



Anionic ligand-induced chirality in perovskite nanoplatelets†

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Thi Kim Tran Tran,^a Joseph A. Adewuyi,^a Yongchen Wang,^a
M. Daniela Morales-Acosta,^b Tomoyasu Mani,^b Gaël Ung^a and Jing Zhao^{*a}

Perovskite materials passivated by chiral ligands have recently shown unique chiroptical activity with promising optoelectronic applications. However, the ligands have been limited to chiral amines. Here, chiral phosphate molecules have been exploited to synthesize CsPbBr₃ nanoplatelets. The nanoplatelets showed a distinct circular dichroism signal and maintained their chiroptical properties after purification with anti-solvent.

Halide perovskites are known for their outstanding electronic and optical properties with promising applications in photovoltaics and optoelectronics such as solar cells,¹ light-emitting diodes (LEDs),² and photodetectors.³ Their general chemical formula is ABX₃, where A is a monovalent cation such as methylammonium CH₃NH₃⁺ (MA⁺), formamidinium HC(NH₂)₂⁺ (FA⁺), or cesium (Cs⁺), B is a divalent cation (*e.g.* Pb²⁺ or Sn²⁺, *etc.*), and X is a halide anion (Cl[−], Br[−], or I[−]). Among different perovskites, halide perovskite materials with chiral properties are attractive for spintronic devices,⁴ circularly polarized photodetectors⁵ and circularly polarized light sources.⁶ Chirality in halide perovskites is typically obtained by incorporating chiral organic molecules into perovskite structures to break their inversion symmetry. As a result, chirality is induced in the inorganic structures so that they exhibit chiroptical properties in the visible to near-IR region.^{7,8}

Up to now, there are two approaches to induce chirality in perovskite materials. One is by introducing chiral organic cations into the A sites of the perovskite framework. These cations isolate the single metal halide octahedral ([BX₆]^{4−}) layers, which get stacked by van der Waals interactions between the chiral organic cations. For example, *R/S*-methylbenzylammonium (*R/S*-MBA) cations were placed in the A-sites to induce the chirality

in two-dimensional (2D) lead- and tin-based perovskite thin films^{9–12} and bulk single crystals.¹³ Besides MBA, the other chiral ammonium cations used to build chiral perovskites were derived from (*R/S*)-(+)-*sec*-butylamine,¹⁰ (*R/S*)-β-methylphenethylamine,^{14,15} and (*R/S*)-1-(2-naphthyl)ethylamine.¹¹ However, these 2D perovskite films have shown low photoluminescence quantum yields due to significant nonradiative recombination resulting from surface and defect states.¹⁶ The second approach was developed to overcome this problem, where the perovskite materials are passivated with chiral cation ligands. For example, *R/S*-MBA and (*R/S*)-1-(2-naphthyl)ethylamine were used as chiral ligands to enclose MAPbBr₃^{4,17} and MAPbI₃¹⁸ 2D perovskites, respectively. This approach was also applied in chiral three-dimensional perovskite nanocrystal (NC) synthesis, such as (*R/S*)-1,2-diaminocyclohexane for CsPb(I/Br)₃ NCs,¹⁹ (*R/S*)-α-octylamine for CsPbBr₃ NCs²⁰ and FAPbBr₃ NCs.²¹ These NCs all showed chiroptical properties and higher photoluminescence quantum yields. Although (*R/S*)-α-octylamine-capped and FAPbBr₃ NCs²¹ have shown the highest degree of circularly polarized emission, purification of the NCs with anti-solvent (ethyl acetate) removed a considerable amount of the chiral amine ligands and extinguished the chiroptical properties.²¹

