High-bandwidth Perovskite Photonic Sources on Silicon

Aobo Ren[1,2,†], Hao Wang[3,†], Linjie Dai[4], Junfei Xia[3], Xinyu Bai[4], Edward Butler-Caddle[5], Joel A. Smith[6], Huagui Lai[7], Junzhi Ye[4], Xiang Li[3,8], Shijie Zhan[3], Chunhui Yao[3], Zewei Li[4], Mingchu Tang[9], Xueping Liu[2], Jinxin Bi[2], Bowei Li[2], Shen Kai[1,10], Rui Chen[3], Han Yan[11], Jintao Hong[3], Liming Yuan[12], Igor P. Marko[2,13], Adrian Wonfor[3], Fan Fu[7], Steve A. Hindmarsh[5], Ana M. Sanchez[5], James Lloyd-Hughes[5], Stephen J. Sweeney[2,13], Akshay Rao[4], Neil C. Greenham[4], Jiang Wu[1,10*], Yanrong Li[10,14], Qixiang Cheng[3*], Richard H. Friend[4], Richard V. Penty[3], Ian H. White[3,15], Henry J. Snaith[6*], Wei Zhang[2*]

[1]Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu, China

[2]Advanced Technology Institute, University of Surrey, Guildford, UK

[3]Division of Electrical Engineering, Department of Engineering, University of Cambridge, Cambridge, UK

[4]Cavendish Laboratory, University of Cambridge, Cambridge, UK

[5]Department of Physics, University of Warwick, Coventry, UK

[6]Clarendon Laboratory, Department of Physics, University of Oxford, Oxford, UK

[7]Laboratory for Thin Films and Photovoltaics, Empa-Swiss Federal Laboratories for Materials Science and Technology, Duebendorf, Switzerland

[8]School of Mechanical Engineering and Electronic Information, China University of Geosciences, Wuhan 430074, China

[9]Department of Electronic and Electrical Engineering, University College London, London, UK

[10]State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu, China

[11]Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, UK

[12]State Key Laboratory of Optical Technologies on Nano-fabrication and Micro-engineering, Institute of Optics and Electronics, Chinese Academy of Sciences, Chengdu, China

[13]Department of Physics, University of Surrey, Guildford, UK

[14]Northwestern Polytechnical University, Xi'an 710072, China

[15]Vice-Chancellor's Office, University of Bath, Bath, UK

[†]These authors contributed equally: Aobo Ren and Hao Wang

[*]Corresponding author: jiangwu@uestc.edu.cn (J.W.); qc223@cam.ac.uk (Q.C.); henry.snaith@physics.ox.ac.uk (H.J.S.); wz0003@surrey.ac.uk (W.Z.)

Abstract

Light-emitting diodes (LEDs) are ubiquitous in modern society, with applications spanning from lighting and displays, to medical diagnostics and data communications. Metal halide perovskites are promising materials for LEDs because of their excellent optoelectronic properties and solution processability. Whilst research has progressed significantly in optimising external quantum efficiency, the modulation characteristics of perovskite LEDs remain unclear. Here we report a holistic approach for realising fast perovskite photonic sources on silicon based on tailoring alkylammonium cations in perovskite systems. We reveal the recombination behaviour of charged species at various carrier density regimes relevant for their modulation performance. By integrating a Fabry–Pérot microcavity on silicon, we demonstrate perovskite devices with efficient light-outcoupling. We achieve device modulation bandwidths of up to 42.6 MHz and data rates above 50 Mbps, with further analysis suggesting that the bandwidth may exceed gigahertz levels. The principles developed here will support the development of perovskite light sources for the next-generation data communication architectures. The demonstration of solution processed perovskite emitters on silicon substrates also opens up the possibility of integration with micro-electronics platforms.

Main

Future applications of light-emitting diodes (LEDs) will never be limited to the fields of lighting and displays. Previous efforts have proven that they are an up-and-coming candidate for transmitters in optical data communications[1–3]. With billions of Internet of Things (IoT) devices already connected, costs and compatibility are sometimes prioritised over speed in current communication scenarios[4]. Metal halide perovskites have shown versatile applications in high-performance photovoltaics, photodetectors and LEDs[5–7]. Another distinct advantage of perovskites is that these materials can be solution-processed on various substrates[6]. The simple low-temperature processing, coupled with high optoelectronic quality may enable perovskites to address the challenge in light emission on silicon that could facilitate low-cost on-chip photonic links. This potentially brings a further benefit that the integrated device could leverage the well-developed micro-electronics technology for photonic-electronic co-integration. However, a fast on-chip perovskite source is yet to be realised, and relevant mechanisms determining modulation performance from material to device level have remained elusive.

The application of LED-based photonic sources for communications has been challenged by the demand for high modulation bandwidth. The -3 dB bandwidth f_{-3dB} of an LED device is primarily limited by its resistor–capacitor time constant τ_{RC} and/or effective charge carrier recombination lifetime τ_{eff}[1],

$$f_{-3dB} = \frac{1}{2\pi\tau}, \tag{1}$$

where τ exhibits a strong correlation with the value of either the τ_{RC} or the τ_{eff}, depending on which is the dominant factor limiting the f_{-3dB}. The τ_{RC} can be directly reduced by shrinking the device active area to decrease the geometric capacitance. The τ_{eff} can vary significantly depending on the choice of emitters. We note that a high-level charge carrier injection into the emissive region of an LED can effectively reduce both the τ_{RC} (decrease the diode resistance) and the τ_{eff}. Although this concept has long been understood in III-V nitride light sources[8], it has brought additional challenges for use in halide perovskite-based light sources due to their distinct physical properties (e.g., soft ionic crystal structures[9], charge scattering[10], etc). One major challenge is how the recombination dynamics in perovskites affect the two aforementioned time-related constants, and further, the modulation performance. Auger recombination process, which occurs at high carrier densities, becomes significant during high-speed operation. Increased Auger process may theoretically lead to a reduction in τ_{eff}. However, in perovskites, issues caused by such process are serious (e.g., device stability reduction and efficiency roll-off). The role of Auger recombination in determining the achievable bandwidths in perovskites remains to be identified. Additionally, another challenge lies in the fact that the device architecture engineering lags far behind that of conventional III-V light sources. The issues of unbalanced charge injection, high outcoupling loss, and poor thermal management still need to be addressed. The intensified Joule heating and the efficiency roll-off make it extremely difficult to maintain continuously operating devices at high injection conditions[11]. To this end, a combination of an emitter with fast radiative recombination and high charge carrier mobility, along with a low τ_{RC} device architecture and an efficient light outcoupling layout must be achieved simultaneously.

In this work, we select caesium lead tribromide ($CsPbBr_3$) as the model material for developing high-speed devices due to its fast recombination rate and decent thermal stability[12]. However, the significant nonradiative recombination of neat $CsPbBr_3$ prevent its emissive property and device modulation performance. The incorporation of alkylammonium cations has been considered as an efficient approach for film quality improvement[13]. The widely used bulky ammonium cations have shown a notable electronic passivation effect on trap states, while free charge carries would undergo strong Coulombic interactions[14]. Such quantum and dielectric confinement not only enhance excitonic recombination but also many-body interactions[15] (e.g., Auger recombination) and phonon scattering[16] (e.g., Fröhlich coupling), hindering device performance under high-injection levels. Here we explore how rational cation tailoring can facilitate their interaction with defective sites while preserving optimal recombination dynamics. We showcase how the behaviour of charge carriers in pristine $CsPbBr_3$ can be manipulated by a range of representative alkylammonium cations. Through probing the fluence-dependent charge carrier kinetics of the alkylammonium cation-modified perovskite emitters, we uncover the recombination mechanisms that underpin the modulation performance. We design a low τ_{RC} device architecture with a Fabry–Pérot microcavity on silicon. We demonstrate greatly improved perovskite LEDs (PeLEDs) with modulation bandwidths of up to 42.6 MHz, enabling a maximum data rate over 50 Mbps in a guided-wave data transmission link.

