

1 **CsPbBr<sub>3</sub> nanocrystal films: deviations from bulk vibrational and optoelectronic**  
2 **properties**

3

4 *Silvia G. Motti, Franziska Krieg, Alexandra J. Ramadan, Jay B. Patel, Henry J. Snaith,*  
5 *Maksym V. Kovalenko, Michael B. Johnston, Laura M. Herz\**

6

7 Dr. Silvia G. Motti, Dr. Alexandra Ramadan, Dr. Jay Patel, Prof. Henry Snaith, Prof. Michael  
8 B. Johnston, Prof. Laura Herz

9 Department of Physics, University of Oxford, Clarendon Laboratory, Parks Road, Oxford  
10 OX1 3PU, United Kingdom

11 Email: \*laura.herz@physics.ox.ac.uk

12

13 Franziska Krieg, Prof. Maksym V. Kovalenko

14 Institute of Inorganic Chemistry, Department of Chemistry and Applied Biosciences, ETH  
15 Zürich, Vladimir Prelog Weg 1, CH-8093 Zürich, Switzerland

16 Laboratory for Thin Films and Photovoltaics, Empa - Swiss Federal Laboratories for  
17 Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland

18

19 Keywords: perovskite, nanocrystals, charge-carrier dynamics, mobility

20

21

22 Metal halide perovskites (MHP) are highly promising semiconductors for light-emitting and  
23 photovoltaic applications. The colloidal synthesis of nanocrystals (NC) is an effective  
24 approach for obtaining nearly defect-free MHP that can be processed into inks for low cost,  
25 high performance device fabrication. However, disentangling the effects of surface ligands,  
26 morphology and boundaries on charge-carrier transport in thin films fabricated with these  
27 high-quality NCs is inherently difficult. To overcome this fundamental challenge, terahertz

1 (THz) spectroscopy is employed here to optically probe the photoconductivity of CsPbBr<sub>3</sub>  
2 nanocrystal films. The vibrational and optoelectronic properties of the NCs are compared with  
3 those of the corresponding bulk polycrystalline perovskite and significant deviations are  
4 found. Charge-carrier mobilities and recombination rates are demonstrated to vary  
5 significantly with the nanocrystal size. Such dependences derive from the localized nature of  
6 charge-carriers within nanocrystals, with local mobilities dominating over inter-particle  
7 transport. It is further shown that the colloiddally synthesized NCs have distinct vibrational  
8 properties with respect to the bulk perovskite, exhibiting blue-shifted optical phonon modes  
9 with enhanced THz absorption strength that also manifest as strong modulations in the THz  
10 photoconductivity spectra. Such fundamental insights into NC versus bulk properties will  
11 guide the optimization of nanocrystalline perovskite thin films for optoelectronic applications.

12

### 13 **1. Introduction**

14 The colloidal synthesis of metal halide perovskite (MHP) semiconductor nanocrystals (NC)  
15 has proven to be an interesting and effective approach for yielding nearly defect-free  
16 materials. Perovskite NCs show high photoluminescence quantum yields (PLQY) and tunable  
17 band gap over all the visible range, among other desirable properties for light emitting  
18 applications.<sup>[1-3]</sup> The fabrication of high-quality conductive thin films by processing the  
19 colloidal NCs as inks has paved the way for an extension of their application to photovoltaics  
20 and photodetectors.<sup>[4,5]</sup> However, the long-range electronic conductivity of these  
21 nanocrystalline thin films depends crucially on interparticle conduction and thus should be  
22 greatly affected by the choice of ligands and deposition methods.<sup>[5,6]</sup> Such insulating ligands  
23 may form barriers between the semiconducting NCs and metallic electrodes that hamper  
24 charge transport in devices.

1 While the optimization of long-range conductivity is a developing topic with its own ongoing  
2 efforts, the investigation of the fundamental charge transport within individual NCs is also  
3 crucial, since both intra- and inter-particle charge motion will affect the performance of  
4 perovskite NC devices. In addition, an understanding of the interplay between electronic  
5 confinement and charge transport is important for the design of NC solids that can still fully  
6 exploit the size-dependent bandgap tunability. Previous studies showed that appreciable  
7 conductivity can be achieved from perovskite NC films with the use of short capping ligands  
8 (chains of 8 carbons or less) or by removal/exchange of ligands after film deposition.<sup>[4,7,8]</sup>

9 While these approaches facilitate interparticle charge transport, they also lead to partial  
10 sintering of NCs,<sup>[9]</sup> which in turn is expected to result in loss of quantum confinement and  
11 higher density of structural defects. Such effects may be particularly undesirable for light-  
12 emitting applications, while they may potentially be more tolerable for photovoltaic devices.

13 The development of zwitterionic ligands has been proposed as an effective approach to obtain  
14 stable colloidal NCs and allowing for the deposition of smooth conductive films while  
15 preserving nanocrystal structural integrity.<sup>[5]</sup> Zwitterionic ligands may therefore be  
16 particularly suitable for balancing the trade-off between preserving nanocrystalline  
17 optoelectronic properties and maintaining effective charge-carrier transport.

18 In this work, we investigate the vibrational and optoelectronic properties of colloiddally  
19 synthesized cuboid CsPbBr<sub>3</sub> NCs of edge lengths 6 nm, 7.5 nm and 10 nm, deposited on  
20 quartz substrates. Such NCs fall within the range of weak quantum confinement, approaching  
21 bulk-like properties with increasing crystal size. Furthermore, the synthesis of NCs in this  
22 range of sizes yields optimum crystal quality and colloidal stability. To investigate the effects  
23 of nanoscale interfaces, we compare our findings with those for a spin-coated polycrystalline  
24 CsPbBr<sub>3</sub> film exhibiting average crystallite size of ~100 nm. We apply a combination of  
25 absorption and photoluminescence studies with Optical-Pump Terahertz-Probe (OPTP)  
26 spectroscopy to unravel the charge-carrier dynamics and photoconductivity in the perovskite

1 NCs and bulk films. The THz radiation can access the energy and time scales of charge carrier  
2 motion and lattice vibrations that can affect charge transport. Moreover, the THz probe allows  
3 us to optically probe the time resolved photoconductivity of the material after photoexcitation  
4 without the need for electrical contacts.<sup>[10–13]</sup>

5 Our findings reveal distinct structural and vibrational properties in NCs compared to the bulk  
6 material. We observe a blue-shift of the optical phonon modes probed in the THz spectral  
7 range and stronger coupling of the THz radiation to these modes with respect to the bulk. In  
8 addition to wider band gaps and higher recombination rates resulting from quantum  
9 confinement, we also report a size dependence of the effective charge-carrier mobilities. We  
10 demonstrate that the charge transport within the NCs in the THz frequency is dominated by  
11 backscattering off NC boundaries, even after film annealing, highlighting the dominance of  
12 intra- over inter-particle transport in these NC solids. These two aspects, the localized  
13 character of charge carriers and the distinct vibrational properties of NCs, are reflected in the  
14 frequency dependence of the THz photoconductivity spectra. In particular, upon  
15 photoexcitation we observe a modification of the phonon response, which result in strong  
16 modulations on the photoconductivity spectra. These photoinduced changes are also enhanced  
17 in the NCs with respect to the bulk, reflecting the stronger coupling of the polar lead-bromide  
18 sublattice to the THz probe.

19

## 20 **2. Results and discussion**

### 21 **2.1 Sample fabrication and characterization**

22 Cuboid shaped CsPbBr<sub>3</sub> NCs of average size 6 nm, 7.5 nm and 10 nm were synthesized  
23 colloiddally, using a hot-injection approach. Anhydrous cesium oleate, lead oleate and a  
24 zwitterionic ligand were dissolved in 1-octadecene and heated under vacuum to 130°C, where

1 the atmosphere was changed to nitrogen. Once the desired reaction temperature was reached,  
2 trioctylphosphine dibromide adduct was injected and the reaction was cooled to room  
3 temperature immediately thereafter; an ice-water bath was used. Full details of the synthesis,  
4 isolation and purification procedures are provided in Section 1 in Supporting Information.  
5 The sizes (edge lengths) of the NCs were determined by transmission electron microscopy  
6 (TEM) to be  $6\pm 2$  nm,  $7.5\pm 2$  nm and  $10\pm 2$  nm. The PLQY values measured for NCs in  
7 colloidal solutions were 67%, 75% and 75%, respectively. For the fabrication of nanocrystal  
8 films, the NCs were deposited on z-cut quartz substrates<sup>[14]</sup> by spin-coating from the colloidal  
9 solution. After deposition, the measured PLQY on the films were slightly reduced, to 50%,  
10 47% and 26%, for the 6, 7.5 and 10 nm NCs, respectively. The center wavelength of the PL  
11 emission did not change after deposition, indicating preservation of confinement and hence  
12 preservation of the structural integrity of the NCs.

