

Flexible Polymer-Assisted Mesoscale Self-Assembly of Colloidal CsPbBr₃ Perovskite Nanocrystals into Higher Order Superstructures with Strong Inter-Nanocrystal Electronic Coupling

Yang Yang,^{§,1} Jacob T. Lee,^{§,1} Thakshila Liyanage,¹ and Rajesh Sardar*^{1,2}

¹Department of Chemistry and Chemical Biology, Indiana University-Purdue University Indianapolis, Indianapolis, Indiana 46202, United States

²Integrated Nanosystems Development Institute, Indiana University-Purdue University Indianapolis, Indianapolis, Indiana 46202, United States

Abstract: Surface passivating ligands, although ubiquitous to colloidal nanocrystal (NCs) synthesis, play a role in assembling NCs into higher-order structures and hierarchical superstructures, which has not been demonstrated yet for colloidal CsPbX₃, (X= Cl, Br, and I) NCs. In this work, we report that functional polyethylene glycols (PEG₆-Y, Y = -COOH and -NH₂) represent unique surface passivating ligands enabling the synthesis of near uniform CsPbBr₃ NCs with diameters of 3.0 nm. The synthesized NCs are assembled into individual pearl necklaces, bundled pearl necklaces, lamellar, and nanorice superstructures, *in-situ*. It is believed a variety of forces, including van der Waals attractions between hydrophilic PEG tails in a nonpolar solvent and dipole-dipole attraction between NCs, drive mesoscale assembly to form superstructures. Furthermore, post-synthetic ligand treatment strengthens the argument for polymer-assisted mesoscale assembly as pearl necklace assemblies can be successfully converted into either lamellar or nanorice structures. We observe an ~240 meV bathochromic shift in the lowest energy absorption peak of CsPbBr₃ NCs when they are present in the lamellar and nanorice assemblies, representing strong inter-NC electronic coupling. Moreover, pearl necklace structures are spontaneously assembled into micrometer length scale twisted ribbon hierarchical superstructures during storage of colloidal CsPbBr₃ NCs. The results show that the self-assembled superstructures of CsPbBr₃ NCs are now feasible to prepare via template free synthesis, as self-assembled structures emerge in the bulk solvent, a process that mimics biological systems except for the use of non-biological surface ligands (PEG₆-Y). Taken together, emergent optoelectronic properties and higher-order superstructures of CsPbBr₃ NCs should aid their potential use in solid-state devices and simplify scalable manufacturing.

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INTRODUCTION

Fascinating size and composition dependent optoelectronic properties,¹⁻³ interfacial charge transfer⁴⁻⁶ along with improved colloidal stability of all-inorganic, highly ionic cesium lead bromide perovskite (CsPbX_3 , X= Cl, Br, and I) nanocrystals (NCs) make them attractive candidates for solar-cells, light-emitting diodes, and lasing applications.⁷⁻¹¹ The high temperature hot injection method developed by Kovalenko and coworkers¹² for the synthesis of CsPbX_3 NCs has prompted a new approach for the preparation of NCs of varying shapes (e.g., spherical, cubes, wires, and platelets). Currently, most synthetic methods produce an ordered-assembly of CsPbX_3 nanocubes, nanowires, and nanoplatelets.¹²⁻²³ These assemblies are formed mostly due to cooperative (dipole-dipole, hydrophobic, and van der Waals (vdW)) interactions between the long aliphatic chains of surface passivating ligands.²⁴⁻²⁷ Recently, we reported that surface ligand chemistry profoundly impacts the self-organization of methylammonium lead bromide ($\text{CH}_3\text{NH}_3\text{PbBr}_3$) perovskite NCs, leading to stacked nanoplatelets and bundles of nanowires as hierarchically organized superstructures.^{28, 29} The programmable assembly of either CsPbX_3 or $\text{CH}_3\text{NH}_3\text{PbBr}_3$ NCs into higher order superstructures via modification of surface ligand chemistry has not yet been demonstrated, but are important to the field in order to understand how these highly ionic NCs are electronically interacted inside the hierarchical superstructures that could lead to the fabrication of efficient solid-state devices.

In this work, we report the synthesis of flexible polymeric ligand-passivated cubic-phase and monodisperse CsPbBr_3 NCs with ~ 3.0 nm diameters, which are assembled into individual pearl necklaces, bundled pearl necklaces (~ 550 nm in length), close-packed, lamellar, and nanorice assemblies. To our knowledge, this is the first example in which a spontaneous self-assembly of polymer-passivated highly ionic inorganic NCs has resulted in one-dimensional, individual and bundled pearl necklaces without applying any external fields or performing covalent attachment through template-free chemical and/or polymerization reactions.³⁰⁻³⁷ Thermodynamically-driven, surface passivating ligand-controlled mesoscale assembly processes circumvent two technical challenges in order to prepare various assemblies of colloidal NCs, including metal and metal chalcogenide NCs: (1) avoiding widely adopted ligand exchange process and (2) performing additional chemical transformations. The *in-situ* self-assembly process of either fully inorganic or inorganic-organic hybrid perovskite NCs is important because these highly ionic NCs are extremely susceptible to undergo degradation in polar solvents and/or ionic environments that are required for ligand exchange, and chemical and/or polymerization reactions. Together, we also show that three important structural parameters (i.e., chain length, concentration, and

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3 binding head groups) of the flexible polymers are critically controlling the *in-situ* self-assembly
4 process of CsPbBr₃ NCs that together promote the formation of higher order superstructures
5 through a combination of cooperative interactions between individual polymer-passivated NCs.
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9 Developing unique surface ligand chemistry capable of organizing NCs into complex and higher
10 order structures through self-assembly opens new possibilities of achieving emergent
11 optoelectronic and electrical properties at the nanoscale that are different from the individual
12 components. Polymeric materials are frequently used for embedding NCs over multiple length
13 scales through self-assembly processes.^{33, 38-42} Moreover, inter-NC interaction can be controlled
14 inside the polymer-NC organic-inorganic hybrid material superstructures, thus laying a
15 foundation for preparation of the first perovskite-based artificial solids with unique functions. The
16 optical band-gap (E_{op}) of CsPbBr₃ NCs in an individual pearl-necklace ($E_{op} = 2.57$ eV) is ~70
17 meV red-shifted compared to bundled pearl necklace ($E_{op} = 2.64$ eV) structures. Furthermore,
18 lamellar and nanorice structures display the highest and lowest E_{op} of 2.70 and 2.46 eV,
19 respectively, whereas NCs in close-packed self-assembly show E_{op} of 2.51 eV. Therefore, we
20 hypothesize the overall 240 meV change in the E_{op} is due to inter-NC electronic coupling
21 through excitonic wavefunction delocalization in the higher order structures.
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31 Over the last three years, significant attention has been given to the production of fatty acid-
32 and/or amine-passivated fully inorganic perovskite NCs through colloidal synthetic methods,^{12,}
33 ⁴³⁻⁴⁶ however, less effort has been devoted on the use of surface ligand chemistry to control NC
34 assemblies during synthesis. As mentioned above, since ligand exchange chemistry of CsPbX₃
35 NCs has not been explored yet, direct synthesis of perovskite NCs with unique surface
36 passivating ligands is critical to appropriately functionalizing their surface and controlling inter-
37 NC interactions. This should provide a unique opportunity to create various molecular
38 interactions that result from the self-assembly of individual NC into higher order superstructures,
39 which would then eventually promote charge transport efficiency of solid-state devices made
40 with perovskite NCs, as this has well documented for metal chalcogenide NCs.⁴⁷⁻⁴⁹ To prepare
41 such higher order superstructures, functional polyethylene glycol (PEG₆-Y, Y = -COOH and
42 NH₂)-passivated CsPbBr₃ NCs are synthesized at a moderately low temperature (~60 °C). We
43 selected PEG₆-Y because acids and amines are known to interact with surface Pb and Br sites,
44 respectively,^{28, 50, 51} which in turn can provide colloidal stability and improved optoelectronic
45 properties of CsPbBr₃ NCs. Additionally, the oxygen within the glycol units can datively interact
46 with the Pb of CsPbBr₃ in order to wrap the NCs with flexible polymer chains similar to a
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3 “meatball and spaghetti” model.^{52, 53} Finally, PEG is a hydrophilic polymer and thus
4 thermodynamically favorable interactions between PEG chains on adjacent NCs in hydrophobic
5 solvents should drive the self-assembly process. Utilizing these inherent properties of PEG, we
6 are able to successfully transform individual pearl-necklaces structures into lamellar and
7 nanorice structures through post-synthetic ligand treatment. Taken together, we propose that a
8 combination of dipole-dipole interactions between CsPbBr₃ NCs and van der Waals (vdW)
9 attraction between surface passivating ligands induce the mesoscale assembly of spherical NCs
10 into individual and bundled pearl-necklaces, and lamellar structures. In addition to these two
11 forces, ionic interactions between COOH and –NH₂ binding head groups of PEG₆ are
12 responsible for the formation of nanorice structures. Finally, during storage of microscale pearl-
13 necklace assemblies in colloidal suspension, twisted ribbon structures are spontaneously
14 formed. Therefore, the current work on template-free synthesis of hierarchical superstructures
15 could be compared with biological systems where nature produces many complex higher order
16 structures. Moreover, such programmable transformation of NC assemblies, in particular
17 perovskite NCs, has not yet been reported in literature. Additionally, various assemblies could
18 be considered as “nanocomposites” that should provide two advantages (1) structural benefit of
19 the polymer^{52, 54} (flexible glycol units of PEG chains and ability to transport charge) as compared
20 to NCs, which are passivated with small, insulating organic ligands; and (2) unique
21 optoelectronic properties of CsPbBr₃ NCs.
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35 Results and Discussion

