITO.



Figure 2. (a) Measurement of circular dichroism on (S)- and (R)-film samples (red and blue, respectively), showing the dissymmetry factor  $g_{abs}$  as a function of wavelength. (b) Top, circularly polarized photoluminescence on the same samples used in panel a, measured by exciting the films with unpolarized light at 365 nm with a Hg lamp. The dissymmetry factor  $g_{PL}$  is reported. Each data point and its corresponding error bar were obtained by repeating the measurement 20 times at each wavelength. See the Methods section and Figure S3 in the Supporting Information for more information on the measurement. (b) Bottom, unpolarized photoluminescence from the same (R)-film sample used in panels a and b, measured in an integrating sphere, by exciting with an unpolarized continuous-wave laser source at 405 nm, with a power of 8 mW. All the measurements were performed at room temperature and in air.

semiconducting perovskites,  $^{10-12}$  and chiral perovskites have been theoretically and experimentally investigated.  $^{12-17}$ 

Chiroptical spectroscopy is a powerful way to investigate the electronic properties of chiral systems. Circular dichroism (CD) and circularly polarized luminescence (CPL) are complementary tools to probe chirality in the ground state and excited state, respectively.<sup>18,19</sup> In particular, these chiroptical methods provide information on the magnetic transition dipole moment of an optical transition, a quantity that is otherwise practically inaccessible because of the inherent weakness of magnetic dipole transitions. CD and CPL have been observed on chiral semiconducting perovskites.<sup>12–14,20</sup> However, CPL has been reported so far only at cryogenic temperatures<sup>12,14</sup> or in nanocrystal dispersions.<sup>21,22</sup> Other studies have investigated CPL in achiral perovskites by

using selectively polarized photoexcitation.<sup>23,24</sup> CPL on chiral perovskite thin films at room temperature and using unpolarized photoexcitation has yet to be reported. This is partially due to the experimental difficulties inherent with CPL measurements.<sup>25</sup> Such characterization is needed to explore the effect of chirality on the electronic structure of perovskites.

Here we employ a standard, but sensitive, technique to accurately measure CPL on chiral perovskite films, and we report CPL measured at room temperature on solution-deposited bulk films of chiral perovskites. We use a chiral cation derived from 1-(1-naphthyl)ethylamine, in the enantiomerically pure forms *S* and *R* (*S/R*-NEA); we mix *S/R*-NEABr with CsBr and PbBr<sub>2</sub> to obtain Ruddlesden–Popper perovskite films composed of cubic nanocrystals (with side lengths of 15–30 nm). In these films, we measure CPL by using unpolarized



Figure 3. (a) Linear polarization of photoluminescence on an (S)-film on glass. The wavelength scan is repeated two times on the same sample. (b) Circularly polarized photoluminescence on an achiral perovskite film fabricated using the achiral organic ligand NMA. Both measurements were performed by exciting the films with unpolarized light at 365 nm from an Hg lamp. All the measurements were performed at room temperature and in air.

photoexcitation, and we record it as a function of wavelength, carefully ruling out measurement artifacts. The dissymmetry in photoluminescence  $(g_{PL})$  reaches values up to  $3 \times 10^{-3}$ . We use these measurements to estimate the magnetic dipole moment associated with the optical transition, which we find being  $\geq 0.1$  Bohr magnetons. We explain the observed CPL as originating from the charge in the photogenerated Wannier exciton orbiting in a chiral environment: because of the broken symmetry, one handedness of the emitted light prevails over the other, depending on the enantiomer of NEA used in the synthesis of the perovskite thin films.

#### **RESULTS AND DISCUSSION**

Figure 1a shows the chemical structure of the chiral ligand used in this study. Both *S* and *R* versions of NEA were used in this study, enantiomerically pure. Perovskite films were obtained by mixing PbBr<sub>2</sub>:CsBr:(*S*/*R*)-NEABr in a 1:1:2 molar ratio in dimethyl sulfoxide (DMSO). A mix of CsBr and (*S*/*R*)-NEABr was used to obtain Ruddlesden–Popper reduced dimensionality perovskite films with n > 1, where *n* is the number of inorganic layers in between organic sheets. Throughout the rest of this article, thin film samples will be indicated as (*S*)-film and (*R*)-film, with *S* and *R* indicating the absolute configuration of the organic ligand used. Further details on fabrication are provided in the Methods section.

