

Mesoscale Growth and Assembly of Bright Luminescent Organolead Halide Perovskite Quantum Wires

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Supporting Information



ABSTRACT: The long carrier lifetimes and low nonradiative recombination rates of organic-inorganic hybrid perovskites have opened new avenues in fabrication of highly efficient solar cells, light-emitting diodes, and lasers. Controlling shapes and organization of newly synthesized perovskite nanostructures should greatly expand their practical application. Here, we report a colloidal synthetic approach to the preparation of methylammonium lead bromide (CH₃NH₃PbBr₃) quantum wires by controlling their surface ligand chemistry to achieve well-defined superstructures. Quantum wire formation was proceeded by the appearance of pearl-necklace assemblies of spherical CH₃NH₃PbBr₃ nanocrystals as intermediates formed mainly through dipolar interactions. The diameter of the quantum wires (~3.8 nm) was found to be larger than the precursor spherical CH₃NH₃PbBr₃ nanocrystals (~2.4 nm). Our experimental findings support mesoscale growth and assembly into CH₃NH₃PbBr₃ quantum wires driven by cooperative interactions between nanocrystals caused by van der Waals interactions and chain interdigitation of surface passivating ligands. The quantum wires displayed an aspect ratio as high as 250 with photoluminescence quantum yield of ~60% and lifetime of ~90 ns, and were aligned in bundles. Our simple colloidal synthetic approach and detailed characterization will inspire rational design of methodologies to prepare diverse anisotropic semiconductor perovskite nanostructures and superstructures, which together will increase the versatility and performance of perovskite materials in optoelectronic and photovoltaic device applications.

■ INTRODUCTION

The early work by Mitzi and co-workers¹ on semiconductor organic-inorganic lead halide perovskites has expedited the synthesis of Earth-abundant organometal perovskite bulk materials, which have shown promise in their application in fabrication of efficient light-emitting diodes² and lasers.³ Following the first report,⁴ organolead halide perovskites are now successfully used as light absorbers in solar cells devices⁵⁻¹³ with certified power conversion efficiency of 20.1%.¹⁴ The long carrier diffusion lengths,^{12,15,16} faster charge carrier mobility,^{12,17} larger absorption cross-section, and ambipolar charge transport character¹⁸ make organic–inorganic

lead halide perovskites ideal materials to design highly efficient solar cells with power conversion efficiency as high as 30%, as demonstrated for silicon and gallium arsenide materials.¹⁴ However, the charge transport properties and carrier lifetimes of the mesoscopic perovskite bulk materials in these solid-state devices can be further improved through understanding the influence of shape on photophysical and electronic properties

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Figure 1. Structural characterization of organic–inorganic hybrid perovskite quantum wires: (A) TEM image of $CH_3NH_3PbBr_3$ quantum wires prepared via the colloidal synthetic approach (scale bar = 100 nm); (B) experimental XRD pattern corresponding to the cubic-phase of the perovskite quantum wires (red) and bulk $CH_3NH_3PbBr_3$ perovskite (black) prepared according to literature procedures¹⁶ (the broad peak (red) centered near 20° is due to the glass coverslip); and (C) high-resolution TEM image of a portion of a quantum wire showing cubic-phase lattice spacing (scale bar = 2 nm).

by synthesis and characterization of one-dimensional (1D) perovskite quantum wires, which are yet to be explored.

Comparing various anisotropic nanostructures such as platelets and rods, nanowires of various materials^{19–25} have shown great promise in the fabrication of field-effect transistors,^{26–28} optoelectronic devices,^{24,25,29} and sensors,^{22,30} because of their unique optical and electronic properties. Nanowires are also able to transport photogenerated charge carriers over a long distance with minimum hopping, which is an ideal electronic property for fabrication of high efficiency solar cells. Over the past two decades, synthetic methods have focused on carbon nanotubes,^{31,32} and metal oxide^{24,33} and semiconductor^{34–36} nanowires. Here, we report a colloidal-based, bright-green light emitting, hybrid organic–inorganic methylammonium lead bromide (CH₃NH₃PbBr₃) quantum wire synthesis with aspect ratio as high as 250 and photoluminescence (PL) lifetimes of ~90 ns.

Unlike point-initiated uniaxial growth of metal oxide or semiconductor crystals into nanowire materials,^{21,23,34,37} our quantum wire growth was driven by the spontaneous selforganization of spherical perovskite nanocrystals. Our solutionbased hybrid organic—inorganic lead bromide quantum wire synthesis is simple and reproducible with remarkable optical and photophysical properties (absorption and emission peaks, quantum yields, and PL lifetimes) that are different from those recently reported for solid-phase crystallization approaches to methylammonium lead iodide (CH₃NH₃PbI₃) nanowire synthesis.³⁸⁻⁴⁰ We suggest that dipole-dipole interactions between spherical nanocrystals and van der Waals interactions between surface-stabilizing ligands drive the mesoscale assembly of spherical nanocrystals into high-quality singlecrystalline bundles of quantum wires with high quantum yield and long PL lifetime. Although colloidal synthetic approachs 41,42 have been attempted for preparation of CH₃NH₃PbBr₃ nanowires, control over structure and optical properties, especially as they relate to structural dimensionality, remains key scientific challenges to fully understand the charge transport properties of this new type of nanostructure, specifically for high-performance device applications.

