Perovskites

International Edition: DOI: 10.1002/anie.201909109
German Edition: DOI: 10.1002/ange.201909109

Halogen Vacancies Enable Ligand-Assisted Self-Assembly of Perovskite Quantum Dots into Nanowires

Jun Pan⁺, Xiyan Li⁺, Xiwen Gong⁺, Jun Yin, Dianli Zhou, Lutfan Sinatra, Renwu Huang, Jiakai Liu, Jie Chen, Ibrahim Dursun, Ahmed M. El-Zohry, Makhsud I. Saidaminov, Hong-Tao Sun, Omar F. Mohammed, Changhui Ye, Edward H. Sargent,^{*} and Osman M. Bakr^{*}

Abstract: Interest has been growing in defects of halide perovskites in view of their intimate connection with key material optoelectronic properties. In perovskite quantum dots (PQDs), the influence of defects is even more apparent than in their bulk counterparts. By combining experiment and theory, we report herein a halide-vacancy-driven, ligand-directed self-assembly process of CsPbBr₃ PQDs. With the assistance of oleic acid and didodecyldimethylammonium sulfide, surface-Br-vacancy-rich CsPbBr₃ PQDs self-assemble into nanowires (NWs) that are 20–60 nm in width and several millimeters in length. The NWs exhibit a sharp photoluminescence profile (≈ 18 nm full-width at-half-maximum) that peaks at 525 nm. Our findings provide insight into the defect-correlated dynamics of PQDs and defect-assisted fabrication of perovskite materials and devices.

Lead halide perovskites have attracted attention as promising optoelectronic materials for photovoltaics (PV),^[1] photodetectors,^[2] light-emitting diodes,^[3] and X-ray detectors.^[4] The performance of these optoelectronic devices is dependent on the photophysical properties of the perovskite active layer. Defects negatively impact photophysical properties by acting as non-radiative recombination centers, deteriorating the device efficiency.^[5] They also act as initiation points for device degradation.^[6]

Perovskite quantum dots (PQDs), with their soft lattice and low energy of formation, possess more labile ligand dynamics and more prevalent defects than conventional semiconductor QDs.^[7] Defects (particularly surface vacancies), which can act as surface traps, are generated across PQD synthesis approaches.^[8] These surface vacancies also play a role in the colloidal stability of PQDs, which stems from the ligand binding dynamics on the PQD surface.^[9] The dynamic equilibrium between free and bound ammonium bromide ligand pairs on the PQD surface is readily shifted during long-term storage and by repeated isolation and purification of the PQDs. This leads to increased surface traps and results in agglomeration, degrading optoelectronic properties.

Up to now, several strategies, including self-assembly, have been developed to passivate surface traps and minimize defects with the goal of enhanced device performance.^[10] However, the mechanism behind the PQD self-assembly process is under studied. Single particle self-assembly is explained through oriented attachment, induced by organic additives or dipole-dipole interaction.^[11] We find herein that, by contrast, surface halide vacancies can mediate assembly. We first modulate the density of surface halide vacancies in CsPbBr₃ PQDs by engineering the surface ligand; after which we direct PQD self-assembly into nanowires (NWs) with the assistance of oleic acid and didodecyldimethylammonium sulfide (DDA-S). Through fine control over experimental conditions, we achieve NWs that are uniform in width (20–60 nm) and that are several millimeters in length, all achieved using PQDs having a high density of surface halide vacancies. In contrast, well-passivated PQDs with vacancy-poor surfaces remained dispersed.

We started by preparing two kinds of PQDs with different synthetic methods: one with the conventional hot-injection method,^[8a] and the other using additional organic ammonium halide salt,^[12] Both kinds of PQDs exhibit identical crystal structure and similar morphology, as confirmed by transmission electron microscopy (TEM, Figure S1 in the Supporting Information) and X-ray diffraction (XRD, Figure S2), respectively. Despite the structural similarities, the PQDs which used oleylammonium bromide as an additional halide source (referred to as halide-rich PQDs, HRPQDs) displayed higher PLQY ($98 \pm 2\%$) than the PQDs with the conventional hot-injection method (referred to as halide-vacancy-rich PQDs, HVPQDs; $PLQY = 50 \pm 4\%$). We posited that the enhanced PLQY of HRPQDs stems from the lower defect density.