We investigated the nanoscale structural composition of the perovskite films by means of ultraviolet-visible (UV-vis) absorption and scanning electron microscopy (SEM) (Figure 1b,c). Here we present results on (R)-film samples, noting that virtually identical results were obtained on (S)-film samples (Figure S1 in Supporting Information). The UV-vis absorption spectrum measured on a (R)-film sample reveals an absorption band starting at ~520 nm, which we attribute to direct band gap absorption from the CsPbBr<sub>3</sub> perovskite bulk semiconductor.<sup>26,27</sup> We observe a further band peaked at 410 nm, consistent with absorption from bound excitons in reduced-dimensionality Ruddlesden-Popper perovskites: it has been previously shown that a layered Ruddlesden-Popper system with n = 2 and chemically similar to ours presents a bound-exciton absorption band peaked at 380 nm.<sup>12</sup> Because in our case the absorption peak from bound excitons is at longer wavelengths, we conclude it must originate from a phase in the film with  $n \ge 2$ .<sup>28</sup> We therefore conclude that our films consist of a reduced-dimensionality RP perovskite containing

two phases: one with  $n \ge 2$  responsible for the absorption peak at 410 nm, and another with n > 4, which results in the absorption at 520 nm typical of delocalized Wannier excitons in quasi-3*D* or 3*D* perovskites.<sup>29</sup> The absence of other absorption peaks excludes other phases being present in the films.<sup>30</sup>

We performed scanning electron microscopy (SEM) on our chiral perovskite films (Figure 1c) and observed that the films comprise nanocrystals with 15 to 30 nm sides and cubic shapes, randomly oriented throughout the film. The size of these nanocrystals is large enough to make the influence of quantum confinement on the optical properties negligible.<sup>27,31</sup>

We then studied the chiroptical properties of these films. Figure 2a shows the circular dichroism (CD) measured on (S)-film and (R)-film samples; here the  $g_{abs}$  is reported, defined as the difference in absorbance A of left- and right-circularly polarized light, divided by the total absorbance:

$$g_{abs} = \frac{A_L - A_R}{\frac{1}{2}(A_L + A_R)}$$
(1)

(S)-Film and (R)-film samples show clear and virtually identical CD, with opposite sign and with peak  $|g_{abs}|$  on the order of  $10^{-3}$ . The CD signal in the 200–350 nm region is assigned to absorption from the organic chiral ligand, similarly to what observed previously by other groups.<sup>12,13</sup> CD is also present at longer wavelengths up to 525 nm, where the perovskite band-edge absorption band is (Figure 1b). (S)-Film and (R)-film show CD spectra that are symmetric with respect to the *x*-axis, consistently with the opposite handedness of the chiral ligand used. The fact that CD is present at the wavelength corresponding to band-edge absorption indicates that chirality has been impinged on the electronic structure of the perovskite semiconductor.

We measured circularly polarized photoluminescence (CPL) on the same samples (Figure 2b, top). The films were excited with UV light from a Hg lamp, selected at 365 nm using bandpass filters and depolarized using an optical fiber bundle. A clear CPL signal was measured on both (*S*)-film and (*R*)-film samples, with signal appearing between 500 and 560 nm, peaking at 540 nm. The sign of  $g_{PL}$  coincides with that of  $g_{abs}$  at the band-edge absorption (ca. 520 nm) and their intensity is in the same order of magnitude (10<sup>-3</sup>). As in CD, the CPL

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spectra of the two samples are virtually identical and opposed in sign. Analogously to  $g_{abs}$ ,  $g_{PL}$  is defined as

$$g_{PL} = \frac{I_L - I_R}{\frac{1}{2}(I_L + I_R)}$$
(2)

where  $I_{\rm L}$  and  $I_{\rm R}$  are the intensity of luminescence with left- and right-handed polarization, respectively. CPL was measured by means of a photoelastic modulator (PEM) and digital photon counting, to accurately determine the small circular polarization (see Methods section for further details).