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37 **Synthesis and Characterization of Flexible Polymer-Passivated Perovskite NCs.** We
38 synthesized PEG₆-NH₂ and PEG₆-COOH in our laboratory using literature procedures.^{55, 56}
39 Supporting Information file provides experimental procedure and ¹H NMR spectra (**Figure S1**
40 **and S2**). In our initial investigation, we use a mixture of PEG₆-NH₂ (0.2 millimole, mmol) and
41 PEG₆-COOH (0.03 mmol) as surface passivating ligands in the synthesis of cesium lead
42 bromide perovskite at 60 °C The purified perovskite material is soluble in chloroform, forming a
43 yellow solution. Transmission electron microscopy (TEM) analysis of the product shows the
44 presence of nearly monodispersed NCs with an average diameter of 3.0 ± 0.4 nm (**Figure 1A**).
45 Furthermore, on the TEM grid the NCs are observed as a two-dimensional (2D) close-packed
46 structure with an average 2.3 nm inter-NC spacing (**Figure S3**). As shown in the low-
47 magnification TEM image (**Figure S4**) the 2D structures are micrometer-sized in dimension.
48 Elemental analysis through energy dispersive X-ray spectroscopy (data not shown) confirms a
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3 Cs:Pb:Br ratio of 1:1:3.1, confirming the formation of CsPbBr₃ NCs. **Figure 2** (Panel A)
4 represents the X-ray diffraction (XRD) patterns of CsPbBr₃ NCs that correlates to a cubic
5 structure (PDF# 84-0464). Interestingly, the XRD peaks of NCs are slightly shifted to lower
6 angles; this can be related to strain in the lattice structure due to adsorption of -COOH and/or -
7 NH₂ head group containing ligands, as previously shown for metal chalcogenide NCs.^{57, 58} FTIR
8 spectroscopy was used to characterize surface ligand chemistry. **Figure S5** exhibits the FTIR
9 spectra of ligand-passivated CsPbBr₃ NCs and shows that the characteristic -C=O and -N-H
10 stretches related to PEG₆-COOH and PEG₆-NH₂, respectively, are observed, confirming the
11 NCs are mixed ligand passivated. Importantly, the FTIR spectra also indicate electronic
12 interactions between the carboxylic acid group and NC, and not negatively charged PEG-COO⁻
13 .⁵⁹ The UV-visible absorption and narrow photoluminescence (PL) spectra of the synthesized
14 CsPbBr₃ NCs display peaks at 494 nm (2.51 eV) and 504 nm (2.46 eV), respectively (**Figure**
15 **1B**). This 50 meV Stokes' shift can be related to surface defects. The appearance of a sharp
16 absorption peak supports the narrow size distribution of CsPbBr₃ NCs. UV-visible absorption
17 spectrum shows long tailing at longer wavelengths, indicating the presence of higher-order
18 structures in solution further supporting the TEM analysis mentioned above. Importantly, ligand-
19 passivated CsPbBr₃ NCs displaying the lowest energy, a sharp absorption peak at 2.51 eV,
20 should correlate to a size of 6-8 nm in diameter, as reported in the literature both experimentally
21 and theoretically.¹² In contrast, we observe nearly similar band-gap for our mixed PEG₆-COOH-
22 and PEG₆-NH₂-passivated, 3.0 nm diameter CsPbBr₃ NCs. According to quantum confinement
23 theory, ~3.0 nm diameter NCs should display larger band-gap than 2.51 eV. We hypothesize
24 this deviation of the experimentally observed optical band gap from theory is a consequence of
25 the delocalization of exciton (electron and/or hole) wavefunction of NCs, which increases the
26 confinement box size and allows strong inter-NC electronic coupling. It has been reported that
27 the "solvent-like" properties of PEGs allow strong inter-NC electronic coupling resulting from the
28 delocalization of excitonic wavefunctions.⁶⁰ Furthermore, dipole-dipole interactions between NCs
29 could also lead to red-shifts (bathochromic shifts) in the absorption peak. We discuss this
30 interesting optoelectronic property below.
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49 **Polymer-Assisted Formation of Higher-Order Assemblies of CsPbBr₃ NCs and Their**
50 **Optoelectronic Properties.** As schematically shown in **Figure 3**, we explore the role of
51 surface passivating ligands in the in-situ synthesis of CsPbBr₃ NCs by manipulating two reaction
52 conditions: (i) use PEG₆-NH₂ only as an added ligand, and (ii) use both PEG₆-NH₂ and PEG₆-
53 COOH as ligands, but increase the concentration of the latter component as compared to our
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3 initial studies. PEG₆-NH₂ concentrations in the reaction mixture were varied from 0.2 to 0.4
4 mmol. TEM characterization shows the formation of sub-micrometer length scale individual
5 pearl necklaces, bundled pearl necklaces, and lamellar assemblies of CsPbBr₃ NCs in the
6 presence of just PEG₆-NH₂ as a surface passivating ligand (**Figure 4A-C**). In contrast, nanorice
7 assemblies containing spherical CsPbBr₃ NCs form when both PEG₆-NH₂ and PEG₆-COOH are
8 present (see **Figure 4D**). These higher order superstructures are made with a nearly identical
9 size of ~3.0 nm diameter CsPbBr₃ NCs (see supporting Information for size analysis) with a
10 cubic crystal phase (see **Figure 2**). Additional TEM images are provided in the Supporting
11 Information, see **Figure S6-S9**. Importantly, we also attempt to synthesize CsPbBr₃ NCs in the
12 presence of just PEG₆-COOH as ligands with relatively higher concentrations that results in an
13 organically insoluble white solid. Use of higher concentrations of PEG₆-NH₂ in the synthesis
14 provides a highly viscous yellow material, and we found it to be difficult to purify the NCs.
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24 Utilizing the chemical structures of surface ligands, gold^{31, 32, 34-37} and magnetic^{30, 33}
25 nanoparticles, and CdTe quantum dots²⁶ have been organized into one-dimensional chains
26 (pearl necklace assembly). However, the work herein represents the first example in which
27 polymer-passivated CsPbBr₃ NCs are organized into either individual or bundled pearl necklace
28 assemblies. It should be noted that all the above-mentioned works on template-free synthesis of
29 pearl necklace assembly of various nanoparticles require: (1) ligand exchange reaction to attach