^[*] Dr. J. Pan,^[+] Dr. J. Yin, D. Zhou, Dr. L. Sinatra, Dr. R. Huang, J. Liu, Dr. J. Chen, Dr. I. Dursun, Dr. A. El-Zohry, Prof. O. Mohammed, Prof. O. Bakr
Division of Physical Science and Engineering (PSE), King Abdullah University of Science and Technology (KAUST)
Thuwal, Jeddah, 23955 (Saudi Arabia)
E-mail: osman.bakr@kaust.edu.sa

Dr. X. Li,^[+] Dr. X. Gong,^[+] Dr. M. Saidaminov, Prof. E. Sargent
Department of Electrical and Computer Engineering
University of Toronto
Toronto, Ontario M5S 3G4 (Canada)
E-mail: ted.sargent@utoronto.ca

Prof. H. Sun
College of Chemistry, Chemical Engineering and Materials Science, Soochow University
Suzhou, Jiangsu 215123 (P. R. China)

Dr. J. Pan,^[+] Prof. C. Ye
College of Materials of Science and Engineering
Zhejiang University of Technology
Hangzhou, Zhejiang 310014 (P. R. China)

^[†] These authors contributed equally to this work.

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/anie.201909109>.

To prove our hypothesis, we first performed density function theory (DFT) calculations to determine the defect formation energies in PQDs. Since the bulk defects in PQDs were reported to have negligible impact on non-radiative recombination compared to the surface defects,^[13] we thus focused on the latter in this work. We first identified the terminating facets of PQDs by comparing the surface energies of different crystal planes. We found that the (100) slab of CsPbBr₃ with CsBr-termination is the lowest energy surface in comparison to the (110) slab and is thus the dominant surface of CsPbBr₃ PQDs.

We then turned to study the formation of Br vacancy (V_{Br}) as they are the predominant defects in Cs-Pb-Br perovskites.^[14] As shown in Figure 1 a, the formation energy of V_{Br}

Figure 1. a) Defect formation energies for orthorhombic-CsPbBr₃ with Br vacancy (V_{Br}) in the bulk and on the surface. b) Defect charge-transition levels for V_{Br} in orthorhombic-phase CsPbBr₃. c) Calculated density of states for orthorhombic-phase CsPbBr₃ (100) slab without and with surface V_{Br} . The insets show the electronic charge density for valence band minimum (VBM) and conduction band minimum (CBM) with surface V_{Br} in CsPbBr₃ (100) slab. All the calculations are performed at HSE + SOC level of theory.

on the (100) surface in CsPbBr₃ is very close to that of the bulk, but much smaller than that on the (110) surface, showing that the formation energies decrease as the chemical potential shifts from the Br-rich to Br-poor side and indicating the higher possibility to form V_{Br} under Br-poor condition. While the V_{Br} in the bulk shows a shallow charge-transition level (see Figure 1 b), the level becomes a deep one when V_{Br} is generated on the (100) and (110) surfaces. In the case of surface (100), the charge density for the valence band maximum (VBM) is delocalized along the whole slab, while the charge density for the conduction band minimum (CBM) is highly localized on the top surface layers, leading to the formation of a surface trap state (Figure 1 c). Such surface defect states can act as non-radiative centers that depreciate the PL.

To further prove the difference of V_{Br} density in these two kinds of dots, X-ray photoelectron spectroscopy (XPS) and positron annihilation spectroscopy (PAS) were employed to investigate the surface chemical composition of the aforementioned two PQD samples. The HVPQDs showed a Pb/Br ratio of 1:2.52, while HRPQDs one owns a ratio of 1:3.1, suggesting the V_{Br} rich surface of HVPQDs. The positron lifetime of PAS reflects the position of the vacancy level inside a material. From Table S1, the positron average lifetime of HRPQDs is 70 ps shorter than that in the

HVPQDs, which is indicative of higher defect density in HVPQDs.

We also performed femtosecond time-resolved transient absorption (fs-TA) to probe the density of defects in PQDs (Figure S4). Both PQDs share some common spectral features, with a strong stimulated emission (SE) peak around 515 nm and a positive excited state absorption spectrum extend from 380 to 900 nm. Fitting the extracted kinetic traces at SE showed average lifetimes of 365 ps and 1100 ps for HVPQDs and HRPQDs, respectively. The longer lifetime of HRPQDs implies a lower trap density on the HRPQD surface. Hence, a suite of spectroscopy techniques corroborated the hypothesis of lower surface defect density in HRPQDs than in HVPQDs.