On the same films, we also recorded unpolarized photoluminescence (PL) by using a continuous-wave laser at 405 nm with low power (8 mW): Figure 2b, bottom shows the unpolarized PL measured on a (*R*)-film sample. The PL is blue-shifted compared with CPL and peaks at 525 nm. This is the wavelength at which bulk CsPbBr<sub>3</sub> emits,<sup>27</sup> and no other secondary peaks are observed: we therefore conclude that photoexcitation of the film leads to emission from the phase with n > 4.<sup>12,29,30</sup> The blue-shift of PL with respect to  $g_{PL}$ suggests that the latter originates from a subset of states in the semiconductor. The wavelength dependence of  $g_{PL}$  is a commonly observed feature in chiral molecular materials,<sup>32,33</sup> indicating that light-emission is associated with more than one electronic transition matrix element.

The films presented an excellent stability in air, allowing for the measurement to be repeated several time at each wavelength (Figure S3 in Supporting Information). Given the small values of  $g_{PI}$ , we performed additional measurements to evaluate possible artifacts. A common source of artifacts in CPL measurements is the presence of linear polarization in the luminescence signal, which can originate an apparent CPL with magnitude comparable to the real CPL;<sup>25</sup> we ruled out this artifact by observing an amount of linear polarization of PL ((S)-film, Figure 3a) that we can consider negligible, as it would not allow to account for the observed  $g_{PL}$  (see Supporting Information for a full discussion). Furthermore, we fabricated an achiral perovskite film by using an achiral organic ligand, 1-naphthylmethylamine (NMA), similar in chemical structure to (S/R)-NEA: on this sample, we did not detect any CPL (Figure 3b). Finally, we note that the observation of CD or CPL does not allow one, per se, to state that the underlying absorber/emitter is chiral: indeed it has been shown that achiral crystals can present chiroptical response under specific measurement angles.<sup>34</sup> In our films, however, the perovskite nanocrystals present a random distribution of orientations (Figure 1c), and therefore, such effects would cancel out. Having evaluated all the above aspects, we can therefore establish that the CD and CPL measured on (S)- and (R)-film samples are real and testify that chirality impacts the 3D (i.e., large n) electronic structure of the perovskite films. Because at wavelengths corresponding to the band edge  $g_{abs}$  and  $g_{PL}$  have the same sign and similar magnitude, we conclude that the CD and CPL in this wavelength range relate to the same ground and excited state manifolds in the quasi-3D/3D semiconductor. This observation also indicates that possible energy transfer from the lower dimensionality phase to the 3D phase does not impact the CPL.

The dissymmetry factor  $g_{PL}$  relates to the electric and magnetic dipole moments of the optical transition via the formula:

$$g_{pL} = \frac{4m\mu\cos(\theta)}{m^2 + \mu^2}$$
(3)

where *m* and  $\mu$  are the norms of the magnetic and electric dipole moment, respectively, and  $\theta$  is the angle between the moments.<sup>35</sup> Having measured  $g_{PL}$ , it is thus possible to extract the value of the magnetic dipole moment by using eq 3, provided that the electric dipole moment  $\mu$  is known. To estimate the value of the magnetic dipole moment *m*, we therefore set out to measure  $\mu$ .

In a monomolecular recombination regime, the electric dipole moment  $\mu$  is related to the radiative recombination rate of the transition by

$$k_{rad}(\omega) = \frac{\omega^3 n^3 |\mu|^2}{3\pi\varepsilon_0 \hbar c^3}$$
(4)

where  $\omega$  is the frequency at which the decay rate is measured, n is the refractive index of the medium at frequency  $\omega$ ,  $\varepsilon_0$  is the vacuum permittivity, and c is the speed of light in vacuum. Here we set n to 2.3 based on previous reports.<sup>36</sup>

To obtain  $k_{rad}$ , we measured the lifetime of PL at 540 nm (i.e., close to the peak of CPL) (Figure 4) and the PL quantum



Figure 4. Time-resolved photoluminescence measured on a (R)-film on glass, with the fit to a biexponential decay (see also Table 1). The measurement was performed at room temperature in air, using a pulsed laser source at 407 nm, with peak power of 4.3 mW.

efficiency (PLQE) of the films. PLQE and time-resolved PL were measured at room temperature, by using a similar (407 nm) excitation wavelength and a similar peak excitation power, to study the system under a comparable density of excitations. From these measurements, the radiative rate can be extracted by using eq 5:

$$PLQE = \frac{k_{rad}}{k_{meas}} = \frac{k_{rad}}{k_{rad} + k_{nr}}$$
(5)

where  $k_{nr}$  is the nonradiative decay rate, and  $k_{meas} = k_{rad} + k_{nr}$  is the total decay rate obtained in time-resolved PL as the reciprocal of the measured PL lifetime  $(k_{meas} = 1/\tau)$ .

