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Corresponding Author:	William Tisdale Massachusetts Institute of Technology Cambridge, Massachusetts UNITED STATES
Corresponding Author's Institution:	Massachusetts Institute of Technology
Corresponding Author E-Mail:	tisdale@mit.edu
Order of Authors:	Seung Kyun Ha William Tisdale
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TITLE:

Facile Synthesis of Colloidal Lead Halide Perovskite Nanoplatelets via Ligand-Assisted Reprecipitation

AUTHORS AND AFFILIATIONS:

Seung Kyun Ha¹ and William A. Tisdale¹

¹Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA

Corresponding Author:

William A. Tisdale

tisdale@mit.edu

Email Addresses of authors:

Seung Kyun Ha (skha89@mit.edu)

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SUMMARY:

This work demonstrates facile room-temperature synthesis of colloidal quantum-confined lead halide perovskite nanoplatelets by ligand-assisted reprecipitation method. Synthesized nanoplatelets show spectrally narrow optical features and continuous spectral tunability throughout the visible range by varying the composition and thicknesses.

ABSTRACT:

In this work, we demonstrate a facile method for colloidal lead halide perovskite nanoplatelet synthesis (Chemical formula: $L_2[ABX_3]_{n-1}BX_4$, L: butylammonium and octylammonium, A: methylammonium or formamidinium, B: lead, X: bromide and iodide, n : number of $[BX_6]^{4-}$ octahedral layers in the direction of nanoplatelet thickness) via ligand-assisted reprecipitation. Individual perovskite precursor solutions are prepared by dissolving each nanoplatelet constituent salt in N,N-dimethylformamide (DMF), which is a polar organic solvent, and then mixing in specific ratios for targeted nanoplatelet thickness and composition. Once the mixed precursor solution is dropped into nonpolar toluene, the abrupt change in the solubility induces the instantaneous crystallization of nanoplatelets with surface-bound alkylammonium halide ligands providing colloidal stability. Photoluminescence and absorption spectra reveal emissive and strongly quantum-confined features. X-ray diffraction and transmission electron microscopy confirm the two-dimensional structure of the nanoplatelets. Furthermore, we demonstrate that the band gap of perovskite nanoplatelets can be continuously tuned in the visible range by varying the stoichiometry of the halide ion(s). Lastly, we demonstrate the flexibility of the ligand-assisted reprecipitation method by introducing multiple species as surface-capping ligands. This methodology represents a simple procedure for preparing dispersions of emissive 2D colloidal semiconductors.

INTRODUCTION:

In the past decade, fabrication of lead halide perovskites solar cells¹⁻⁶ has effectively highlighted the excellent properties of this semiconductor material, including long carrier diffusion lengths⁷⁻¹⁰, compositional tunability^{4,5,11} and low-cost synthesis¹². In particular, the unique nature of defect tolerance^{13,14} makes lead halide perovskites fundamentally different from other semiconductors and thus highly promising for next-generation optoelectronic applications.

In addition to solar cells, lead halide perovskites have been shown to make excellent optoelectronic devices such as light-emitting diodes^{6,15-22}, lasers²³⁻²⁵, and photodetectors²⁶⁻²⁸. Especially, when prepared in the form of colloidal nanocrystals^{18,29-43}, lead halide perovskites may exhibit strong quantum- and dielectric-confinement, large exciton binding energy^{44,45}, and bright luminescence^{17,19} along with facile solution processability. Various reported geometries including quantum dots²⁹⁻³², nanorods^{33,34} and nanoplatelets^{18,35-41,43} further demonstrate the shape tunability of lead halide perovskite nanocrystals.

Among those nanocrystals, colloidal two-dimensional (2D) lead halide perovskites, or “perovskite nanoplatelets”, are especially promising for light-emitting applications due to strong confinement of charge carriers, large exciton binding energy reaching up to hundreds of meV⁴⁴, and spectrally narrow emission from thickness-pure ensembles of nanoplatelets³⁹. Additionally, anisotropic emission reported for 2D perovskite nanocrystals⁴⁶ and other 2D semiconductors^{47,48} highlights the potential of maximizing outcoupling efficiency from perovskite nanoplatelet-based light-emitting devices.