To explore the function of surface vacancies on self-assembly behavior, we then used the above PQDs with different vacancy densities for self-assembly.^[10a] No changes occurred for the HRPQDs over one week after adding oleic acid (OA) and didodecyldimethylammonium sulfide (DDAS). However, we observed the formation of precipitates after 180 minutes of OA and DDAS addition in HVPQDs solution, signaling a self-assembly process (Figure S5). We used high-resolution transmission electron microscopy (HR-TEM) to reveal the self-assembly mode by observing the microscopic structure of the formed precipitates at different times after the addition of OA and DDAS (Figure 2 a–d).

Figure 2. TEM images of different samples obtained at different time a) pristine HVPQDs, b) 5 min, c) 60 min, d) 180 min. e) High resolution single NW image. f) HR-SEM image of NWs. g, h) Energy-filtered TEM element mapping of single NW: Pb mapping (g), S mapping (h).

Increased particle size was observed in HVPQDs $t = 5$ min. The nanoparticles further fused with each other along one direction and the distinctive shape of nanowires appeared at $t = 60$ min. With the passage of time, the nanoparticles were consumed and transformed into NWs with widths around 20–60 nm and lengths up to several μm scale (Figure 2 d and S6). A redshift of the PL peak of the precipitates with time is observed and is consistent with the reduction quantum confinement that is expected in the self-assembled products (Figure S7 and S8). The NWs are in the orthorhombic phase (Figure S9), consistent with the pristine HVPQDs. The lattice fringes of CsPbBr₃ NW in all the directions are very clear and periodic, which indicate the as-grown NWs are single crystalline crystallites, and have very good crystalline quality. (Figure 2 e). Interestingly, we observed that the NW surface was covered by an organic shell (Figure 2 f). Energy-filtered

transmission electron microscopy (EFTEM) shows that sulfur is distributed uniformly on the wire surface, while lead is situated in the main NW framework (Figure 2g and h). Furthermore, quaternary ammonium group (DDA^+), due to its high-affinity to negative sites, can replace the pristine organic ligand group,^[10a,b] leading to less ligand weight loss between 160–350 °C in NWs than in HVPQDs, as seen in thermogravimetric analysis (TGA) (Figure S10). Hence, we speculate that sulfur fills the V_{Br} and assists HVPQD self-assembly, while DDA^+ passivates the NW surface.

We used ex-situ grazing incidence small angle X-ray scattering (GISAXS) to further probe the self-assembly process. We obtained the GISAXS patterns of self-assembled quantum dots at time = 20 min and 180 min, respectively (Figure 3a and b). The reflection at $0.75 \text{ \AA}^{-1}$ is ascribed to the diffraction from unfused QD with unit size of $L = 8 \text{ nm}$, and the peaks with smaller Q values correspond the lattice constant of $d = 2L, 3L, 5L$, indicating the formation of the superlattice of HVPQDs. It should be noted that NWs with lengths more than $5L$ are beyond the detection limit of the GISAXS set-up utilized in this work. Figure 3c shows the 1D profile along Q_z direction with different self-assembly time in real space. The diffraction peaks result from the scattering of single unit cells and the superlattices of CsPbBr_3 PQDs. As a simplified size distribution model, we take only the three well-defined peaks at $d = L, 2L$, and $5L$ into account, and study their temporal revolution by probing the relative ratio against the self-assembly time. The relative ratio of $d = L, d = 2L, d = 5L$ was calculated by normalizing the intensity of each peak to the sum of the intensity of the three peaks. Figure 3d shows the ratio of the HVPQD-unit ($L = a$) keeps decreasing with time while the longer wire component ($L = 5a$) increases. The time-dependent evolution studied by GISAXS and TEM provide a consisted picture of the initial steps during the formation of self-assembled NWs.