30 specific surface functionalization groups, which could covalently link to form one-dimensional
31 structures; (2) living free-radical polymerization reaction to connect individual nanoparticles into
32 a pearl necklace assembly.⁶¹ In contrast, our PEG ligand-driven *in-situ* formation of pearl
33 necklace assemblies of CsPbBr₃ NCs does not require polymerization and/or ligand exchange
34 reactions, specifically circumventing the latter case that is found to be extremely challenging for
35 perovskite NCs in general.⁶² Particularly, ligand exchange reactions may not be as
36 straightforward for perovskite NCs as compared to metal and metal oxide nanoparticles and
37 metal chalcogenide quantum dots because there are several factors, such as concentration and
38 binding head group of surface passivating ligands, and the solvent system that all control the
39 exchange processes. Moreover, new ligand passivation may hinder the appropriate solubility
40 property of NCs for complete ligand exchange in order for the self-assembly processes to take
41 place. Then, stability of CsPbBr₃ NCs during the exchange reaction is another issue. Taken all
42 the factors together, we believe that the demonstrated *in-situ* self-assembly process for CsPbBr₃
43 NCs should be applicable to prepare different assemblies of other ionic nanoparticles beyond
44 perovskite NCs.
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3 UV-visible spectroscopy characterizations of different assemblies of CsPbBr₃ NCs reveal non-
4 size dependent optoelectronic properties. The E_{op} of lamellar, bundled and individual pearl
5 necklace, close-packed, and nanorice structures are 460 nm (2.70 eV), 470 nm (2.64 eV), 483
6 nm (2.57 eV), 494 nm (2.51 eV) and 505 nm (2.46 eV), respectively (see **Figure 4E-H**). **Table 1**
7 summarizes the assembly dependent optical properties of ~3.0 nm diameter CsPbBr₃ NCs
8 under our optimized reaction conditions. Importantly, E_{op} of our ~3.0 nm diameter CsPbBr₃ NCs
9 in lamellar assembly is in agreement with the E_{op} reported by Kovalenko group.¹² Surprisingly,
10 the lowest band-gap (2.46 eV) observed for ~3.0 nm diameter CsPbBr₃ NCs is in the nanorice
11 assembly, which is significantly red-shifted (~2.0 eV) as compared to the theoretical value of
12 4.46 eV for a discrete 3.0 nm CsPbBr₃ NC, as determined from effective mass approximation
13 calculations.⁶³ Therefore, our CsPbBr₃ NCs behave more like bulk perovskite materials (E_{op} =
14 2.25 eV)⁶⁴ while maintaining nanoscale properties as similar to “artificial solids”. Moreover, as
15 mentioned above, while all of these assemblies are made with nearly identical size, ~3.0 nm
16 CsPbBr₃ NCs we observe a large difference in their E_{op}-gaps. Hence, we hypothesize that the
17 ~240 meV bathochromic shifts in the lowest energy absorption peak between lamellar and
18 nanorice assembly are due to delocalization of excitonic wavefunctions in the NCs that increase
19 the confinement box size. The exciton binding energy of CsPbBr₃ NCs are relatively small (<100
20 meV).^{65, 66} Moreover, kinetic energy of excitons (electrons and/or holes) within NCs at their
21 relatively small size range (≤4.0 nm diameter semiconductor NCs) are considered to be higher
22 than that of columbic interaction energy.^{67, 68} Under this condition, wavefunctions of a photo-
23 excited electron and/or hole could occupy the entire NC volume and leak outside of the fully
24 inorganic perovskite core boundary. Escaped wavefunctions then entangle, resulting in
25 electronic coupling between neighboring NCs and the formation of extended delocalization
26 states (minibands), and thus increasing the confinement box size and cause bathochromic shifts
27 in the lowest energy absorption peak, as reported for only metal chalcogenide quantum dots^{60,}
28 ⁶⁹⁻⁷² but yet to be demonstrated for CsPbBr₃ NCs. Solvent-like properties and low hydrodynamic
29 radii of PEG should facilitate such electronic coupling. Under such circumstances, where inter-
30 NC electronic coupling is the major contributor to observed bathochromic shifts of 3.0 nm
31 diameter CsPbBr₃ NCs in various assemblies, one would expect a strong relationship between
32 the spatial distance (NC edge-to-edge separation) and E_{op}. This is due to the fact that as the
33 spacing increases, electronic coupling strength decreases, and therefore E_{op} increases (less
34 influence on the E_{op}). **Figure 5A** illustrates a near linear relationship between inter-NC spacing
35 and E_{op} for four different assemblies in which the highest reduction of optical band-gap is
36 observed for 2D closed-packed assemblies. We are unable to determine inter-CsPbBr₃ NC
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spacing in the nanorice assembly due to their highly closely packed and overlapping spatial organization. The PL characterization also shows continuous red-shifting in the peak position from lamellar to nanorice assembly (see **Figure 4E-H**). However, these shifts can be related to a variable degree of surface defects. Unless the NCs are completely defect free, it is highly qualitative to determine the electronic coupling from the PL analysis. It is also important to mention that the dipole-dipole interaction between NCs^{73, 74} and changes in the local refractive index⁷⁵⁻⁷⁷ of NCs have the potential to induce bathochromic shifts. However, we used exactly identical chain lengths of PEG₆-NH₂ and PEG₆-COOH as ligands, therefore refractive index-related E_{op} modulation can be neglected. It is important to mention that our observed exciton wavefunction delocalization of CsPbBr₃ NCs in pearl necklace assemblies is a further example of a previously reported phenomenon, as polymer-functionalized gold nanoparticles organized into one-dimensional networks also show increased delocalization of excitons.⁷⁸ Taken together, the pearl necklace assembly of CsPbBr₃ NCs organized in one-dimensional chains having the ability to delocalize excitonic wavefunctions and provide efficient charge separation should allow long distance charge transport, and thus potentially aid fabrication of advanced optoelectronic devices.