Results and discussion

High-level injection conditions are essential for LED-based photonic sources to achieve higher bandwidths for efficient communications. It is therefore vital for perovskite films to maintain sufficient photoluminescence quantum efficiencies (PLQEs) under high charge carrier densities. We first evaluate the luminescence behaviours of $CsPbBr_3$ (hereafter denoted as the control), and those modified with three representative organic salts (single-carbon, long-chain and short-chain): methylammonium bromide (MABr), phenethylammonium bromide (PEABr), and *tert*-butylammonium bromide (*t*-BABr). In Fig. 1a-c, the PLQE maps show the distinct recombination features at different excitation power densities. The presence of all three alkylammonium cations results in a notable enhancement in PLQE across all excitation intensities when $x > 0.2$, in line with the results of favourable passivation of defects[14,17,18]. For the PEABr-modified films with $x > 0.6$, two distinct absorption and emission features become evident, assigned to the formation of n=2 and n=3 quasi-two-dimensional (2D) Ruddlesden-Popper phases (n is the number of $[PbBr_6]^{4-}$ octahedral sheets between the organic spacer planes) (Fig. 1d-f, Extended Data Fig. 1). The PEABr-based films exhibit high PLQEs of ~60-70% with less dependence upon power densities in the low excitation density regime (Fig. 1b). It is because of the electronic isolation and efficient passivation of emissive domains within the perovskites, facilitating efficient radiative geminate exciton recombination[19]. The efficient localisation of charges significantly increases the carrier density at recombination centres. Unfortunately, it also leads to increased polydispersity and lowers the threshold of nonradiative

Auger process. Remarkably, the MABr and *t*-BAB films with three-dimensional (3D) phases show similar recombination behaviours with considerably high PLQEs of ~50% and ~60% even at power density (10^3 mWcm^{-2}). We emphasise that such a scenario, where radiative bimolecular recombination dominates over Auger recombination at high carrier densities, is desirable for fast photonic sources.

We observe the broadening of the excitonic absorption features (Fig. 1d-f) and the PL peaks (Extended Data Fig. 1) for the films with excess bulky cations compared to the strong excitonic absorption peaks of the control films (Supplementary Fig. 1). Thus, we extract the absorption-related energy states, including the lowest-energy 1*s* excitonic transition and unbound continuum absorption, based on the Elliott theory[20] (Supplementary Fig. 2-4). Previous studies have shown that high exciton binding energies, which result in strong electron-hole Coulomb interactions, directly contribute to an increased propensity for Auger recombination process[21]. The molar ratio-dependent exciton binding energy (E_b) suggests that organic cation additives can weaken the Auger process via reducing the excitonic oscillator strength ($x \leq 0.5$). Further increasing the cation ratio ($x > 0.5$) leads to an increase of E_b and excitonic disorder parameter[22,23] (Supplementary Fig. 5). We find that $(MABr)_{0.5}CsPbBr_3$, $(PEABr)_{0.4}CsPbBr_3$ and $(t\text{-}BABr)_{0.4}CsPbBr_3$ (referred to as MA, PEA and *t*-BA hereafter) films show reduced PLQE roll-off at high power densities (Supplementary Fig. 6), consistent with their suppressed electron-hole interaction.

We fabricated perovskite sources based on the optimal alkylammonium cation-modified perovskite films discussed above. Both the PEA and *t*-BA films show a significant decrease in grain size (less than 50 nm) and compact surface coverage as seen by scanning electron microscopy (SEM), atomic force microscopy (AFM) and elemental depth profiles (Supplementary Fig. 7-9). X-ray diffraction (XRD) measurements (Extended Data Fig. 2a, b) show similar peaks at around 15.2° and 21.5° for all films, corresponding to the reflections from the orthorhombic $CsPbBr_3$ perovskite phase. Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements (Extended Data Fig. 2c-f) reveal that the perovskite crystal domains have different orientations with each additive. By identifying unique Bragg spots for each film that are also present in simulated scattering patterns (Supplementary Fig. 10 and 11), we observe that the crystal domains are primarily oriented along (002) for the PEA film and (110) for the *t*-BA film. To enhance the light outcoupling, a surface-emission configuration was devised by situating the perovskite layer within a Fabry–Pérot microcavity, employing a high reflective Au anode and a semi-transparent Ag cathode[24,25] (Fig. 2a, Supplementary Fig. 12, 13). Cross-sectional scanning transmission electron microscopy (STEM) (Fig. 2b, Supplementary Fig. 14) and element-mapping images (Extended Data Fig. 3) show a well-defined layer-by-layer stack. The thickness of the functional layers was carefully tuned for a balanced charge injection (Supplementary Fig. 15).

Figure 2c shows the current density-voltage (*J*-*V*) characteristics of the LED devices. The maximum external quantum efficiency (EQE) values achieved are 4.1% (control), 17.2% (MA), 20.2% (PEA), and 19.6% (*t*-BA), respectively (Fig. 2d, Supplementary Fig. 16). Strikingly, but consistent with the intensity-dependent PL findings, the *t*-BA device sustains high EQEs under high injection levels. Additionally, we infer that the chemically inert and hydrophobic polystyrene layer also passivated the grain boundaries of the perovskite films (Supplementary Fig. 17). The elemental depth profiles of the *t*-BA devices indicate that the insertion of such a capping layer can effectively suppress the migration of Ag and Pb ions (Extended Data Fig. 4). The resulting *t*-BA device displayed exceptional long-term stability with a -3 dB lifetime of ~88 h (Supplementary Fig. 18) benefiting from its balanced charge injection and efficient thermal dissipation, prerequisites for achieving fast and stable data transmissions.

We modelled the light outcoupling efficiency η_{out} and optical power dissipation using the finite-difference time-domain (FDTD) method (Extended Data Fig. 5). Isotropic, horizontally oriented $p_{x/y}$ dipoles contribute the most to the extracted light from the device, whereas vertical p_z dipoles show low light outcoupling due to total internal reflection. The angular-spectral radiated power patterns of the cavity, showing non-Lambertian emission profiles, closely match the measured angle-dependent electroluminescence profiles. This indicates that the resonance wavelength is blue-shifted with increasing viewing angle. The simulated power distribution among different optical modes of the device shows a peak outcoupling efficiency of 29.04% (Fig. 2e). This excellent light extraction is attributed to the elimination of the waveguide mode (perovskite layer <200 nm) and the enhancement of the surface plasmon polariton (SPP) mode at the air/Ag interface (Fig. 2f).

To assess the modulation performance of the devices, we examined their frequency response characteristics under various injection levels. Directly decreasing the active area seems to be the most straightforward solution to improve the device modulation bandwidth (Extended data Fig. 6a-d). However, this approach comes with the trade-off of a reduction in power intensity. We measured the voltage-dependent frequency responses of our smallest devices (0.028 mm^2) (Extended data Fig. 6e-h). As the bias increases from 3.5 to 7.5 V, the bandwidths of the MA and *t*-BA devices increase from 1.9 and 2.1 MHz to 21.3 and 37.6 MHz, respectively. This is a direct consequence of their significantly lowered τ_{RC}s at high injections. In contrast, the bandwidths of both the control and PEA devices drop at a high bias of 7.5 V due to the deterioration of device performance under high injections. Through reducing the active device area while maintaining high injection levels, the best performing control, MA, PEA and *t*-BA devices attained bandwidths of 16.0, 23.1, 12.9, 42.6 MHz, respectively (Fig. 3a).