To identify the crucial elements in the self-assembly process, several control experiments were further conducted (Table S2). When we replaced the bivalent S in DDAS with the monovalent Br (DDAB) (Figure S11), no NWs were formed, though PQDs underwent a similar ligand exchange

Figure 3. QD self-assembly study using GISAXS. a,b) Diffraction pattern of the samples with different assembly time. c) 1D profiles of the diffraction patterns along Q_z direction at different time. d) The normalized ratio between the particles with lengths (L) equals to a and $5a$, respectively, as a function of time. With self-assembly proceeding, the ratio of $L = 5a$ increasing, indicating single QD gradually forms longer unit.

process according to our previous work.^[10b] Furthermore, when we reduced the amount of OA, taper-shaped structure appeared (Figure S12a and S12b). Moreover, fewer short wires were obtained with decreased amount of DDA-S (Figure S12c and S12d), indicating that sulfur facilitates the longitudinal growth of NW. However, when we only added DDAS into HVPQDs, no NWs were observed. In summary, uniform long NWs were formed with co-existence of OA and DDA-S , indicating sulfur with proper amount of OA is key factors for HVPQD self-assembly.

Combined with above results, we found HVPQDs aggregate into NWs rather than nanocubes because of the different density of vacancies on two most prominent surfaces of QDs.

Scheme 1. QD Self-assembly mechanism.

DFT calculation shows that the formation energy of V_{Br} on the CsPbBr₃ (110) surface is much larger than that on the (100) surface, that is, (100) has larger density of vacancies. Therefore, the assembly of HVPQDs becomes anisotropic, as also shown by the above ex-situ GISAXS data. Hence, we propose the following dynamic ligand and V_{Br} assisted Scheme as the mechanism of the self-assembly process. As shown in Scheme 1, OA was added to alter the equilibrium of the HVPQDs' ionic surface, forming an acid-base complex with oleylammonium weakly bonded on the HVPQDs' surface.^[10b,15] The detachment of oleylammonium creates more space for DDA-S to attach on the surface of the QDs, while the S^{2-} group from DDA-S occupies the Br vacancy. Two adjacent HVPQD monomers are then attracted to one another by the bivalency of sulfur, thus inducing the self-assembly of HVPQDs. DDA⁺ has a high affinity for the sulfur sites and, subsequently, even replaces the original OLA sites to form an organic shell on the NW surface.^[10a,b]

To conclude, in this work, we utilized the surface defects as ionic anchoring sites to assemble PQDs into NWs. We further unveiled the mechanism and identified the function of the key elements of the self-assembly process. OA alters the dynamics of the surface ligands on PQDs, which then affords sulfur anions to fill in bromine vacancies of HVPQDs. Sulfide bivalent anions bridge the adjacent HVPQDs through binding with one halide vacancy from each PQDs, hence facilitate the self-assembly. This vacancy induced self-assembly sheds new light on the surface chemistry of the PQDs and opens new prospects for fabricating perovskite NWs for optoelectronic applications.

Acknowledgements

The authors acknowledge funding support from KAUST.

Conflict of interest

The authors declare no conflict of interest.

Keywords: CsPbBr₃ · halide vacancy · nanowire · perovskite quantum dot · self-assembly

- [1] a) X. Li, M. I. Dar, C. Y. Yi, J. S. Luo, M. Tschumi, S. M. Zakeeruddin, M. K. Nazeeruddin, H. W. Han, M. Gratzel, *Nat. Chem.* **2015**, *7*, 703–711; b) Q. A. Akkerman, M. Gandini, F. Di Stasio, P. Rastogi, F. Palazon, G. Bertoni, J. M. Ball, M. Prato, A. Petrozza, L. Manna, *Nat. Energy* **2017**, *2*, 16194; c) M. Y. Li, Y. M. Shi, C. C. Cheng, L. S. Lu, Y. C. Lin, H. L. Tang, M. L. Tsai, C. W. Chu, K. H. Wei, J. H. He, W. H. Chang, K. Suenaga, L. J. Li, *Science* **2015**, *349*, 524–528; d) A. Swarnkar, A. R. Marshall, E. M. Sanehira, B. D. Chernomordik, D. T. Moore, J. A. Christians, T. Chakrabarti, J. M. Luther, *Science* **2016**, *354*, 92–95; e) H. Tan, A. Jain, O. Voznyy, X. Lan, F. P. Garcia de Arquer, J. Z. Fan, R. Quintero-Bermudez, M. Yuan, B. Zhang, Y. Zhao, F. Fan, P. Li, L. N. Quan, Y. Zhao, Z.-H. Lu, Z. Yang, S. Hoogland, E. H. Sargent, *Science* **2017**, *355*, 722–