RESULTS AND DISCUSSION

Colloidal Synthesis of CH₃NH₃PbBr₃ Quantum Wires. Our approach is based on general colloidal synthetic methods that included use of organic ligands as stabilizers to control the size, morphology, and organization of the resulting nanostructures.^{43,44} Figure 1A illustrates the transmission electron microscopy (TEM) image of the resulting CH₃NH₃PbBr₃ quantum wires with lengths of 300-900 nm and 3.8 ± 0.4 nm in diameter. X-ray diffraction (XRD) characterization was performed to analyze the phase structure of the quantum wires and then compared with single-crystal CH₂NH₃PbBr₃ bulk perovskite that was synthesized according to the literature.¹⁶ Their XRD characterization is shown in Figure 1B. The diffraction peaks in quantum wires were broadened, compared to bulk perovskite, which suggest their nanometer-size structure, while the positions of the diffraction peaks correspond to cubic phase. The broad XRD pattern of our CH₃NH₃PbBr₃ quantum wires is similar to the literature report of 3.3-nm-diameter CH₃NH₃PbBr₃ nanocrystals⁴⁵ but markedly different from CH₃NH₃PbBr₃ nanowires where extremely sharp peaks were detected.⁴¹ The high-resolution TEM analysis of our CH₃NH₃PbBr₃ is shown in Figure 1C, giving an interplanar distance fringe separation of \sim 5.9 Å, which is characteristic of (001) planes in the cubic phase structure of CH₃NH₃PbBr₃ perovskite. The formation of these CH₃NH₃PbBr₃ quantum wires occurred within the 240 s interval after the injection of PbBr₂ in N₂N-dimethylformamide (DMF) into the reaction mixture containing oleic acid, octylammonium bromide, and methylammonium bromide, which were all dissolved in 1octadecene at 95 °C.

In order to investigate the mechanism of quantum wire formation, we characterized the time dependence of both the optical spectroscopic and TEM analyses of the reaction mixture under synthesis conditions. Figures 2A and 2B show ultra-



Figure 2. Time-dependent, solution-phase spectroscopic characterizations of organic–inorganic perovskite nanostructures. (A) UV-vis absorption and (B) normalized photoluminescence spectra of perovskite $CH_3NH_3PbBr_3$ quantum wire at different reaction times. Inset: Solution color of $CH_3NH_3PbBr_3$ quantum wires dissolved in toluene under illumination at 350 nm. The black, blue, red, and purple lines in panels (A) and (B) represent synthesis progression at 30, 60, 120, and 240 s, respectively.

violet-visible (UV-vis) and PL spectra, respectively, of the resulting perovskite material after quenching and purification at different time points. The 30 s reaction sample displayed its absorption peak at 426 nm and band-edge PL maximum at 428 nm, along with a long tail covering the visible region of the spectrum. These optical properties are markedly different from bulk CH₂NH₂PbBr₃ materials¹⁶ and likely indicate the formation of nanocrystals in the solution.^{46,47} Furthermore, the long tail suggests that the surface of the nanocrystals was not fully passivated, and this optical feature most likely originates from surface-related mid-gap trap states, rather than a large size distribution of the nanocrystals in solution, as was previously reported for ultrasmall CdSe nanocrystals of similar size. $^{48-51}$ The 60 s reaction sample displayed a welldefined absorption peak at 495 nm and its band-edge PL peak at 514 nm with a 93 meV Stokes shift. As the reaction progressed to 240 s, both the absorption and band-edge PL peaks red-shifted to 522 and 524 nm, respectively. These red shifts are expected in the case of formation of one-dimensional (1D) nanostructures (Figure 1A) and Table 1. We believe that the progressive red-shift of these peaks was due to the transformation of ultrasmall nanocrystals into 1D nanostructures⁵² and the resulting reduction in quantum confinement. The negligible Stokes shift (10 meV) (see Figure S1 in the Supporting Information) of the quantum wires is an indication that their surface was nicely passivated with ligands with a low population of trap states, which is important in the context of longer charger carrier lifetimes and transport of photogenerated carriers.

Structural Characterization of CH₃NH₃PbBr₃ Quantum Wires. The formation of CH₃NH₃PbBr₃ quantum wires was also investigated by time-dependent TEM analysis. The 30 s reaction sample displayed nearly monodispersed, ultrasmall spherical $CH_3NH_3PbBr_3$ nanocrystals with 1.5 ± 0.1 nm diameter (Figure 3A). A narrow size distribution should provide a sharp band-edge emission peak in the PL spectrum, rather than a combination of band-edge and broad-band PL peaks. We believe that the broad PL peak measured with the 30 s reaction sample is related to the surface structure of our 1.5nm-diameter nanocrystals and not their size distribution. In the ultrasmall size range, a large percentage of atoms occupy surface nanocrystal sites. Any unpassivated surface sites would result in the formation of surface midgap trap states^{50,51} where photogenerated holes could be trapped, and perhaps recombine with photoexcited electrons far from the band-edge. Such recombination could display a broad tail in the PL spectra, as previously observed for ultrasmall CdSe nanocrystals (1.6 nm in diameter).⁴⁹ After another 30 s, the diameter increased to 2.4 \pm 0.2 nm. These data are in agreement with the absorption and PL peak shifts from 426 nm to 495 nm and from 428 nm to

Table 1. Comparison of Absorption, Photoluminescence, and Excited State Properties of CH₃NH₃PbBr₃ Perovskite Nanostructures at Various Time Points during the Synthesis

reaction time (s)	abs. max (nm)	PL max (nm)	PL peak fwhm (nm)	$PLQY$ $(\%)^a$	PL lifetime (ns) ^b	radiative rate constant $(s^{-1})^c$	nonradiative rate constant $(s^{-1})^d$
30	426	428	20	~1.3	$\tau_{\text{fast}} = 4 \pm 1; \ \tau_{\text{slow}} = 9 \pm 2$	1.4×10^{6}	109.6×10^{6}
60	495	514	22	16 ± 2	$\tau_{\rm fast}$ = 9 ± 2; $\tau_{\rm slow}$ = 50 ± 5	3.2×10^{6}	16.8×10^{6}
120	511	517	22	44 ± 3	$\tau_{\text{fast}} = 10 \pm 1; \tau_{\text{slow}} = 63 \pm 8$	6.8×10^{6}	8.9×10^{6}
240	522	524	25	59 ± 7	$\tau_{\text{fast}} = 11 \pm 1;$ $\tau_{1} = 89 \pm 13$	6.6×10^{6}	4.6×10^{6}

^{*a*}The average PLQY was determined from three different batches of perovskite nanostructures. ^{*b*}Same samples were used to determine the PL lifetimes. ^{*c*}Radiative rate constant (k_r) was determined by using PLQY/ τ_{slow} . ^{*d*}Nonradiative rate constant was determined by using $k_r + k_{nr} = 1/\tau_{slow}$.