Here, we demonstrate a protocol for the simple, universal, room-temperature synthesis of colloidal lead halide perovskite nanoplatelets via a ligand-assisted reprecipitation technique^{36,38,49}. Perovskite nanoplatelets incorporating iodide and/or bromide halide anions, methylammonium or formamidinium organic cations, and variable organic surface ligands are demonstrated. Procedures for controlling the absorption and emission energy and the thickness purity of the colloidal dispersion are discussed.

PROTOCOL:

NOTE: Simpler notations of ‘ $n = 1$ BX’ and ‘ $n = 2$ ABX’ will be used from here instead of the complex chemical formula of L_2BX_4 and $L_2[ABX_3]BX_4$, respectively. For better stability and optical properties of resulting perovskite nanoplatelets, it is recommended to complete the whole procedure under inert conditions⁴⁹ (i.e., a nitrogen glovebox).

1. Preparation of perovskite nanoplatelet precursor solution

1.1. Prepare ~1 mL of 0.2 M solutions of methylammonium bromide (MABr), formamidinium bromide (FABr), lead bromide ($PbBr_2$), butylammonium bromide (BABr), octylammonium bromide (OABr), methylammonium iodide (MAI), formamidinium iodide (FAI), lead iodide (PbI_2), butylammonium iodide (BAI), and octylammonium iodide (OAI) in N,N-dimethylformamide

(DMF) either by dissolving each salt in DMF or by diluting commercially available solutions.

1.1.1. PbBr_2 is not readily soluble in DMF at room temperature, keep the solution at 80 °C for 10 min or longer for complete dissolution. Once dissolved, cool the solution back to room temperature before use.

NOTE: Concentration of individual precursor solutions can be increased to synthesize more nanoplatelets, but the maximum concentration is usually limited by the solubilities of PbBr_2 and PbI_2 in DMF.

1.2. Mix those individual precursor solutions in specific volumetric ratios for each target thickness and composition.

1.2.1. To synthesize bromide-only or iodide-only nanoplatelets, see **Table 1**, which summarizes the volumetric ratios for $n = 1$ and $n = 2$ bromide and iodide nanoplatelets.

1.2.2. To synthesize nanoplatelets with mixed halide compositions, combine bromide-only and iodide-only perovskite nanoplatelet precursor solutions of the same thickness at desired volumetric ratio for the target composition. For example, to make 30%-bromide-70%-iodide $n = 2$ perovskite nanoplatelets, mix the precursor solutions of $n = 2$ MAPbBr and $n = 2$ MAPbI at a 3:7 volumetric ratio.

NOTE: Changing the organic cation does not significantly affect the optical transition energies¹³. Absorption and luminescence are primarily tuned by changing the halide composition or nanoplatelet thickness.

2. Synthesis of perovskite nanoplatelets via ligand-assisted reprecipitation method

2.1. Inject 10 μL of mixed precursor solution into 10 mL of toluene under vigorous stirring. Nanoplatelets will instantaneously crystallize due to the abrupt change in the solubility.

NOTE: The amount of mixed precursor solution injected into toluene can be increased up to ~ 100 μL . Total amount of injected precursor solution and injection speed do not seem to significantly affect perovskite nanoplatelet morphology (**Figure S1**). However, injection of too much DMF increases the polarity of the solution and reduces the crystallization.

2.2. Leave the solution under stirring for 10 min until no further color change is observed from the solution to ensure complete crystallization of perovskite nanoplatelets.

NOTE: Freshly synthesized perovskite nanoplatelets from freshly prepared precursor solutions usually show the best photoluminescence quantum yield and photostability⁴⁹. And over time, nanoplatelets will slowly aggregate (**Figure S2**), deteriorating colloidal stability. Thus, it is recommended to use nanoplatelet solutions as soon as possible once synthesized.