- 726; f) A. O. El-Ballouli, O. M. Bakr, O. F. Mohammed, *Chem. Mater.* **2019**, *31*, 6387–6411; g) Z. Chen, B. Turedi, A. Y. Alsalloum, C. Yang, X. Zheng, I. Gereige, A. AlSaggaf, O. F. Mohammed, O. M. Bakr, *ACS Energy Lett.* **2019**, *4*, 1258–1259. [2] a) L. T. Dou, Y. Yang, J. B. You, Z. R. Hong, W. H. Chang, G. Li, Y. Yang, *Nat. Commun.* **2014**, *5*, 5404; b) L. Gao, K. Zeng, J. S. Guo, C. Ge, J. Du, Y. Zhao, C. Chen, H. Deng, Y. S. He, H. S. Song, G. D. Niu, J. Tang, *Nano Lett.* **2016**, *16*, 7446–7454; c) M. Shoaib, X. H. Zhang, X. X. Wang, H. Zhou, T. Xu, X. Wang, X. L. Hu, H. W. Liu, X. P. Fan, W. H. Zheng, T. F. Yang, S. Z. Yang, Q. L. Zhang, X. L. Zhu, L. T. Sun, A. L. Pan, *J. Am. Chem. Soc.* **2017**, *139*, 15592–15595. [3] a) H. Cho, S.-H. Jeong, M.-H. Park, Y.-H. Kim, C. Wolf, C.-L. Lee, J. H. Heo, A. Sadhanala, N. Myoung, S. Yoo, S. H. Im, R. H. Friend, T.-W. Lee, *Science* **2015**, *350*, 1222–1225; b) M. J. Yuan, L. N. Quan, R. Comin, G. Walters, R. Sabatini, O. Voznyy, S. Hoogland, Y. B. Zhao, E. M. Beauregard, P. Kanjanaboos, Z. H. Lu, D. H. Kim, E. H. Sargent, *Nat. Nanotechnol.* **2016**, *11*, 872–877; c) 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, Z. Wei, *Nature* **2018**, *562*, 245–248; d) Y. Cao, N. Wang, H. Tian, J. Guo, Y. Wei, H. Chen, Y. Miao, W. Zou, K. Pan, Y. He, H. Cao, Y. Ke, M. Xu, Y. Wang, M. Yang, K. Du, Z. Fu, D. Kong, D. Dai, Y. Jin, G. Li, H. Li, Q. Peng, J. Wang, W. Huang, *Nature* **2018**, *562*, 249–253; e) X. M. Li, Y. Wu, S. L. Zhang, B. Cai, Y. Gu, J. Z. Song, H. B. Zeng, *Adv. Funct. Mater.* **2016**, *26*, 2435–2445; f) J. Song, J. Li, X. Li, L. Xu, Y. Dong, H. Zeng, *Adv. Mater.* **2015**, *27*, 7162–7167; g) X. L. Yang, X. W. Zhang, J. X. Deng, Z. M. Chu, Q. Jiang, J. H. Meng, P. Y. Wang, L. Q. Zhang, Z. G. Yin, J. B. You, *Nat. Commun.