Figure 3. Time-dependent transformation of perovskite nanocrystals into quantum wires and their excited state lifetimes, as depcited in TEM images of intermediate states of the $CH_3NH_3PbBr_3$ nanocrystal to quantum wire transition: (A) 30 s of reaction, (B) 60 s of reaction, and (C) 120 s of reaction (scale bars are each 50 nm). (D) Normalized photoluminescence decay measurements at the highest emission maxima (inset shows a confocal microscopy image of a bundle of $CH_3NH_3PbBr_3$ quantum wires). Scale bar = 1 mm. The black, blue, red, and purple lines in panel (D) represent synthesis progression at 30, 60, 120, and 240 s, respectively.

514 nm, respectively, in accordance with the known relationship between size and optical peak wavelength of perovskite nanocrystals.47,53 These results strongly support our expectation that, at the early stages of synthesis, ultrasmall nanocrystals are formed in the reaction mixture. In the 60 s sample, "pearl-necklace" assemblies consisting of spherical nanocrystals were observed (Figure 3B). Similar pearl-necklace assemblies were observed previously with the growth of CdTe nanowires from spherical quantum dots.⁵² Therefore, we believe that CH₃NH₃PbBr₃ quantum wires were formed neither through "oriented attachment" of spherical CH₃NH₃PbBr₃ nanocrystals directly to the ends of the quantum wires, nor through point-initiated vectorial growth. In the case of oriented attachment, the diameter of the CH₃NH₃PbBr₃ quantum wires should be smaller than the diameter of the spherical nanocrystals. The oriented attachment-driven growth involves direct crystal-to-crystal interactions causing crystalline fusion to form a single-crystal lattice.^{54,55} Under this growth condition, the width and/or diameter of the anisotropic nanostructures (nanorods, nanoplatelets, nanowires) should be identical or lower in width/diameter to the spherical nanocrystals.^{54,56,57} However, instead, we observed a second intermediate stage where quantum wires were formed having a diameter of 3.2 \pm 0.2 nm in the same sample that the spherical nanocrystals (Figure 3C) were observed. The increased diameter of CH₃NH₃PbBr₃ quantum wires nicely corroborated the red shifts in both the absorbance and emission spectra found with

spherical nanocrystals 2.4 nm in diameter. Thus, because we found (i) the same crystallographic structure (cubic) for $CH_3NH_3PbBr_3$ spherical nanocrystals (see Figure S2 in the Supporting Information) and quantum wires, (ii) appearance of pearl-necklace assemblies, and (iii) an increase in diameter during the growth of quantum wires, we propose that $CH_3NH_3PbBr_3$ quantum wires were formed through cooperative interactions between the spherical nanocrystals causing "mesoscale growth and assembly".^{58,59} It is important to mention that the $CH_3NH_3PbBr_3$ quantum wires were extremely stable under prolonged exposure (at least 30 min) to the electron beam during the TEM analysis (see Figure S3 in the Supporting Information). Apparently, our observation is markedly different from recent studies on $CH_3NH_3PbBr_3$ nanoplates, where crystalline spherical nanocrystals were formed from nanoplates during the TEM analysis.^{41,47}

Based on our structural characterizations, we hypothesize that both octylammonium ions (OAMIs) and oleic acid are prerequisite to control the formation of spherical nanocrystals, as well as the mesoscale growth and assembly to $CH_3NH_3PbBr_3$ quantum wires. During the preparation of this article, colloidal synthesis of $CsPbBr_3$ nanowires was reported.⁶⁰ However, their synthetic procedure (150 °C), nanowire structural properties (orthorhombic phase), and 1D morphology (~10 nm in diameter) were completely different than our organic–inorganic hybrid $CH_3NH_3PbBr_3$ quantum wires, as discussed above.



Figure 4. Surface chemistry of organic–inorganic hybrid perovskite quantum wires. X-ray photoelectron spectroscopic (XPS) analysis of $CH_3NH_3PbBr_3$ quantum wires. The Pb 4f (A), Br 3d (B), and N 1s (C) spectral profile of the $CH_3NH_3PbBr_3$ quantum wires. The solid lines are the experimental data and dotted lines are the fits. (D) A representative energy dispersive X-ray (EDX) spectroscopy analysis of $CH_3NH_3PbBr_3$ quantum wires. (E) FTIR characterization of pure oleic acid (blue) and $CH_3NH_3PbBr_3$ quantum wires (red).

