




Cite this: *Nanoscale*, 2024, **16**, 1115Received 17th October 2023,
Accepted 11th December 2023

DOI: 10.1039/d3nr05232j

rsc.li/nanoscale

Simultaneously improved photoluminescence, stability, and carrier transport of perovskite nanocrystals by post-synthetic perfluorobutanesulfonic acid treatment†

Xiao Huang, Xinli Wang, Jie Gao, Yang Sun, Jun Zhan, Yi Wang,  * Xi-Cheng Ai 
and Jian-Ping Zhang 

We report a post-synthetic treatment method based on perfluorobutanesulfonic acid (PFBA) to ameliorate the photophysical performance of perovskite nanocrystals. By virtue of the PFBA treatment, both the photoluminescence efficiency and stability of perovskite quantum dot-based colloidal solutions and the electrical conductivity of their close-packed films are simultaneously improved.

Cesium lead halide perovskite (CsPbX_3 , $X = \text{Cl, Br, I}$) quantum dots (QDs) offer a myriad of advantages, including a high photoluminescence quantum yield (PLQY), tunable emission wavelengths with narrow emission profiles, and facile hot-

injection synthesis procedures, making them promising emission media for optical imaging, displays, and lasing.^{1–5} However, because of the soft ionic lattice and low formation energy,⁶ perovskite QDs are susceptible to humidity, light, and temperature, leaving behind the stability problem in practice.^{7,8} Although the method of encapsulating perovskite QDs with hydrophobic molecules, such as trifluoroethyl methacrylate,⁹ covalent organic frameworks (COFs),¹⁰ and (3-iodopropyl)trimethoxysilane,¹¹ has been proposed for promoting robustness against humidity and oxygen, the terrible electroconductivity of the capping layers makes them lose their usefulness in electronic and photoelectronic applications.¹²

On the other hand, surface modification of perovskite QDs with organic ligands is essential for trap state passivation and PLQY enhancement.¹³ Nevertheless, the interaction between perovskite QDs and the most widely used organic ligands (*e.g.*, oleylamine and oleic acid) is weak,¹⁴ which leads to severe ligand detachment during the purification of solution-processed perovskite QDs and hence poses the issues of chemical decomposition, physical agglomeration, and emission intensity decline.^{15,16} To overcome this obstacle without losing the dispersibility in nonpolar solvents, it has been suggested in several works to replace oleylamine and oleic acid with ligands that can tightly bind to the lead-rich surface of perovskite QDs, such as dodecylbenzene sulfonic acid,¹⁴ porphyrin-thiol,¹⁷ and soy lecithin.¹⁸ Unfortunately, despite the effectiveness of these ligands in terms of defect passivation and waterproofing, their long alkyl chains play the role of spacers in the as-prepared perovskite QD films and hinder the charge carrier transport through the active layer at the device level.^{19,20}

In this work, we propose a novel ligand, perfluorobutanesulfonic acid (PFBA), to modify the as-synthesized perovskite QDs. The sulfonic acid terminal group shows a much stronger interaction with the lead-rich surface than the conventional carboxylic acid,¹⁴ and the carbon–fluorine bond can effectively insulate polar solvents and humidity,²¹ which collectively give rise to the simultaneous promotion of PLQY and stability of perovskite QDs. More importantly, the short alkyl chain of

Key Laboratory of Advanced Light Conversion Materials and Biophotonics,
Department of Chemistry, Renmin University of China, Beijing 100872, China.
E-mail: ywang@ruc.edu.cn

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d3nr05232j>



Yi Wang

Yi Wang is an associate professor in the Department of Chemistry at Renmin University of China. He obtained his B.S. and Ph.D. degrees at Renmin University of China in 2011 and 2016, respectively. From 2016 to 2018, he conducted postdoctoral research in the Department of Chemistry at the National University of Singapore. From 2019 to 2020, he worked as a research assistant professor in the Department of Chemistry at

the University of Tokyo. His current research interests include the photophysics of photovoltaic devices, chemical synthesis and optical applications of semiconductor nanocrystals, and the methodology of ultrafast spectroscopy and optical microscopy.