So far, all of the chiral molecules used to induce chirality in perovskite NCs are amines.^{7,8} In order to understand and develop chiral perovskite materials for optical applications, it is necessary to expand the selection of chiral ligands. Some studies have shown that axially chiral binaphthyl derivatives could induce chirality in metal clusters, nanoparticles and nanorods.^{22–25} Therefore, we adopted these anionic binaphthyl-based ligands for perovskite NC synthesis in this work. In particular, (*R*)-(-)-1,1'-binaphthyl-2,2'-diyl hydrogenphosphate (*R*-BNP) and *S*-BNP molecules (see the structures in Fig. 1a) were prepared following a published protocol²⁶ and characterized by nuclear magnetic resonance (NMR) (see details in the ESI†). They were then used to synthesize CsPbBr₃ nanoplatelets (NPLs). The NPLs with the *R*- and *S*-BNP ligands exhibit circular dichroism (CD) signals of opposite signs at 350–460 nm wavelengths beyond the absorption range of BNPs, demonstrating their chiral properties. Moreover, the chirality of the NPLs was

^a Department of Chemistry, University of Connecticut, 55 North Eagleville Rd., Storrs Mansfield, Connecticut 06269-3060, USA. E-mail: jing.zhao@uconn.edu

^b Institute of Materials Science, University of Connecticut, Storrs Mansfield, Connecticut 06269, USA

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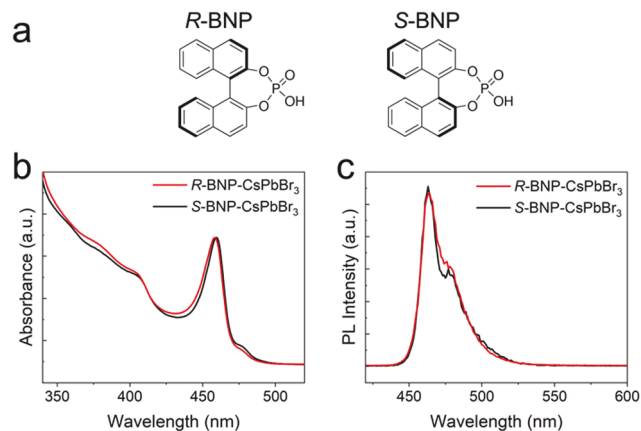


Fig. 1 (a) Chemical structures of BNP ligands with (*R*) and (*S*) enantiomers. (b) The absorption and (c) photoluminescence (PL) spectra of *R*- (red curves) and *S*- (black curves) BNP- CsPbBr_3 NPLs in hexane.

maintained after purification with anti-solvents because the phosphate groups are known to have high binding affinity to the CsPbBr_3 perovskite NC surface in various binding modes.^{27–31} Furthermore, the NPLs show linearly polarized emission in their PL, which is ascribed to their anisotropic shape. This work provides alternative means to develop chiral perovskite materials.

The NPLs were synthesized using a hot injection method modified from the protocol reported by Protesescu *et al.*³² Firstly, Cs-OA-R/S-BNP precursor in 1-octadecene (ODE) was prepared by dissolving Cs_2CO_3 , oleic acid (OA) and *R/S*-BNP in ODE at 110 °C. In a separate three-necked flask attached to a Schlenk line, PbBr_2 was mixed with a 1:1 molar ratio of oleylamine (OLAm) and *R/S*-BNP and dissolved in solvent ODE. After degassing at 110 °C for 1 h, the mixture was heated to 175 °C under N_2 for 30 mins in order to ensure complete dissolution. The temperature of the mixture was brought down to 120 °C and the Cs-OA-R/S-BNP precursor was swiftly injected. After 7 s, the reaction mixture was quenched by a water-ice bath. The NPLs were purified from the reaction mixture through precipitation with *tert*-butanol as the anti-solvent and centrifugation. The precipitates were redispersed in hexane for characterization.

The UV-vis absorption and PL spectra of *R*- and *S*-BNP- CsPbBr_3 NPLs in hexane are shown in Fig. 1b and c. The corresponding spectra look almost identical for the *R*- and *S*-BNP NPL samples, suggesting that the morphologies of the two samples are similar. The absorption spectra peak at 460 nm and the PL peak at 464 nm correspond to 5 unit-cell thickness of CsPbBr_3 NPLs as shown in a previous report.³³ The sharp excitonic absorption is the result of quantum confinement effects in the NPLs with the thickness much less than the bulk CsPbBr_3 Bohr exciton diameter (7 nm³²). The shoulders in the absorption and PL spectra at 475 and 479 nm, respectively, coincide with each other, presumably caused by accumulation and transformation of some of the thin NPLs to thicker ones during the purification step. A similar phenomenon was observed by Wang *et al.*³⁴ Thus, the final product primarily