3. Characterization sample preparation and purification of colloidal perovskite nanoplatelet solution.

3.1. Transmission electron microscopy (TEM) sample preparation.

3.1.1. Centrifuge the solution at 2050 x *g* for 10 min.

3.1.2. Discard the supernatant.

3.1.3. Redisperse the nanoplatelets in 1 mL of toluene.

3.1.4. Drop 1 droplet on a TEM grid.

3.1.5. Dry the sample under vacuum.

3.2. X-ray diffraction (XRD) sample preparation

3.2.1. Centrifuge the solution at 2050 x *g* for 10 min.

3.2.2. Discard the supernatant.

3.2.3. Redisperse the nanoplatelets in 30 μ L of toluene.

3.2.4. Dropcast on a glass slide.

3.2.5. Dry the sample under vacuum.

3.3. General purification

3.3.1. Centrifuge the solution at 2050 x *g* for 10 min.

3.3.2. Discard the supernatant.

3.3.3. Redisperse the nanoplatelets in desired amount of solvent depending on the usage.

NOTE: Depending on the usage of nanoplatelets, the volume of the redispersing solvent can be freely adjusted and other nonpolar organic solvents such as hexane, octane or chlorobenzene can be used instead of toluene.

REPRESENTATIVE RESULTS:

Schematic illustration of perovskite nanoplatelets and synthesis procedure gives an overview of the material and synthetic details (**Figure 1**). Pictures of colloidal perovskite nanoplatelet solutions under ambient light and UV (**Figure 2**), combined with photoluminescence and absorption spectra (**Figure 3**) further confirm the emissive and absorptive nature of

nanoplatelets. TEM images (**Figure 4**) and XRD patterns (**Figure 5**) are used to estimate the lateral dimensions and stacking spacings of nanoplatelets, respectively, while also confirming the two-dimensional structure. Absorption spectra of perovskite nanoplatelet solutions with mixed halides demonstrate tunability of the bandgap (**Figure 6**). Insensitivity of the photoluminescence spectrum to the chemical identity of organic surface-capping ligands highlights the compositional flexibility of these materials (**Figure 7**).

FIGURE AND TABLE LEGENDS:

Table 1. Formulation guidelines for perovskite nanoplatelet precursor solutions. Numbers in the table indicate the volumetric equivalents of each precursor solution (columns) that should be combined to achieve the targeted nanoplatelet (rows), according to the concentration specifications in the protocol text.

Figure 1. Perovskite nanoplatelet structure and synthesis procedure. (a) Illustration of perovskite unit cell and nanoplatelet structure. (b) Schematic illustration of colloidal perovskite nanoplatelet synthesis. Reprinted (adapted) with permission from Ref. 48. Copyright 2019 American Chemical Society.

Figure 2. Colloidal perovskite nanoplatelet solutions illuminated by UV light. Emission from the nanoplatelets can be clearly seen along the beam path. Reprinted (adapted) with permission from Ref. 48. Copyright 2019 American Chemical Society.

Figure 3. Photoluminescence and absorption spectra of colloidal perovskite nanoplatelet solutions. Bandgap of the nanoplatelets can be tuned with thickness and composition. Longpass filter (Cut-on wavelength: 400 nm) was used to filter out excitation UV light before photoluminescence spectrum collection and it could have slightly altered $n = 1$ lead bromide nanoplatelet emission spectrum.

Figure 4. Transmission electron microscopy (TEM) images of perovskite nanoplatelets. Images show randomly-overlapping nanoplatelets. See also **Figure S7**.

Figure 5. X-ray diffraction (XRD) patterns and d-spacings of perovskite nanoplatelets. XRD patterns are dominated by nanoplatelet stacking peaks which confirm the two-dimensional nature of the nanoplatelets and their face-to-face self-assembly in dropcasted films.

Figure 6. Absorption spectra of colloidal perovskite nanoplatelet solutions with mixed halides. Continuous shift of first excitonic absorption features shows bandgap tunability with halide composition.

Figure 7. Photoluminescence spectra of $n = 1$ PbBr and $n = 2$ MAPbBr nanoplatelets synthesized with different ligand species. The reprecipitation method can be easily extended to other ligand chemistries. See also **Table S2** for formulation guidelines. Longpass filter (Cut-on wavelength: 400 nm) was used to filter out excitation UV light before photoluminescence spectrum collection and it could have slightly altered $n = 1$ lead bromide nanoplatelet emission spectrum.

Supplementary file. Supporting information.