PFBA is desirable for fabricating high-conductivity close-packed QD films, as mirrored by the elevated charge transfer efficiency and reduced series resistance of the PFBA-treated perovskite QD film. The dilemma among the light emission performance, working stability, and charge transport efficiency can be judiciously circumvented through the proposed ligand engineering method, which is believed to provide new insights into the perovskite QD-based electronic and photoelectronic techniques.

CsPbBr₃ perovskite QDs are synthesized based on the reported hot-injection method,²² and the protocol of the PFBA post-treatment is detailed in the ESI†. The molecular structures of traditional oleic acid and the proposed PFBA are schematically illustrated in Fig. 1a. Compared with oleic acid, the substantial difference of PFBA, besides the short alkyl chain length, is the carbon–fluorine bond and sulfonic acid terminal group. This is well uncovered by the infrared absorption spectra (Fig. 1b), where the characteristic peaks related to the C–F stretching vibration around 1250 cm^{−1} and the S–O stretching vibration at 1050 cm^{−1} are unambiguously seen in the PFBA-treated sample.^{23–25} The interaction between PFBA and CsPbBr₃ perovskite QDs is further investigated by X-ray photoelectron spectroscopy as seen in Fig. 1c. In addition to the appearance of the F[−] 1s peak at 688.01 eV, the binding energies of Pb²⁺ 4f_{5/2} and 4f_{7/2} are shifted from 138.05 eV and 142.90 eV to 138.20 eV and 143.10 eV, respectively, indicating a strong interaction between PFBA and the surface of CsPbBr₃ nanocrystals.^{26,27} A closer inspection implicates that the Br-to-Pb ratio is increased from 2.61 to 2.92 after the PFBA treat-

ment. Transmission electron microscopy images (Fig. 1d and e) show that the cubic shape of the nanocrystals is well sustained upon the PFBA treatment, although the average edge length is slightly reduced. Fig. 1f presents the corresponding ultraviolet-visible (UV-vis) absorption and photoluminescence (PL) emission spectra. Despite the barely changed spectral profile, a drastic enhancement in the PL intensity for the PFBA-treated sample is observed. Closer spectral interrogation manifested that by virtue of the PFBA post-treatment, the PLQY is improved from 68% to 95% (Fig. S1, ESI†), and the PL lifetime is prolonged from 3.78 ns to 6.54 ns (Fig. 1g), which can be attributed to the trap state passivation effect of PFBA that suppresses nonradiative exciton recombination.

As mentioned above, CsPbBr₃ perovskite QDs generally suffer from ligand detachment during the purification process; as a result, the purified samples exhibit chemical decomposition, physical agglomeration, and PL decline.^{28,29} As seen in Fig. 2a and Fig. S2 (ESI†), with the increase in purification times, the colloidal solution becomes turbid and much less emissive under UV-light excitation. In contrast, on the basis of the PFBA post-treatment, the CsPbBr₃ QD solution remains well-dispersed and bright after purifying several times (Fig. 2b). X-ray diffraction (XRD) results (Fig. S3, ESI†) and UV-vis absorption spectra (Fig. S4, ESI†) further illustrate that PFBA prevents CsPbBr₃ QDs from precipitating. With respect to the PL performance, the untreated sample shows a bathochromic emission (Fig. 2c) and shortened PL lifetime (Fig. 2e), which are attributable to physical agglomeration and severe nonradiative exciton recombination, respectively, in view of