13 For comparison with bulk perovskite properties, bulk polycrystalline CsPbBr<sub>3</sub> films were  
14 fabricated by spin-coating of a Cs-Pb-Br-precursor solution in DMSO onto the quartz  
15 substrates at 4000 rpm for 40 s followed by a solvent annealing step using chloroform (see  
16 Section 1.5 in SI for more details). The average crystallite size within the bulk film was ~100  
17 nm as determined by atomic force microscopy (**Error! Reference source not found.**).

18 As a first characterization step, absorption and photoluminescence spectra were taken, as  
19 shown in **Figure 1.a**. As expected, with decreasing crystal size the NCs show an increasing  
20 blue shift of the absorption onset and the PL peak position with respect to the data for the bulk  
21 CsPbBr<sub>3</sub> film, confirming the presence of weak confinement.<sup>[1]</sup> We also note a broadening of  
22 the PL emission and the excitonic feature in the absorption spectra of the NC films with  
23 respect to those of the bulk thin film. Such broadening is related to the size distribution ( $\pm 1-2$   
24 nm, see **Error! Reference source not found.** and Figure S13 in SI) of the nanocrystals, and  
25 more pronounced in the case of the smaller NCs.

## 1 2.2 Size dependence of structural and vibrational properties

2 The low dimensionality and the high surface-to-volume ratio of semiconductor nanocrystals  
3 has been shown to have an effect on their crystal lattice.<sup>[15-17]</sup> To investigate such effects, we  
4 examined the structural properties of the bulk and nanocrystalline perovskite films by X-ray  
5 diffraction (XRD). The diffraction patterns obtained for the polycrystalline CsPbBr<sub>3</sub> and 10  
6 nm NCs deposited on quartz are shown in Figure 1.b (see **Error! Reference source not**  
7 **found.** in SI for complete diffraction data for all NC sizes). No peaks related to PbBr<sub>2</sub> or other  
8 impurities were detected. We observe broadening of the diffraction peaks with decreasing  
9 crystal size, as is typical in nanocrystals.<sup>[18,19]</sup> Interestingly, we can also notice a shift of the  
10 diffraction peaks to lower angles with respect to the bulk CsPbBr<sub>3</sub>. Such a shift is related to  
11 longer distances between planes, and usually associated with lattice strain.<sup>[20]</sup> In order to  
12 properly analyze the position and broadening of the diffraction peaks, we must take into  
13 account the crystalline phase and peak superpositions. It has been shown that CsPbBr<sub>3</sub> NCs  
14 fabricated from colloidal synthesis adopt an orthorhombic structure, analogous to the bulk  
15 material.<sup>[21,22]</sup> According to the expected diffraction pattern for orthorhombic CsPbBr<sub>3</sub>,<sup>[23]</sup> we  
16 fitted the peaks and calculated the d-spacings for the (101), (121) and (202) planes and  
17 noticed that the NC films exhibit slightly but consistently larger plane distances than the bulk  
18 perovskite (see **Error! Reference source not found.**). We then used the fitted peak positions  
19 and broadenings to create Williamson-Hall plots<sup>[24]</sup> for bulk and NC films and found no  
20 significant presence of micro-strain (see **Error! Reference source not found.** in SI),  
21 suggesting good crystallite quality and insignificant defect-related distortion. Considering the  
22 negligible contribution of micro-strain and inhomogeneities, the increased d-spacings indicate  
23 a lattice expansion in the NCs with respect to the bulk. The expansion of the lattice in  
24 nanocrystals has been previously reported in different systems,<sup>[15,25,26]</sup> including lead halide  
25 perovskites,<sup>[16,27]</sup> and has been attributed to a decrease in electrostatic forces between the  
26 atoms induced by the reduced valence of atoms at the NC surfaces.<sup>[26]</sup>

1 The differences in lattice expansion combined with reduced particle size and high surface-to-  
2 volume ratio is expected to have an effect on the vibrational properties of semiconductor  
3 nanocrystals.<sup>[15,28]</sup> To elucidate such effects, we investigated the optical phonon modes  
4 associated with the lead-bromide sub-lattice in both the NCs and bulk CsPbBr<sub>3</sub> by measuring  
5 the absorption of the films in the terahertz (THz) region. As Figure 1.c shows, the THz  
6 absorption spectra of the NCs are broader and the modes appear to be blue-shifted compared  
7 to those of the bulk. We propose that such broadening of the phonon modes in the NCs is  
8 related to shorter phonon lifetimes (given the energy-time uncertainty relation  $\Delta E / \hbar = 1 / \tau$ )  
9 that result from confinement effects and increased surface scattering in nanocrystals.<sup>[15,29]</sup> The  
10 broadening of the THz absorption increases with decreased NC size (see **Error! Reference**  
11 **source not found.** in SI), which directly implies a decrease of the phonon lifetime in smaller  
12 NCs.

13 Regarding the blue-shift of the THz spectra, the absence of size dependence between NCs  
14 suggests that phonon confinement is not the dominant cause of the shift over the studied size  
15 range. Intriguingly, the lattice expansion observed for the NCs in the XRD patterns also fails  
16 to explain the blue-shift of the optical phonon modes, given that the reduced electrostatic  
17 force is expected to induce a softening of the phonon modes (*i.e.* red-shift) instead of the  
18 observed blue-shift. We therefore propose that the observed effect may instead derive mostly  
19 from changes in the direct coupling of radiation across the multitude of optical photon modes  
20 that is present in lead halide perovskites,<sup>[30,31]</sup> which have numerous atoms per unit cell  
21 leading to the existence of many acoustic and optical modes. In support of this conclusion, we  
22 note that the relative effective absorption coefficients of the phonon modes (obtained by  
23 comparing the absorption in the THz region relative to the edge of the optical gap) is higher  
24 by a factor of 2 in the NCs compared to the bulk (see **Error! Reference source not found.**).  
25 This more efficient coupling of the lattice modes to THz radiation can be a result of distinct  
26 selection rules in NC films or distinct phonon distributions, and has an effect on the THz

1 photoconductivity spectra, as we will discuss in Section 2.4 further below. Such changes  
2 therefore suggest that the perceived blue-shift of optical phonon modes in the NCs may derive  
3 from complex changes to the vibrational frequencies and coupling strengths of optical modes  
4 to infrared radiation. We note that since significant broadening of the optical modes persists  
5 even at low temperature (**Error! Reference source not found.** in SI), individual phonon  
6 modes could not be resolved.

7 The higher absorption coefficients and blue shift of the phonon modes in NCs reveal the  
8 distinct vibrational properties of NCs with respect to the bulk. In addition, the lack of size  
9 dependence of the optical phonon mode absorption fingerprint (Figure 1c) indicates that the  
10 fabrication methods might also play a role in determining surface and morphological  
11 properties.