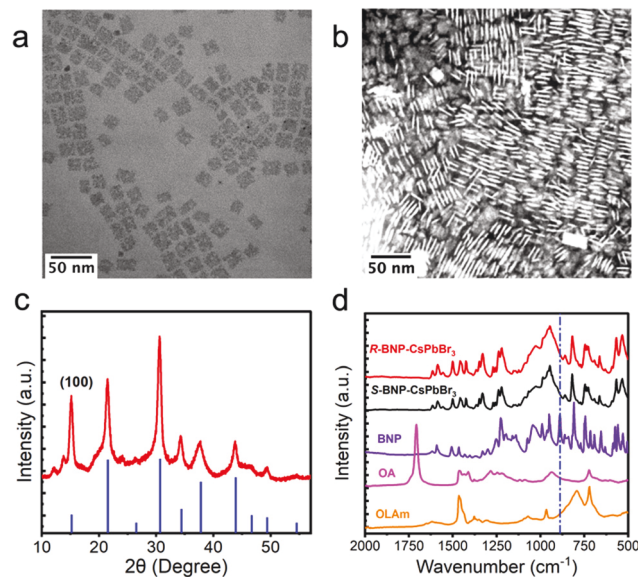


Fig. 2 (a) The TEM image of BNP- CsPbBr_3 NPLs lying on their "flat" side. (b) The STEM dark-field image of BNP- CsPbBr_3 NPLs in stacks. (c) The XRD spectrum of BNP- CsPbBr_3 NPLs. The reference cubic crystal structure of CsPbBr_3 is shown in blue lines, PDF 00-054-0752. (d) The FTIR spectra of OLAm, OA, BNP and BNP- CsPbBr_3 NPLs.

consists of 5 unit-cell thick NPLs, with a small portion of aggregates. The PL quantum yield is 43% and 34% with respect to *R*- and *S*-BNP NPLs. The PL lifetimes of the *R*- and *S*-BNP NPLs were 5.89 ns and 6.14 ns, respectively, determined by fitting a bi-exponential function of the PL decays. The fitting parameters are listed in Table S1 (ESI†).

The morphology of the NPLs was studied with transmission electron microscopy (TEM). The TEM images were acquired from a diluted sample where the NPLs lay flat on the TEM grid (Fig. 2a) and from a concentrated sample where the NPLs stacked (Fig. 2b). The TEM images revealed the platelet morphology of the BNP- CsPbBr_3 NCs, with a lateral dimension of 10–20 nm and an average thickness of 2.7 ± 0.4 nm (see thickness distribution in Fig. S6, ESI†). The X-ray diffraction (XRD) peaks of the BNP- CsPbBr_3 NPLs in Fig. 2c match well with those of cubic CsPbBr_3 . In the cubic phase, the lattice constant of the CsPbBr_3 NPL unit cells, which is equal to the lattice spacing between the {100} planes, is calculated to be 0.585 nm. Therefore, the thickness of the BNP- CsPbBr_3 NPLs (~2.7 nm) corresponds to approximately 5 unit cells, which is in agreement with the previous report³³ and the features in the UV-vis absorption spectra in Fig. 1b.

To study the surface chemistry of the BNP- CsPbBr_3 NPLs, FTIR spectroscopy was performed and the spectra are shown in Fig. 2d and Fig. S6 (ESI†). The spectra of the BNP-NPLs show much similarity to that of the BNP molecules, proving that BNP molecules have been successfully incorporated in the NPLs. Specifically, the stretching vibration of P–O–H at 889 cm^{–1} disappeared in the BNP-NPLs in contrast to BNP ligand, suggesting the deprotonation of the hydrogen phosphate group of BNP by OLAm.³⁵ Meanwhile, the stretching vibration mode