Electronic Properties of CH₃NH₃PbBr₃ Quantum Wires. We compared the optical band gap of our nanocrystals obtained at different time point during the quantum wires synthesis (spherical nanocrystals, quantum wires, and the mixture of both) with effective mass approximation (EMA) theory,⁶¹ with the consideration that all the nanocrystals maintained quantum well properties. However, our experimental data do not agree with the EMA calculation (see Figure S4 in the Supporting Information). This could be due to reduction in the dimension of the nanocrystals, as well as the role of surface passivating ligands in modulating confinement energy. Recently, a similar disagreement was found for CH₃NH₃PbBr₃ nanoplates with different thickness, and the authors suggested that the exciton wave functions could escape from the inorganic core boundary of the plates and hybridize with neighboring nanoplates.47 This exciton delocalization mechanism and deviation of optical properties from theoretical calculations are further supported by a recent investigation of CsPbBr₃ nanoplates.⁶² In this context, we have reported that the smallest size CdSe nanocrystals (1.6-2.5 nm in diameter) displayed the highest delocalization and hybridization of electron and/or hole wave functions with adjacent nanocrystals, resulting in the largest shift in the optical band gap.⁶ Therefore, we believe that the change in optical band gap of 0.42 eV for a difference in diameter of 0.9 nm between the spherical nanocrystals of CH₃NH₃PbBr₃ at the early stages of the synthesis could be caused by a combination of both nanocrystal size and identity of surface passivating ligands affecting quantum confinement. Nevertheless, such deviation of the optical band gap from a simple EMA calculation was also observed for CsPbBr3 nanocubes in the strong confinement regime (<5 nm in edge-length).53 Therefore, modeling the complex photophysical properties of our CH₃NH₃PbBr₃ nanocrystals and quantum wires requires a sophisticated mathematical model with a variety of possible spacial

organization (e.g., pearl-necklace, bundle-type), which is not within the scope of this work.

The CH₃NH₃PbBr₃ quantum wires displayed a bright green color under illumination with 350 nm light and an absolute PL quantum yield (ϕ) of 59% \pm 7% (Table 1). The increase in ϕ from spherical nanocrystals to quantum wires is due to their more-crystalline character (Figure 1B), dimensionality, and surface passivation, which would together cause an increase in the PL lifetime (see Figure 3D), as was observed from the biexponential fits with $\tau_{\text{fast}} = 11$ ns and $\tau_{\text{slow}} = 89$ ns (see Figure S5 in the Supporting Information). Perhaps, among all these parameters, we believe that surface ligand chemistry played a major role in producing the high ϕ and PL lifetime of our quantum wires, as discussed below. Importantly, the PL lifetime of CH₃NH₃PbBr₃ quantum wires was at least 25 times greater than CH₃NH₃PbI₃ nanowires grown on a solid surface.⁴² The ϕ of our quantum wires was higher than those found with directband-gap CdSe (diameter = 2.0 nm, $\phi = 15\%$)⁶⁴ and CdTe (diameter = 3.5 nm, ϕ = 16.2%)⁵² semiconductor nanowires, CH3NH3PbBr3 nanowires with diameters larger than ours (diameter = 47 nm, ϕ = 13%),⁴¹ and CH₃NH₃PbBr₃ spherical nanocrystals (diameter = 6.0 nm, ϕ = 17%).⁶⁵ Furthermore, $CH_3NH_3PbI_3$ nanowires (diameter = 10-200 nm) prepared via the solid-phase crystallization approach displayed a ϕ value of 0.012% and a PL lifetime of <10 ns,^{38,39} which are markedly different than our CH₃NH₃PbBr₃ quantum wires. The CH₃NH₃PbBr₃ quantum wires were imaged via confocal microscopy (Figure 3D, inset) and emitted bright green color throughout their entire length. By comparison with Figure 1A, we believe the image displays a bundle of individual quantum wires.

The sharp band-edge PL peak, high quantum yield, and long PL lifetime (Table 1) of the $CH_3NH_3PbBr_3$ quantum wires together suggest that the surface of the quantum wires was nicely passivated with OAMIs (see Figure S6 in the Supporting Information), which eliminated the surface defects and

nonradiative trap states, and thus PL decay occurred through radiative exciton recombination. We believe that the OAMIs are directly attached to the quantum wires via electrostatic interactions with surface bromide ions. Furthermore, oleic acid likely interacts with the ammonium head groups of OAMIs as part of an OAMI bilayer-type structures, as discussed later. As shown in Table 1 for CH₃NH₃PbBr₃ perovskite, ϕ and PL lifetime increased dramatically from our 1.5-nm-diameter spherical nanocrystals to the 3.8-nm-diameter quantum wires. It is known that, as the size decreases, the surface-to-volume ratio increases, which results in a larger percentage of atoms residing on the surface. Any unpassivated surface atoms create nonpassivated trap states, which reduce radiative (k_r) and enhance nonradiative (k_{nr}) decay rates. Under our experimental conditions, the $k_{\rm nr}$ value was found to be ~80 times higher than k_r for ultrasmall (1.5-nm-diameter) spherical nanocrystals, whereas k_r was the dominating factor for CH₃NH₃PbBr₃ quantum wires. These experimental data are in agreement with the proposed surface chemistry and surface structure of spherical nanocrystals and quantum wires in which better surface passivation reduces surface defects and nonradiative trap states, resulting in higher ϕ , PL lifetime, and k_r (Table 1).