## 12 **2.3 Charge carrier dynamics**

13 In addition to wider bandgaps and structural variations, another characteristic effect of  
14 confinement commonly observed in semiconductor nanocrystals is higher charge-carrier  
15 recombination rates with decreasing size.<sup>[32,33]</sup> To investigate the size dependence of charge  
16 carrier dynamics in CsPbBr<sub>3</sub>, we first measured the transient PL decays of the bulk and NC  
17 films, following photoexcitation with 3.1eV ( $\lambda=400\text{nm}$ ) photons. As can be observed in  
18 Figure 1.d, the polycrystalline bulk CsPbBr<sub>3</sub> film shows shorter PL lifetimes than the  
19 nanocrystal films, which can be attributed to the high prevalence of defects in polycrystalline  
20 lead bromide perovskite films.<sup>[34–36]</sup> While the higher surface-to-volume ratio in NCs is  
21 associated with a higher density of boundaries and dangling bonds, the attached ligands  
22 effectively passivate the crystal surfaces,<sup>[37]</sup> ultimately resulting in a lower defect density with  
23 respect to the bulk. It can also be observed that the smaller NCs show shorter PL lifetimes  
24 than larger NCs. Given that the PLQY values were similar or higher for smaller crystals, the  
25 shorter PL lifetimes for smaller NCs must be associated with higher radiative rates. No



1 significant fluence dependence was observed in the PL dynamics (see **Error! Reference**  
2 **source not found.** in SI) at these excitation densities indicating a predominance of a mono-  
3 molecular recombination mechanism. Given that rates appear to be dominated by a radiative  
4 mechanism, we therefore suggest that this mono-molecular mechanism is to a large extent  
5 associated with excitonic recombination. We assume, however, that both excitons and free  
6 carriers can co-exist in the material. In the case of nanocrystals at these low excitation  
7 fluences (between 1 to 100 nJ/cm<sup>2</sup>), we estimate that an average of less than 0.02 photo-  
8 excitations are initially generated per crystal (see Section 4 in SI for details) which explains  
9 the absence of any high-order effects. However, we note that instead of mono-exponential  
10 (first-order) decays intuitively expected from mono-molecular recombination, all NCs present  
11 very stretched PL dynamics. Such complex dynamics are most likely associated with  
12 inhomogeneities of size distribution, photon reabsorption and charge diffusion between NCs  
13 in the film.<sup>[11,38–40]</sup>

14 To investigate higher-order charge-carrier recombination processes across a wider range of  
15 carrier densities and with higher time resolution, we performed OPTP spectroscopy for the  
16 range of NC sizes allowing us to probe the transient photoconductivity of the films following  
17 pulsed photoexcitation. The THz radiation is a non-contact probe sensitive to the photo-  
18 generated charge-carrier population density and the effective charge-carrier mobility (see  
19 Section 3 in SI for details),<sup>[10,12]</sup> making it ideal for the study of NCs, where the insulating  
20 ligands and contact barriers would greatly affect the results obtained from electrical  
21 measurements. The measurements were performed with photoexcitation by 35 fs pulses of  
22 3.1 eV ( $\lambda=400\text{nm}$ ) photons for a range of different excitation fluences. The transients were  
23 fitted with a dynamic model that describes the charge-carrier population decay with a  
24 combination of first, second and third order recombination rates, with rate constants  $k_1$ ,  $k_2$  and  
25  $k_3$ , respectively (see Section 1.5.1 in SI for details).<sup>[10,12,13]</sup> **Figure 2** shows the OPTP  
26 dynamics obtained from the NCs of different sizes together with best fits based on this model.

1 We were able to obtain good-quality fits assuming a negligible first-order rate constant  $k_1$   
2 (which relates to a combination of excitonic and non-radiative recombination pathways) in  
3 agreement with the observation of flat photoconductivity decay at the lowest fluences. The  
4 absence of first-order recombination can be explained by the 1-ns time window over which  
5 the OPTP transients are recorded, which is significantly shorter than the approximate first-  
6 order decay constant ( $\tau \sim 4$  ns) describing the initial decay of the PL transients. Therefore,  
7 mono-molecular recombination has little influence on the shape of the OPTP transients.

8 Given the higher fluences employed during the OPTP measurements, the estimated carrier  
9 densities suggest the presence of more than one excitation per crystal with increasing fluences  
10 (see Section 4 in SI for details). In such cases, we expect higher contributions from second  
11 and third order ( $k_2$  and  $k_3$ ) recombination processes. The values for the effective rate constants  
12  $k_2$  and  $k_3$  extracted from these fits are shown in Figure 2.d, e, which highlight notable  
13 increases in both  $k_2$  and  $k_3$  with decreasing NC size. Such higher recombination rate constants  
14 may result from the stronger overlap of electron and hole wavefunctions caused by  
15 confinement effects,<sup>[41,42]</sup> which results from a combination of confinement-induced state  
16 mixing, enhanced Coulomb coupling and increasing surface-to-volume ratio.<sup>[43]</sup> In addition,  
17 these values may be affected by increasing excitonic effects with decreasing NC size because  
18 the values of  $k_2$  and  $k_3$  determined in OPTP are factored with the photon-to-charge branching  
19 ratio, which may increase with increasing exciton binding energy (see Section 3 in SI for  
20 details).

#### 21 **2.4. Charge carrier mobility and localization**

22 We may further examine how charge-carrier confinement in the NCs affects the effective  
23 charge carrier mobility by evaluating the differential THz transmission ( $-\Delta T_{\text{THz}}/T_{\text{THz}}$ )  
24 amplitude immediately after photoexcitation. The magnitude of the  $-\Delta T_{\text{THz}}/T_{\text{THz}}$  signal is  
25 proportional to photo-induced conductivity and therefore the product of the charge-carrier

1 mobility  $\mu$  and the charge-carrier population. We are thus able to determine an effective  
2 charge-carrier mobility  $\phi\mu$  from the initial photoconductivity signal immediately after  
3 excitation, before significant charge-carrier recombination has occurred. Here,  $\phi$  is the  
4 photon-to-charge-carrier generation ratio, which accounts for the unknown conversion factor  
5 of photons absorbed to charge-carriers generated (see Section 3 in SI for details)<sup>[10,12]</sup> and  $\mu$  is  
6 the sum of the electron and hole mobilities. As shown in **Figure 3.a**, the effective  $\phi\mu$  values  
7 obtained for the 10 nm, 7.5 nm and 6 nm NCs decrease with decreasing crystal size from 2.8  
8 to 0.7 cm<sup>2</sup>/Vs, indicating increasing localization of charge carriers within the confines of the  
9 nanocrystals. We note that such a reduction in  $\phi\mu$  can be the result of both increasing  
10 excitonic effects (decreasing  $\phi$ ) and increasing proximity of physical barriers (decreasing  $\mu$ )  
11 with decreasing NC size.

12 To investigate further why the nanocrystal size has an effect on the effective charge-carrier  
13 mobilities, we examined the influence of ligands and how the barriers between NCs affect  
14 charge-carrier localization. We obtained the effective terahertz mobilities of NC films of one  
15 particular size (7.5 nm) but prepared with different ligands. Ligand 1 is the C3 sulfobetaine  
16 system (3-(N,N-dimethyloctadecylammonio)propanesulfonate) used in the samples presented  
17 so far. Ligand 2, lecithin, has twice as many tails per head group at similar surface ligand  
18 density, thus resulting in more effective insulation between crystals. The films with ligand 3  
19 were obtained by solid state ligand exchange with a di-zwitterionic ligand (3,3'-(hexane-1,6-  
20 diylbis(dimethylammoniumdiyl))bis propane-1-sulfonate) and are expected to be less  
21 insulating than the ligands 1 and 2 (See Section 1.1 in SI for details). As Figure 3.b indicates,  
22 no significant difference in effective charge-carrier mobility with ligand type was observed.  
23 We then subjected one film of 7.5 nm NCs with ligand 1 to annealing at 150°C for 10  
24 minutes. We observed a red shift of the optical bandgap (see **Error! Reference source not**  
25 **found.** in SI) following annealing, evidencing loss of confinement due to ligand extraction  
26 and/or merging of crystals. Surprisingly, however, no significant increase of effective

1 mobility was observed (Figure 3.b). Taken together, these observations demonstrate that the  
2 effective THz mobilities of NC films are dominated by intra-NC motion of charge carriers,  
3 rather than migration between NCs. While interparticle charge-carrier diffusion probably does  
4 occur (as indicated by the stretched PL decays and long-range photoconductivity in these  
5 films<sup>[5]</sup>), we suggest that the associated inter-particle mobility of charge-carriers is still  
6 substantially lower than the intra-particle mobility. As a result, the measured effective THz  
7 mobility mostly reflects carrier motion within individual particles, which is limited by the  
8 boundaries of the NCs. We note that such observations (of significantly larger high-frequency  
9 than low-frequency carrier mobility) have also been typical of metal oxide nanoparticle  
10 films.<sup>[44]</sup>

11 We also investigated the charge-carrier mobility for the CsPbBr<sub>3</sub> bulk polycrystalline film for  
12 comparison and obtained a value of  $\phi\mu=9.1$  cm<sup>2</sup>/Vs, similar to that determined elsewhere for  
13 lead bromide perovskite films<sup>[12]</sup> with a range of A-cation choices. While this effective  
14 mobility is higher than that measured for the larger NCs, it is significantly lower than the  
15 theoretically predicted upper limit for mobility of  $\sim 200$  cm<sup>2</sup>/Vs (or 400 cm<sup>2</sup>/Vs when probing  
16 the sum of electron and hole mobilities, such as in our case) for CsPbBr<sub>3</sub> expected for the case  
17 when only Fröhlich interactions with longitudinal phonons are operational.<sup>[45,46]</sup> Given that  
18 the measured mobility does not vary with excitation fluence (see **Error! Reference source**  
19 **not found.** in SI), we can disregard the contribution of carrier-carrier scattering. We therefore  
20 infer that the charge-carrier mobility in the polycrystalline film investigated here is limited by  
21 carrier scattering with defects, which may include grain boundaries that could potentially  
22 have an effect analogous to that of the surfaces of NCs.