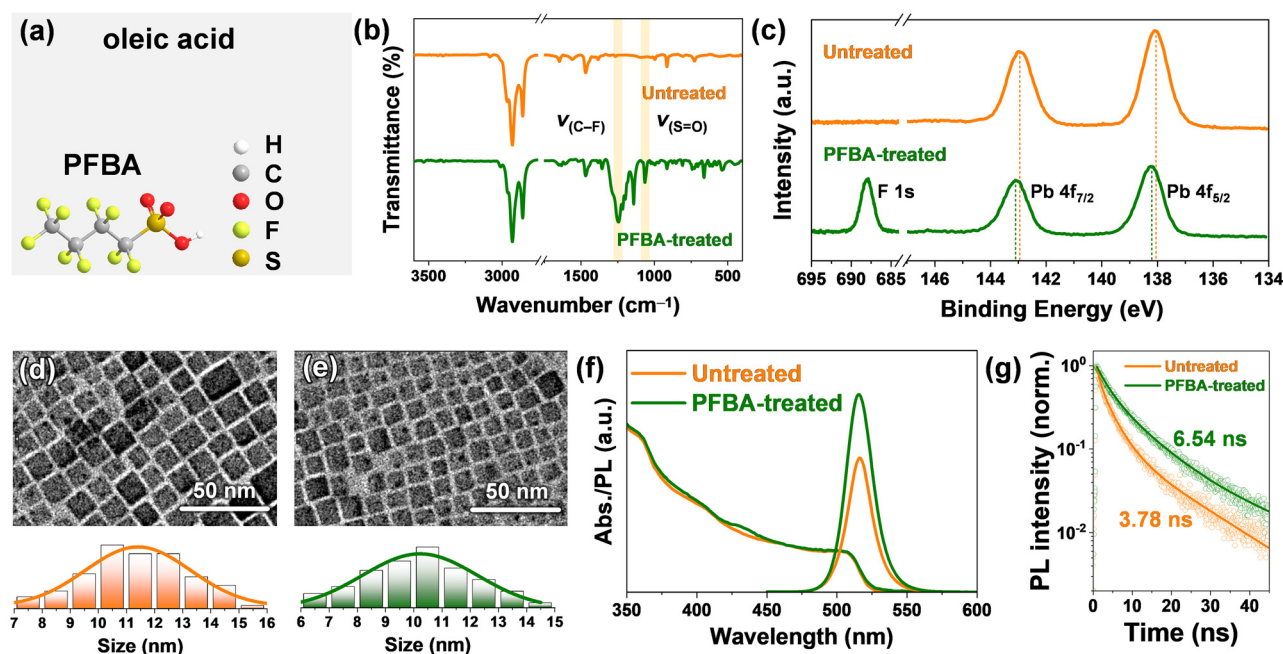


Fig. 1 (a) Molecular structures of the conventionally used oleic acid ligand and the proposed PFBA ligand. (b) Infrared absorption spectra with characteristic peaks of PFBA shaded by yellow, (c) X-ray photoelectron spectra, (d and e) transmission electron microscopy images and size distribution histograms, (f) steady-state UV-vis absorption and PL emission spectra, and (g) time-resolved PL profiles of CsPbBr₃ perovskite QD solutions without (orange) and with (green) the PFBA post-treatment.