We calculated the vdW interaction strength (V_{vdW}) between two spherical NCs (considered as hard balls) as described in literature, without considering the ligand effects in the calculation.^{79, 80} Our calculations show a nearly three-fold difference in V_{vdW} between closed-packed and lamellar assemblies (**Figure 5B**). Although V_{vdW} between CsPbBr₃ NCs in chloroform dispersion is low but it is an attractive one. As mentioned earlier, dipole-dipole and charge-dipole interactions may also play a significant role in the overall mesoscale assembly processes, which result in a high coupling energy. We are able to calculate the van der Waals interaction, and analysis of dipole-dipole and charge-dipole interactions are ongoing and we hope to report them in future works.

Experiments were undertaken to characterize the spatial organization of surface passivating ligands (e.g., PEG₆-NH₂) on the surface of CsPbBr₃ NCs that lead to in-situ formation of pearl necklace assemblies. By using a ninhydrin-based assay (**Figure S10**)⁸¹ and reported a molar extinction coefficient of $\sim 1.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ of CsPbBr₃ NCs,⁸² we determine that about ~ 0.7 PEG₆-NH₂/nm² are bound on 3.0 nm diameter CsPbBr₃ NCs. Supporting information file provides detailed experimental procedure for the ninhydrin-based assay and polymer grafting density calculations. According to the Flory model, such a low density of polymer grafting,

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3 specifically for the shorter chain length polymers (i.e., PEG₆-NH₂) leads to a “mushroom”
4 structure in which polymers lay flat on the solid surface while wrapping the NCs.⁸³ This result
5 supports our proposed meatball-spaghetti model (vide infra).
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9 Based on the structural characterizations presented above, we propose the mesoscale
10 assembly model as the basis for the formation of various nanoscale assemblies under our
11 experimental conditions.²⁴ The mechanism underlying mesoscale assembly of individual
12 inorganic NCs into higher order assemblies through cooperative interactions is controlled by the
13 short-range vdW forces between surface passivating ligands, along with dipole-dipole and
14 charge-dipole forces between NCs.^{24, 84, 85} We believe vdW interactions between surface
15 passivating ligands induce mesoscale assembly and drive adjacent CsPbBr₃ NCs closer
16 together to form pearl necklace assemblies with regular inter-NC spacing (**Figure 4A**).
17 Importantly, this assembly is only observed when PEG₆-NH₂ is present in the reaction medium.
18 PEG₆-NH₂ is hydrophilic in nature; therefore some excess ligands are expected to be present in
19 NCs even after purification in hydrophobic solvent (hexane/toluene mixture). Furthermore, the
20 chloroform (a non-polar solvent) in which CsPbBr₃ NCs are dispersed should favor vdW
21 interactions between PEG₆ chains. Additionally, a cubic CsPbBr₃ crystal has an inherent dipole
22 moment,⁸⁶ that would assist dipole-dipole interactions between NCs. The hydrodynamic radii of
23 PEG₆ in solution is 0.6 nm and it forms coil structures.⁶⁰ The inter-CsPbBr₃ NC spacing in an
24 individual pearl-necklace assembly is 2.4 nm, which is ~1.0 nm larger than twice the
25 hydrodynamic radii of PEG₆. This may also suggest the presence of excess PEG₆ between NCs,
26 possibly as interdigitated structures leading to vdW interactions, which readily facilitate the
27 thermodynamically controlled mesoscale assembly of NCs into higher order superstructures. As
28 shown in **Figure S6B**, pearl-necklace assemblies are present in a long-range linear array. This
29 is only possible because of the size monodispersity of NCs that helps crystal-face specific
30 interactions between the hydrophilic tails of surface-bound PEG₆ ligands. Additionally,
31 sufficiently high binding affinity between -NH₂ and surface Br⁻ of CsPbBr₃ NC, along with dative
32 interactions between Pb²⁺ and glycol units (-CH₂-CH₂-O-) of PEG₆ provide high stability of NCs.
33 This results in no further crystal growth within the pearl-necklace assembly, as previously
34 observed for CdTe nanowire formation from the corresponding pearl necklace structures.²⁶
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52 The formation of bundled pearl necklace assemblies of CsPbBr₃ NCs, in which long pearl
53 necklace structures retain their one-dimensional arrangement, are observed (see **Figure 4B**)
54 when the synthesis was performed in the presence of a slightly higher concentration of PEG₆-
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3 NH_2 . Although the passivating ligand $\text{PEG}_6\text{-NH}_2$ is hydrophilic in nature, it is still soluble in
4 chloroform due to a unique solubility property.⁶⁰ In this context, the solvent layer from the
5 surface of ligand-passivated NCs is expected to be repelled by $\text{PEG}_6\text{-NH}_2$. Therefore, the
6 existing cooperative interactions between individual pearl-necklace assemblies is expected to
7 increase, pushing pearl necklace assemblies towards each other, and this result in the
8 formation of bundled assemblies of $\text{CsPbBr}_3\text{ NCs}$.⁸⁷ Further increasing $\text{PEG}_6\text{-NH}_2$
9 concentrations in the reaction mixture produces lamellar assemblies in which $\text{CsPbBr}_3\text{ NCs}$ are
10 uniformly distributed throughout the structure (see **Figure 4C**). A continuous increase in inter-
11 NC spacing is observed from individual necklace to bundled necklace and then to lamellar
12 assemblies (**Figure 5**) due to presence of extra PEG_6 between NCs. When both $\text{PEG}_6\text{-NH}_2$ and
13 $\text{PEG}_6\text{-COOH}$ were used in the synthesis, nanorice assemblies are formed rather than one-
14 dimensional assemblies of $\text{CsPbBr}_3\text{ NCs}$. This is presumably because of the strong electrostatic
15 and hydrogen bonding interactions between $-\text{COOH}$ and $-\text{NH}_2$ groups. Although these
16 attractive forces bring the NCs closer, individual NCs are not fused together and they form
17 aggregated structures. Soft and flexible PEG chains passivate the surface of NCs through
18 multiple dative bonds - Pb of CsPbBr_3 could datively interact with the oxygen in the glycol units-
19 similar to a meatball and spaghetti structure. Overall, solution-based self-assembly of NCs into
20 higher order superstructures through the thermodynamically-driven mesoscale assembly
21 process lies in the delicate interplay between the various forces discussed above, including the
22 polarity of the solvent. Additionally, presence of excess ligands in the purified $\text{CsPbBr}_3\text{ NC}$
23 samples plays a significant role in the mesoscale assembly process, which could be difficult to
24 achieve through a post-synthetic ligand exchange reaction. Nevertheless, precise quantification
25 of these interactions is beyond the scope of this article. We should mention that other
26 parameters such as reaction temperature and the rate of solvent evaporation could also
27 influence the mesoscale assembly process. In this work, all syntheses were performed under
28 identical temperature and all TEM samples were prepared using the same protocol (see
29 Supporting Information). Therefore, we believe temperature and microscopy sample preparation
30 do not influence the formation of higher order superstructures of $\text{CsPbBr}_3\text{ NCs}$.
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49 As described above, it is suggested that all higher order superstructures of spherical ~ 3.0 nm
50 $\text{CsPbBr}_3\text{ NCs}$ are driven and stabilized through various interactions of surface passivating
51 ligands, and not by cross-linking between individual PEG_6 units. Therefore, we hypothesize that
52 one type of assembly (e.g., pearl necklace) can be converted to other assemblies (e.g., lamellar
53 and/or nanorice) by controlling ligand interactions (e.g., vdW) through post-synthetic ligand
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3 treatment (**Figure 3**). To further examine the unique role of surface passivating ligands in the
4 mesoscale assembly, individual pearl necklace assemblies were prepared by using 0.2 mmol of
5 PEG₆-NH₂. Samples were treated separately with (i) 0.4 mmol of PEG₆-NH₂ and (ii) 0.2
6 mmol PEG₆-COOH. As shown in Figure **6A-B**, lamellar and nanorice assemblies are formed in
7 the presence of PEG₆-NH₂ and PEG₆-COOH, respectively. These control experiments definitely
8 support our proposed model of ligand-controlled mesoscale assembly of CsPbBr₃ NCs and
9 formation of superstructures. If the entire hypothesis holds true we then expect that methyl-
10 terminated PEG (PEG₆-CH₃) - with an identical chain length of PEG₆-NH₂ – should drive the
11 mesoscale assembly and convert individual pearl necklace structure to either bundled pearl
12 necklace or lamellar assemblies, as shown in **Figure S11**. Overall, these control experiments
13 prove that the appropriate selection of surface passivating ligands in the colloidal synthesis of
14 CsPbBr₃ NCs has the unique ability to participate in various interactions and promote mesoscale
15 assembly processes in solution, thereby resulting in the formation of higher-order
16 superstructures.
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Template-Free Hierarchical Self-Assembly of CsPbBr₃ NCs into Superlattice Structures. It

27
28 is noteworthy to mention that within nearly 24 h, the storage of individual pearl necklace
29 assemblies of CsPbBr₃ NCs in chloroform dispersion produce hierarchical, twisted ribbon
30 structures (**Figure 6C**), similar to CdTe/CdS structures reported in the literature.⁸⁸ The ribbons
31 are extended to micron length forming superlattice structures. A closer look (**Figure S12**)
32 reveals the presence of individual necklaces at the ribbon's top. The formation of higher order
33 superstructures can also be observed for nanorice assemblies in which individual rice is
34 connected to form chain-like structures (**Figure 6D**). The hierarchical superstructure formation
35 can be monitored visually by the appearance of turbidity in the originally clear solution of
36 CsPbBr₃ NCs. We do not fully understand what parameters drive the hierarchical superstructure
37 formation, but we speculate that PEG₆- PEG₆ (NC surface bound and/or free unbound)
38 interactions within the hydrophobic solvent of the template-free process may play a significant
39 role. Nevertheless, a more detailed investigation, possibly including time-dependent microscopic
40 characterization, may unravel the mechanism underlying the hierarchical superstructure
41 formation; this represents ongoing research within our laboratory.
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CONCLUSIONS