23 To investigate whether the mechanisms leading to carrier scattering in NCs films differ from  
24 those limiting charge-carrier mobilities in the bulk polycrystalline films, we investigate the  
25 frequency dependence of the photoconductivity. Photoconductivity spectra are able to

1 differentiate cleanly between strong localization effects and random scattering events on  
2 charge-carrier motion. In the case of random scattering events, the complex conductivity ( $\sigma$ )  
3 of metals and semiconductors under an alternating electric field of frequency  $\omega$  can usually be  
4 described by the Drude model as

$$5 \quad \sigma(\omega) = \frac{Ne^2}{m^*} \frac{i}{\omega + i\gamma} \quad (1)$$

6 where  $m^*$  is the charge-carrier effective mass and  $\gamma$  is the scattering rate, which relates to the  
7 mobility  $\mu$  by

$$8 \quad \mu = \frac{e}{m^*\gamma} \quad (2)$$

9 This model assumes a simple acceleration of a charge carrier in an electric field subject to its  
10 momentum being randomized through scattering events at average time intervals  $1/\gamma$ . Figure  
11 4.a shows the complex THz photoconductivity spectrum of a bulk CsPbBr<sub>3</sub> film taken ~20 ps  
12 after photoexcitation. No spectral variations over time delay were found to occur (Figures S23  
13 and S24). The solid lines are spectra simulated with the Drude model according to equation  
14 (1) considering the effective mass for electrons and holes to be  $0.15 m_e$ <sup>[1]</sup> and fixing the  
15 scattering rate according to the experimentally measured value for the effective mobility in  
16 the bulk polycrystalline CsPbBr<sub>3</sub> of  $9.1 \text{ cm}^2/\text{Vs}$ . Despite some modulations in the spectra, the  
17 photoconductivity of the bulk perovskite shows good agreement with the Drude model,  
18 displaying a positive real, and a near-zero imaginary part of the spectrum.

19 The frequency-dependent photoconductivity of the NCs (Figure 4.b), on the other hand,  
20 deviates strongly from such Drude-like spectra. We observe that the conductivity at low  
21 frequency, instead of reaching a maximum, as expected from the Drude model, tends to zero  
22 in the case of the NCs. This is a common observation in semiconductor nanoparticles and can  
23 be associated with charge-carrier localization, where the presence of barriers significantly  
24 reduces the DC conductivity.<sup>[47–50]</sup> Another striking characteristic of this behavior is the

1 negative imaginary part of the spectra. One approach for evaluating this deviation from Drude  
2 behavior is by calculating the Drude quality factor  $f_{Drude}$ , which essentially compares the  
3 absolute magnitudes of the real and imaginary parts of the complex THz spectra (as described  
4 in <sup>[51]</sup>). While  $f_{Drude} = 1$  indicates ideal Drude behavior, deviations are indicated by values  
5 lower than 1. The values for  $f_{Drude}$  obtained from the THz spectra up to 2 THz are 0.97 for the  
6 bulk film and 0.58 for the NC film. These values demonstrate the difference in charge  
7 transport mechanism between the two cases and the localized nature of carriers in the NC  
8 film. We consider two models that are typically able to reproduce such behavior. First, we  
9 may investigate an exclusively excitonic character of the photoexcited carriers in the NCs and  
10 describe the frequency dependence of the THz photoconductivity as a Lorentz oscillator. In  
11 this case, a maximum of the real photoexcited THz spectra and a zero-crossing of the  
12 imaginary part would correspond to an intra-excitonic transition resonance which is directly  
13 related to the exciton binding energy.<sup>[52]</sup> We are unable to observe any zero-crossing in the  
14 imaginary part of the spectra obtained from the NCs within the 3.5 THz range over which the  
15 spectra are recorded. However, this absence of an observable resonance peak and crossing  
16 may potentially derive from the exciton binding energy being larger than 20 meV,<sup>[52]</sup> in which  
17 case these intra-excitonic absorption features would fall outside our observation window.  
18 Since relatively large exciton binding energies have been observed for lead bromide  
19 perovskites, and electronic confinement will enhance these further,<sup>[53–56]</sup> a clear resonance  
20 would therefore not be expected to fall within our observation window. However, the spectra  
21 could still be influenced by the low-frequency tail of such an excitonic response.

22 As a second example of a localized response, we consider the Drude-Smith model,<sup>[50,57]</sup> a  
23 phenomenological adaptation of the Drude model that accounts for backscattering to  
24 reproduce the behavior of localized charge-carriers (See Section 1.5 in SI). The Drude-Smith  
25 model extends the Drude model by considering scattering anisotropy according to

$$\sigma(\omega) = \frac{Ne^2}{m^*} \frac{i}{\omega + i\gamma} \left[ 1 + \sum_{p=1}^{\infty} \frac{c_p}{(1 - i\omega / \gamma_{DS})^p} \right] \quad (3)$$

2 where  $\gamma_{DS}$  is the Drude-Smith scattering rate,  $p$  is the number of scattering events and  $c_p$  is the  
 3 fraction of the initial velocity retained by carriers after each scattering event. For Drude-like  
 4 photoconductivity,  $c_p = 0$ . In systems where charges are localized,  $c_p$  can be negative (from 0  
 5 to -1), representing preferential backwards scattering (See Section 3.2 in SI for more details).  
 6 Upon attempting to fit a Drude-Smith expression according to Eqn. (3) to the  
 7 photoconductivity spectra of the NC films, we find adequate agreement with the data only for  
 8 the low-frequency range (<1 THz). Furthermore,  $c_p$  tends towards -1, indicating strong  
 9 charge-carrier localization effects (Figure 4 shows a Drude-Smith spectrum for  $c_p = -1$  as a  
 10 dashed line). We note that while an intrinsic charge-carrier mobility value  $\mu_{DS}$  can in principle  
 11 be extracted from the Drude-Smith model according to  $\mu_{DS} = (1 + c_p) \frac{e}{m^* \gamma_{DS}}$ , in the limit of  
 12  $c_p = -1$  this value will tend to infinity. Therefore, in cases of strong carrier localization, such  
 13 as the NCs presented here, such derivations of intrinsic charge-carrier mobilities that could be  
 14 attained in the absence of carrier backscattering off NC surfaces would be largely  
 15 overestimated and are therefore avoided here.

16 The experimental photoconductivity spectrum from the NC film shows clear evidence of  
 17 charge localization on the low frequency side, which qualitatively agrees with the Drude-  
 18 Smith model. However, it deviates from both the Drude model and the Drude-Smith model at  
 19 higher frequencies, where it is affected by very strong modulations. The line-shape of the  
 20 experimental spectra and the deviations from the theoretical predictions are not representative  
 21 of charge transport phenomena, but rather of the combined interaction of the THz probe beam  
 22 with the lattice and with the charge-carrier population. The response of the THz probe to  
 23 charge-carrier motion is superimposed with modulations of the THz transmission caused by  
 24 photoinduced changes to the lattice component in the absorption of the THz radiation. The  
 25 photoinduced changes to the THz transmission can also be appreciated as a shift in the THz

1 peak in the time domain (see **Error! Reference source not found.** in SI). While no  
2 significant shift can be perceived in the bulk material, in the case of the NCs the THz  
3 transmission peak slightly shifts to earlier times after photoexcitation, indicating a decrease in  
4 refractive index in the THz region in the presence of photogenerated charge carriers. It is  
5 important to highlight that the experiments were carried out at comparable charge carrier  
6 densities ( $\sim 10^{17} \text{ cm}^{-3}$ ) in both bulk and NCs. Photoinduced changes to the lattice response to  
7 the THz radiation have been previously observed in lead halide perovskites,<sup>[58]</sup> and can be  
8 indicative of the existence of a photoinduced modification of the vibrational properties. In  
9 other words, the presence of charge carriers has an effect on the lattice phonon modes,  
10 changing either the phonon oscillator strengths or shifting the resonance frequencies in  
11 relation to the ground state distribution.