We fitted the time evolution of PL at 540 nm from an (*R*)film sample to a biexponential decay function (Figure 4 and Table 1): the decay is dominated by one decay-time with a lifetime  $\tau_1$  of 1.2 ns and a corresponding lifetime-weighted fractional intensity of 0.89, indicating a largely monomolecular recombination process that is therefore appropriate to be used in eq 4. We attribute the second, longer lifetime  $\tau_2$  (8.2 ns) to nongeminate recombination at lower excitation densities. The PLQE on the same film amounted to 7.2%. Using eq 5, one www.acsnano.org

Table 1. Fit Parameters of Time-Resolved PL Decay Traces at 540 nm on (R)-Film Sample<sup>a,b</sup>

$\lambda_{\rm em}~({\rm nm})$	$ au_1$ (ns)	$\alpha_1^{c}$	$\tau_2$ (ns)	$\alpha_2^{c}$	adj. R-square
540 nm	1.2	0.89	8.2	0.11	0.92

<sup>*a*</sup>Traces fitted to a biexponential decay function  $y(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ . <sup>*b*</sup>Measurements performed at room temperature, in air, with excitation wavelength 407 nm and with peak power 4.3 mW. The recorded trace recorded is shown in Figure 4. <sup>*c*</sup> $\alpha_i$  are the lifetime-weighted fractional intensities of each component of the multi-exponential fit, calculated as  $\alpha_i = \frac{A_i r_i}{\sum_i A_i r_i}$ .

obtains  $k_{rad}$  (540 nm) = 6.2 × 10<sup>7</sup> s<sup>-1</sup>, which substituted in eq 4 gives a value for the electric dipole moment of  $\mu$  = 1.6 D (Debye). This value is reasonable for a delocalized photoexcitation (a Wannier exciton) and is indeed much lower than in organic semiconductors and other confined-excitation systems such as quantum dots.<sup>37–39</sup> Thus, using  $\mu$  = 1.6 D and  $g_{PL}$  = 3 × 10<sup>-3</sup> (i.e., the value measured at 540 nm) in eq 3, while setting  $\theta$  = 0°, we find m = 0.1  $\mu_B$ , where  $\mu_B$  is the Bohr magneton. Note that, by using  $\theta$  = 0°, this is an estimation of a lower limit for the value of m.

We propose that the excess in handedness of emitted light (CPL) from our films originates from charges in delocalized Wannier excitons forming noncentrosymmetric orbitals (with nonzero orbital momentum), which indicates that the chiral ligand has successfully imparted chirality on the semiconductor and its electronic structure. If the charges in the excitons were forming centrosymmetric orbitals, equal numbers of left and right circularly polarized photons would be emitted, and no net CPL would be observed on the films. Note that the Bohr radius of Wannier excitons in CsPbBr<sub>3</sub> perovskites has been estimated to be 3.5 nm;<sup>31</sup> charges in exciton electron–hole pairs can therefore probe a substantial volume of the chiral perovskite nanocrystals in our films.

Because we use fully unpolarized excitation light, no net angular momentum is conveyed to the exciton in the perovskite by the excitation photon: therefore, optical angular momentum of the excitation light cannot be the source of the circular polarization observed. Owing to strong spin—orbit coupling (SOC), a change in the spin of the electron upon electronic excitation may contribute, together with orbital momentum, to the measured magnetic transition dipole moment.<sup>35</sup> On the other hand, as electrons and holes formed upon photoexcitation may move in every direction relative to the randomly oriented crystallites in the solid, Rashba SOC, if present, should not result in net spin polarization of the charge carriers. Hence, the Rashba mechanism cannot account for the observed circular polarization of the luminescence.