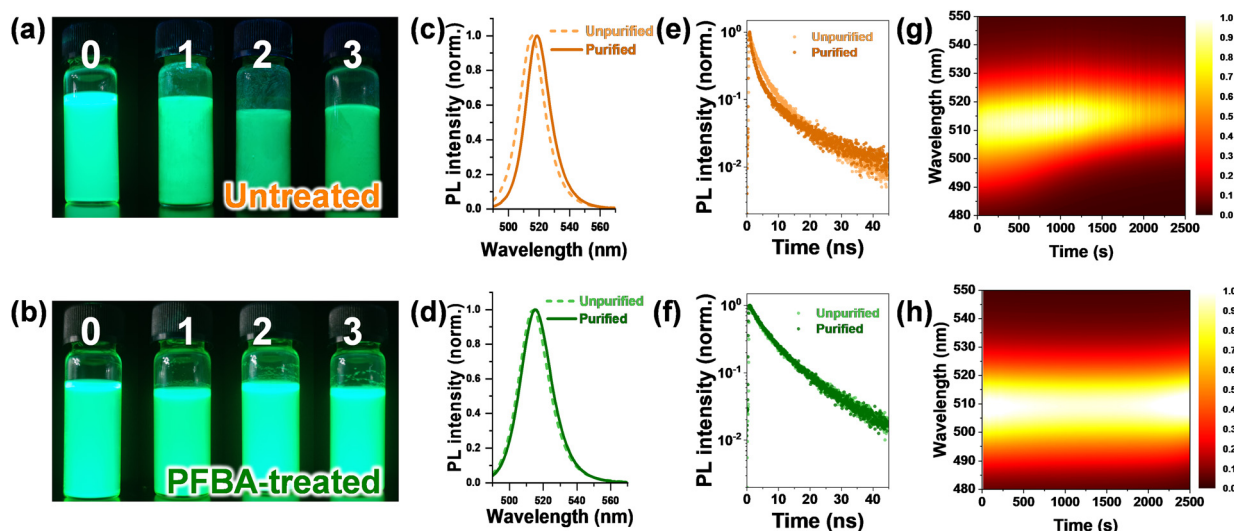


Fig. 2 Photographs of CsPbBr₃ QD solutions without (a) and with (b) the PFBA post-treatment under UV light irradiation as a function of purification times. (c and d) PL emission spectra and (e and f) time-resolved PL profiles of CsPbBr₃ perovskite QD solutions before and after purification, where the orange and green colours denote untreated and PFBA-treated samples, respectively. Real-time, *in situ* PL emission spectra of without (g) and with (h) the PFBA post-treatment under a CW laser excitation (excitation wavelength: 450 nm, power density: 4 W cm⁻²).

ligand detachment. As a comparison, the variation of emission wavelength (Fig. 2d) and PL lifetime (Fig. 2f) becomes negligible for the PFBA-treated sample, demonstrating a substantial improvement in the chemical stability of CsPbBr₃ QDs. In addition, the photostability is inspected by real-time, *in situ* PL emission spectroscopy, where the PL spectra of CsPbBr₃ QDs are consecutively recorded under the illumination of a strong continuous-wave (CW) laser beam (see details in the ESI†). The as-acquired PL mappings are shown in Fig. 2g for the untreated sample and in Fig. 2h for the PFBA-treated sample. Following the CW excitation for 2500 s, similar to the case of purification, the emission wavelength is shifted from 512 nm to 517 nm, accompanying a decrease of PL intensity to ~50% of the initial value for the untreated CsPbBr₃ QD solution. As expected, both the PL redshift and intensity loss under continuous light illumination are avoided by the PFBA post-treatment.³⁰ In a similar manner, the stability against heating (Fig. S5a, ESI†) and storage time (Fig. S5b, ESI†) was also elevated for the PFBA-treated QDs.

Having elaborated on the success of PFBA in ameliorating the photophysical properties and stability of perovskite QD solutions, we moved forward to the QD film that has been widely used as the active layer for light emitting devices and photovoltaics. In terms of QD-based photoelectronic and photonic applications, the device performance is not only limited by the nonradiative charge/exciton recombination, but also highly restricted by the poor carrier transport.^{31–34} Perovskite QDs are generally capped with long-chain organic ligands, which hinders the connection among the nanocrystals and thus exacerbates the carrier transport issue.^{35–37} Fig. 3a and b show the PL spectra and time-resolved PL profiles of perovskite QD films spin-coated on a silica substrate or a ZnO-coated glass substrate.³⁸ By replacing silica with a ZnO-coated

glass, owing to the electron transfer from CsPbBr₃ to ZnO, the PL intensity is reduced by a factor of 17% (44%), and the PL lifetime is shortened from 3.04 ns (6.13 ns) to 2.65 ns (3.56 ns) for the untreated (PFBA-treated) sample. The variations of both PL intensity and PL lifetime are more remarkable after the PFBA post-treatment, indicative of a higher electron transfer efficiency.^{39,40} Space charge limited current results indicate that the trap-filling limit voltage (V_{TFL}) decreases from 2.8 V to 1.6 V (Fig. 3c), as per the passivation of trap states by PFBA (Fig. S6, ESI†).⁴¹ Similar results are also observed for the hole transporting layer-only devices (Fig. S7, ESI†). Fig. 3d displays the Nyquist plots of CsPbBr₃ QD films extracted from the electrochemical impedance spectroscopy results, which give a series resistance (R_s) of 22 Ω for the untreated film and 16 Ω for the PFBA-treated film within the framework of the equivalent circuit analysis (Fig. S8, ESI†). The smaller R_s implies that carrier transport through the active layer is promoted,^{42,43} in agreement with the steady-state PL and time-resolved PL studies shown in Fig. 3a and b, which can be assigned to the reduced chain length of PFBA.