* **2018**, *9*, 570; h) N. N. Wang, L. Cheng, R. Ge, S. T. Zhang, Y. F. Miao, W. Zou, C. Yi, Y. Sun, Y. Cao, R. Yang, Y. Q. Wei, Q. Guo, Y. Ke, M. T. Yu, Y. Z. Jin, Y. Liu, Q. Q. Ding, D. W. Di, L. Yang, G. C. Xing, H. Tian, C. H. Jin, F. Gao, R. H. Friend, J. P. Wang, W. Huang, *Nat. Photonics* **2016**, *10*, 699–704. [4] a) Q. S. Chen, J. Wu, X. Y. Ou, B. L. Huang, J. Almutlaq, A. A. Zhumeckenov, X. W. Guan, S. Y. Han, L. L. Liang, Z. G. Yi, J. Li, X. J. Xie, Y. Wang, Y. Li, D. Y. Fan, D. B. L. Teh, A. H. All, O. F. Mohammed, O. M. Bakr, T. Wu, M. Bettinelli, H. H. Yang, W. Huang, X. G. Liu, *Nature* **2018**, *561*, 88–93; b) Y. C. Kim, K. H. Kim, D. Y. Son, D. N. Jeong, J. Y. Seo, Y. S. Choi, I. T. Han, S. Y. Lee, N. G. Park, *Nature* **2017**, *550*, 87–91; c) W. C. Pan, H. D. Wu, J. J. Luo, Z. Z. Deng, C. Ge, C. Chen, X. W. Jiang, W. J. Yin, G. D. Niu, L. J. Zhu, L. X. Yin, Y. Zhou, Q. G. Xie, X. X. Ke, M. L. Sui, J. Tang, *Nat. Photonics* **2017**, *11*, 726–732; d) H. T. Wei, Y. J. Fang, P. Mulligan, W. Chuirazzi, H. H. Fang, C. C. Wang, B. R. Ecker, Y. L. Gao, M. A. Loi, L. Cao, J. S. Huang, *Nat. Photonics* **2016**, *10*, 333–339; e) Y. Zhang, R. Sun, X. Ou, K. Fu, Q. Chen, Y. Ding, L.-J. Xu, L. Liu, Y. Han, A. V. Malko, X. Liu, H. Yang, O. M. Bakr, H. Liu, O. F. Mohammed, *ACS Nano* **2019**, *13*, 2520–2525. [5] a) F. Wang, S. Bai, W. Tress, A. Hagfeldt, F. Gao, *npj Flexible Electron.* **2018**, *2*, 22; b) T. Zhao, C. C. Chueh, Q. Chen, A. Rajagopal, A. K. Y. Jen, *ACS Energy Lett.* **2016**, *1*, 757–763. [6] a) N. Aristidou, C. Eames, I. Sanchez-Molina, X. Bu, J. Kosco, M. S. Islam, S. A. Haque, *Nat. Commun.* **2017**, *8*, 15218; b) N. Li, S. Tao, Y. Chen, X. Niu, C. K. Onwudinanti, C. Hu, Z. Qiu, Z. Xu, G. Zheng, L. Wang, Y. Zhang, L. Li, H. Liu, Y. Lun, J. Hong, X. Wang, Y. Liu, H. Xie, Y. Gao, Y. Bai, S. Yang, G. Brocks, Q. Chen, H. Zhou, *Nat. Energy* **2019**, *4*, 408–415. [7] a) Y. Wei, Z. Cheng, J. Lin, *Chem. Soc. Rev.* **2019**, *48*, 310–350; b) M. V. Kovalenko, L. Protesescu, M. I. Bodnarchuk, *Science* **2017**, *358*, 745–750; c) J.-P. Ma, J. Yin, Y.-M. Chen, Q. Zhao, Y. Zhou, H. Li, Y. Kuroiwa, C. Moriyoshi, Z.-Y. Li, O. M. Bakr, O. F. Mohammed, H.-T. Sun, *ACS Mater. Lett.* **2019**, *1*, 185–191. [8] a) L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh, M. V. Kovalenko,