Statistically, with the same active area and injection level, the *t*-BA devices always exhibit the largest bandwidths (Fig. 3b). Such a large difference in bandwidth is, in part, due to the variation of charge carrier mobility[26]. The effective carrier mobility $\varphi\sum\mu$ (where $\sum\mu$ is the sum of the electron and hole mobilities; φ is the free charge-carrier branching ratio) was probed by examining the differential terahertz (THz) photoconductivity (Fig. 3c, Extended Data Fig. 7). Notably, $\varphi\sum\mu$ of the *t*-BA film (21.4 $cm^2V^{-1}s^{-1}$) is 2-3 times larger than those of other compositions under low pump excitation density. Charge carrier mobility is expected to be influenced by scattering events[16,27]. The high $\varphi\sum\mu$ of the *t*-BA film is consistent with a reduction in the strength of electron-phonon Fröhlich coupling (Supplementary Fig. 19, 20) responsible for charge carrier scattering within the crystalline material[16].

The trap states within the devices, capable of being charged and discharged by the modulation signals (extra capacitance)[28], were evaluated by thermal admittance spectroscopy (Extended Data Fig. 8a-d). The trap density of states (tDOS) can thereby be deduced from the differential capacitance spectra at characteristic peaks (Fig. 3d, Extended Data Fig. 8e-j). As expected, all three cations-modified devices exhibit lower trap densities of ~$0.7\text{-}1.2\times10^{16}$ $cm^{-3}ev^{-1}$ (compared to the control device of 3.8×10^{16} $cm^{-3}ev^{-1}$) in the shallower energy regions. The interaction between the cations with the defects on the grain surfaces is further confirmed by density functional theory (DFT) calculations. It is evident that these three cations can effectively eliminate the in-gap states as observed in the electronic structures (Supplementary Fig. 21-24). We note that the measured capacitance of all devices drops abruptly with increasing frequency, enabling a further reduction in their τ_{RC}s. This is resulting from fewer trap states that can respond to the modulation signals toward high frequencies[29].

Beyond reducing τ_{RC}, it is important to note that τ_{eff} also imposes limitations on bandwidth[1]. To gain insights into the processes governing the τ_{eff}s, we considered the various recombination pathways occurring in the perovskite emissive layers, combined in a general recombination rate equation,

$$-\frac{dn}{dt} = k_1 n + k_2 n^2 + k_3 n^3, \quad (2)$$

where k_1 is the monomolecular recombination rate constant, k_2 is the radiative bimolecular recombination rate constant, k_3 is the Auger recombination rate constant, and the charge carrier recombination rate $\frac{dn}{dt}$ strongly depends on the charge carrier density n. We carried out transient absorption (TA) measurements over the pico- to nanosecond time scale (Extended Data Fig. 9a-l). We spliced the carrier density-dependent recombination rates for all pump fluences to fit the rate constants k_1, k_2 and k_3 with the rate equation (Extended Data Fig. 9m-p). Notably, the TA-derived rate constants (Fig. 4a, Supplementary Fig. 25) are in good agreement with the k_1 derived from the low-fluence time-resolved photoluminescence (TRPL) (Supplementary Fig. 26), as well as the k_2 and k_3 derived from optical pump terahertz probe (OPTP) spectroscopy (Extended Data Fig. 7a-d).

τ_{eff} can be the derivative of the recombination rate with respect to n,

$$\tau_{eff}{}^{-1} = k_1 + 2k_2 n + 3k_3 n^2. \quad (3)$$

Combined with equation (1), we can obtain the f_{-3dB} as a function of n based on our measured rate constants (Fig. 4b-e, Supplementary Note 1). The reconstructed f_{-3dB} boundaries from the rate constants are well agreed with the fluence-dependent τ_{eff}s (Supplementary Fig. 27, 28). The device differential resistance reduces with increasing carrier density (Supplementary Fig. 29), leading to a lower τ_{RC} and, consequently, a higher f_{-3dB}. The highest k_1 value of the control film implies a dominant nonradiative recombination process resulting from the existence of unpassivated defects. Such a high k_1 value dominating the f_{-3dB} at low injection level ($n<10^{15}$ cm^{-3}) comes at the cost of sacrificing efficiency, rendering it not useful. We observe an increase in the effective k_2 for the films containing the organic cations. The increased k_2 validates the enhanced band-to-band radiative recombination, especially for the *t*-BA film. The quasi-2D/3D PEA film with low-dimensional phases result in "charge funnelling" into the lower band gap 3D domains, and an increase in the carrier density, and hence bimolecular recombination within 3D domains[30]. However, the noticeably increased k_3 in the PEA film indicates a more significant Auger recombination at high carrier densities ($n > 10^{17}$ cm^{-3}). Though such a process has theoretical benefits for increasing the intrinsic f_{-3dB} (equation (3)), it significantly impedes devices from reaching high current density operating regimes for both high brightness and fast radiative bimolecular recombination. In contrast, the excellent luminescence properties of the *t*-BA film are again validated, showcasing the fast bimolecular recombination, strongly suppressed Auger recombination and solid photo-stability (Supplementary Fig. 30). Overall, we find that the bandwidths of our devices are mostly τ_{RC} dominant. Interestingly, the bandwidths of the *t*-BA devices with the smallest area have reached the boundary of the material's intrinsic f_{-3dB}, suggesting that their bandwidths tend to be both τ_{RC} and τ_{eff} dominant. We expect the potential device bandwidth can achieve gigahertz range exceeding the current state-of-the-art high-speed LEDs (Fig. 4f)[9,31,32]. The supressed Auger recombination rate in the *t*-BA film can be attributed to its reduced dielectric constant gap between the organic cation and inorganic framework, further weakening the Columbic force of electron–hole pairs (Supplementary Fig. 31). We show the reported Auger rate constants k_3 for some direct band gap compound semiconductors (Supplementary Fig. 32), and is approximately an order of magnitude lower than that of the previously reported perovskite emitters[14,33–36].

We lastly evaluated the data transmission performance of our on-chip photonic sources by constructing a guided-wave data transmission link (Supplementary Fig. 33). The measured data rates of the devices for each category are all bound by a similar trend as their respective modulation bandwidths (Extended Data Fig. 10a). The control, MA and PEA devices achieved data rates exceeding 20, 30, 16 Mbps, respectively. The *t*-BA devices provide optimal transmission performance (Extended Data Fig. 10b-d), exhibiting a maximum data rate of over 53 Mbps with a modulation bandwidth of 41.3 MHz. Furthermore, the energy consumption is in the range of 90-150 pJ per bit at the high injection regimes (>30 Mbps). We note that this value is significantly reduced to 300-400 fJ per bit at the low injection regimes (~1-2 Mbps), which can still offer more than enough bandwidth and ultralow load for some IoT and smart device applications[37,38].