Surface Ligand Chemistry of CH₃NH₃PbBr₃ Quantum Wires. We characterized the CH₃NH₃PbBr₃ quantum wire surface ligand chemistry, which is generally known to directly influence the nucleation and growth processes of nanostructures, as well as long-term colloidal stability. The X-ray photoelectron spectroscopy (XPS) analysis (Figures 4A-C) of five randomly selected areas of two different preparations showed an average Pb-to-Br atomic ratio of 1:3.4 with higher bromide ion concentration at the surface of 3.8-nm-diameter CH₃NH₃PbBr₃ quantum wires. Our experimental data are in agreement with the previously reported XPS results on 3.3 nm diameter CH₃NH₃PbBr₃ nanocrystals in which the Pb-to-Br atomic ratio was found to be 1:3.5.⁴⁵ For CH₃NH₃PbBr₃ bulk material, the ratio is 1:3.^{1,7-9} Because CH₃NH₃PbBr₃ perovskite consists of [PbBr₆]⁴⁻ octahedral unit cells, the excess bromide ions in the quantum wires were assigned to bromide ions residing on the surface. The appearance of two sharp Pb 4f peaks (binding energies: 138 and 148 eV) without any shoulder suggests the nanosized structure of the synthesized materials.⁴⁵ The broad Br 3d peak was fitted to two peaks (binding energies: 67.8 and 68.9 eV) with the higher intensity peak at 68.9 eV indicating a bromide-rich surface and the peak at 67.8 eV corresponding to core bromide ions.⁴⁵ In the N 1s spectrum, two peaks were observed with binding energies at 399.1 and 401.7 eV, which correspond to the nitrogen from OAMI and CH₃NH₃⁺, respectively.⁴⁵ Taken together, the appearance of two sharp peaks in our CH₃NH₃PbBr₃ quantum wires in Pb 4f region, the broad Br 3d peak, and the two N 1s peaks are all in agreement with the literature of nanosized CH₃NH₃PbBr₃ crystals.⁴⁵ Our energy-dispersive X-ray analysis (EDX) of the same samples confirmed that the average stoichiometric Pb:Br composition ratio was 1:3.3 (Figure 4D). This ratio is higher than the ideal 1:3 ratio for either CH₃NH₃PbBr₃ bulk perovskite material¹⁶ or CsPbBr₃ nanocrystals and nanocubes.⁵³ However, the 1:3.3 EDX ratio is consistent with the XPS analysis where the Pb:Br ratio was found to be 1:3.4. The bromide-rich surface and presence of OAMI, which has a cationic headgroup, suggest that the OAMI acted as a surface passivating ligand coordinating with surface bromide ions through electrostatic interaction.^{45,47} These data are consistent with our proposed structure.

As illustrated in Figure S7 in the Supporting Information, we observed a broad proton signal from the carboxylic acid group at 11.87 ppm in the ¹H NMR spectrum. Pure oleic acid showed proton signals associated with both the double bond and the carboxylic acid resonances at 5.34 and 11.87 ppm, respectively. The peaks corresponding to the same resonances in the CH₃NH₃PbBr₃ quantum wires sample were much broader. Such peak broadening is generally observed when organic ligands are attached onto the surface of inorganic nanostructures.^{49,66,67} The broadening of the resonance peaks is likely due to a combination of spin–spin relaxation broadening and dipole broadening, as well as a distribution of chemical shifts.^{68,69} Sharp resonances at 1–3 ppm are from alkane hydrogens and perhaps from residual solvents.

FTIR spectroscopy was used to confirm the existence of oleic acid and *n*-octylammonium cations as surface passivating ligands of our quantum wires, as shown in Figure 4E. The peak at 1735 cm⁻¹ in the quantum wire spectrum (red diamond), which was assigned to the C=O stretching band of a carboxylic acid group, was 26 cm⁻¹ higher than 1709 cm⁻¹ found in the pure oleic acid (blue diamond),⁷⁰ indicating that the acid group is involved in an electronic interaction but not the negatively charged oleate ion. The presence of oleic acid bound to the surface of the quantum wires as passivating ligands was also confirmed by the appearance of the O-H stretch at 970 cm⁻¹ (dotted circle in Figure 4E).⁷⁰ Pure oleic acid showed asymmetric and symmetric C-H stretching bands at 2925 and 2853 cm⁻¹, respectively, which were also present in quantum wires. The new broad intense peaks appearing at 3143 and 3196 cm⁻¹ were assigned to the NH₃⁺ symmetric stretching bands from OAMI.^{71,72} The peaks at 1653 and 1584 cm^{-1} were attributed to the asymmetric and symmetric NH_3^+ deformations, respectively, from OAMI.^{71,72} The peak 3419 cm⁻¹ could be assigned to the effects of hydrogen bonding between the -COOH group of oleic acid and $- NH_3^+$ of OAMI, which will be discussed later.

In order to fabricate efficient solid-state devices in the future, it will be important to investigate, in detail, the stability of our CH₃NH₃PbBr₃ quantum wires. The quantum wires (see Figure S8 in the Supporting Information) were stored under normal laboratory conditions in darkness. We did not observe any noticeable change in the absorption and PL peak positions and shapes over the course of almost two months. Moreover, during this time period, only a 4% decrease in ϕ was observed. We believe this excellent long-term stability of our organolead bromide perovskite quantum wires is likely due to suitable surface passivation that inhibited degradation by moisture. However, complete degradation of the PL and ϕ of CH₃NH₃PbBr₃ quantum wires was observed within a week when the colloidal solution (in toluene) was kept in air and light (data not shown). Perhaps a more comprehensive and systematic study, e.g., varying humidity,⁷³ light exposure, and solvent, is required to properly address the stability of these quantum wires.

Proposed Growth Mechanism of $CH_3NH_3PbBr_3$ Quantum Wires. The appearance of two distinct intermediate steps in the $CH_3NH_3PbBr_3$ quantum wire formation—i.e., (1) the pearl-necklace assemblies and (2) the mixed aggregates of quantum wires and spherical nanocrystals—suggests that cooperative interactions between nanocrystals at the early stage of quantum wire formation are very critical. Previously, the formation of one-dimensional (1D) CdTe nanowires from spherical quantum dots was described as follows:

(i) The detachment of surface passivating ligands during solvent precipitation creates unpassivated quantum dots inducing the dipole-dipole interaction and reducing electrostatic repulsion between them. These interactions between quantum dots are strong and long-range, as opposed to hydrogen bonding or weak van der Waals interactions, resulting in the appearance of pearl-necklace assemblies.⁵²

(ii) Naked, multiple quantum dots in the assembly fuse together to form single-crystal CdTe nanowires. Thus, the last step in CdTe growth is dominated by an aggregation process.