- Nano Lett.* **2015**, *15*, 3692–3696; b) G. H. Ahmed, J. K. El-Demellawi, J. Yin, J. Pan, D. B. Velusamy, M. N. Hedhili, E. Alarousu, O. M. Bakr, H. N. Alshareef, O. F. Mohammed, *ACS Energy Lett.* **2018**, *3*, 2301–2307; c) J.-P. Ma, J. Yin, Y.-M. Chen, Q. Zhao, Y. Zhou, H. Li, Y. Kuroiwa, C. Moriyoshi, Z.-Y. Li, O. M. Bakr, O. F. Mohammed, H.-T. Sun, *ACS Mater. Lett.* **2019**, *1*, 185–191 ■■■ see ref [7c] ■■■.
- [9] a) J. De Roo, M. Ibáñez, P. Geiregat, G. Nedelcu, W. Walravens, J. Maes, J. C. Martins, I. Van Driessche, M. V. Kovalenko, Z. Hens, *ACS Nano* **2016**, *10*, 2071–2081; b) S. R. Smock, T. J. Williams, R. L. Brutchey, *Angew. Chem. Int. Ed.* **2018**, *57*, 11711–11715; *Angew. Chem.* **2018**, *130*, 11885–11889.
- [10] a) J. Pan, S. P. Sarmah, B. Murali, I. Dursun, W. Peng, M. R. Parida, J. Liu, L. Sinatra, N. Alyami, C. Zhao, E. Alarousu, T. K. Ng, B. S. Ooi, O. M. Bakr, O. F. Mohammed, *J. Phys. Chem. Lett.* **2015**, *6*, 5027–5033; b) J. Pan, L. N. Quan, Y. B. Zhao, W. Peng, B. Murali, S. P. Sarmah, M. J. Yuan, L. Sinatra, N. M. Alyami, J. K. Liu, E. Yassitepe, Z. Y. Yang, O. Voznyy, R. Comin, M. N. Hedhili, O. F. Mohammed, Z. H. Lu, D. H. Kim, E. H. Sargent, O. M. Bakr, *Adv. Mater.* **2016**, *28*, 8718–8725; c) G. Li, F. W. R. Rivalola, N. J. L. K. Davis, S. Bai, T. C. Jellicoe, F. de la Peña, S. Hou, C. Ducati, F. Gao, R. H. Friend, N. C. Greenham, Z.-K. Tan, *Adv. Mater.* **2016**, *28*, 3528–3534; d) J. Pan, Y. Shang, J. Yin, M. De Bastiani, W. Peng, I. Dursun, L. Sinatra, A. M. El-Zohry, M. N. Hedhili, A.-H. Emwas, O. F. Mohammed, Z. Ning, O. M. Bakr, *J. Am. Chem. Soc.* **2018**, *140*, 562–565; e) D. P. Nenon, K. Pressler, J. Kang, B. A. Koscher, J. H. Olshansky, W. T. Oso-wiecki, M. A. Koc, L.-W. Wang, A. P. Alivisatos, *J. Am. Chem. Soc.* **2018**, *140*, 17760–17772; f) B. A. Koscher, J. K. Swabeck, N. D. Bronstein, A. P. Alivisatos, *J. Am. Chem. Soc.* **2017**, *139*, 6566–6569; g) X. Y. Chin, A. Perumal, A. Bruno, N. Yantara, S. A. Veldhuis, L. Martínez-Sarti, B. Chandran, V. Chirvony, A. S.-Z. Lo, J. So, C. Soci, M. Grätzel, H. J. Bolink, N. Mathews, S. G. Mhaisalkar, *Energy Environ. Sci.* **2018**, *11*, 1770–1778; h) S. Yuan, Z.-K. Wang, M.-P. Zhuo, Q.-S. Tian, Y. Jin, L.-S. Liao, *ACS Nano* **2018**, *12*, 9541–9548; i) X. Zheng, Y. Hou, H.-T. Sun, O. F. Mohammed, E. H. Sargent, O. M. Bakr, *J. Phys. Chem. Lett.* **2019**, *10*, 2629–2640; j) A. Dutta, R. K. Behera, P. Pal, S. Baitalik, N. Pradhan, *Angew. Chem. Int. Ed.* **2019**, *58*, 5552–5556; *Angew. Chem.* **2019**, *131*, 5608–5612; k) G. Almeida, I. Infante, L. Manna, *Science* **2019**, *364*, 833; l) J. Shamsi, A. S. Urban, M. Imran, L. De Trizio, L. Manna, *Chem. Rev.* **2019**, *119*, 3296–3348.
- [11] a) Y. Tong, B. J. Bohn, E. Bladt, K. Wang, P. Muller-Buschbaum, S. Bals, A. S. Urban, L. Polavarapu, J. Feldmann, *Angew. Chem. Int. Ed.* **2017**, *56*, 13887–13892; *Angew. Chem.* **2017**, *129*, 14075–14080; b) K.-S. Cho, D. V. Talapin, W. Gaschler, C. B. Murray, *J. Am. Chem. Soc.* **2005**, *127*, 7140–7147; c) J. Liu, K. Song, Y. Shin, X. Liu, J. Chen, K. X. Yao, J. Pan, C. Yang, J. Yin, L.-J. Xu, H. Yang, A. M. El-Zohry, B. Xin, S. Mitra, M. N. Hedhili, I. S. Roqan, O. F. Mohammed, Y. Han, O. M. Bakr, *Chem. Mater.* **2019**, *31*, 6642–6649; d) K. J. Williams, W. A. Tisdale, K. S. Leschies, G. Haugstad, D. J. Norris, E. S. Aydil, X. Y. Zhu, *ACS Nano* **2009**, *3*, 1532–1538.
- [12] A. Dutta, R. K. Behera, S. K. Dutta, S. Das Adhikari, N. Pradhan, *J. Phys. Chem. Lett.* **2018**, *9*, 6599–6604.
- [13] J. Kang, L. W. Wang, *J. Phys. Chem. Lett.* **2017**, *8*, 489–493.
- [14] a) C. C. Stoumpos, C. D. Malliakas, J. A. Peters, Z. F. Liu, M. Sebastian, J. Im, T. C. Chasapis, A. C. Wibowo, D. Y. Chung, A. J. Freeman, B. W. Wessels, M. G. Kanatzidis, *Cryst. Growth Des.* **2013**, *13*, 2722–2727; b) A. Filippetti, A. Mattoni, *Phys. Rev. B* **2014**, *89*, 125203; c) J. Yin, H. Yang, K. Song, A. M. El-Zohry, Y. Han, O. M. Bakr, J.-L. Brédas, O. F. Mohammed, *J. Phys. Chem. Lett.* **2018**, *9*, 5490–5495.
- [15] A. Dong, X. Ye, J. Chen, Y. Kang, T. Gordon, J. M. Kikkawa, C. B. Murray, *J. Am. Chem. Soc.* **2011**, *133*, 998–1006.