of $\text{P}=\text{O}$ ($\sim 1000\text{ cm}^{-1}$) and $\text{P}-\text{O}$ ($\sim 750\text{ cm}^{-1}$) and the bending vibration mode of $\text{O}-\text{P}-\text{O}$ ($\sim 550\text{ cm}^{-1}$) in the BNP-NPLs are present but broader than those of the BNP molecules, likely because of the different local chemical environments around the BNP molecules after they were attached to the NPL surface.³⁵ Moreover, even though OA was used in cesium precursor preparation, the stretching vibration of $\text{C}=\text{O}$ at 1706 cm^{-1} was not observed probably due to lower affinity to the NPL surface of carboxyl groups compared to phosphorus-based ones.³¹ The broad peak at 3159 cm^{-1} (Fig. S7, ESI†) was attributed to N^+-H_3 stretching vibrations of ammonium groups of protonated OLAM on the NPLs.³⁶ Therefore, BNP and OLAM ligands are present on the NPL surface.

The chirality of the NPLs was evaluated by circular dichroism (CD) spectroscopy, in which the difference in absorbance of left- and right-handed circularly polarized light of a sample was recorded. CD spectroscopy is used to study the chiroptical properties of materials in their ground state.³⁷ The CD spectra of BNP- CsPbBr_3 NPLs and the precursors are shown in Fig. 3. The *R*-BNP and *S*-BNP-capped NPLs exhibit CD spectra above 350 nm that are mirror images with almost equal intensity. In contrast, the CD signals of free *R/S*-BNP molecules and precursors in the synthesis only have peaks below 340 nm. The Cotton effect, which is a characteristic change of CD sign in the vicinity of an absorption band of a substance, is observed at 461 nm, which is around the first excitonic absorption of the NPLs. Moreover, NPLs were also prepared with a racemic mixture of the *R/S*-BNP ligands and they showed no CD features. Therefore, we confirmed that the chirality of the NPLs has been induced by the *R/S*-BNP ligands.

In previous studies of chiral CsPbBr_3 perovskite NCs, it was proposed that chiral ammonium ligands occupy the A-site of the perovskite structure and transfer chirality *via* two mechanisms. One is asymmetric lattice distortions up to five atomic unit cells deep into the perovskite NCs by chiral ammonium ligands.³⁸ The other one is the electronic state hybridization between the valence band of the perovskite NCs and the HOMOs of the chiral ligands.³⁹ In this study, the BNP molecules have two bulky naphthyl groups and a bridged structure of two oxygen atoms connected at the 2,2'-positions of the binaphthyl rings *via* a $-\text{P}(\text{O})(\text{OH})$ moiety. Considering steric hindrance, it is likely that BNP molecules only bind to uncoordinated Pb^{2+} and Cs^+ on the NPL surface and do not get into

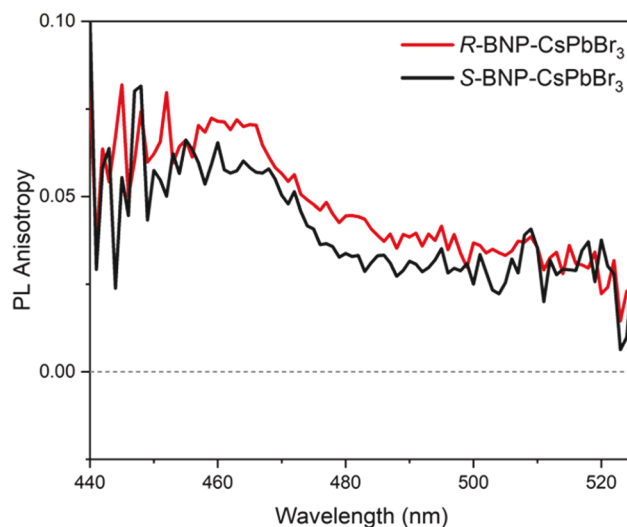


Fig. 4 Photoluminescence anisotropy of CsPbBr_3 NPLs.

halide vacancies on the surface. Still, BNP molecules on the NPL surface can induce chirality in CsPbBr_3 perovskite NCs *via* both mechanisms mentioned above. Future mechanistic studies are necessary to elucidate the interaction between the anionic BNPs and the CsPbBr_3 NCs.