In summary, we have demonstrated a facile colloidal synthetic method for the preparation of flexible polymer-passivated, nearly monodispersed CsPbBr₃ NCs. Depending on the concentration and binding head group of the surface passivating ligand PEG₆-NH₂/COOH, various self-assembled structures of NCs such as individual and bundled pearl-necklaces, lamellar, nanorice are formed in-situ. In the thermodynamically controlled mesoscale assembly process, vdW interactions between polymeric passivating ligands and dipole-dipole interactions of NCs contribute substantially to the formation of these uniquely organized assemblies. Although, we have studied the effects of concentration and binding head group of the surface passivating ligand on the assembly formation, one would expect that the chain length of PEG ligands should produce different structures because of the variable degree of cooperative interactions. As a proof-of-concept, we conducted the synthesis using additionally three different chain lengths PEG_n-NH₂ (n = 4, 12, and 18). We have observed the formation of nanowires for PEG₄-NH₂, and pearl necklaces and micro-size nanosheets containing individual spherical NCs for PEG₁₂-NH₂ and PEG₁₈-NH₂, respectively (data not shown). Importantly, strong electronic coupling between NCs, due to delocalization and entanglement of excitonic wavefunctions in the close-packed assembly has resulted in significant alteration of optical band-gaps and the higher-order hybrid nanostructures obtained behave more like artificial solids. Finally, both pearl-necklace and/or nanorice assembly form hierarchical superstructures that can be further refined to produce complex and unique self-assembled structures that mimic those found in the nature. Taken together, our work on polymer-assisted synthesis of higher order superstructures of CsPbBr₃ NCs consisting of regular ordering and with strong inter-NC electronic coupling leading to collective optoelectronic properties, along with the reported facile charge transport abilities of PEGs^{89, 90} may enhance the efficiency of photovoltaic and light emitting devices.⁷⁻¹¹

EXPERIMENTAL SECTION

Chemicals. Poly(ethylene glycol) methyl ethers (PEG₆-OH), *p*-toluene sulfonyl chloride (>99%), lead bromide (PbBr₂, >99%), potassium phthalimide (98%), cesium carbonate (99.9%), hydrazine monohydrate (98%), succinic anhydride, 4-(dimethylamino)pyridine, triethyl amine, 1,4 dioxane, carbon tetrachloride (99.9%), 1-octadecene (90% technical grade), anhydrous acetonitrile (CH₃CN, >99.8%), toluene (99.9%) hexane (99%), ethanol (98.5%), chloroform (>99%), and dichloromethane (DCM, >99%) were purchased from Aldrich and used without further purification. Different chain length PEG_n-amines (n = 4, 12, and 18) were purchased from Biochempeg, MA. Tetrahydrofuran (99.9%), sodium hydroxide, sodium sulphate anhydrous, and

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3 methanol (99.9%) were purchased from Fisher and used without further purification. Organic
4 solvents were purged with N₂ for 30 min prior to use.
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8 **Synthesis of Cesium Lead Bromide Perovskite Nanocrystals.** In a 25 mL round bottom
9 flask, 3.0 mL ODE along with desired amount of PEG₆-amine (60-120 μL) and PEG₆-acid (0-20
10 μL) were mixed together and then the reaction mixture was heated at 65° C for 45 min under
11 stirring. Separately, 5.0 mg of PEG₆-COO-Cs was placed in a small vial and dispersed in ODE
12 (200 μL) by sonication then injected into the round bottom flask, and the reaction mixture was
13 stirred for an additional 30 min. Next, 25.0 mg PbBr₂ was dissolved in 200 μL DMSO and
14 injected into the flask and allowed to react for 15 sec. At this point, the reaction mixture was
15 injected into 5.0 mL hexane and toluene mixture (7:3 volume ratio) to quench the reaction. The
16 product was isolated through centrifugation at 5000 rpm for 5 min, and the resulting product was
17 then redissolved in chloroform and centrifuged again at 5000 rpm for 5 min to remove any
18 insoluble materials. The yellow supernatant was collected for spectroscopy and microscopy
19 analyses.
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28 **UV-vis Absorbance, Photoluminescence, and NMR Analyses.** The absorption spectra were
29 collected using a Varian-Cary 50 Scan UV-visible spectrophotometer with 1 cm quartz cuvettes
30 over a range of 300-800 nm. All spectra were recorded in chloroform, and chloroform was used
31 as a background for all measurements. The photoluminescence emission (PL) spectra were
32 collected using a Cary Eclipse fluorescence spectrophotometer from Varian Instruments with 1
33 cm quartz cuvettes. H¹ NMR spectra were recorded on a Bruker Avance III 500 instrument at
34 500 MHz frequency using CDCl₃ as solvent.
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39 **Elemental Analysis.** A field emission scanning electron microscopy system (Hitachi S-4700),
40 which was equipped with an energy dispersive X-ray (EDS) analyzer, was used to determine
41 the Cs:Pb:Br ratio.
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45 **Powder X-ray Diffraction (PXRD) Analysis.** Wide-angle PXRD was recorded on a Rigaku
46 MiniFlexTM II (Cu Kα) instrument. Samples were prepared by drop-casting the purified
47 perovskite nanocrystals on cleaned glass coverslips. All samples were run from 10°- 60° with
48 0.015° increments at 1.5 s per step.
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52 **Transmission Electron Microscopy (TEM) Characterization.** The samples for TEM analysis
53 were prepared by placing 10 μL of the sample dissolved in chloroform onto a carbon-coated
54 copper grid (Electron Microscopy Science). The sample was allowed to set for 30 seconds and
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3 any excess solution was removed by wicking with a Kimwipe in order to avoid particle
4 aggregation. Images were acquired using a JEOL-3200FS-JEM instrument operating at 200 kV.
5 At least 300 NCs were analyzed for diameter averaging. At least 100 inter-NC spacing were
6 used to determine average and standard deviation.
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10 ASSOCIATED CONTENT

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14 **Supporting Information.** Detailed experimental procedures for ligands synthesis, various
15 spectroscopy and microscopy characterizations, histograms for size and dimension analyses,
16 and additional micrographs. These materials are available free of charge. (PDF)
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21 AUTHOR INFORMATION

22 Corresponding Author

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26 *Rajesh Sardar; Email: rsardar@iupui.edu
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29 Author Contributions

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32 [§]These authors contributed equally to this work.
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Figures and Table