In conclusion, we propose a novel organic ligand, PFBA, with a sulfonic acid terminal group, hydrophobic carbon-fluorine bonds, and a short chain length, to modify perovskite QDs, which results in a remarkable improvement of the photophysical performances in terms of three aspects. First, the strong interaction between the sulfonic acid terminal group of PFBA and the lead-rich surface of perovskite QDs effectively passivates surface trap states, giving rise to the enhancement of PLQY from 68% to 95%. Second, the carbon-fluorine bonds protect the QDs from being degraded by a polar solvent or humidity and hence notably improve their stability. And thirdly and more importantly, thanks to the short alkyl chain of PFBA, the electrical conductivity of the QD film is increased,

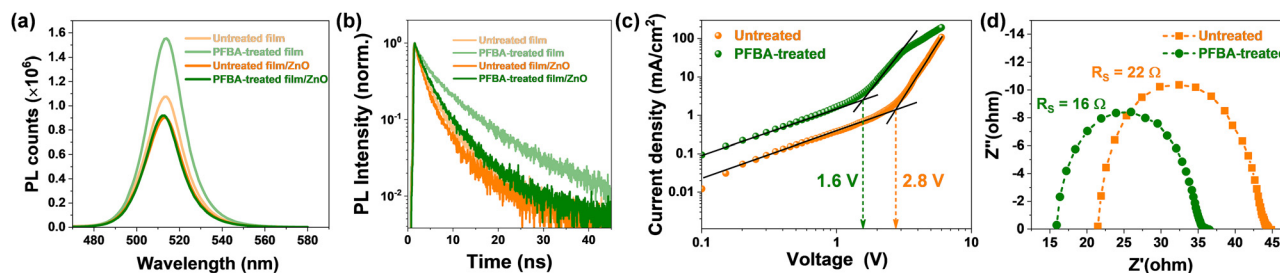


Fig. 3 (a) Steady-state PL emission spectra and (b) time-resolved PL profiles of CsPbBr₃ QD films without (orange) and with (green) the PFBA post-treatment spin-coated on a silica substrate or a ZnO-coated glass substrate. (c) Dark current–voltage responses and (d) Nyquist plots of CsPbBr₃ QD films without (orange) and with (green) the PFBA post-treatment.

which results in a smaller series resistance and more efficient electron transfer at the interface between the QD layer and the electron transport layer. The facile post-treatment strategy established in this work is believed to advance the practical application of perovskite QD-based electronic and photoelectric devices.

Author contributions

Y. W. conceived the idea and supervised the project; X. H. monitored all the experiments; X. W. provided help in film fabrication and ligand exchange methodology; J. G. provided help in quantum dot synthesis; Y. S. provided help in *in situ* spectroscopy measurements; J. Z. provided help in electrical measurements; X. H. performed data analysis; Y. W. and X. H. drafted the manuscript; X.-C. A. and J.-P. Z. provided suggestions for the manuscript revision; Y. W. finalized the manuscript; and all authors discussed the results and provided comments on the manuscript.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (NSFC) (Grant No. 22103096, 22273119, and 22203103), the Beijing Natural Science Foundation (Grant No. 2232008), and the Research Funds of Renmin University of China (22XNKJ08).