In addition to chirality in the ground state absorption of the NPLs, we observed fluorescence anisotropy in the excited state of NPLs as shown in Fig. 4. Fluorescence anisotropy has been observed in some anisotropic semiconductor nanocrystals such as CsPbBr_3 and CdSe/CdS core/shell nanorods;^{40,41} however, this property has yet to be explored in halide perovskite NPLs. In our experiments, linearly polarized emission of the NPLs was characterized by exciting them with linearly polarized light and comparing the photoluminescence intensity through parallel and perpendicular polarizers (see details in the Experimental section in the ESI†). The NPLs of 5 monolayer thick achieve a fluorescence anisotropy value of ~ 0.06 . In contrast, fluorescence anisotropy was not observed in cube-shaped CsPbBr_3 NCs (see Fig. S8, ESI†). Thus, the fluorescence anisotropy is attributed to the in-plane orientation of the transition dipole moments⁴² and the small height of the NPLs compared to their base. Both chirality in the ground state and linearly polarized emission from the excited state of the *R/S*-BNP- CsPbBr_3 NPLs open more possibilities for using them in display applications.

In conclusion, we developed a new approach to fabricate chiral perovskite NCs by using anionic ligands with high affinity to the perovskite surface. The *R/S*-BNP ligands successfully induced chiroptical activity in five-unit cell CsPbBr_3 NPLs. The BNP- CsPbBr_3 NPLs showed CD signals after purification with *t*-butanol as the anti-solvent. Linearly polarized emission of the NPLs was also observed and ascribed to their anisotropic shape. This study has expanded the choice of chiral ligands for perovskite NCs from cationic amine to anionic phosphate. It opens up the possibility to achieve chiroptical perovskite NCs using chiral phosphorus-based ligands with high affinity to the perovskite surface.

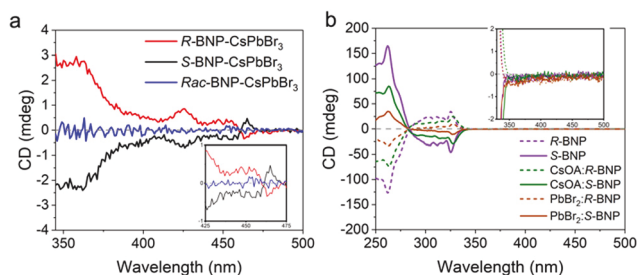


Fig. 3 The CD spectra of (a) *R*- and *S*-BNP- CsPbBr_3 NPLs (inset 425–475 nm) and (b) precursors (inset 330–500 nm).

T. K. T. T. and J. Z. initiated the project. T. K. T. T. conducted the NPL synthesis, and characterization and analyzed the results under the supervision of J. Z. J. A. A. synthesized the BNP molecules and performed the NMR characterization of BNP under the supervision of G. U. Y. W. and T. K. T. T. collected the TEM images. M. D. M-A. and T. K. T. T. carried out the XRD measurements. T. M. performed the linearly polarized emission measurements. All the authors contributed to the manuscript preparation. All the authors gave approval to the final version of the manuscript.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