We finally note that chiral perovskite semiconductors have features that clearly distinguish them from the systems on which CPL has been most studied in the past: organic chromophores. In organic chromophores, the electric transition dipole moment  $\mu$  is large (typically several Debye) and the optical transition between the lowest excited singlet state and the ground state is allowed; in this way, nonradiative decay pathways are outcompeted by the radiative ones and bright fluorescence is achieved. At the same time, spin—orbit coupling is very weak for molecules consisting mainly of carbon and hence electron spin hardly contributes to the magnetic transition dipole moment. Furthermore, organic molecules often have low symmetry, with three-fold or higher rotation axes being absent. As a result, angular momentum in organic molecules is quenched, and magnetic transition dipole moments are small. In combination with high  $\mu$ , the small value of the magnetic transition dipole moment *m* thus limits the degree of circular polarization for bright organic chromophore emitters,<sup>35</sup> that is, results in low  $g_{PL}$  (eq 3). We propose that chiral perovskites, instead, have the potential to be light sources with high brightness and high  $g_{PL}$  because the low electric transition dipole moments can in principle be combined with low nonradiative recombination rates in highpurity films.<sup>1</sup> Additionally, the delocalized nature of excitons in perovskites could allow to engineer both *m* and the relative orientation  $\theta$  between  $\mu$  and *m*, which in bound Frenkel excitons in organic chromophores is typically close to 90° and further limits  $g_{PL}$ .<sup>35</sup>

# **CONCLUSIONS**

We have observed circular polarization of photoluminescence at room temperature from chiral Ruddlesden-Popper perovskite thin films, excited with unpolarized light. We recorded the full spectrum of CPL, which showed an asymmetry factor  $g_{PL}$ peaking at  $3 \times 10^{-3}$ , on films based on opposite enantiomers of a chiral organic ligand. We propose that CPL is originated by charges in the photogenerated Wannier exciton orbiting in the chiral semiconductor and we extract a lower limit for the value of the transition magnetic dipole moment, amounting to 0.1  $\mu_B$ . Our results demonstrate that the chiral organic ligands used in the synthesis of perovskite films impart chirality into the electronic structure of the semiconductor, breaking symmetry and allowing an excess of handedness in the emitted photon. Further studies will be needed to address the impact of the chiral perovskite nanostructure on the exciton properties and hence on the amount of CPL; such studies will allow one to assess if chiral perovskites can be a good candidate as bright sources of strongly circularly polarized light.

Our results provide an accurate characterization of chirality in practical perovskite-based systems, that is, in solutionprocessed thin films at room temperature; this characterization will be useful for future investigations into their electronic and spintronic properties. Finally, our findings on chiral perovskites have wider implications for the study of perovskites in general, as we present a method to directly measure magnetic dipole moments in this class of semiconductors.

# **METHODS**

**Materials and Synthesis.** PbBr<sub>2</sub> ((99.999%, metals basis)), CsBr (99.999%, metals basis), dimethyl sulfoxide (DMSO, 99.9%), and HBr (99.99% metals basis, 48 wt % in water) were purchased from Sigma-Aldrich and used as received. (S)-(-)-1-(1-Naphthyl)-ethylamine ((S)-NEA) and (R)-(+)-1-(1-naphthyl)ethylamine ((R)-NEA) were purchased from Tokyo Chemical Industry. (S)-NEABr was synthesized by adding 2.16 g of hydroiodic acid to a stirring solution of (S)-NEA (6.36 mmol) in ethanol (anhydrous, 25 mL) at 0 °C for 2 h. The (S)-NEA Br precipitate was obtained by evaporating the solution at 50 °C, which was washed by ethanol three times and then dried under vacuum at 40 °C for 24 h. (R)-NEABr was synthesized by using the same method with (R)-NEA in place of (S)-NEA.