Conclusion

In summary, we provide a versatile approach for developing fast perovskite photonic sources, encompassing strategies for material tailoring, device engineering, and methodologies for establishing a relationship between photophysical processes and modulation performance. This has enabled us to demonstrate the devices processed directly on silicon chips with a maximum modulation bandwidth of 42.6 MHz and a data transmission rate of over 50 Mbps within a guided-wave link. This work has showcased the high-bandwidth capability of perovskites and is likely to be broadly applicable to widespread communication solutions. Furthermore, our investigations may also boost the development of high-speed perovskite photodetectors[39] or continuous-wave pumped perovskite lasers[40].

References (main)

1. Ren, A. *et al.* Emerging light-emitting diodes for next-generation data communications. *Nature Electronics* **4**, 559–572 (2021).
2. Karunatilaka, D., Zafar, F., Kalavally, V. & Parthiban, R. LED based indoor visible light communications: State of the art. *IEEE Communications Surveys and Tutorials* **17**, 1649–1678 (2015).
3. Rajbhandari, S. *et al.* A review of gallium nitride LEDs for multi-gigabit-per-second visible light data communications. *Semiconductor Science and Technology* **32**, 023001 (2017).
4. Cisco, T. & Internet, A. *Cisco: 2020 CISO Benchmark Report*. *Computer Fraud & Security* vol. 2020 (2020).
5. Park, N.-G. & Zhu, K. Scalable fabrication and coating methods for perovskite solar cells and solar modules. *Nature Reviews Materials* **5**, 333–350 (2020).
6. García De Arquer, F. P., Armin, A., Meredith, P. & Sargent, E. H. Solution-processed semiconductors for next-generation photodetectors. *Nature Reviews Materials* **2**, 1–16 (2017).
7. Liu, X. K. *et al.* Metal halide perovskites for light-emitting diodes. *Nature Materials* **20**, 10–21 (2021).
8. Barlow, I. A., Kreouzis, T. & Lidzey, D. G. High-speed electroluminescence modulation of a conjugated-polymer light emitting diode. *Applied Physics Letters* **94**, 11–14 (2009).
9. Fu, Y. *et al.* Metal halide perovskite nanostructures for optoelectronic applications and the study of physical properties. *Nature Reviews Materials* **4**, 169–188 (2019).
10. Lee, W. *et al.* Ultralow thermal conductivity in all-inorganic halide perovskites. *Proceedings of the National Academy of Sciences of the United States of America* **114**, 8693–8697 (2017).
11. Qin, J., Liu, X.-K., Yin, C. & Gao, F. Carrier Dynamics and Evaluation of Lasing Actions in Halide Perovskites. *Trends in Chemistry* **3**, 34–46 (2021).
12. Wolf, C. & Lee, T.-W. Exciton and lattice dynamics in low-temperature processable CsPbBr3 thin-films. *Materials Today Energy* **7**, 199–207 (2018).
13. Lee, J.-W., Tan, S., Seok, S. Il, Yang, Y. & Park, N.-G. Rethinking the A cation in halide perovskites. *Science* **375**, (2022).

14. Jiang, Y. jpclett. 5b02290. pd. *et al.* Reducing the impact of Auger recombination in quasi-2D perovskite light-emitting diodes. *Nature Communications* **12**, 1–10 (2021).

15. Herz, L. M. Charge-Carrier Dynamics in Organic-Inorganic Metal Halide Perovskites. *Annual Review of Physical Chemistry* **67**, 65–89 (2016).

16. Wright, A. D. *et al.* Electron–phonon coupling in hybrid lead halide perovskites. *Nature Communications* **7**, 11755 (2016).

17. Lin, K. *et al.* Perovskite light-emitting diodes with external quantum efficiency exceeding 20 per cent. *Nature* **562**, 245–248 (2018).

18. Wang, Z. *et al.* Manipulating the Trade-off Between Quantum Yield and Electrical Conductivity for High-Brightness Quasi-2D Perovskite Light-Emitting Diodes. *Advanced Functional Materials* **28**, 1–10 (2018).

19. Xing, G. *et al.* Transcending the slow bimolecular recombination in lead-halide perovskites for electroluminescence. *Nature Communications* **8**, 14558 (2017).

20. Elliott, R. J. Intensity of Optical Absorption by Excitons. *Physical Review* **108**, 1384–1389 (1957).

21. Chen, X., Lu, H., Yang, Y. & Beard, M. C. Excitonic Effects in Methylammonium Lead Halide Perovskites. *The Journal of Physical Chemistry Letters* **9**, 2595–2603 (2018).

22. Warby, J. H. *et al.* Revealing Factors Influencing the Operational Stability of Perovskite Light-Emitting Diodes. *ACS Nano* **14**, 8855–8865 (2020).

23. Wehrenfennig, C., Liu, M., Snaith, H. J., Johnston, M. B. & Herz, L. M. Homogeneous Emission Line Broadening in the Organo Lead Halide Perovskite CH 3 NH 3 PbI 3− x Cl x. *The Journal of Physical Chemistry Letters* **5**, 1300–1306 (2014).

24. Schubert, E. F. *et al.* Highly Efficient Light-Emitting Diodes with Microcavities. *Science* **265**, 943–945 (1994).

25. Wen, C. P. Coplanar Waveguide, a Surface Strip Transmission Line Suitable for Nonreciprocal Gyromagnetic Device Applications. *1969 G-MTT International Microwave Symposium* 110–115 (1969) doi:10.1109/GMTT.1969.1122668.

26. Yoshida, K. *et al.* 245 MHz bandwidth organic light-emitting diodes used in a gigabit optical wireless data link. *Nature Communications* **11**, 1171 (2020).

27. Herz, L. M. Charge-Carrier Mobilities in Metal Halide Perovskites: Fundamental Mechanisms and Limits. *ACS Energy Letters* **2**, 1539–1548 (2017).

28. Boix, P. P. *et al.* Determination of gap defect states in organic bulk heterojunction solar cells from capacitance measurements. *Applied Physics Letters* **95**, 233302 (2009).

29. Stallinga, P. *Electrical Characterization of Organic Electronic Materials and Devices*. *Electrical Characterization of Organic Electronic Materials and Devices* (John Wiley & Sons, Ltd, 2009). doi:10.1002/9780470750162.

30. Yuan, M. *et al.* Perovskite energy funnels for efficient light-emitting diodes. *Nature Nanotechnology* **11**, 872–877 (2016).

31. Wan, R. *et al.* Improving the Modulation Bandwidth of GaN-Based Light-Emitting Diodes for High-Speed Visible Light Communication: Countermeasures and Challenges. *Advanced Photonics Research* **2**, 2100093 (2021).

32. Yu, L. *et al.* High-speed micro-LEDs for visible light communication: challenges and progresses. *Semiconductor Science and Technology* **37**, 023001 (2022).

33. Wehrenfennig, C., Eperon, G. E., Johnston, M. B., Snaith, H. J. & Herz, L. M. High Charge Carrier Mobilities and Lifetimes in Organolead Trihalide Perovskites. *Advanced Materials* **26**, 1584–1589 (2014).

34. Richter, J. M. *et al.* Enhancing photoluminescence yields in lead halide perovskites by photon recycling and light out-coupling. *Nature Communications* **7**, 13941 (2016).

35. Ban, M. *et al.* Solution-processed perovskite light emitting diodes with efficiency exceeding 15% through additive-controlled nanostructure tailoring. *Nature Communications* **9**, 1–10 (2018).

36. Du, P. *et al.* Efficient and large-area all vacuum-deposited perovskite light-emitting diodes via spatial confinement. *Nature Communications* **12**, 4751 (2021).

37. Minotto, A. *et al.* Visible light communication with efficient far-red/near-infrared polymer light-emitting diodes. *Light: Science & Applications* **9**, 70 (2020).