- 1 J. Y. Kim, J.-W. Lee, H. S. Jung, H. Shin and N.-G. Park, *Chem. Rev.*, 2020, **120**, 7867–7918.
- 2 G. Pacchioni, *Nat. Rev. Mater.*, 2021, **6**, 108.
- 3 J. Miao and F. Zhang, *J. Mater. Chem. C*, 2019, **7**, 1741–1791.
- 4 G. Long, C. Jiang, R. Sabatini, Z. Yang, M. Wei, L. N. Quan, Q. Liang, A. Rasmita, M. Askerka, G. Walters, X. Gong, J. Xing, X. Wen, R. Quintero-Bermudez, H. Yuan, G. Xing, X. R. Wang, D. Song, O. Voznyy, M. Zhang, S. Hoogland, W. Gao, Q. Xiong and E. H. Sargent, *Nat. Photonics*, 2018, **12**, 528–533.
- 5 C. Chen, L. Gao, W. Gao, C. Ge, X. Du, Z. Li, Y. Yang, G. Niu and J. Tang, *Nat. Commun.*, 2019, **10**, 1927.
- 6 I. C. Seo, Y. Lim, S.-C. An, B. H. Woo, S. Kim, J. G. Son, S. Yoo, H.-K. Park, J. Y. Kim and Y. C. Jun, *ACS Nano*, 2021, **15**, 13781–13793.
- 7 Y. Dong, Y. Zhang, X. Li, Y. Feng, H. Zhang and J. Xu, *Small*, 2019, **15**, 1902237.
- 8 G. Long, R. Sabatini, M. I. Saidaminov, G. Lakhwani, A. Rasmita, X. Liu, E. H. Sargent and W. Gao, *Nat. Rev. Mater.*, 2020, **5**, 423–439.
- 9 J. Ma, C. Fang, C. Chen, L. Jin, J. Wang, S. Wang, J. Tang and D. Li, *ACS Nano*, 2019, **13**, 3659–3665.
- 10 J. Ahn, E. Lee, J. Tan, W. Yang, B. Kim and J. Moon, *Mater. Horiz.*, 2017, **4**, 851–856.
- 11 J. Ahn, S. Ma, J.-Y. Kim, J. Kyhm, W. Yang, J. A. Lim, N. A. Kotov and J. Moon, *J. Am. Chem. Soc.*, 2020, **142**, 4206–4212.
- 12 H. Lu, C. Xiao, R. Song, T. Li, A. E. Maughan, A. Levin, R. Brunecky, J. J. Berry, D. B. Mitzi, V. Blum and M. C. Beard, *J. Am. Chem. Soc.*, 2020, **142**, 13030–13040.
- 13 Y. Dang, X. Liu, Y. Sun, J. Song, W. Hu and X. Tao, *J. Phys. Chem. Lett.*, 2020, **11**, 1689–1696.
- 14 H. Ren, Y. Wu, C. Wang and Y. Yan, *J. Phys. Chem. Lett.*, 2021, **12**, 2676–2681.
- 15 C. Yuan, X. Li, S. Semin, Y. Feng, T. Rasing and J. Xu, *Nano Lett.*, 2018, **18**, 5411–5417.
- 16 G. Xing, B. Wu, X. Wu, M. Li, B. Du, Q. Wei, J. Guo, E. K. L. Yeow, T. C. Sum and W. Huang, *Nat. Commun.*, 2017, **8**, 14558.
- 17 Z. N. Georgieva, B. P. Bloom, S. Ghosh and D. H. Waldeck, *Adv. Mater.*, 2018, **30**, 1800097.
- 18 T. Liu, W. Shi, W. Tang, Z. Liu, B. C. Schroeder, O. Fenwick and M. J. Fuchter, *ACS Nano*, 2022, **16**, 2682–2689.
- 19 T. He, J. Li, X. Li, C. Ren, Y. Luo, F. Zhao, R. Chen, X. Lin and J. Zhang, *Appl. Phys. Lett.*, 2017, **111**, 151102.
- 20 W. Chen, S. Zhang, M. Zhou, T. Zhao, X. Qin, X. Liu, M. Liu and P. Duan, *J. Phys. Chem. Lett.*, 2019, **10**, 3290–3295.
- 21 Y.-H. Kim, Y. Zhai, E. A. Gauding, S. N. Habisreutinger, T. Moot, B. A. Rosales, H. Lu, A. Hazarika, R. Brunecky, L. M. Wheeler, J. J. Berry, M. C. Beard and J. M. Luther, *ACS Nano*, 2020, **14**, 8816–8825.
- 22 A. Nemati, S. Shadpour, L. Querciagrossa, T. Mori, C. Zannoni and T. Hegmann, *ACS Nano*, 2019, **13**, 10312–10326.
- 23 C. Gautier, R. Taras, S. Gladiali and T. Bürgi, *Chirality*, 2008, **20**, 486–493.