We believe our CH₃NH₃PbBr₃ quantum wire formation involves (1) dipole-dipole interactions between nanocrystals that results in pearl-necklace assemblies and (2) surface ligandcontrolled cooperative interactions causing mesoscale transformation of CH₃NH₃PbBr₃ nanocrystals to quantum wires. In both cases, the presence of pearl-necklace assemblies is critical; however, our transformation of spherical nanocrystals to quantum wires (mesoscale growth) is substantially different than with CdTe nanowire growth from spherical quantum dots, which can be considered as recrystallization of multiple quantum dots in linear aggregates.⁵¹ Moreover, mesoscaledriven growth does not require detachment of ligands from the surface of the nanocrystals, as demonstrated for CdTe nanowire growth. The entropically controlled mesoscale growth is governed by the cooperative interactions between nanocrystals caused by van der Waals interactions and chain interdigitation of surface passivating ligands. Therefore, the presence of passivating ligands attached onto the surface of the nanocrystals throughout the growth process is extremely important.

To determine structural parameters that may cause dipoledipole interactions between our 2.4-nm-diameter spherical perovskite CH₃NH₃PbBr₃ nanocrystals, we performed their EDX analysis (Figure S9 in the Supporting Information), which showed them to be highly bromide rich (Pb-to-Br was 1:3.8). This excess in bromide could have induced a dipole moment, even though the crystal lattice was symmetrical,⁷⁴ because the cationic ligand OAMI would be strongly adsorbed onto the inorganic quantum wire surface. Therefore, pearl-necklace assemblies (see Figures 3B and 5B, as well as Figure S10A in the Supporting Information) of hybrid organic-inorganic perovskite nanocrystals would be formed due to polarization in the crystal structure. The high surface charge would induce cooperative interactions between inorganic spherical nanocrystals and surface passivating ligands, e.g., OAMIs and oleic acid, which together would lead to mesoscale transformation to wiretype structures (see Figures 3C and 5C, as well as Figure S10B), as demonstrated previously for the formation of BaSO₄ nanofilaments.⁷⁵ The driving force for the cooperative mesoscale transformation of spherical nanocrystals to quantum wires could be reduction of curvature that allows van der Waals contacts between the aligned surface passivating ligands. The last stage of the CH3NH3PbBr3 quantum wire formation involves continuous attachment of spherical nanocrystals to quantum wires via mesoscale growth by the influence of cooperative interaction, where van der Waals attractive forces and interdigitation of surface passivating ligands resulted in mesoscale assembly of quantum wire bundles (see Figures 1A and 5D).

We investigated the key role of surface passivating ligands in the formation of $CH_3NH_3PbBr_3$ quantum wires. We hypothesize that the presence of both oleic acid and OAMIs in the reaction mixture is a prerequisite for the formation of $CH_3NH_3PbBr_3$ quantum wires, in that they play stabilizing



Figure 5. Proposed pathway of mesoscale self-assembly of perovskite quantum wires:⁵⁸ (A) ~1.5 nm CH₃NH₃PbBr₃ nanocrystals are formed after 30 s, which grow into ~2.4 nm nanocrystals that undergo pearl-necklace assembly via dipolar interaction; (B) quantum wires (~3.2 nm diameter) are formed via cooperative interaction of the 2.4 nm nanocrystals that undergo a mesoscale transformation; (C) the quantum wires continue to grow both in diameter and length via mesoscale growth while maintaining their spatial organization through surface ligand chemistry; and (D) bundle-like superstructures, made with perovskite quantum wires, are formed. Throughout the growth process, the presence of passivating ligands attached onto the surface of the nanocrystals is extremely important for the cooperative interactions between nanocrystals caused by van der Waals interactions and chain interdigitation.

and formative roles. Our two control experiments were confirmatory. First, the presence of oleic acid and absence of OAMI in the reaction mixture resulted in the formation of bulk perovskite CH₃NH₃PbBr₃ materials with a Pb:Br ratio of 1:3 in EDX analysis (Figure S11 in the Supporting Information). Thus, OAMI acts as a stabilizing ligand, providing stability to spherical CH₃NH₃PbBr₃ nanocrystals, and oleic acid alone is not sufficient to retain the colloidal properties of the spherical nanocrystals that formed at the early stage in the reaction mixture. Second, the reaction mixture containing OAMI but no oleic acid showed the formation of CH₃NH₃PbBr₃ quantum platelets ($\phi \approx 45\%$) without any spherical nanocrystals or quantum wires either 60 or 240 s after the addition of PbBr₂ (Figure S12 in the Supporting Information). Thus, both OAMI and oleic acid participate directly in the cooperative interaction and mesoscale growth.

We performed another control synthesis experiment by using octanoic acid, instead of oleic acid, while keeping the other experimental conditions identical. Our working hypothesis of quantum wire formation is based on the cooperative interaction and interdigitation of surface passivating ligands. Therefore, reducing the alkyl chain length (from $(CH_2)_{17}$ in oleic acid to $(CH_2)_7$ in octanoic acid) should reduce the van der Waals attractive forces and interdigitation of surface passivating ligands, resulting in disruption in the cooperative interaction. Using octanoic acid, a purified sample from the 4 min reaction mixture was characterized by optical spectroscopy and displayed absorption and emission peaks centered at 505 and 515 nm, respectively (Figure S13A in the Supporting Information). Both these peaks were blue-shifted, in comparison to CH₃NH₃PbBr₃ quantum wires. TEM analysis of this sample showed the formation of polydispersed spherical $CH_3NH_3PbBr_3$ nanocrystals 7.4 \pm 2.8 nm in diameter without

the appearance of any quantum wires (Figure S13B). These data are consistent with the colloidal synthesis of nanocrystals in which aggregation of nanocrystals would be observed during the growth process if shorter-chain surface passivating ligands were present.^{44,76} This aggregation is likely caused by the low diffusion barrier of the shorter-chain ligand (octanoic acid). This result supports the concept that the mixed surface ligation of OAMI and oleic acid is the key to the synthesis of CH₃NH₃PbBr₃ quantum wires through the occurrence of the two crucial intermediate steps of cooperativity and chain interdigitation. Taken together, the appropriate selection of surface ligand chemistry enables control of the van der Waals attractive forces between coated anisotropic nanostructures, which will result in the formation of new hybrid nanomaterials with unique electronic properties.