38. Li, N. *et al.* Ultra-low-power sub-photon-voltage high-efficiency light-emitting diodes. *Nature Photonics* **13**, 588–592 (2019).

39. Dou, L. *et al.* Solution-processed hybrid perovskite photodetectors with high detectivity. *Nature Communications* **5**, 1–6 (2014).

40. Qin, C. *et al.* Stable room-temperature continuous-wave lasing in quasi-2D perovskite films. *Nature* **585**, 53–57 (2020).

Methods

Materials

All chemicals were used as received without further purification. Caesium bromide (CsBr, 99.999%), 2-propanol (anhydrous, 99.5%), dimethyl sulfoxide (DMSO, 99.5%), Bathocuproine (BCP, 99.99%), Poly(ethylene glycol) (PEG), Polyvinylpyrrolidone (PVP), Polystyrene (PS) and Polyethylene glycol tert-octylphenyl ether (Triton X-100) were purchased from Sigma-Aldrich. Lead bromide ($PbBr_2$, 98%) was purchased from TCI. Toluene (99.85%) was purchased from Acros Organics. Methylammonium bromide (MABr, 99.99%), phenethylammonium bromide (PEABr, 99%) and *tert*-butylammonium bromide (*t*-BABr, 99%) were purchased from Greatcell Solar Materials Pty Ltd. PEDOT:PSS (Clevios PV P AI4083) was purchased from Heraeus.

Preparation of perovskite precursor

The control perovskite precursor was prepared by dissolving 110.1 mg CsBr, 76.6 mg $PbBr_2$ (1.2:1 molar ratio) and 5 mg PEG in 1mL DMSO (0.3 M). Different amounts of MABr, PEABr or *t*-BABr were added to the control solution. The molar ratio of alkylammonium bromide to $PbBr_2$ is varied from 0.1-1 with a step of 0.1. All the precursor was stirred overnight at room temperature.

Device fabrication

Commercial silicon wafers (100 mm, Si-Mat) with 300 nm wet thermal oxide (SiO_2) on both wafer sides were used as substrates for the devices. The silicon substrates were cleaned in a sequential process involving detergent, deionised water, acetone and 2-propanol (IPA) in an ultrasonic cleaner for 30 min. Subsequently, the substrates were transferred into an electron-beam evaporation system for the deposition of a Ti adhesion layer (5 nm) followed by an Au layer (100 nm). The as-deposited substrates underwent the same cleaning process, followed by 10 min of O_2 plasma ashing. To enhance surface wettability and electrical conductivity, PEDOT:PSS was doped with 0.5 wt% surfactant Triton X-100. The PEDOT:PSS was spin-coated onto the $Si/SiO_2/Au$ substrates at 4,000 rpm (2000 rpm s^{-1}) for 30 s and annealed at 150 °C for 15 min in air. The coated substrates were then transferred into a N_2-filled glove box. PVP (1 mg mL^{-1}) in IPA was spin-coated at 3,000 rpm (1500 rpm s^{-1}) for 30 s and annealed at 150 °C for 20 min to form a thin hydrophilic buffer layer. For each substrate, 30 μL of perovskite precursor was spread over the PVP layer at 3,000 rpm (1500 rpm s^{-1}) for 90 s and annealed at 60 °C for 5 min. PS (2 mg mL^{-1}) in toluene was then spin-coated at 4,000 rpm (2000 rpm s^{-1}) for 30 s and annealed at 60 °C for 15 min to form a thin hydrophobic buffer layer. Finally, a layer of BCP (30 nm) and Ag (20 nm) were sequentially deposited using a thermal evaporation system. The different active areas of the devices were defined as the area of overlap between the Au and Ag electrodes (Supplementary Fig. 12, 13).

Elliott modelling

The absorption spectrum of a direct bandgap semiconductor can be described by the Elliott formula[20], as the sum of the absorption of continuum states (α_c) and absorption of excitonic bound states (α_b),

$$\alpha(\hbar\omega) = A \cdot \Theta\left(\hbar\omega - E_g\right) \cdot D_{CV} \cdot \left(\frac{\pi e^{\pi x}}{sinhsinh\ \pi x}\right) + A \cdot E_b \sum_{n=1}^{\infty} \frac{4\pi}{n^3} \delta\left(\hbar\omega - E_g + \frac{E_b}{n^2}\right),$$

where A is a constant related to the transition matrix element, Θ is the step function, $\hbar\omega$ is the photon energy, E_g is the bandgap, D_{CV} is the joint density of valence and conduction bands states, x is defined as $x = \left[\frac{E_b}{(\hbar\omega - E_g)}\right]^{\frac{1}{2}}$, E_b is the exciton binding energy and δ is the Dirac delta function (Supplementary Note 2).

PL and UV–vis absorption spectroscopy

UV–vis absorption spectra were measured using a Cary 5000 UV-Vis-NIR spectrophotometer. PL spectra were measured using a Cary Eclipse Fluorescence spectrometer with a fixed excitation intensity and wavelength (400nm). The temperature-dependent PL spectra were measured by a fluorescence spectrophotometer (FLS980, Edinburgh Instruments) excited by a 375-nm laser. Further details of the temperature dependence of PL linewidth for extracting the electron–phonon coupling strength (Supplementary Note 3).

PLQE measurement

The steady-state PLQEs of the perovskite samples were measured using an integrating sphere method[41]. A continuous-wave 405nm diode laser with excitation power varying from 0.5 to 3000 μW and a focused beam spot of ~0.138 mm^2 was used to excite the samples. The emission was measured using an Andor iDus DU420A-BVF detector.

XRD and GIWAXS measurements

XRD and GIXRD patterns of the perovskite films on silica substrates were collected by an X-ray diffractometer (PANalytical X'Pert Pro) with Cu Kα (λ = 0.154187 nm) radiation.

GIWAXS data were acquired with a Rigaku SmartLab diffractometer. A 3 kW Cu source with CBO-f optics was incident on perovskite films, using a 2D-XRD attachment head (including a knife-edge to prevent air scatter and a beamstop). X-ray scattering was detected using a HyPix-3000 hybrid pixel-array 2D detector with a sample-to-detector distance of 65 mm. Sample widths were reduced to ~4mm to minimise sample footprint broadening. Data were collected at an incidence angle of 1.5° and the detector was rotated on a goniometer arm through 2θ angles from 0° to 30° in 1° steps. The detected images were then resampled into Q-space and combined using scripts based on the PyFAI and pygix libraries[42,43].

1D powder XRD patterns were calculated using VESTA[44], using the standard crystallographic information files (CIFs) for $CsPbBr_3$ (PDF Card - 01-085-6500), Cs_4PbBr_6 (PDF Card - 01-086-3013) and $CsPb_2Br_5$[45]. 2D GIWAXS simulations were performed using the WAXS package in the SimDiffraction Matlab toolbox[46], using the above CIFs. All simulations used a uniaxial preferential orientation model with a pseudo-Voigt distribution, with the marked lattice planes aligned parallel to the substrate (reciprocal lattice vectors perpendicular).

Morphological characterisation

The surface morphology of the samples was measured by a Veeco Dimension-3100 atomic force microscopy (AFM) in tapping-mode. Secondary electron (SE) and backscattered electrons (EBS) images of perovskite films were obtained in an ultra-high resolution Zeiss Gemini SEM. Cross-section specimens were prepared using a TESCAN Focus Ion Beam system. TEM and STEM images were recorded in a double CEOS-corrected Schottky emission JEOL ARM-200F microscope operating at 200 kV. Annular Dark Field signals were collected in the range between 45–180 mrad, with a probe forming a convergence semi-angle of 21 mrad. Energy dispersive spectroscopy (EDS) analyses were performed and collected with an Oxford Instruments X-Max Silicon Drift Detector with an area of 100 mm^2.