12 The more pronounced modulations in the THz photoconductivity spectra of NCs as opposed  
13 to the bulk film are likely related to the stronger coupling of THz radiation to the lattice (as a  
14 result of higher absorption coefficients or distinct selection rules) observed in the dark  
15 absorption of NCs in the THz range. Additionally, the impact of photogenerated charges on  
16 the THz refractive index in NCs indicate stronger coupling between the lattice and charge  
17 carriers compared to the bulk perovskite. We could also confirm that these modulations  
18 appear in the photoconductivity spectra immediately after photoexcitation and persist for at  
19 least several picoseconds (see **Error! Reference source not found.** in SI). Such fast response  
20 is counterevidence of the role of photostriction in the modulations, as the lattice  
21 reorganization would be expected to occur over longer timescales.<sup>[59–61]</sup>

22 It is worth noting that the  $\mu$  values obtained from the OTP measurements (Figure 3) are  
23 calculated from the frequency averaged  $\Delta T/T$  signal (see Section 3 in SI for details). This  
24 shows that performing and interpreting THz measurements on these materials require care.  
25 While the evidence of carrier localization on the low frequency side of the THz



1 photoconductivity and the increasing  $\mu$  with increasing crystal size are reliable observations,  
2 the absolute values reported are likely affected by such modulations in the intensity of the  
3  $\Delta T_{\text{THz}}/T_{\text{THz}}$  signal.

4 The contrast between bulk and NC mobility values and photoconductivity spectra illustrates  
5 two important points concerning charge transport in these systems. One is the localization of  
6 charge carriers within nanoscale crystals, observed even after annealing. Such localization  
7 limits the charge transport in the THz range (*i.e.* picosecond timescales) and indicates that  
8 long range conductivity relies on interparticle hopping. However, localization may need to be  
9 tolerated in particular in applications for which optoelectronic properties arising from the  
10 nanocrystalline dimensions are important, as for example in light-emitting diodes. The second  
11 point is the distinct vibrational properties of colloiddally synthesized NCs, which are reflected  
12 in the photoconductivity spectra in the form of strong modulations. As shown in Section 2.2,  
13 the phonon absorption spectra of NCs are blue-shifted and the coupling of THz radiation to  
14 the lattice is twice as strong as in the bulk. Such differences are likely related to the reduced  
15 size, increased surface-to-volume ratio, and the lattice expansion in colloidal NCs. The  
16 distinct coupling of THz radiation to optical phonons in colloidal NCs can be an indication of  
17 fundamental differences in optoelectronic properties with respect to the bulk, in addition to  
18 the charge-carrier localization effects. In particular, the blue-shift of the THz spectra can be a  
19 result of more efficient coupling of light to specific modes of the lattice due to reduced size or  
20 orientation. Alternatively, it can also indicate a higher frequency of the phonon modes, which  
21 could suggest higher fundamental upper limits for the charge-carrier mobility with respect to  
22 that of the bulk.<sup>[45]</sup> However, further work is required to investigate in details how the  
23 structural and vibrational properties impact the charge-carrier mobility in perovskite  
24 nanocrystals.

### 25 **3. Conclusion**

1 In summary, we have investigated the optoelectronic properties of bulk CsPbBr<sub>3</sub> and  
2 colloiddally synthesized NCs in the weak confinement regime (6, 7.5 and 10 nm). We  
3 demonstrate how the structural, vibrational and charge transport properties of NCs deviate  
4 from the bulk material and how these are affected by the crystal size. In addition to wider  
5 band gaps and higher charge-carrier recombination rates resulting from confinement effects,  
6 we also observed a lattice expansion and distinct phonon spectra in the NCs compared to the  
7 bulk, which is likely related both to the reduced crystal size and to the crystal formation  
8 dynamics during colloidal synthesis in contrast to spin-coating methods. The phonon  
9 absorption spectra in the THz region of the NCs show a blue shift, broadening and higher  
10 effective relative absorption coefficients with respect to those of the bulk material. In addition  
11 to these differences in the dark spectra, we report a photoinduced modification of the phonon  
12 modes that can be seen as strong modulations on the photoexcited THz spectra, superimposed  
13 with the photoconductivity response. We also report an increase of the effective charge-carrier  
14 mobility with increasing crystal size and no dependence on the nature of the ligands or on  
15 film annealing. The obtained values for charge-carrier mobility and the shape of the  
16 photoconductivity spectra in the THz region demonstrate that the THz probe is sensitive to  
17 localized phenomena and that the carrier motion in these nanocrystalline materials is  
18 dominated by backscattering. Thus, the long-range photoconductivity of thin films made from  
19 NC inks depends on the competition between interparticle hopping and the enhanced  
20 recombination rates within NCs. This understanding of charge-carrier dynamics and transport  
21 represent an important step towards the optimization of nanocrystalline perovskite thin films  
22 for specific optoelectronic applications. In particular, light-emitting applications based on  
23 nanocrystals may benefit from films in which nanocrystals retain their mostly intra-particle  
24 optoelectronics properties, as investigated here, while photovoltaic applications may be better  
25 served by sintered nanocrystal films that approach bulk properties. Our findings therefore

1 provide valuable information that will guide further fundamental research on perovskite  
2 nanocrystals for specific applications.

3

#### 4 **Supporting Information**

5 Supporting Information is available from the Wiley Online Library or from the author.

6

#### 7 **Acknowledgements**

8 The authors gratefully acknowledge support from the Engineering and Physical Sciences  
9 Research Council (EPSRC) and the European Union's Horizon 2020 research and innovation  
10 programme under the Marie Skłodowska-Curie grant agreement No. 675867 (INFORM).  
11 SGM and AJR thank EPSRC Prosperity Partnership (EP/S004947/1) and AJR thanks EPSRC  
12 SPACE (EP/M015254/2). L.M.H. thanks the Alexander-von-Humboldt Foundation for a  
13 Friedrich-Wilhelm-Bessel Research Award.

14

15 Received: ((will be filled in by the editorial staff))

16 Revised: ((will be filled in by the editorial staff))

17 Published online: ((will be filled in by the editorial staff))

18

19

20

#### 21 **References**

22 [1] L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X.  
23 Yang, A. Walsh, M. V. Kovalenko, *Nano Lett.* **2015**, *15*, 3692.

24 [2] S. Yakunin, L. Protesescu, F. Krieg, M. I. Bodnarchuk, G. Nedelcu, M. Humer, G. De  
25 Luca, M. Fiebig, W. Heiss, M. V. Kovalenko, *Nat. Commun.* **2015**, *6*, 8056.

26 [3] N. Wang, L. Cheng, R. Ge, S. Zhang, Y. Miao, W. Zou, C. Yi, Y. Sun, Y. Cao, R.