Mesoscale Assembly of CH₃NH₃PbBr₃ Quantum Wire to Superstructure. We performed grazing-incidence smallangle X-ray scattering (GISAXS) of CH₃NH₃PbBr₃ quantum wires (Figure 6A) to investigate the bundle-type assemblies observed in Figure 1A. The center of the peak (blue curve) was determined by subtracting the blank sample and then fitting with a Gaussian function (dotted red), and was found to be 0.206 $Å^{-1}$. Interestingly, the GISAXS scattering pattern corroborated the parallel alignment of CH₃NH₃PbBr₃ quantum wires shown in Figure 1A, and gave a 3.2 nm separation with the possibility that OAMI and oleic acid are present between the wires in a bilayer-type structure in the bundle of individual quantum wires. n-Alkylammonium bromides are known to be shape-directing surfactants, which form a bilayer on the surface of the gold nanorods.⁷⁷ We believe our mesoscale growth is one-dimensional along the (011) direction rather than forming three-dimensional (3D) nanostructures, because OAMI forms an ordered monolayer on the flat (001) wire surface.^{57,60} Our average interquantum wires separation was calculated from the TEM image to be 3.1 nm, which is consistent with the GISAXS value and is more than two times longer than the fully extended hydrocarbon chain length of OAMI (2.18 nm). This separation suggests participation of oleic acid in the bilayer-type structure, which would increase the separation of the quantum wires. The OAMI monolayer has positively charged ammonium groups that could interact through hydrogen bonding with the carboxylic acid groups of oleic acid. This addition of oleic acid would lead to bilayer-type structure of mixed composition of oleic acid and OAMIs between the CH₃NH₃PbBr₃ quantum wires (Figure 6B) and perhaps expand the bilayer thickness. The formation of a bilayer-type structure by oleic acid is known to occur even when it is attached to the surface of nanostructures.^{57,78} An electrostatic interaction between bromide ions and OAMI amine groups would allow substantial adsorption of surface passivating ligands onto the surface of the nanostructures, which is thermodynamically favorable due to release of adsorption enthalpy, and van der Waals interaction would help drive hydrocarbon tail association, partial interdigitation, and bilayer-type structure formation.

CONCLUSION

In nanocrystal synthesis, many experimental parameters control the size and shape of the resulting nanomaterials and their interactions, and the type and strength of these interactions define the final assembly of the nanocrystals. In this study, the experimental data presented have established the mechanism of formation of the first organic—inorganic hybrid CH₃NH₃PbBr₃ quantum wires, which importantly exhibit unprecedented



Figure 6. Characterization of mesoscale assembly of $CH_3NH_3PbBr_3$ quantum wires: (A) GISAXS pattern of perovskite $CH_3NH_3PbBr_3$ quantum wires showing 3.2 nm wire separation, and (B) proposed surface ligand attachment and interdigitation of $CH_3NH_3PbBr_3$ quantum wires. The bromide-rich surface interacts electrostatically with OAMI, which acts as a stabilizing ligand. The hydrophobic C_8 carbon chain apparently participates in a bilayer-type structure. The interquantum wires spacing calculated from Figure 1A, 3.1 nm, is almost 1.0 nm wider than the theoretically calculated length for two fully stretched OAMI molecules (2.18 nm, as determined from ChemBioDraw 14.0). Therefore, oleic acid was crucial in the formation of the bilayer like-structure between $CH_3NH_3PbBr_3$ wires, which was stabilized through multiple hydrogen bonding interactions with the OAMI amine groups (dotted circles) and through van der Waals interactions between long alkyl chains.

quantum yield and PL lifetime. Excess surface charge on the inorganic moiety of the $CH_3NH_3PbBr_3$ quantum wires, van der Waals interactions between adsorbed surface ligands, and the likely bilayer-type structure of these surface passivating ligands together cause the formation of quantum wire bundles from spherical nanocrystals through cooperative interactions and mesoscale growth and assembly. We believe that our demonstration of ligand-controlled growth and assembly will inspire rational design of colloidal synthetic methods, allowing the preparation of diverse ionic, anisotropic semiconductor perovskite nanostructures, as observed for BaSO₄ and BaClO₄ nanocrystals⁵⁹ with their assembly into higher-order superstructures.⁷⁹ Thus, our findings will help expedite the fabrication of highly efficient solid-state devices.

EXPERIMENTAL SECTION

Chemicals. Lead(II) bromide (PbBr₂, 99.999%), methylamine solution (CH₃NH₂, 2.0 M in THF), hydrobromic acid (HBr, 48%), *n*-octylamine (CH₃(CH₂)₇NH₂, 99%), oleic acid (99%), octanoic acid (99%), 1-octadecene (1-ODE, 90%), acetone (99.5%, ACS reagent) and toluene (99.5%, ACS reagent) were purchased from Sigma–Aldrich. *N*,*N*-dimethylformamide (DMF) was purchased from Fisher Scientific. All measurements were conducted inside a N₂-filled glovebox. Before use, ODE was kept under high vacuum overnight and transferred to the glovebox under N₂ atmosphere. All solvents were purged with N₂ for 30 min prior to use.