DISCUSSION:

The product of this synthesis is colloidal lead halide nanoplatelets capped by alkylammonium halide surface ligands (**Figure 1a**). **Figure 1b** demonstrates the synthetic procedure of colloidal perovskite nanoplatelets via ligand-assisted reprecipitation. To summarize, constituent precursor salts were dissolved in a polar solvent DMF in specific ratios for desired thickness and composition, and then injected into toluene, which is nonpolar. Due to the abrupt change in solubility, colloidal perovskite nanoplatelets started to crystallize instantaneously. When preparing the mixed precursor solution, ratios between constituent precursors primarily determined the thickness of resulting nanoplatelets (**Figure S3**), and the presence of excess ligands in precursor solution was crucial to ensure the thickness homogeneity of the product (**Figure S4**). In general, any polar solvent can be used to dissolve perovskite precursor salts while any nonpolar solvent can be used to disperse colloidal nanoplatelets. However, miscibility of those nonpolar and polar solvents is crucial for homogeneous synthesis of colloidal perovskite nanoplatelets, and thus we chose DMF and toluene. Also, it is important to have nonpolar solvent in large excess to the added polar solvent for the crystallization of perovskite nanoplatelets to occur. Adding too much polar solvent increases the polarity of the resulting solvent mixture (i.e. DMF + toluene), which can dissolve the nanoplatelets. Chloride- and cesium-incorporating nanoplatelets can also be synthesized by this approach (**Figure S5**), though the chloride-containing nanoplatelets are nonemissive and the cesium-based nanoplatelets suffer from inferior stability and thickness homogeneity relative to the methylammonium-based nanoplatelets when synthesized via this method³⁸. Finally, we note that only the $n = 1$ and $n = 2$ members have been synthesized with good thickness homogeneity by this method; attempts at making thicker ($n \geq 3$) nanoplatelets typically yield mixed-thickness dispersions (**Figure S6**).

Figure 2 shows the images of as-synthesized colloidal perovskite nanoplatelet solutions illuminated by UV light, where the emission of the nanoplatelets can be clearly seen along the beam path. **Figure 3** shows the normalized photoluminescence (PL) and absorption spectra of colloidal perovskite nanoplatelet solutions, which are consistent with previous reports^{37,38,50,51}, demonstrating the tunability of perovskite nanoplatelets with thickness and constituent species. For all nanoplatelets, strong excitonic features in the absorption spectra and significant blue-shift of the spectra compared to bulk perovskites³⁵ were observed due to strong quantum- and dielectric-confinement. Changing the organic cation from methylammonium to formamidinium did not significantly affect the band gap – either for bromide or iodide nanoplatelets – in agreement with understanding of the valence electronic structure in lead halide perovskites¹³. **Table S1** summarizes the photoluminescence quantum yields (PLQYs) of those colloidal perovskite nanoplatelet solutions.

The two-dimensional structure of the perovskite nanoplatelets was confirmed by TEM and XRD. In **Figure 4**, TEM images show partially overlapping two-dimensional perovskite nanoplatelets, with individual lateral dimensions ranging from a few hundred nanometers to a micrometer. The image contrast and random configuration of nanoplatelets on the TEM grid suggests that they are dispersed in solution as individual sheets – rather than stacked lamellar crystals. Small, dark

spherical dots appeared upon electron beam irradiation as observed in **Figure 4**, and they are believed to be metallic Pb as previously reported^{36,52}. Due to the large lateral dimensions of perovskite nanoplatelets, they preferentially lay flat on top of each other when cast into a film, and periodic stacking peaks dominated the XRD pattern as shown in Figure 5. Considering that the lattice constant for the cubic perovskite unit cell is $\sim 0.6 \text{ nm}^{53}$, it can be deduced that the organic ligand layer is 1 nm thick in stacked nanoplatelet films regardless of the nanoplatelet species³⁸.

The absorption and emission resonance could be continuously tuned by varying the halide composition. **Figure 6** shows the normalized absorption spectra of colloidal $n = 1$ PbX and $n = 2$ MAPbX nanoplatelet solutions with varying ratios of bromide and iodide. Clear excitonic absorption peaks indicate strong confinement of carriers in nanoplatelets, and continuous shift of those peaks with halide composition demonstrates band gap tunability through halide composition variation (**Figure S8**). However, photoluminescence spectra of mixed-halide nanoplatelets exhibit broad or multiple features (**Figure S9**), which is possibly due to photoinduced halide segregation.⁵⁴

The ligand-assisted reprecipitation method is particularly amenable to changing the identity of the long-chain capping ligand, as shown in **Figure 7**. This opens up the possibility of tuning the nature of the surface-bound organic species for the optimized performance of a specific device or application⁵⁵. We note, however, that the ratios between individual precursors may require slight adjustment when employing new ligand species for the best thickness homogeneity of the resulting system (**Figure S10** and **Table S2**).