- 1 Yang, Y. Wei, Q. Guo, Y. Ke, M. Yu, Y. Jin, Y. Liu, Q. Ding, D. Di, L. Yang, G.  
2 Xing, H. Tian, C. Jin, F. Gao, R. H. Friend, J. Wang, W. Huang, *Nat. Photonics* **2016**,  
3 *10*, 699.
- 4 [4] Q. A. Akkerman, M. Gandini, F. Di Stasio, P. Rastogi, F. Palazon, G. Bertoni, J. M.  
5 Ball, M. Prato, A. Petrozza, L. Manna, *Nat. Energy* **2017**, *2*, 16194.
- 6 [5] F. Krieg, S. T. Ochsenbein, S. Yakunin, S. ten Brinck, P. Aellen, A. Süess, B. Clerc, D.  
7 Guggisberg, O. Nazarenko, Y. Shynkarenko, S. Kumar, C.-J. Shih, I. Infante, M. V  
8 Kovalenko, *ACS Energy Lett.* **2018**, *3*, 641.
- 9 [6] J. Li, L. Xu, T. Wang, J. Song, J. Chen, J. Xue, Y. Dong, B. Cai, Q. Shan, B. Han, H.  
10 Zeng, *Adv. Mater.* **2017**, *29*, 1603885.
- 11 [7] D. V. Talapin, J.-S. Lee, M. V. Kovalenko, E. V. Shevchenko, *Chem. Rev.* **2010**, *110*,  
12 389.
- 13 [8] L. M. Wheeler, E. M. Sanehira, A. R. Marshall, P. Schulz, M. Suri, N. C. Anderson, J.  
14 A. Christians, D. Nordlund, D. Sokaras, T. Kroll, S. P. Harvey, J. J. Berry, L. Y. Lin, J.  
15 M. Luther, *J. Am. Chem. Soc.* **2018**, *140*, 10504.
- 16 [9] S. Dastidar, D. A. Egger, L. Z. Tan, S. B. Cromer, A. D. Dillon, S. Liu, L. Kronik, A.  
17 M. Rappe, A. T. Fafarman, *Nano Lett.* **2016**, *16*, 3563.
- 18 [10] C. Wehrenfennig, G. E. Eperon, M. B. Johnston, H. J. Snaith, L. M. Herz, *Adv. Mater.*  
19 **2014**, *26*, 1584.
- 20 [11] S. G. Motti, T. Crothers, R. Yang, Y. Cao, R. Li, M. B. Johnston, J. Wang, L. M. Herz,  
21 *Nano Lett.* **2019**, *19*, 3953.
- 22 [12] L. M. Herz, *ACS Energy Lett.* **2017**, *2*, 1539.
- 23 [13] M. B. Johnston, L. M. Herz, *Acc. Chem. Res.* **2016**, *49*, 146.

- 1 [14] C. L. Davies, J. B. Patel, C. Q. Xia, L. M. Herz, M. B. Johnston, *J. Infrared,*  
2 *Millimeter, Terahertz Waves* **2018**, *39*, 1236.
- 3 [15] D. Wang, J. Zhao, B. Chen, C. Zhu, *J. Phys. Condens. Matter* **2008**, *20*, 085212.
- 4 [16] L. Dou, A. B. Wong, Y. Yu, M. Lai, N. Kornienko, S. W. Eaton, A. Fu, C. G. Bischak,  
5 J. Ma, T. Ding, N. S. Ginsberg, L.-W. Wang, A. P. Alivisatos, P. Yang, *Science (80-. )*.  
6 **2015**, *349*, 1518.
- 7 [17] E. S. Parrott, J. B. Patel, A.-A. Haghighirad, H. J. Snaith, M. B. Johnston, L. M. Herz,  
8 *Nanoscale* **2019**, *11*, 14276.
- 9 [18] D. Di, K. P. Musselman, G. Li, A. Sadhanala, Y. Ievskaya, Q. Song, Z.-K. Tan, M. L.  
10 Lai, J. L. MacManus-Driscoll, N. C. Greenham, R. H. Friend, *J. Phys. Chem. Lett.*  
11 **2015**, *6*, 446.
- 12 [19] L. Polavarapu, B. Nickel, J. Feldmann, A. S. Urban, *Adv. Energy Mater.* **2017**, *7*,  
13 1700267.
- 14 [20] T. W. Jones, A. Osherov, M. Alsari, M. Sponseller, B. C. Duck, Y.-K. Jung, C. Settens,  
15 F. Niroui, R. Brenes, C. V. Stan, Y. Li, M. Abdi-Jalebi, N. Tamura, J. E. Macdonald,  
16 M. Burghammer, R. H. Friend, V. Bulović, A. Walsh, G. J. Wilson, S. Lilliu, S. D.  
17 Stranks, *Energy Environ. Sci.* **2019**, *12*, 596.
- 18 [21] P. Cottingham, R. L. Brutchey, *Chem. Commun. Chem. Commun* **2016**, 5246, 5246.
- 19 [22] F. Bertolotti, L. Protesescu, M. V. Kovalenko, S. Yakunin, A. Cervellino, S. J. L.  
20 Billinge, M. W. Terban, J. S. Pedersen, N. Masciocchi, A. Guagliardi, *ACS Nano* **2017**,  
21 *11*, 3819.
- 22 [23] C. C. Stoumpos, C. D. Malliakas, J. A. Peters, Z. Liu, M. Sebastian, J. Im, T. C.  
23 Chasapis, A. C. Wibowo, D. Y. Chung, A. J. Freeman, B. W. Wessels, M. G.

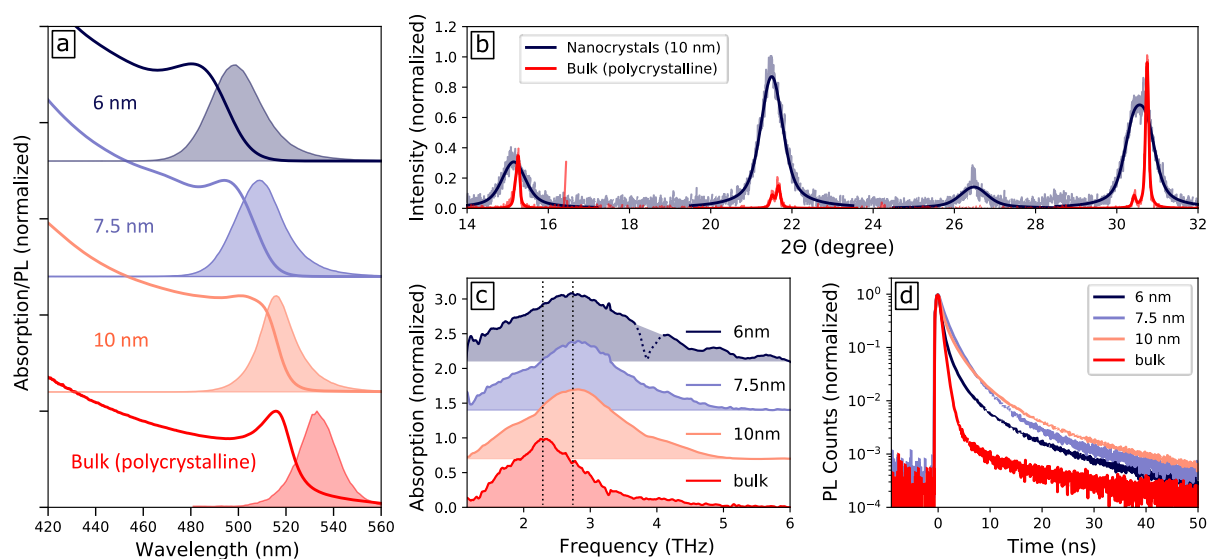
- 1 Kanatzidis, *Cryst. Growth Des.* **2013**, *13*, 2722.
- 2 [24] W. H. Hall, *Proc. Phys. Soc. Sect. A* **1949**, *62*, 741.
- 3 [25] P. M. Diehm, P. Ágoston, K. Albe, *ChemPhysChem* **2012**, *13*, 2443.
- 4 [26] S. Tsunekawa, K. Ishikawa, Z.-Q. Li, Y. Kawazoe, A. Kasuya, *Phys. Rev. Lett.* **2000**,  
5 85, 3440.
- 6 [27] A. Swarnkar, A. R. Marshall, E. M. Sanehira, B. D. Chernomordik, D. T. Moore, J. A.  
7 Christians, T. Chakrabarti, J. M. Luther, *Science (80-. )*. **2016**, *354*, 92.
- 8 [28] L. Saviot, B. Champagnon, E. Duval, I. A. Kudriavtsev, A. I. Ekimov, *J. Non. Cryst.*  
9 *Solids* **1996**, *197*, 238.
- 10 [29] H. Richter, Z. P. Wang, L. Ley, *Solid State Commun.* **1981**, *39*, 625.
- 11 [30] M. A. Pérez-Osorio, R. L. Milot, M. R. Filip, J. B. Patel, L. M. Herz, M. B. Johnston,  
12 F. Giustino, *J. Phys. Chem. C* **2015**, *119*, 25703.
- 13 [31] M. A. Pérez-Osorio, Q. Lin, R. T. Phillips, R. L. Milot, L. M. Herz, M. B. Johnston, F.  
14 Giustino, *J. Phys. Chem. C* **2018**, *122*, 21703.
- 15 [32] V. I. Klimov, *Science (80-. )*. **2000**, *287*, 1011.
- 16 [33] M. Li, S. Bhaumik, T. W. Goh, M. S. Kumar, N. Yantara, M. Grätzel, S. Mhaisalkar,  
17 N. Mathews, T. C. Sum, *Nat. Commun.* **2017**, *8*, 14350.
- 18 [34] Y. Yamada, T. Nakamura, M. Endo, A. Wakamiya, Y. Kanemitsu, *J. Am. Chem. Soc.*  
19 **2014**, *136*, 11610.
- 20 [35] S. D. Stranks, V. M. Burlakov, T. Leijtens, J. M. Ball, A. Goriely, H. J. Snaith, *Phys.*  
21 *Rev. Appl.* **2014**, *2*, 034007.
- 22 [36] S. G. Motti, M. Gandini, A. J. Barker, J. M. Ball, A. R. Srimath Kandada, A. Petrozza,