UV-vis Absorbance, Photoluminescence, Excited-State Lifetime, and Absolute Quantum Yield Measurements. Absorption spectra were collected with a UV-vis spectrophotometer (Varian Cary, Model 50 Scan), using a 1 cm quartz cuvette over a wavelength range of 300-800 nm. All spectra were collected in toluene, which was used as a background for these measurements. The photoluminescence emission (PL) spectra were acquired using a Cary Eclipse fluorescence spectrophotometer (Varian Instruments), using a 1 cm quartz cuvette. The lifetime measurements were recorded using a time-correlated single photon counting (TCSPC) experimental setup. The data acquisition card (DAO) was obtained from Edinburgh Instruments (Model TCC900). The laser was a 405 nm pulsed laser from PICOQUANT (Model LDH-D-C-405M, CW-80 MHz) with a pulse width of <100 ps. The detector was a photomultiplier tube (PMT) (Hamamatsu, Model H7422-40). The samples were excited at their maximum absorption wavelength and the lifetime decay was measured at the emission wavelength maximum. The following multiexponential equation was used to determine the excited-state lifetime using a time-correlated single photon counting (TCSPC) experimental setup. The χ^2 metric was used to fit the biexponential decay function.¹⁶

$$\chi^{2} = \frac{1}{N} - p - 1 \sum_{i} (y_{i} - f(t_{i}))^{2}$$

Here, Y_i and t_i are the experimental PL counts and time delays, respectively. *N*, *p*, and f(t) are the total number of points, the number of free parameters, and the model fit function, respectively. Absolute quantum yield was measured using an absolute PL spectrophotometer (Hamamatsu, Model C11347) with a 150 W xenon light source and an integrating sphere (Spectralon). A confocal microscope with a 60× objective (Olympus, Model FV1000), equipped with a mercury lamp source (USHIO, Inc. Japan), a 405 nm excitation laser, and a 500 nm wavelength filter was used to image CH₃NH₃PbBr₃ quantum wires. Image acquisition, processing, and analysis were performed using FV-ASV software (Olympus America, PA).

Transmission Electron Microscopy (TEM) Characterization. For high-resolution TEM analysis, samples were prepared inside a glovebox by placing 10 μ L of dissolved CH₃NH₃PbBr₃ perovskite quantum wires in toluene onto a lacey carbon-coated copper grid (Electron Microscopy Science). The sample was allowed to stand for 30 s and any excess solution was removed by wicking with a Kimwipe to avoid particle aggregation. Images were obtained using a JEOL Model 3200FS-JEM instrument at a beam energy of 200 kV. The size of the spherical CH₃NH₃PbBr₃ nanocrystals, and the diameter and length of quantum wires were determined using ImageJ software. At least 500 nanocrystals were counted to determine the average size, and 300 quantum wires were analyzed for diameter and length calculations.

Grazing-Incidence Small-Angle X-ray Scattering (GI-SAXS) of Quantum Wires. GISAXS experiments were carried out utilizing a NanoStar SAXS system (Bruker, Germany). An \sim 8 keV incident beam was incorporated with a 0.4 mm pinhole setup. The sample-to-detector distance (~25 cm) was determine for each measurement using a silver behenate calibration sample. The data was collected using a HiStar xenon gas area detector (1024×1024 pixels) with a photon count of ~1500 photons/second and exposure of ~30 h. Samples were mounted such that the direction normal to the plane of the glass coverslip was perpendicular to the direction of the incident beam. The stage was positioned to align the coated portion of the slide with the X-ray beam. The sample was rotated slightly back and forth along the axis perpendicular to both the direction of the beam and the direction normal to the sample's surface to pass through the orientation angle θ , where we would obtain a maximum scattering intensity. An oriented muscovite crystal was used to verify the direction of the rotational axis of rotation, with respect to the incident beam. The two-dimensional (2D) scattering data was process using FIT2D and plotted using Matlab and Origin software.

Synthesis of Methylammonium and Octylammonium Bromide. Bromide salts of methylamine and *n*-octylamine were prepared by a modified literature procedure.² Hydrobromic acid (10.84 mL, 0.2 mol) was added dropwise to a solution of CH_3NH_2 (7.2 mL, 0.2 mol) or $CH_3(CH_2)_7NH_2$ (32.98 mL, 0.2 mol) in ethanol (20 mL) at 0 °C under stirring, which continued for 3 h. Ethanol was removed by rotary evaporator and the solid was redissolved in ethanol and recrystallized by adding ether. The solid then was dried under vacuum, producing a snow-white crystalline material, which was stored inside the glovebox for further use.

Perovskite CH₃NH₃PbBr₃ Quantum Wires Synthesis. In a two-neck, round-bottom flask, 0.38 mmol of oleic acid was dissolved in 6 mL of 1-octadecene under N2 and the reaction mixture was stirred at 95 °C for 45 min. At this point, 0.06 mmol of solid CH₃(CH₂)₆CH₂NH₃Br was added to the reaction mixture and stirred for another 30 min. Separately, 0.032 mmol of CH₃NH₃Br and 0.037 mmol of PbBr₂ were dissolved in 100 and 200 μ L DMF, respectively. The CH₃NH₃Br solution was added first to the round-bottom flask and then allowed to react for 60 s. PbBr₂ solution then was added, resulting in a light yellow solution. At 240 s, 0.5 mL of the reaction mixture was injected into 5 mL of acetone to quench the reaction. The solid was collected by centrifugation at 5000 rpm for 5 min, dissolved in toluene, and centrifuged at 7000 rpm for 5 min. Finally, the clear yellow supernatant was collected for further characterization.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.6b01793.

Additional experimental procedure, control experiment, XRD, EDS, XPS, NMR characterizations, TEM and SEM images, optical spectra, graphs, and table (PDF)

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Notes

The authors declare no competing financial interest.

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