References

- M. V. Kovalenko, L. Protesescu and M. I. Bodnarchuk, *Science*, 2017, **358**, 745–750.
- Z. Li, L. Kong, S. Huang and L. Li, *Angew. Chem., Int. Ed.*, 2017, **56**, 8134–8138.
- K. Lin, J. Xing, L. N. Quan, F. P. G. de Arquer, X. Gong, J. Lu, L. Xie, W. Zhao, D. Zhang, C. Yan, W. Li, X. Liu, Y. Lu, J. Kirman, E. H. Sargent, Q. Xiong and Z. Wei, *Nature*, 2018, **562**, 245–248.
- X.-K. Liu, W. Xu, S. Bai, Y. Jin, J. Wang, R. H. Friend and F. Gao, *Nat. Mater.*, 2021, **20**, 10–21.
- J. Ren, T. Li, X. Zhou, X. Dong, A. V. Shorokhov, M. B. Semenov, V. D. Krevchik and Y. Wang, *Chem. Eng. J.*, 2019, **358**, 30–39.
- J. S. Manser, M. I. Saidaminov, J. A. Christians, O. M. Bakr and P. V. Kamat, *Acc. Chem. Res.*, 2016, **49**, 330–338.
- C. Zhang, Q. Wan, L. K. Ono, Y. Liu, W. Zheng, Q. Zhang, M. Liu, L. Kong, L. Li and Y. Qi, *ACS Energy Lett.*, 2021, **6**, 3545–3554.
- X. Li, W. Ma, D. Liang, W. Cai, S. Zhao and Z. Zang, *eScience*, 2022, **2**, 646–654.
- Y. Liu, T. Chen, Z. Jin, M. Li, D. Zhang, L. Duan, Z. Zhao and C. Wang, *Nat. Commun.*, 2022, **13**, 1338.
- J. Ren, X. Zhou and Y. Wang, *Chem. Eng. J.*, 2023, **454**, 140285.
- W. Song, D. Wang, J. Tian, G. Qi, M. Wu, S. Liu, T. Wang, B. Wang, Y. Yao, Z. Zou and B. Liu, *Small*, 2022, **18**, e2204763.
- C. Liu, X. Zhou, S. Chen, X. Zhao, S. Dai and B. Xu, *Adv. Sci.*, 2019, **6**, 1801169.
- Y. Bai, M. Hao, S. Ding, P. Chen and L. Wang, *Adv. Mater.*, 2022, **34**, e2105958.
- D. Yang, X. Li, W. Zhou, S. Zhang, C. Meng, Y. Wu, Y. Wang and H. Zeng, *Adv. Mater.*, 2019, **31**, e1900767.
- C. Han, K. Wang, X. Zhu, H. Yu, X. Sun, Q. Yang and B. Hu, *J. Phys. D: Appl. Phys.*, 2018, **51**, 095501.
- L. Xu, J. Li, B. Cai, J. Song, F. Zhang, T. Fang and H. Zeng, *Nat. Commun.*, 2020, **11**, 3902.
- X. Feng, X. Zhao, J. Liu, P. Xu and J. Liu, *Adv. Mater. Interfaces*, 2023, **10**, 2201886.
- F. Krieg, Q. K. Ong, M. Burian, G. Raino, D. Naumenko, H. Amenitsch, A. Suess, M. J. Grotevent, F. Krumeich, M. I. Bodnarchuk, I. Shorubalko, F. Stellacci and M. V. Kovalenko, *J. Am. Chem. Soc.*, 2019, **141**, 19839–19849.
- Y. Liu, Y. Li, X. Hu, C. Wei, B. Xu, J. Leng, H. Miao, H. Zeng and X. Li, *Chem. Eng. J.*, 2023, **453**, 139904.