TRPL measurement

Time-resolved photoluminescence spectra were obtained by exciting the perovskite films with a Pico Quant LDH407 laser diode at 407 nm with a repetition rate of 5 MHz. The emission signal was selected with a monochromator to get the desired wavelength and detected by a Hamamatsu R3809U-50 photomultiplier detector. A neutral density filter was used to ensure that no more than one photon was detected in every photoexcitation cycle. See Supplementary note 4 for an estimate of carrier density. All samples were encapsulated with glass-epoxy in the N_2-filled glove box before measurements to avoid potential degradation of the perovskite films in ambient air.

TA spectroscopy

Femtosecond-to-nanosecond TA. The output of a Ti:sapphire amplifier system (Spectra Physics Solstice Ace) operating at 1 kHz and generating ~100-fs pulses (800 nm) was split into pump pulses and probe pulses. The 400-nm pump pulses were created by sending the 800 nm fundamental beam of the Solstice Ace through a second harmonic generating beta barium borate (BBO) crystal (Eksma Optics). The pump was blocked by a chopper wheel rotating at 500 Hz. The broadband probe (330-700 nm) was generated by focusing the 800 nm fundamental beam onto a CaF_2 crystal (Eksma Optics, 5 mm) connected to a digital motion controller (Mercury C-863 DC Motor Controller). The pump-probe delay (100 fs to 2 ns) was controlled by a mechanical delay stage (Thorlabs DDS300-E/M). The transmitted pulses were collected with a monochrome line scan camera (JAI SW-4000M-PMCL, spectrograph: Andor Shamrock SR-163). All samples were encapsulated with glass-epoxy in the N_2-filled glove box before measurements to avoid potential degradation of perovskite films in ambient air. The carrier densities increase linearly with the pump fluences and no significant nonlinear processes were involved (Supplementary note 5, Supplementary Fig. 34).

Nanosecond-to-microsecond TA. The 355 nm pump operating at 500 Hz was generated from the third harmonic configuration of Picolo (AOT-MOPA 25, Picosecond Nd:YVO Laser System, INNOLAS), and was triggered at desired time delays (pulse duration <800 ps).

OPTP spectroscopy

OPTP measurements were performed using the output of a Ti:Sapphire regenerative Amplifier (Spectra-Physics Spitfire Ace-PA-40, 780-820 nm laser pulses at a repetition rate of 1 kHz, a pulse duration of <40 fs) which was split into three beams. One beam was used to generate THz pulses by exciting a spintronic emitter (W/CoFeB/Pt trilayer), another beam was used to pump an optical parametric amplifier (Light Conversion TOPAS Prime) to generate the 410 nm pulses used to pump the sample, and the third beam was used for electro-optic sampling of the THz pulse in a ZnTe crystal (2mm, <110>). The THz induced change in polarisation of the detection beam was measured using a Wollaston prism and balanced photodiodes, whose output was recorded with an oscilloscope (Picoscope 4262). Mechanical delay stages were used to delay the detection pulse relative to the THz generation pulse (allowing time-resolved sampling of the THz waveform), and to delay both these pulses relative to the pump pulse, giving the pump-probe delay. The THz generation beam and pump beam were mechanically chopped at 500Hz and 250Hz respectively, to give a measurement scheme using four consecutive pulses of the detection beam (1kHz, not chopped). The first two pulses correspond to THz passed and blocked respectively, with the pump pulses hitting the sample for both, and the second two pulses were THz passed and blocked respectively, with the pump beam blocked for both. The difference between the first two pulses is proportional to the THz electric field transmitted when the sample is optically pumped, and the difference between the second pair of pulses is proportional to the THz electric field transmitted when the sample is not optically pumped. Measurements were performed with the THz beam path and the sample under a nitrogen atmosphere.

The spot sizes of the THz and pump beams at the sample position were measured using a knife edge scan, and the derivatives of these scans were fit with Gaussians. For the THz knife edge, the field magnitude of the temporal peak of the THz pulse was measured as a function of knife edge position. For these measurements, the standard deviations of the THz and pump spots were 0.3 mm and 0.85 mm respectively (0.45 mm and 0.75 mm respectively for the PEA sample). The power of the pump beam was measured using a Newport power meter (Detector 919P-003-10, Power Meter 843-R).

The photoinduced THz transmission change is proportional to the charge-carrier population $n(t)$. By estimating the initial free carrier density, $n(t=0)=\varphi n'$, where φ is the photon to charge-carrier branching ratio ($0<\varphi\leq 1$) and n' is the absorbed photon density, one can deduce $n(t)$. In the case of the perovskite films with low exciton binding energy, excitons are easily dissociated at room temperature, and thus $\varphi\approx 1$. The rate constants k_2 and k_3 were obtained through a global fit of the photoconductivity dynamics at various fluences using the rate equation (2). Further details and determination of effective carrier mobility $\varphi\sum\mu$ and carrier diffusion length L can be seen in Supplementary Note 6, Supplementary Fig. 35.

Emission performance characterisation

A programmable source meter (Keithley 2400) was used to apply a DC bias for devices. The J-V characteristics were measured using a voltage sweep from 0 V to 7.5 V in 30 mV steps with a delay time of 20 ms. The electroluminescence spectra were measured using an Ocean Optics HR2000+ fibre-coupled spectrometer (Supplementary Fig. 36). The angular-dependent emission spectra were recorded by a rotary sample stage. The radiant power of the devices was measured by a ILX Lightwave OMM-6810B optical multimeter with a calibrated silicon power head centred over the device pixel[47]. The EQEs was calculated from the radiant power, current density, EL emission spectrum, and angular intensity profile (Supplementary note 7). The operation stability of the devices was measured with simple glass-epoxy encapsulation in the ambient air. The chip temperature was controlled below 278 K by a heat sink to dissipate Joule heating at high driving current density.

Optical simulation

The optical properties were simulated by a classical electromagnetic model as a radiative decay of dipole antennas in the dedicated structure composed of stacked multi-layer films. An analytical model[48] was implemented regarding to the reflectivity and transmissivity of a planar Fabry-Perot microcavity (Supplementary Fig. 37).

The finite-difference time-domain (FDTD) method was used to analysis the electromagnetic fields and power density of the microcavity. The properties of all materials were assumed to be isotropic, thereby the refractive indices of Au, PEDOT:PSS, perovskite, BCP and Ag were set to 0.557+2.2i, 1.5, 1.94, 1.686 and 0.0533+3.41i, respectively. To calculate the total radiated power, the isotropic dipole orientation was assumed under a linear relationship with 2/3 power of the horizontal dipole and 1/3 power of the vertical dipole[49]. The assumption that the emitting medium is non-absorbing was also made due to an intrinsic limitation of the electromagnetic model. The reabsorption effect induced by planar microcavity can be considered in the photoluminescent quantum efficiency independently. The excitons from the reabsorption will convergently decay through either radiative or nonradiative process, and thus it would not affect the results of the out-coupled fraction. Since the dipoles are distributed randomly in the emission layer, an equivalent emitter position where dipoles were placed, was subsequently carried out based on the refractive index and thickness of each layer. The fraction of power in various optical modes was accordingly given by power distribution based on different thicknesses of emitting layer.