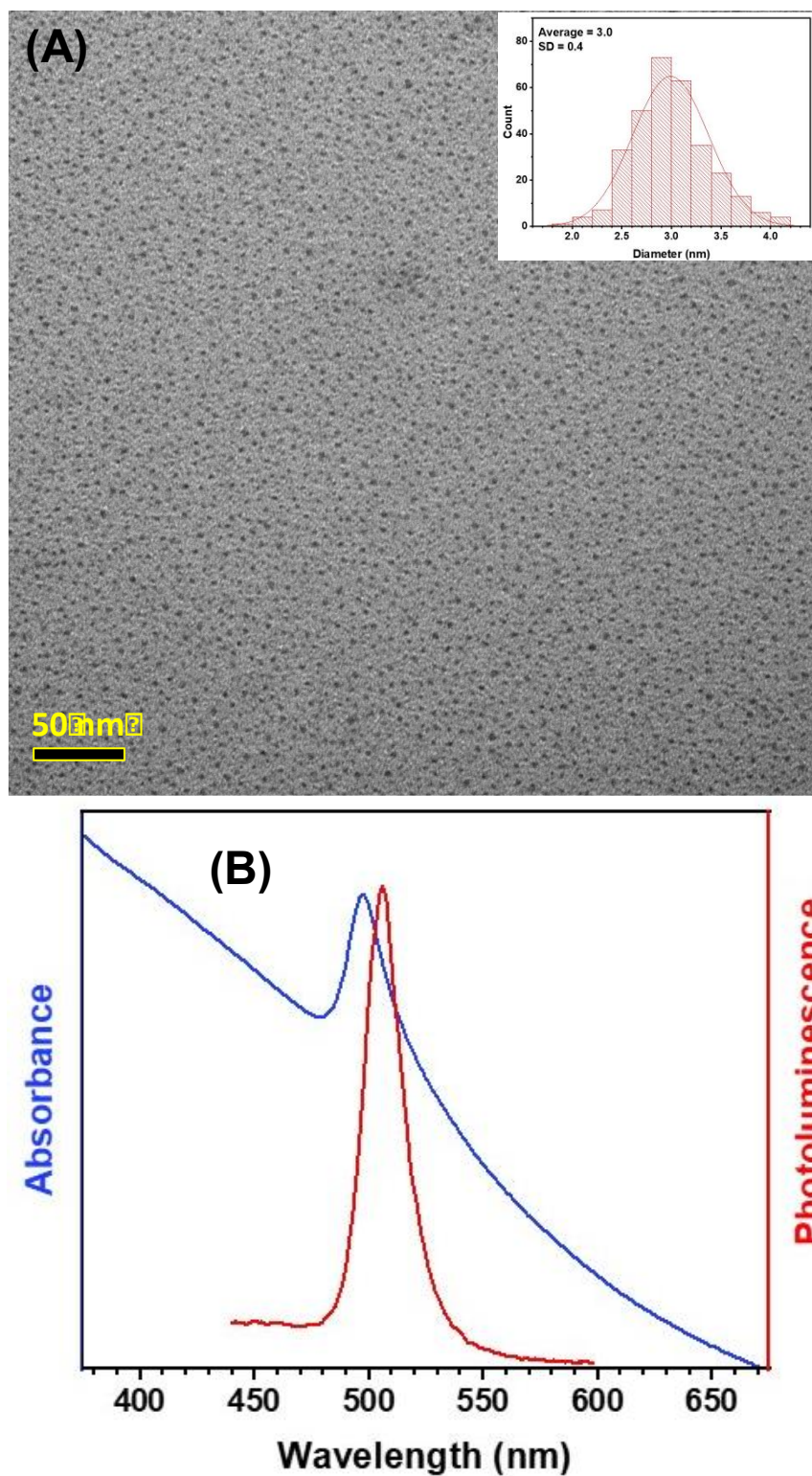
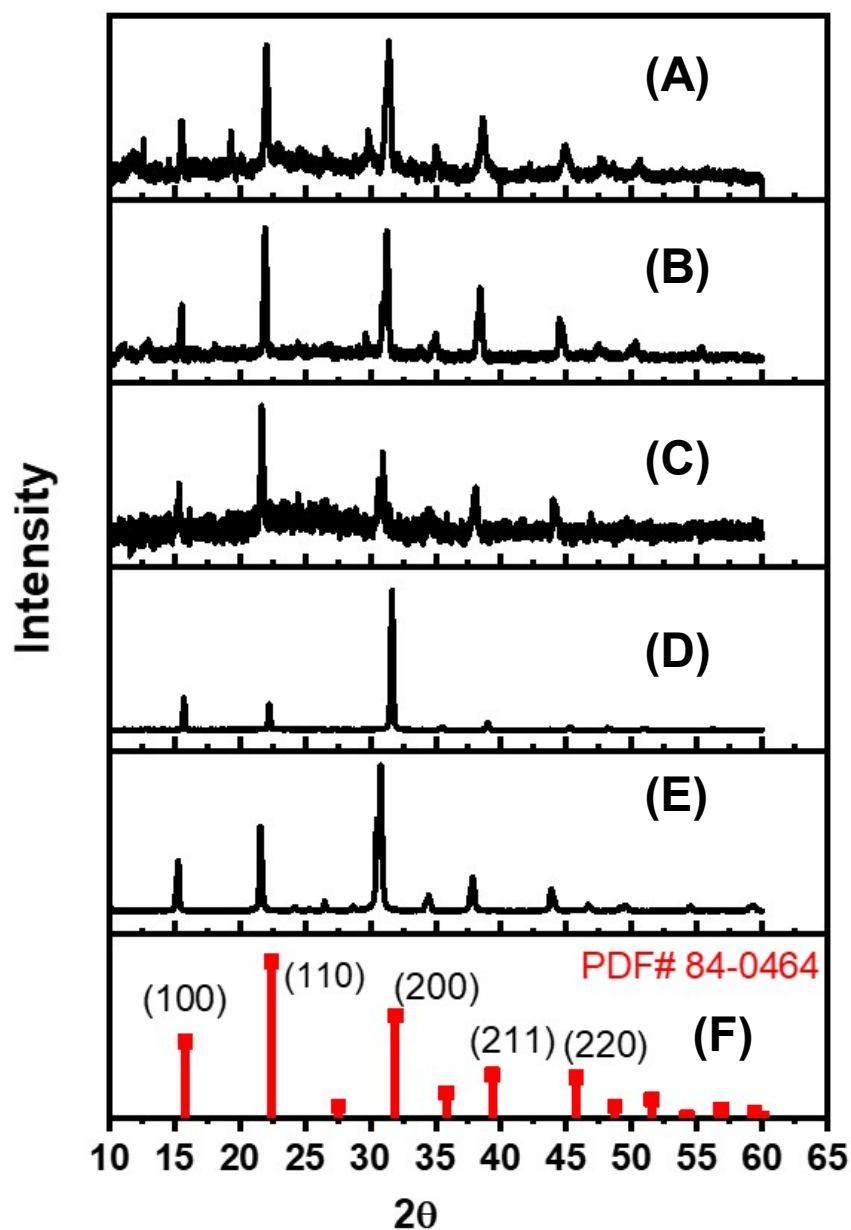


Figure 1. (A) Low-magnification TEM image of CsPbBr₃ NCs synthesized using 10 and 60 μ L of PEG₆-COOH and PEG₆-NH₂, respectively. The inset shows a histogram of size analysis. Approximately 300 NCs were counted to determine the average and standard deviation. (B) UV-