- 20 E. T. Vickers, T. A. Graham, A. H. Chowdhury, B. Bahrami, B. W. Dreskin, S. Lindley, S. B. Naghadeh, Q. Qiao and J. Z. Zhang, *ACS Energy Lett.*, 2018, **3**, 2931–2939.
- 21 B. M. Lefler, S. J. May and A. T. Fafarman, *Phys. Rev. Mater.*, 2020, **4**, 120301.
- 22 M. Zhang, Z.-Q. Tian, D.-L. Zhu, H. He, S.-W. Guo, Z.-L. Chen and D.-W. Pang, *New J. Chem.*, 2018, **42**, 9496–9500.
- 23 C. J. Young, M. D. Hurley, T. J. Wallington and S. A. Mabury, *Chem. Phys. Lett.*, 2009, **473**, 251–256.
- 24 S. Yang, S. Chen, E. Mosconi, Y. Fang, X. Xiao, C. Wang, Y. Zhou, Z. Yu, J. Zhao and Y. Gao, *Science*, 2019, **365**, 473–478.
- 25 E. Elzinga, D. Peak and D. Sparks, *Geochim. Cosmochim. Acta*, 2001, **65**, 2219–2230.
- 26 J. Kim, D. Jung, Y. Park, Y. Kim, D. W. Moon and T. G. Lee, *Appl. Surf. Sci.*, 2007, **253**, 4112–4118.
- 27 J. Y. Woo, Y. Kim, J. Bae, T. G. Kim, J. W. Kim, D. C. Lee and S. Jeong, *Chem. Mater.*, 2017, **29**, 7088–7092.
- 28 Y. Chu, J. Liu and G. Zhao, *J. Alloys Compd.*, 2022, **929**, 167223.
- 29 S. Cheng and H. Zhong, *J. Phys. Chem. Lett.*, 2022, **13**, 2281–2290.
- 30 X. Li, Y. Wang, H. Sun and H. Zeng, *Adv. Mater.*, 2017, **29**, 1701185.
- 31 J. Chen, D. Jia, R. Zhuang, Y. Hua and X. Zhang, *Adv. Mater.*, 2022, **34**, e2204259.
- 32 W. Gong, Y. Li, Y. Yang, H. Guo and X. Niu, *J. Mater. Chem. C*, 2023, **11**, 6963–6970.
- 33 E. A. Duijnste, J. M. Ball, V. M. Le Corre, L. J. A. Koster, H. J. Snaith and J. Lim, *ACS Energy Lett.*, 2020, **5**, 376–384.
- 34 Y. Wang, Y. Teng, P. Lu, X. Shen, P. Jia, M. Lu, Z. Shi, B. Dong, W. W. Yu and Y. Zhang, *Adv. Funct. Mater.*, 2020, **30**, 1910140.
- 35 D. Jia, J. Chen, M. Yu, J. Liu, E. M. J. Johansson, A. Hagfeldt and X. Zhang, *Small*, 2020, **16**, e2001772.
- 36 L. M. Wheeler, E. M. Sanehira, A. R. Marshall, P. Schulz, M. Suri, N. C. Anderson, J. A. Christians, D. Nordlund, D. Sokaras, T. Kroll, S. P. Harvey, J. J. Berry, L. Y. Lin and J. M. Luther, *J. Am. Chem. Soc.*, 2018, **140**, 10504–10513.
- 37 J. Kim, B. Koo, W. H. Kim, J. Choi, C. Choi, S. J. Lim, J.-S. Lee, D.-H. Kim, M. J. Ko and Y. Kim, *Nano Energy*, 2019, **66**, 104130.
- 38 C. Zheng, C. Bi, F. Huang, D. Binks and J. Tian, *ACS Appl. Mater. Interfaces*, 2019, **11**, 25410–25416.
- 39 C. Luo, G. Zheng, F. Gao, X. Wang, C. Zhan, X. Gao and Q. Zhao, *Nat. Photonics*, 2023, **17**, 856–864.
- 40 S. Liu, Y. Chen, W. Gao, W. Li, X. Yang, Z. Li, Z. Xiao, Y. Liu and Y. Wang, *Adv. Mater.*, 2023, **35**, 2303544.
- 41 K.-L. Wang, Y.-G. Yang, Y.-H. Lou, M. Li, F. Igbari, J.-J. Cao, J. Chen, W.-F. Yang, C. Dong and L. Li, *eScience*, 2021, **1**, 53–59.
- 42 L. Hu, L. Duan, Y. Yao, W. Chen, Z. Zhou, C. Cazorla, C. H. Lin, X. Guan, X. Geng, F. Wang, T. Wan, S. Wu, S. Cheong, R. D. Tilley, S. Liu, J. Yuan, D. Chu, T. Wu and S. Huang, *Adv. Sci.*, 2022, **9**, 2102258.
- 43 S. Zhang, Y. J. Yoon, X. Cui, Y. Chang, M. Zhang, S. Liang, C.-H. Lu and Z. Lin, *J. Mater. Chem. A*, 2020, **8**, 26098–26108.