Thermal admittance spectroscopy

Capacitance-frequency measurements were carried out with a constant AC modulation voltage of 30 mV in a frequency range from 20 Hz to 2 MHz in logarithmic steps using an Agilent E4980A LCR meter. Capacitance-voltage measurements were performed with DC bias voltage swept from -0.5 to 2.0 V with an oscillation level of 30 mV. All the capacitance-frequency/voltage measurements were performed using a liquid-nitrogen cooled cryo-system and a temperature-controlled vacuum stage in the dark. The temperatures were set from 208 to 298 K with a step size of 10 K. All the measurements were delayed 15 min to ensure each temperature step was stable. The trap density N_T distribution in demarcation energy E_ω was calculated based on the differential capacitance spectra measured at different temperatures,

$$N_T(E_\omega) = -\frac{V_{bi}}{qW}\frac{dC}{d\omega}\frac{\omega}{k_BT}$$

$$E_\omega = k_BTln\left(\frac{\omega_0}{\omega}\right) = k_BTln\left(\frac{2\pi\upsilon_0T^2}{\omega}\right)$$

where C is the capacitance of the device measured at an angular frequency ω and temperature T; V_{bi} is the built-in voltage and W is the depletion width, which can be extracted from the Mott–Schottky plot; k_B is the Boltzmann's constant; q is the elemental charge; ω_0 denotes the attempt-to-escape frequency and υ_0 is the temperature-independent constant obtained by Arrhenius plots of characteristic frequencies of trap peaks.

Time-of-flight secondary ion mass spectrometry measurement

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements were performed on a ToF-SIMS.5 instrument (IONTOF, Germany), operated in spectral mode using a 25 keV Bi^{3+} primary ion beam with an ion current of 0.38 pA. A mass resolving power in the range of 7000-10000 m/Δm was reached. For depth profiling, a 1000 eV Cs^+ sputter beam with a current of 40 nA was used to remove the material layer-by-layer in interlaced mode from a raster area of 500 µm × 500 µm. Both positive and negative ions were collected for depth profile analysis. The mass-spectrometry was performed on an area of 50 µm × 50 µm in the centre of the sputter crater.

DFT calculation

DFT calculations were performed with the Perdew-Burke-Ernzer (PBE) exchange functional of the plane-wave open-source package QUANTUM ESPRESSO[50]. The "GBRV" ultrasoft potentials[51] were used with an energy cut-off for a wavefunction of 50 Ry and an energy cutoff for a charge density of 300 Ry. The atomic positions in the cubic $CsPbBr_3$ structure were optimised. With the relaxed parameters, the supercell size of the slab model was extended as needed. For the slab supercell calculations, the atomic positions were relaxed until all atomic forces were less than 1 mRy bohr^{-1}. The surface slabs for different molecules adsorbed on $CsPbBr_3$ surfaces were generated using the *pymatgen* package[52] with a slab thickness of 5 Å and minimum vacuum thickness of 15 Å. The Van der Waals (VdW) interactions were also included using the DFT-scattered correction method (DFT-D3 approach)[53]. The 2×1×1 Monkhorst-Pack sampling[54] of each surface slab was calculated from the reciprocal of the ratio of the supercell dimensions constructed with *Pymatgen*. For grain boundary of $CsPbBr_3$, the *k*-

point meshes with grid spacing of $2\pi \times 0.03$ Å^{-1} were used for electronic Brillouin zone integration.

Data transmission measurement

The bandwidths of the perovskite LED sources were measured using a vector network analyser (VNA), as illustrated in Supplementary Fig. 26. The devices were biased to a DC operating point using a source meter and this DC signal was combined with the -10 dBm signal from the VNA via a bias-tee. The output optical signal was butt coupled into a 1 mm diameter plastic optical fibre (POF) 1 m patch cord and fed into an 800 µm diameter avalanche photodiode (APD) via a pair of aspheric optical lenses. The received optical signal was then through a bias-tee before being amplified and fed back into the VNA. The VNA was calibrated such that the output from its S_{21} measurement directly provided the frequency responses of the devices, as the bandwidths of the photodiode, amplifiers and POF are all >650 MHz.

The transmission performance of the perovskite LED sources was evaluated in a similar way as that for bandwidths measurement. An arbitrary waveform generator (AWG) was used at the transmitter side to generate an on-off key (OOK) signal with different Baud rate. The received signal was collected by a digital sampling oscilloscope (DSO) with a sampling rate of 2 GSa s^{-1}. The maximum achievable bit rate was defined at a 7% FEC threshold of 3.8×10^{-3}.

Data availability

All data supporting the findings of this study are available within the article and its supplementary information.

Code availability

The code that supports the findings of this study is available from the corresponding author upon reasonable request.

References (methods)

41. de Mello, J. C., Wittmann, H. F. & Friend, R. H. An improved experimental determination of external photoluminescence quantum efficiency. *Advanced Materials* **9**, 230–232 (1997).

42. Ashiotis, G. *et al.* The fast azimuthal integration Python library: pyFAI. *Journal of Applied Crystallography* **48**, 510–519 (2015).

43. Dane, T. The pygix library. https://github.com/tgdane.

44. Momma, K. & Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *Journal of Applied Crystallography* **44**, 1272–1276 (2011).

45. Zhang, Z. *et al.* Growth, characterization and optoelectronic applications of pure-phase large-area CsPb 2 Br 5 flake single crystals. *Journal of Materials Chemistry C* **6**, 446–451 (2018).

46. Breiby, D. W., Bunk, O., Andreasen, J. W., Lemke, H. T. & Nielsen, M. M. Simulating X-ray diffraction of textured films. *Journal of Applied Crystallography* **41**, 262–271 (2008).

47. Anaya, M. *et al.* Best practices for measuring emerging light-emitting diode technologies. *Nature Photonics* **13**, 818–821 (2019).

48. Neyts, K. A. Simulation of light emission from thin-film microcavities. *Journal of the Optical Society of America A* **15**, 962 (1998).

49. Shi, X. B. *et al.* Optical Energy Losses in Organic–Inorganic Hybrid Perovskite Light-Emitting Diodes. *Advanced Optical Materials* **6**, (2018).

50. Giannozzi, P. *et al.* QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *Journal of Physics: Condensed Matter* **21**, 395502 (2009).

51. Garrity, K. F., Bennett, J. W., Rabe, K. M. & Vanderbilt, D. Pseudopotentials for high-throughput DFT calculations. *Computational Materials Science* **81**, 446–452 (2014).

52. Ong, S. P. *et al.* Python Materials Genomics (pymatgen): A robust, open-source python library for materials analysis. *Computational Materials Science* **68**, 314–319 (2013).

53. Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *Journal of Computational Chemistry* **27**, 1787–1799 (2006).

54. Monkhorst, H. J. & Pack, J. D. Special points for Brillouin-zone integrations. *Physical Review B* **13**, 5188–5192 (1976).

Acknowledgements

This work was supported by the National Key Research and Development Program of China (2021YFA1401100), the National Natural Science Foundation of China (61901268 and 52202165), the '111 Project' (B20030), the Fundamental Research Funds for the Central Universities (ZYGX2019Z018), the Innovation Group Project of Sichuan Province (20CXTD0090), the UESTC Shared Research Facilities of Electromagnetic Wave and Matter Interaction (Y0301901290100201), EPSRC (2015; EP/M015165/1), (2021; EP/V048732/1), (2016; EP/N010825/1), W.Z. acknowledges the EPSRC New Investigator Award (2018; EP/R043272/1) and the Newton Advanced Fellowship (192097) for financial support, L.D. thanks the Cambridge Trust and the China Scholarship Council for funding, E.B.-C. thanks the EPSRC for a studentship, and H.W. thanks G. Ren for the support.