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3 visible absorption (blue line) and photoluminescence (red line) spectra of average 3.1 nm
4 diameter CsPbBr₃ NCs. The photoluminescence spectrum was collected at 380 nm excitation
5 wavelength.
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48 **Figure 2.** XRD pattern of CsPbBr₃ NCs synthesized in the presence of different amount of
49 PEG₆-COOH and PEG₆-NH₂: (A) close-packed, (B) individual pearl necklace, (C) bundled pearl
50 necklace, (D) lamellar, (E) nanorice assemblies and (F) standard XRD pattern.
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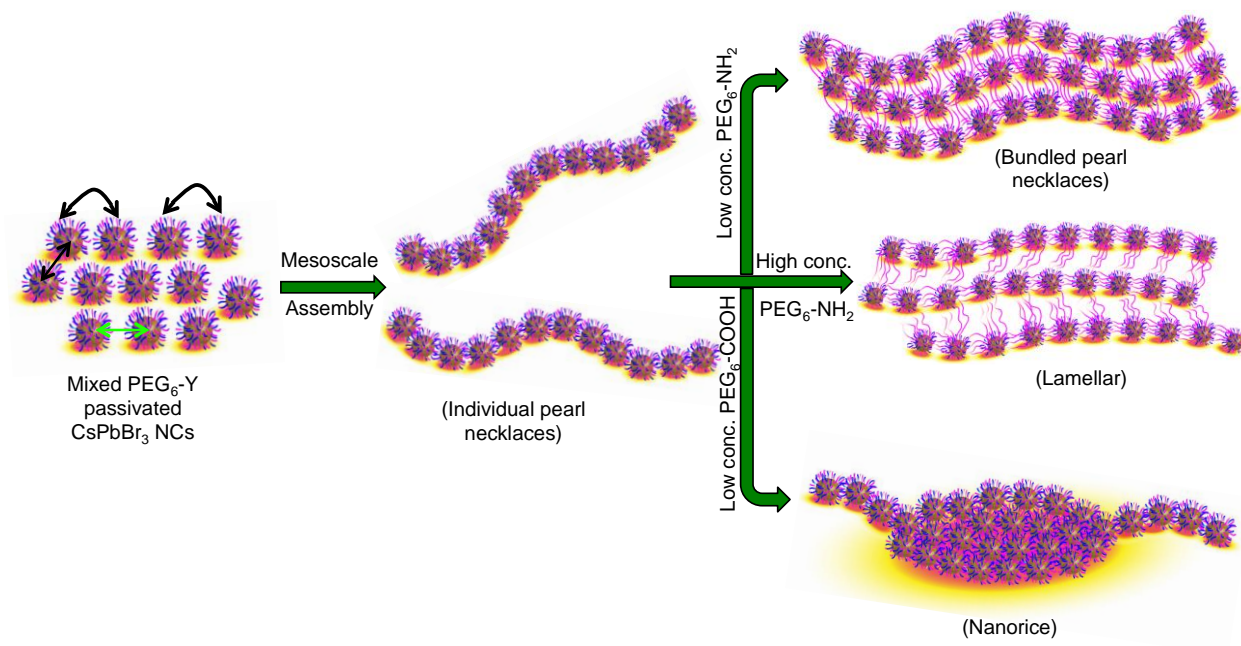


Figure 3. Schematic representation of ligand-assisted mesoscale transformations and formation of higher-order hybrid nanostructures (superstructures). Van der Waals interactions between hydrophilic PEG tails (double-headed black arrows) in a nonpolar solvent, and dipole-dipole attraction between NCs (double-headed green arrows) drive the mesoscale assembly to form superstructures. In the hairy-ball model, blue and purple curves represent PEG₆-COOH and PEG₆-NH₂, respectively. Long-range cooperative interactions between superstructures produce hierarchical superstructures with micron length scale.

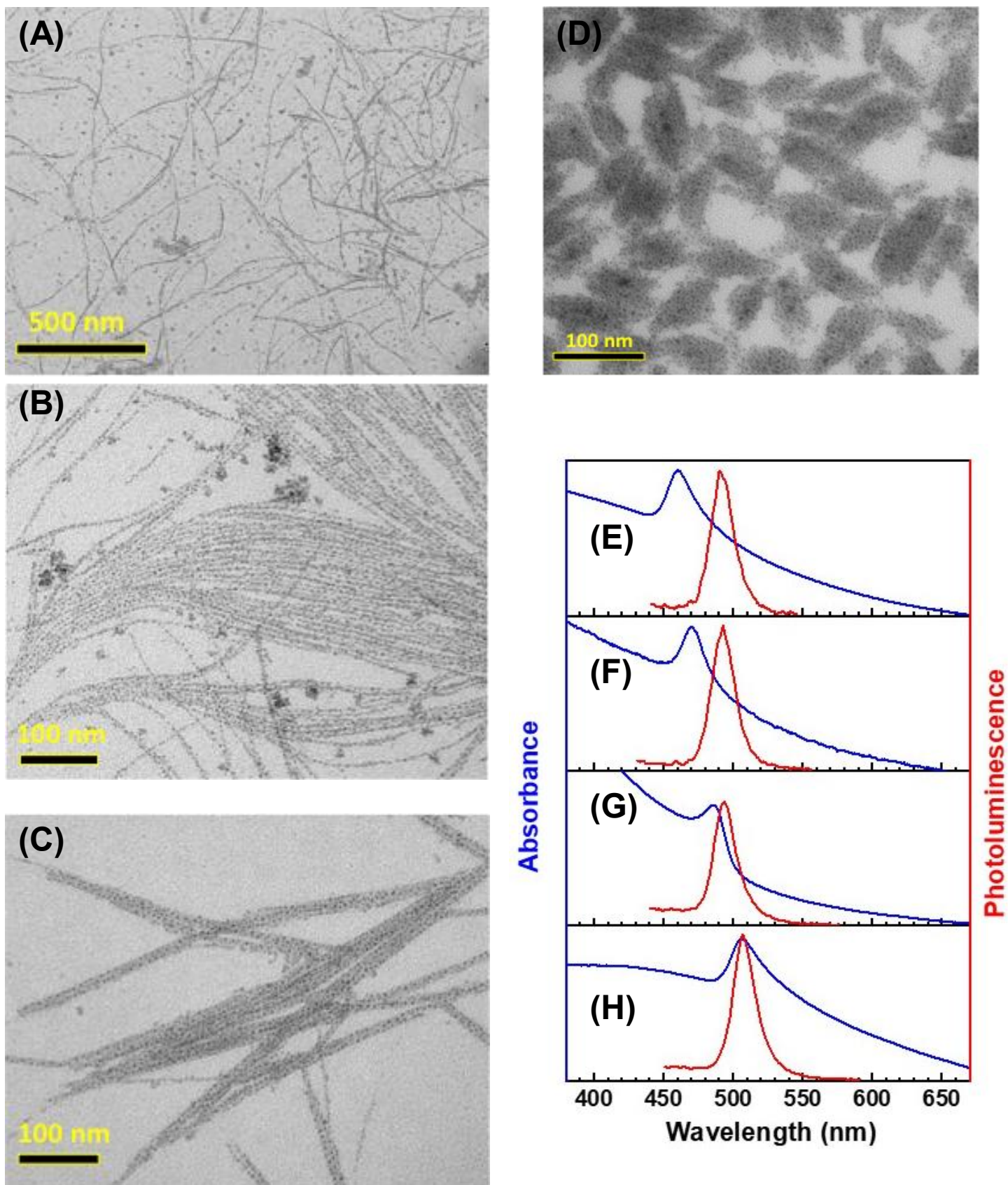


Figure 4. TEM micrographs of pearl-necklace (A), bundled (B), lamellar (C), and nanorice (D) assemblies of CsPbBr₃ NCs synthesized in the presence of different amount of PEG₆-NH₂ (A-C)

but no PEG₆-COOH, and using both PEG₆-COOH and PEG₆-NH₂ (D). UV-visible absorption (blue lines) and photoluminescence (red lines) spectra of lamellar (E), bundled (F), pearl-necklace (G), and nanorice (H) assemblies of CsPbBr₃ NCs.