Manuscript received: July 22, 2019

Revised manuscript received: September 13, 2019

Version of record online: ■■■ ■■■, ■■■■■

Communications

Perovskites

J. Pan, X. Li, X. Gong, J. Yin, D. Zhou,
L. Sinatra, R. Huang, J. Liu, J. Chen,
I. Dursun, A. El-Zohry, M. Saidaminov,
H. Sun, O. Mohammed, C. Ye,
E. Sargent,* O. Bakr* ——— ■■■■-■■■■

Halogen Vacancies Enable Ligand-
Assisted Self-Assembly of Perovskite
Quantum Dots into Nanowires

With the assistance of oleic acid and didodecyldimethylammonium sulfide, surface-Br-vacancy-rich CsPbBr₃ perovskite quantum dots self-assemble into nanowires that are 20–60 nm in width and several millimeters in length.

Perovskite

J. Pan, X. Li, X. Gong, J. Yin, D. Zhou,
L. Sinatra, R. Huang, J. Liu, J. Chen,
I. Dursun, A. El-Zohry, M. Saidaminov,
H. Sun, O. Mohammed, C. Ye,
E. Sargent,* O. Bakr* ——— ■■■■-■■■■

Halogen Vacancies Enable Ligand-
Assisted Self-Assembly of Perovskite
Quantum Dots into Nanowires

Mithilfe von Ölsäure und Didodecyldimethylammoniumsulfid werden CsPbBr₃-Quantenpunkte mit einer großen Zahl an Oberflächen-Bromid-Leerstellen zu Nanodrähten zusammengefügt. Die Nanodrähte sind 20–60 nm breit und erreichen eine Länge von mehreren Millimetern.

SPACE RESERVED FOR IMAGE AND LINK

Share your work on social media! *Angewandte Chemie* has added Twitter as a means to promote your article. Twitter is an online microblogging service that enables its users to send and read short messages and media, known as tweets. Please check the pre-written tweet in the galley proofs for accuracy. If you, your team, or institution have a Twitter account, please include its handle @username. Please use hashtags only for the most important keywords, such as #catalysis, #nanoparticles, or #protein design. The ToC picture and a link to your article will be added automatically, so the **tweet text must not exceed 250 characters**. This tweet will be posted on the journal's Twitter account (follow us @angew_chem) upon publication of your article in its final (possibly unpaginated) form. We recommend you to re-tweet it to alert more researchers about your publication, or to point it out to your institution's social media team.

Please check that the ORCID identifiers listed below are correct. We encourage all authors to provide an ORCID identifier for each coauthor. ORCID is a registry that provides researchers with a unique digital identifier. Some funding agencies recommend or even require the inclusion of ORCID IDs in all published articles, and authors should consult their funding agency guidelines for details. Registration is easy and free; for further information, see <http://orcid.org/>.

Dr. Jun Pan <http://orcid.org/0000-0002-6879-7023>

Dr. Xiyan Li

Dr. Xiwen Gong

Dr. Jun Yin

Dianli Zhou

Dr. Lutfan Sinatra

Dr. Renwu Huang

Jiakai Liu

Dr. Jie Chen

Dr. Ibrahim Dursun

Dr. Ahmed M. El-Zohry

Dr. Makhsud I. Saidaminov

Prof. Hong-Tao Sun

Prof. Omar F. Mohammed

Prof. Changhui Ye

Prof. Edward H. Sargent

Prof. Osman M. Bakr <http://orcid.org/0000-0002-3428-1002>