- 1        *ACS Energy Lett.* **2016**, *1*, 726.
- 2    [37] V. K. Ravi, P. K. Santra, N. Joshi, J. Chugh, S. K. Singh, H. Rensmo, P. Ghosh, A.  
3        Nag, *J. Phys. Chem. Lett.* **2017**, *8*, 4988.
- 4    [38] T. W. Crothers, R. L. Milot, J. B. Patel, E. S. Parrott, J. Schlipf, P. Müller-Buschbaum,  
5        M. B. Johnston, L. M. Herz, *Nano Lett.* **2017**, *17*, 5782.
- 6    [39] Y. Yamada, T. Yamada, L. Q. Phuong, N. Maruyama, H. Nishimura, A. Wakamiya, Y.  
7        Murata, Y. Kanemitsu, *J. Am. Chem. Soc.* **2015**, *137*, 10456.
- 8    [40] L. M. Pazos-Outon, M. Szumilo, R. Lamboll, J. M. Richter, M. Crespo-Quesada, M.  
9        Abdi-Jalebi, H. J. Beeson, M. Vru ini, M. Alsari, H. J. Snaith, B. Ehrler, R. H. Friend,  
10       F. Deschler, *Science (80-. )*. **2016**, *351*, 1430.
- 11   [41] Y. Li, T. Ding, X. Luo, Z. Chen, X. Liu, X. Lu, K. Wu, *Nano Res.* **2019**, *12*, 619.
- 12   [42] J. A. Castañeda, G. Nagamine, E. Yassitepe, L. G. Bonato, O. Voznyy, S. Hoogland,  
13        A. F. Nogueira, E. H. Sargent, C. H. B. Cruz, L. A. Padilha, *ACS Nano* **2016**, *10*, 8603.
- 14   [43] I. Robel, R. Gresback, U. Kortshagen, R. D. Schaller, V. I. Klimov, *Phys. Rev. Lett.*  
15        **2009**, *102*, 177404.
- 16   [44] P. Tiwana, P. Docampo, M. B. Johnston, H. J. Snaith, L. M. Herz, *ACS Nano* **2011**, *5*,  
17        5158.
- 18   [45] S. Poncé, M. Schlipf, F. Giustino, *ACS Energy Lett.* **2019**, *4*, 456.
- 19   [46] M. Sendner, P. K. Nayak, D. A. Egger, S. Beck, C. Müller, B. Epding, W. Kowalsky,  
20        L. Kronik, H. J. Snaith, A. Pucci, R. Lovrinčić, *Mater. Horizons* **2016**, *3*, 613.
- 21   [47] G. M. Turner, M. C. Beard, C. A. Schmittenmaer, *J. Phys. Chem. B* **2002**, *106*, 11716.
- 22   [48] M. C. Beard, G. M. Turner, C. A. Schmittenmaer, *Nano Lett.* **2002**, *2*, 983.

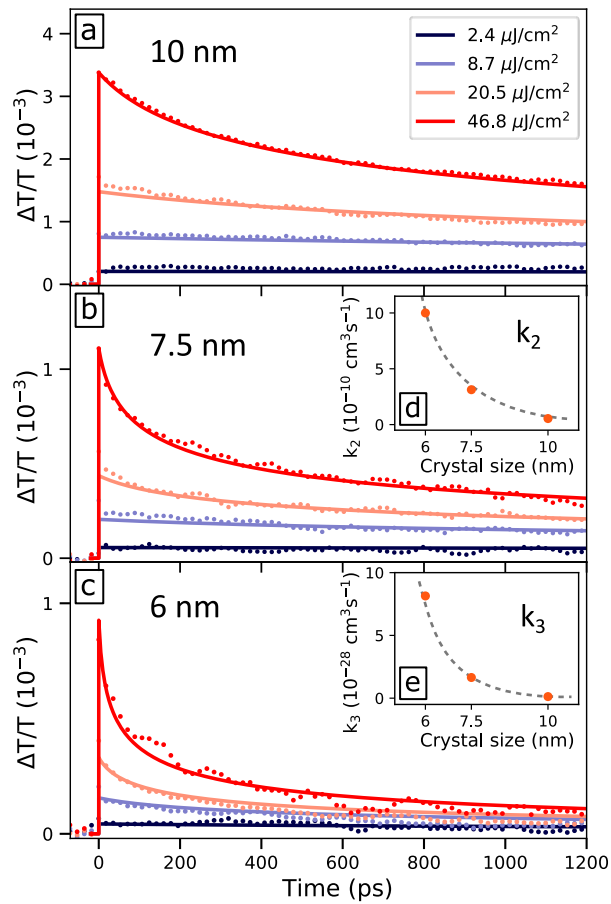
- 1 [49] J. Lloyd-Hughes, T.-I. Jeon, *J Infrared Milli Terahz Waves* **2012**, *33*, 871.
- 2 [50] H. J. Joyce, J. L. Boland, C. L. Davies, S. A. Baig, M. B. Johnston, *Semicond. Sci.*  
3 *Technol.* **2016**, *31*, 103003.
- 4 [51] R. L. Milot, G. E. Eperon, H. J. Snaith, M. B. Johnston, L. M. Herz, *Adv. Funct. Mater.*  
5 **2015**, *25*, 6218.
- 6 [52] C. L. Davies, J. Borchert, C. Q. Xia, R. L. Milot, H. Kraus, M. B. Johnston, L. M.  
7 Herz, *J. Phys. Chem. Lett.* **2018**, *9*, 4502.
- 8 [53] M. V. Kovalenko, L. Protesescu, M. I. Bodnarchuk, *Science (80-. )*. **2017**, *358*, 745.
- 9 [54] J. Li, L. Luo, H. Huang, C. Ma, Z. Ye, J. Zeng, H. He, *J. Phys. Chem. Lett.* **2017**, *8*,  
10 1161.
- 11 [55] K. Zheng, Q. Zhu, M. Abdellah, M. E. Messing, W. Zhang, A. Generalov, Y. Niu, L.  
12 Ribaud, S. E. Canton, T. Pullerits, *J. Phys. Chem. Lett.* **2015**, *6*, 2969.
- 13 [56] K. Tanaka, T. Takahashi, T. Ban, T. Kondo, K. Uchida, N. Miura, *Solid State*  
14 *Commun.* **2003**, *127*, 619.
- 15 [57] N. Smith, *Phys. Rev. B* **2001**, *64*, 155106.
- 16 [58] Y. Lan, B. J. Dringoli, D. A. Valverde-Chávez, C. S. Ponseca, M. Sutton, Y. He, M. G.  
17 Kanatzidis, D. G. Cooke, *Sci. Adv.* **2019**, *5*, eaaw5558.
- 18 [59] Y. Zhou, L. You, S. Wang, Z. Ku, H. Fan, D. Schmidt, A. Rusydi, L. Chang, L. Wang,  
19 P. Ren, L. Chen, G. Yuan, L. Chen, J. Wang, *Nat. Commun.* **2016**, *7*, 11193.
- 20 [60] T.-C. Wei, H.-P. Wang, T.-Y. Li, C.-H. Lin, Y.-H. Hsieh, Y.-H. Chu, J.-H. He, *Adv.*  
21 *Mater.* **2017**, *29*, 1701789.
- 22 [61] H. Tsai, R. Asadpour, J.-C. Blancon, C. C. Stoumpos, O. Durand, J. W. Strzalka, B.



1 Chen, R. Verduzco, P. M. Ajayan, S. Tretiak, J. Even, M. A. Alam, M. G. Kanatzidis,  
2 W. Nie, A. D. Mohite, *Science* (80-. ). **2018**, *360*, 67.