Author contributions

I.H.W. proposed the project initially. J.W., Q.C., H.J.S. and W.Z. conceived the project and supervised the project together with S.J.S., A.R., N.C.G., Y.L., R.H.F., R.V.P. and I.H.W. A.R. and H.W. conducted the experiments and coordinated the collaboration and were assisted by J.W., Q.C., H.J.S. and W.Z. A.R. and H.W. developed the perovskite films and devices. J.Y., Z.L. and A.R. performed the PLQE and analysed the data. A.R. and H.W. performed the absorption and photoluminescence measurements. L.Y., A.R. and H.W. wrote the computational codes and performed the Elliott modelling. S.A.H and A.M.S. performed the SEM and TEM. M.T. performed the AFM. X.L., J.B. and B.L. performed the XRD and GIXRD and analysed the data. J.A.S. performed the GIWAXS and analysed the data. J.X. and C.Y. performed optical modelling and J.X., A.R. and H.W. analysed the data. A.R., H.W., S.Z. and I.P.M. performed the device emission performance measurements and analysed the data. H.L. and F.F. performed the ToF-SIMS and thermal admittance spectroscopy and analysed the data. H.W., R.C., H.Y., J.H. and A.W. performed the data transmission setups. H.W. performed the device modulation bandwidth measurements and A.R. and H.W. analysed the data. X.B. and Z.L. performed the TRPL and X.B. and A.R. analysed the data. E.B.-C. and J.L.-H. performed the OPTP and E.B.-C., J.L.-H., A.R. and H.W. analysed the data. L.D. performed the TA and data analysis under the supervision of N.C.G. H.W. and X.L. performed the data transmission and signal processing measurements and analysed the data. K.S. performed the DFT simulation. A.R. and H.W. drafted the first version of the manuscript, with assistance from J.W., Q.C., H.J.S. and W.Z. All authors have read and commented upon, or contributed to the writing of, the manuscript.

Competing interests The authors declare no competing interests.

Correspondence and requests for materials should be addressed to J.W., Q.C., H.J.S. or W.Z.

Fig. 1 | Emission and absorption properties of perovskite films. a-c, PLQE maps of the perovskite films modified with MABr (**a**), PEABr (**b**) and *t*-BABr (**c**) as a function of the molar ratio of organic cations and excitation power densities. The control $CsPbBr_3$ film was prepared using a precursor solution containing a mixture of CsBr and $PbBr_2$ at a molar ratio of 1.2:1. Alkylammonium cations were added to the control precursor solution with a molar ratio (referred to as *x*) varying from 0 to 1 equivalent with respect to $PbBr_2$. At low power densities, free carriers can be easily captured by non-radiative recombination centres (low PLQEs, region I). With increasing power densities, bimolecular recombination gradually dominates over charge carrier trapping (increased PLQEs, region II). At high power densities, Auger recombination becomes dominant over bimolecular recombination (reduced PLQEs, region III). **d-f**, Absorption maps of the perovskite films as a function of the molar excess of organic cations MABr (**d**), PEABr (**e**) and *t*-BABr (**f**) and photon energy. Absorption onsets decrease in the MABr-modified films ($x \approx 0.4$-0.5) (**d**) is due to the octahedral tilting through the competing mechanisms of partial cation substitution. The absorption features of the $n=2$ and $n=3$ (**e**) indicate the quasi-two-dimensional (2D) phases. The blue shifts of absorption onsets can be observed as the molar ratio of PEABr is increased.

Fig. 2 | Emission characteristics of perovskite sources on silicon. a, Photographs of the PeLEDs on a 100-mm-diameter wafer. Scale bar, 10 mm. Magnified photograph of a single LED pixel. Scale bar, 1 mm. **b**, Schematic architecture and cross-sectional STEM image of the *t*-BA device consisting of Au (100 nm)/PEDOT:PSS (40 nm)/polyvinylpyrrolidone (PVP) (5 nm)/perovskite (50 nm)/polystyrene (PS) (5 nm)/bathocuproine (BCP) (20 nm)/Ag (20 nm). PEDOT:PSS served as a hole transport layer, BCP as an electron transport layer, PVP and PS as a thin hydrophilic buffer layer and a hydrophobic capping layer, respectively. Scale bar, 100 nm. Current density-voltage characteristics (**c**), and current-density dependent EQEs (**d**) of the control, MA, PEA and *t*-BA devices. **e**, Power distribution into different optical modes of the microcavity as a function of the perovskite layer thicknesses. The *t*-BA device with a perovskite layer thickness of 50 nm shows a high outcoupling efficiency of 29.04%. **f**, Dispersion diagram as a function of energy and in-plane wavevector k_x for isotropic dipole radiators in the microcavity. The dashed line denotes the borders of outcoupled air mode. Three different metal electrode-induced surface plasmon polariton (SPP) modes can be observed: SPP1 (air/Ag), SPP2 (Ag/BCP) and SPP3 (PEDOT:PSS/Au).

Fig. 3 | Device modulation performance. a, Frequency responses of the best-performing devices. The corresponding current density: 1.81 A cm^{-2} (control), 3.11 A cm^{-2} (MA), 0.61 A cm^{-2} (PEA), 5.42 A cm^{-2} (*t*-BA). **b**, Effective THz mobilities $\varphi \sum \mu$ of the perovskite films at early times (0-10 ps) under a low-fluence. Error bars represent the standard error obtained from eight independent measurements ($n = 8$). **c**, Size-dependent modulation bandwidth statistics of the control, MA, PEA and *t*-BA devices. The data points of each histogram were collected from 25 devices. **d**, tDOS distributions. The trap-state profiles are fitted with Gaussian function (solid lines). The demarcation energy E_ω established by modulation frequency and temperature marks those trap states.

Fig. 4 | Charge carrier dynamics and modulation characteristics. a, Monomolecular recombination rate constant k_1, bimolecular recombination rate constant k_2 and Auger recombination rate constant k_3 for the control, MA, PEA and *t*-BA films. Three rate constants k_1, k_2 and k_3 were extracted from TA measurements through the rate equation (Extended Data Fig. 9m-p, Supplementary Fig. 25). For comparison, the rate constants k_1 were extracted from the low-fluence TRPL (Supplementary Fig. 26) and the rate constants k_2 and k_3 were extracted from OPTP spectroscopy (Extended Data Fig. 7a-d). Data are presented as best-fit parameters with error bars indicating the 95% confidence intervals of the rate constant value fits. **b-e**, The f_{-3dB} as a function of carrier density of the control (**b**), MABr (**c**), PEABr (**d**) and *t*-BA (**e**) films and devices. The overlaps between dotted lines are the intrinsic f_{-3dB} from derived recombination rate constants. Solid dots are from the measured τ_{eff}s. Open squares are estimated from the measured device f_{-3dB}. **f**, The f_{-3dB} versus current density of the measured PeLEDs in this work and reported studies covering OLEDs and III-V nitride μ-LEDs. The triangles (solid symbols) indicate the calculated resistance-capacitance (RC) f_{-3dB} of the *t*-BA device derived from the measured differential resistance and capacitance. The dash line shows the theoretical f_{-3dB} curve limited by τ_{RC} estimated from the measured results (Supplementary Note 1).