In conclusion, we have demonstrated a simple, versatile method for synthesizing colloidal lead halide perovskite nanoplatelets of varying composition (**Figure S11**). The ligand-assisted reprecipitation approach is potentially amenable to high-throughput synthesis and further data-driven analysis. Thickness-, composition- and ligand-tunability can be achieved without any major modifications in the synthetic protocols. Moving forward, it would be desirable to further increase the photoluminescence efficiency to levels commensurate with other perovskite nanocrystals^{29,32,56}.

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DISCLOSURES:

The authors declare no competing financial interests.

REFERENCES:

309 1 Kim, H. S. *et al.* Lead iodide perovskite sensitized all-solid-state submicron thin film
 310 mesoscopic solar cell with efficiency exceeding 9%. *Scientific Reports*. **2** 591, (2012).

311 2 Zhou, H. *et al.* Interface engineering of highly efficient perovskite solar cells. *Science*. **345**
 312 (6196), 542-546, (2014).

313 3 Yang, W. S. *et al.* Iodide management in formamidinium-lead-halide-based perovskite
 314 layers for efficient solar cells. *Science*. **356** (6345), 1376-1379, (2017).

315 4 Saliba, M. *et al.* Cesium-containing triple cation perovskite solar cells: improved stability,
 316 reproducibility and high efficiency. *Energy & Environmental Science*. **9** (6), 1989-1997, (2016).

317 5 Jeon, N. J. *et al.* Compositional engineering of perovskite materials for high-performance
 318 solar cells. *Nature*. **517** (7535), 476-480, (2015).

319 6 Stranks, S. D., Snaith, H. J. Metal-halide perovskites for photovoltaic and light-emitting
 320 devices. *Nature Nanotechnology*. **10** (5), 391-402, (2015).

321 7 Ma, L. *et al.* Carrier diffusion lengths of over 500 nm in lead-free perovskite CH₃NH₃SnI₃
 322 films. *Journal of the American Chemical Society*. **138** (44), 14750-14755, (2016).

323 8 Dong, Q. *et al.* Electron-hole diffusion lengths > 175 μ m in solution grown CH₃NH₃PbI₃
 324 single crystals. *Science*. **347** (6225), 967-970, (2015).

325 9 Stranks, S. D. *et al.* Electron-Hole Diffusion Lengths Exceeding 1 Micrometer in an
 326 Organometal Trihalide Perovskite Absorber. *Science*. **342** (6156), 341-344, (2013).

327 10 Shi, D. *et al.* Low trap-state density and long carrier diffusion in organolead trihalide
 328 perovskite single crystals. *Science*. **347** (6221), 519-522, (2015).

329 11 McMeekin, D. P. *et al.* A mixed-cation lead mixed-halide perovskite absorber for tandem
 330 solar cells. *Science*. **351** (6269), 151-155, (2016).

331 12 Saidaminov, M. I. *et al.* High-quality bulk hybrid perovskite single crystals within minutes
 332 by inverse temperature crystallization. *Nature Communications*. **6** 7586, (2015).

333 13 Kovalenko, M. V., Protesescu, L., Bodnarchuk, M. I. Properties and potential
 334 optoelectronic applications of lead halide perovskite nanocrystals. *Science*. **358** (6364), 745-750,
 335 (2017).

336 14 Akkerman, Q. A., Rainò, G., Kovalenko, M. V., Manna, L. Genesis, challenges and
 337 opportunities for colloidal lead halide perovskite nanocrystals. *Nature Materials*. **17** 394-405,
 338 (2018).

339 15 Gangishetty, M. K., Hou, S., Quan, Q., Congreve, D. N. Reducing Architecture Limitations
 340 for Efficient Blue Perovskite Light-Emitting Diodes. *Advanced Materials*. **30** (20), 1706226, (2018).