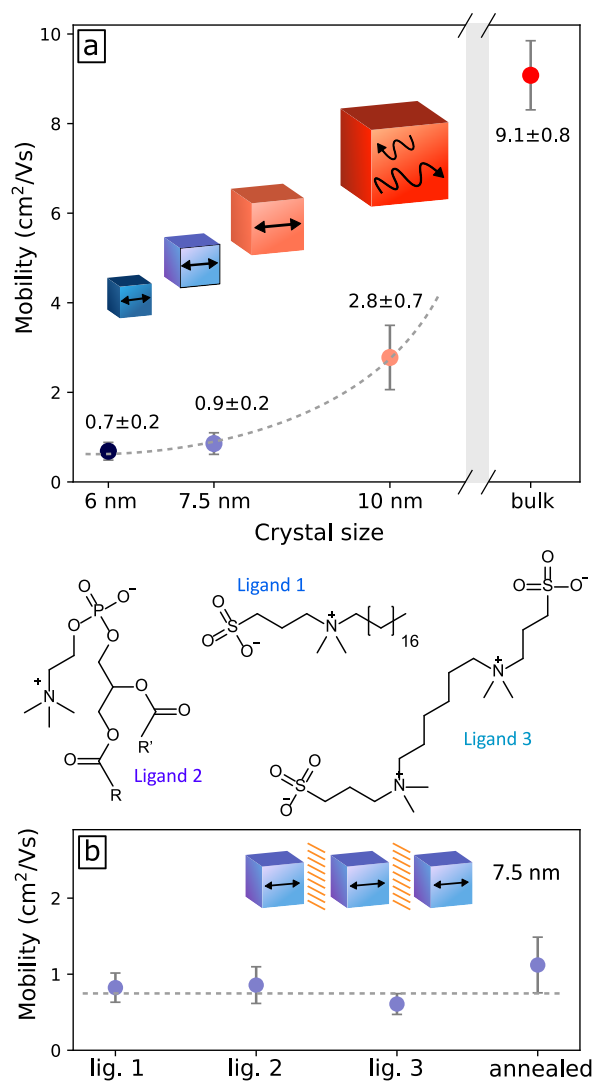


6  
7 **Figure 1.** (a) Absorption and PL spectra of CsPbBr<sub>3</sub> nanocrystals (average size 6, 7.5 and 10  
8 nm) deposited on quartz substrates and spin coated polycrystalline film (average grain size  
9 ~100 nm); b) XRD diffraction pattern obtained from the 10-nm nanocrystals and the spin  
10 coated polycrystalline film, corrected for tilting according to the quartz substrate diffraction  
11 peaks as reference; c) Normalized THz absorption spectra in the dark for the nanocrystals and  
12 the spin coated polycrystalline film; offsets were added for clarity; the dashed line in the 6-nm  
13 NC spectrum is an artifact caused by the absorption of the quartz substrate,<sup>[14]</sup> visible in the  
14 cases of films with lower optical density. d) PL decay dynamics of polycrystalline and  
15 nanocrystalline CsPbBr<sub>3</sub> obtained at excitation fluence ~20 nJ/cm<sup>2</sup>, wavelength 398 nm, 5  
16 MHz repetition rate.



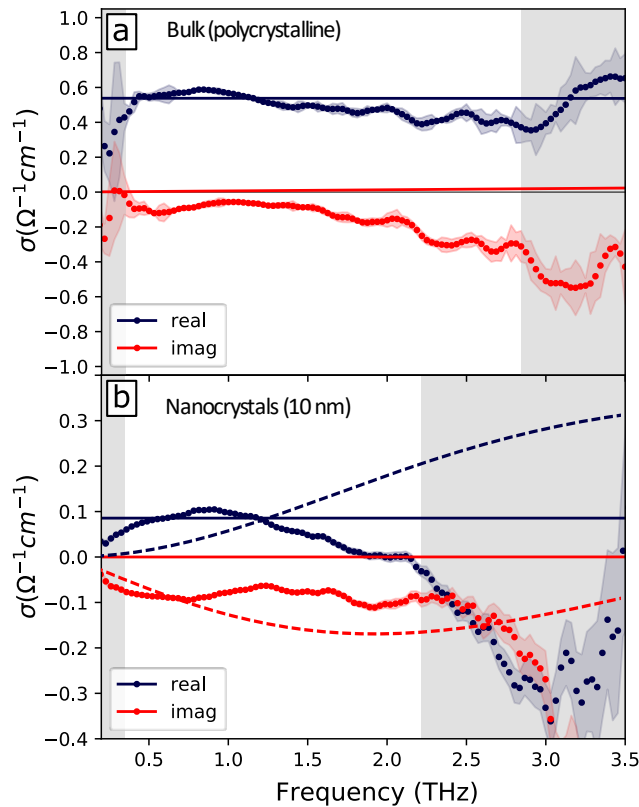
1

2 **Figure 2.** Photoconductivity dynamics (plotted as  $-\Delta T_{\text{THz}}/T_{\text{THz}} \propto \sigma$ ; excitation at 400 nm,  
 3 repetition rate 5 kHz) of CsPbBr<sub>3</sub> nanocrystals of average size (a) 10 nm, (b) 7.5 nm and (c) 6  
 4 nm, deposited on quartz. Dots are experimental data and solid lines are rate equation fits to  
 5 the fluence dependence as described in detail in Section 1.5.1 in SI. Insets show the fitted  
 6 values of rate constants (d)  $k_2$  and (e)  $k_3$ . Dashed grey lines are guides to the eye.



1  
 2 **Figure 3.** (a) Size dependence of the effective THz mobilities obtained from OPTP  
 3 measurements on deposited nanocrystals and (b) Effective THz mobilities of 7.5 nm crystals  
 4 with different ligands and after annealing at 150°C for 10 minutes. The molecular structures  
 5 of the ligands are shown in the middle panel, where R and R' can be different saturated or  
 6 unsaturated 16- or 18-carbon long carbo-hydrate chains (see Section 1 in SI for more details).

7



1

2 **Figure 4.** Real (dark blue) and imaginary (red) parts of THz photoconductivity spectra of (a)  
 3 a polycrystalline thin film and (b) 10 nm nanocrystals of CsPbBr<sub>3</sub> deposited on quartz, ~20 ps  
 4 after photoexcitation at fluence ~40  $\mu\text{J}/\text{cm}^2$ . Dots are experimental data while solid lines are  
 5 simulated spectra from the Drude model and the dashed lines in (b) are obtained with Drude-  
 6 Smith. The grey shaded areas mark regions of lower confidence (at frequencies lower than  
 7 0.35 THz due to focusing artifacts and in regions where the THz transmission is reduced by  
 8 90%). See **Error! Reference source not found.** in SI for other NC sizes.

9

10

11

12

13

14

1 **Table of Contents**

2

3

4 **Keywords:** perovskite, nanocrystals, charge-carrier dynamics, mobility

5

6 S. G. Motti, F. Krieg, A. J. Ramadan, J. B. Patel, H. J. Snaith, M. V. Kovalenko, M. B.

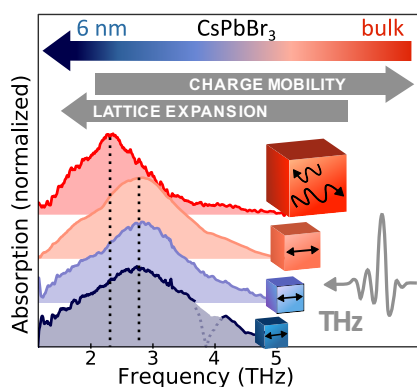
7 Johnston, L. M. Herz\*

8

9 **CsPbBr<sub>3</sub> nanocrystal films: deviations from bulk vibrational and optoelectronic**  
10 **properties**

11

12



13

14

15 The optoelectronic properties of CsPbBr<sub>3</sub> nanocrystal films are investigated in comparison to  
16 those of a bulk polycrystalline film. The terahertz photoconductivity shows localization of  
17 charge carriers in nanocrystals even after partial sintering. The nanocrystals show expansion  
18 of the lattice, blue-shifted phonon spectra and enhanced coupling of phonon modes to the  
19 terahertz probe with respect to the bulk.

20

21

22

23 Copyright WILEY-VCH Verlag GmbH &amp; Co. KGaA, 69469 Weinheim, Germany, 2018.