**Film Deposition.** PbBr<sub>2</sub>, CsBr, and (S/R)-NEABr were mixed in a 1:1:2 molar ratio in DMSO, with 0.23 M, 0.23 and 0.46 M concentrations, respectively. The solutions were stirred at 80 °C for 4 h prior to spin-coating. Thin films were fabricated by spin coating on washed glass substrates, which had undergone an O<sub>2</sub> plasma treatment to improve wettability. The solutions were filtered with a 200 nm PTFE filter prior to spin-coating at 5000 rpm for 150 s, using an acceleration of 3000 rpm/s. Both solution preparation and spin-

coating were performed in a nitrogen-filled glovebox, achieving perovskite films with a thickness of 50-60 nm. The films were kept in glovebox in the dark for over a week before being measured.

Optical Characterization. All optical measurements were conducted at room temperature and in air. Circular dichroism (CD) measurements on films, from which  $g_{abs}$  was extracted, were performed in a Jasco J-815 circular dichroism spectropolarimeter. Circularly polarized photoluminescence was measured using a homebuilt setup employing a photoelastic modulator (PEM) operated at a frequency f = 50 kHz, a linear polarizer in combination with a spectrograph with a 16-channel photomultiplier array involving a photon counting detection scheme. Continuous excitation light at 365 nm was selected from a Hg lamp using appropriate interference and bandpass filters. The excitation light was depolarized by passing it through a bundle of optical fibers. The direction of the excitation was normal to the surface of the film and in line with the direction of emission collection. Linear polarization of photoluminescence was measured on the same samples and in the same setup configuration, but now employing half-wave optical retardation by operating the modulator and signal acquisition at a frequency 2f. The degree of linear polarization is reported as  $p_{lum} = 2(I_V - I_H)/(I_V + I_H)$  with  $I_{V(H)}$ being the intensity of vertically (horizontally) polarized light. Luminescence in this setup was collected by integrating the collected light for 30 s, and 20 consecutive measurements were used to estimate the mean and standard error (as shown in Figure 2b, top).

The absorbance on thin films was measured by using a Hewlett-Packard 8453 spectrometer. Unpolarized photoluminescence (PL) and PL quantum efficiency (PLQE) were measured with the samples in an integrating sphere setup; the samples were excited by using a continuous wave laser diode at 405 nm, with an excitation power of 8 mW obtained by using neutral density filters. The PL emission was collected with an optical fiber and measured using an Andor iDus DU490A spectrometer coupled to a silicon CCD detector.

Time-resolved PL was measured by using a pico-second pulsed laser with wavelength 407 nm (Picoquant PDL-800-B). The laser has a fwhm pulse duration of 40 ps and was operated at 20 MHz repetition frequency; neutral density filters were used to obtain a low peak power (4.3 mW) for excitation densities comparable to those used in the PLQE measurements. The photoluminescence was detected by a single-photon avalanche diode (SPAD) based on silicon (Micro Photon Devices, PDM–PDF version) with an instrument response of ~200 ps. A 420 nm long-pass filter was used to screen-out any scattered laser signal in the optical path.

**Scanning Electron Microscopy (SEM).** SEM measurements were carried out on perovskite films deposited on indium tin oxide (ITO) substrates, using a high-resolution scanning microscope (LEO GEMINI 1530VP FEG-SE).

#### **ASSOCIATED CONTENT**

### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.0c03628.

UV-vis absorption spectrum and SEM image of a sample based on PbBr<sub>2</sub>:CsBr:(S)-NEABr precursor mix, CD spectrum of a sample based on PbBr<sub>2</sub>:CsBr:(R)-NEABr precursor mix, PL/ $g_{PL}$  measurements as function of time under constant photoexcitation (PDF)

# **AUTHOR INFORMATION**

# **Corresponding Author**

Daniele Di Nuzzo – Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, United Kingdom; orcid.org/0000-0002-4462-9068; Email: dd467@ cantab.ac.uk

#### Authors

- Linsong Cui Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, United Kingdom
- Jake L. Greenfield Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, United Kingdom; orcid.org/0000-0002-7650-5414
- Baodan Zhao Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, United Kingdom
- Richard H. Friend Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, United Kingdom; orcid.org/0000-0001-6565-6308
- Stefan C. J. Meskers Institute for Complex Molecular Systems, Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands; orcid.org/0000-0001-9236-591X

Complete contact information is available at: https://pubs.acs.org/10.1021/acsnano.0c03628

### Notes

The authors declare no competing financial interest.

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