- 24 T. Mori, A. Sharma and T. Hegmann, *ACS Nano*, 2016, **10**, 1552–1564.
- 25 M. Tamura and H. Fujihara, *J. Am. Chem. Soc.*, 2003, **125**, 15742–15743.
- 26 J. Jacques and C. Fouquey, Enantiomeric (S)-(+)- and (R)-(–)-1,1'-Binaphthyl-2,2'-diyl hydrogen phosphate, *Org. Synth.*, 1993, **8**, 50; J. Jacques and C. Fouquey, Enantiomeric (S)-(+)- and (R)-(–)-1,1'-Binaphthyl-2,2'-diyl hydrogen phosphate, *Org. Synth.*, 1989, **67**, 1.
- 27 F. Liu, Y. Zhang, C. Ding, S. Kobayashi, T. Izuishi, N. Nakazawa, T. Toyoda, T. Ohta, S. Hayase, T. Minemoto, K. Yoshino, S. Dai and Q. Shen, *ACS Nano*, 2017, **11**, 10373–10383.
- 28 B. Zhang, L. Goldoni, J. Zito, Z. Dang, G. Almeida, F. Zaccaria, J. de Wit, I. Infante, L. de Trizio and L. Manna, *Chem. Mater.*, 2019, **31**, 9140–9147.
- 29 L. Wu, Q. Zhong, D. Yang, M. Chen, H. Hu, Q. Pan, H. Liu, M. Cao, Y. Xu, B. Sun and Q. Zhang, *Langmuir*, 2017, **33**, 12689–12696.
- 30 J. Y. Woo, S. Lee, S. Lee, W. D. Kim, K. Lee, K. Kim, H. J. An, D. C. Lee and S. Jeong, *J. Am. Chem. Soc.*, 2016, **138**, 876–883.
- 31 J. Shamsi, D. Kubicki, M. Anaya, Y. Liu, K. Ji, K. Frohna, C. P. Grey, R. H. Friend and S. D. Stranks, *ACS Energy Lett.*, 2020, **5**, 1900–1907.
- 32 L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh and M. V. Kovalenko, *Nano Lett.*, 2015, **15**, 3692–3696.
- 33 Q. A. Akkerman, S. G. Motti, A. R. Srimath Kandada, E. Mosconi, V. D'Innocenzo, G. Bertonni, S. Marras, B. A. Kamino, L. Miranda, F. de Angelis, A. Petrozza, M. Prato and L. Manna, *J. Am. Chem. Soc.*, 2016, **138**, 1010–1016.
- 34 Y. Wang, X. Li, S. Sreejith, F. Cao, Z. Wang, M. C. Stuparu, H. Zeng and H. Sun, *Adv. Mater.*, 2016, **28**, 10637–10643.
- 35 M. Klähn, G. Mathias, C. Kötting, M. Nonella, J. Schlitter, K. Gerwert and P. Tavan, *J. Phys. Chem. A*, 2004, **108**, 6186–6194.
- 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 Y. Sang, J. Han, T. Zhao, P. Duan and M. Liu, *Adv. Mater.*, 2020, **32**, 1900110.
- 38 Y.-H. Kim, R. Song, J. Hao, Y. Zhai, L. Yan, T. Moot, A. F. Palmstrom, R. Brunecky, W. You, J. J. Berry, J. L. Blackburn, M. C. Beard, V. Blum and J. M. Luther, *Adv. Funct. Mater.*, 2022, **32**, 2200454.
- 39 S. Jiang, Y. Song, H. Kang, B. Li, K. Yang, G. Xing, Y. Yu, S. Li, P. Zhao and T. Zhang, *ACS Appl. Mater. Interfaces*, 2022, **14**, 3385–3394.
- 40 Y. Dou, F. Cao, T. Dudka, Y. Li, S. Wang, C. Zhang, Y. Gao, X. Yang and A. L. Rogach, *ACS Mater. Lett.*, 2020, **2**, 814–820.
- 41 P. D. Cunningham, J. B. Souza Jr, I. Fedin, C. She, B. Lee and D. V. Talapin, *ACS Nano*, 2016, **10**, 5769–5781.
- 42 A. H. Proppe, G. W. Walters, A. Y. Alsalloum, A. A. Zhumekenov, E. Mosconi, S. O. Kelley, F. de Angelis, L. Adamska, P. Umari, O. M. Bakr and E. H. Sargent, *J. Phys. Chem. Lett.*, 2020, **11**, 716–723.