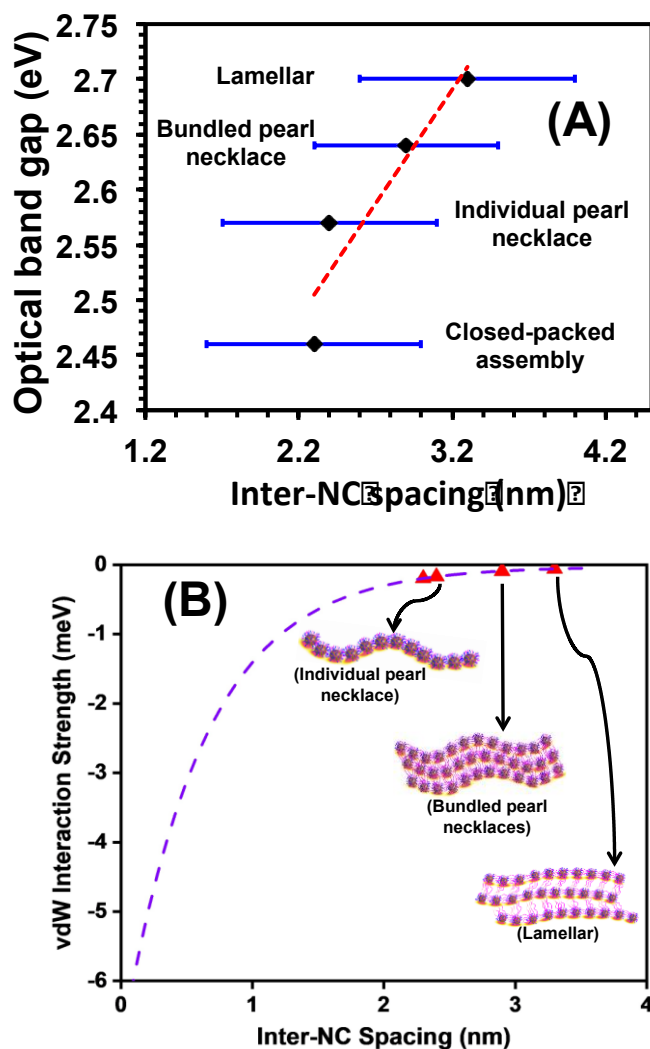


Figure 5. (A) Relationship depicting experimentally determined optical band-gap of CsPbBr₃ NCs as a function of inter-NC spacing. The size of the NCs is ~3.0 nm. Dotted red line shows a linear correlation (R² = 0.956). According to effective mass approximation calculations, the band-gap of 3.0 nm diameter CsPbBr₃ NCs is expected to be 4.46 eV.^{12, 63} Bulk band-gap of CsPbBr₃ perovskite is 2.25 eV.⁶⁴ (B) The red triangles are from a theoretical calculation of V_{vdW} between two adjacent NCs. Insets are the corresponding images of the self-assembly superstructure. Blue dash line illustrates the trend of the change of V_{vdW} with respect to the inter-NC spacing. The dash line represents nonlinear curve fitting based on the calculations.

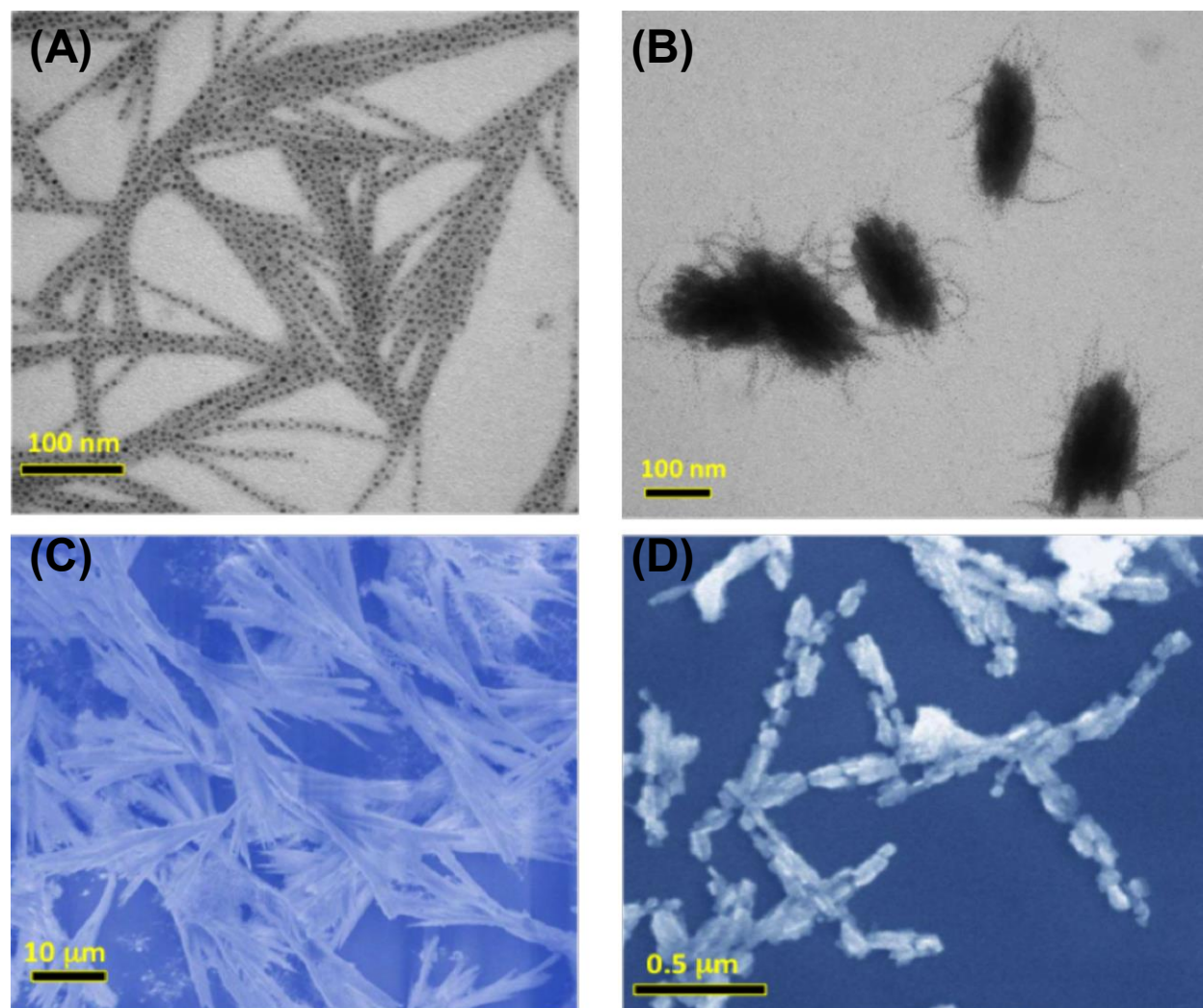


Figure 6. Representative TEM images showing lamellar **(A)** and nanorice **(B)** assemblies of CsPbBr₃ NCs prepared from pearl-necklace assemblies by adding 0.2 mmol PEG₆-NH₂ (A) 0.06 mmol and PEG₆-COOH (B) at room temperature. SEM micrographs of twisted ribbons **(C)** and inter-connected nanorices **(D)** of CsPbBr₃ NCs.

Table 1. Comparison of absorption, Photoluminescence, Size, and Inter-NC Spacing of CsPbBr₃ NCs in Various Assemblies, Which Were Prepared Using PEG₆-NH₂ and/or PEG₆-COOH of Different Concentrations.

reagent concentration	UV-visible absorption peak position, nm (eV)	PL peak position, nm (eV)	NC diameter (nm)	inter-NC spacing (nm)	length (nm)	NC assembly
0.4 mmol PEG ₆ -NH ₂ and no PEG ₆ -COOH	460 (2.70)	490 (2.53)	3.0 ± 0.5	3.3 ± 0.7	N/A	lamellar
0.34 mmol PEG ₆ -NH ₂ and no PEG ₆ -COOH	470 (2.64)	493 (2.52)	3.0 ± 0.5	2.9 ± 0.6	584 ± 150	bundled pearl-necklace
0.2 mmol PEG ₆ -NH ₂ and no PEG ₆ -COOH	483 (2.57)	495 (2.51)	3.0 ± 0.4	2.4 ± 0.7	533 ± 133	individual pearl-necklace
0.03 mmol PEG ₆ -COOH and 0.2 mmol PEG ₆ -NH ₂	494 (2.51)	504 (2.46)	3.0 ± 0.4	2.3 ± 0.7	N/A	closed-packed self-assembly
0.06 mmol PEG ₆ -COOH and 0.2 mmol PEG ₆ -NH ₂	505 (2.46)	508 (2.44)	3.1 ± 0.5	N/A	N/A	nanorice

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TOC Graphic