341 16 Congreve, D. N. *et al.* Tunable Light-Emitting Diodes Utilizing Quantum-Confined Layered
 342 Perovskite Emitters. *ACS Photonics*. **4** (3), 476-481, (2017).

343 17 Kumar, S. *et al.* Ultrapure Green Light-Emitting Diodes Using Two-Dimensional
 344 Formamidinium Perovskites: Achieving Recommendation 2020 Color Coordinates. *Nano Letters*.
 345 **17** (9), 5277-5284, (2017).

346 18 Kumar, S. *et al.* Efficient blue electroluminescence using quantum-confined two-
 347 dimensional perovskites. *ACS Nano*. **10** (10), 9720-9729, (2016).

348 19 Pan, J. *et al.* Bidentate Ligand-Passivated CsPbI₃ Perovskite Nanocrystals for Stable Near-
 349 Unity Photoluminescence Quantum Yield and Efficient Red Light-Emitting Diodes. *Journal of the*
 350 *American Chemical Society*. **140** (2), 562-565, (2018).

351 20 Kim, Y. H. *et al.* Multicolored organic/inorganic hybrid perovskite light-emitting diodes.
 352 *Advanced Materials*. **27** (7), 1248-1254, (2015).

353 21 Pan, J. *et al.* Highly Efficient Perovskite-Quantum-Dot Light-Emitting Diodes by Surface
 354 Engineering. *Advanced Materials*. **28** (39), 8718-8725, (2016).
 355 22 Tsai, H. *et al.* Stable Light-Emitting Diodes Using Phase-Pure Ruddlesden–Popper Layered
 356 Perovskites. *Advanced Materials*. **30** (6), 1704217, (2018).
 357 23 Sutherland, B. R., Hoogland, S., Adachi, M. M., Wong, C. T., Sargent, E. H. Conformal
 358 organohalide perovskites enable lasing on spherical resonators. *ACS Nano*. **8** (10), 10947-10952,
 359 (2014).
 360 24 Deschler, F. *et al.* High photoluminescence efficiency and optically pumped lasing in
 361 solution-processed mixed halide perovskite semiconductors. *The Journal of Physical Chemistry*
 362 *Letters*. **5** (8), 1421-1426, (2014).
 363 25 Zhu, H. *et al.* Lead halide perovskite nanowire lasers with low lasing thresholds and high
 364 quality factors. *Nature Materials*. **14** (6), 636-642, (2015).
 365 26 Fang, Y., Huang, J. Resolving weak light of sub-picowatt per square centimeter by hybrid
 366 perovskite photodetectors enabled by noise reduction. *Advanced Materials*. **27** (17), 2804-2810,
 367 (2015).
 368 27 Shen, L. *et al.* A Self-Powered, Sub-nanosecond-Response Solution-Processed Hybrid
 369 Perovskite Photodetector for Time-Resolved Photoluminescence-Lifetime Detection. *Advanced*
 370 *Materials*. **28** (48), 10794-10800, (2016).
 371 28 Dou, L. *et al.* Solution-processed hybrid perovskite photodetectors with high detectivity.
 372 *Nature Communications*. **5** 5404, (2014).
 373 29 Protesescu, L. *et al.* Nanocrystals of Cesium Lead Halide Perovskites (CsPbX₃, X = Cl, Br,
 374 and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano*
 375 *Letters*. **15** (6), 3692-3696, (2015).
 376 30 Schmidt, L. C. *et al.* Nontemplate synthesis of CH₃NH₃PbBr₃ perovskite nanoparticles.
 377 *Journal of the American Chemical Society*. **136** (3), 850-853, (2014).
 378 31 Imran, M. *et al.* Shape-Pure, Nearly Monodispersed CsPbBr₃ Nanocubes Prepared Using
 379 Secondary Aliphatic Amines. *Nano Letters*. **18** (12), 7822-7831, (2018).
 380 32 Dong, Y. *et al.* Precise Control of Quantum Confinement in Cesium Lead Halide Perovskite
 381 Quantum Dots via Thermodynamic Equilibrium. *Nano Letters*. **18** (6), 3716-3722, (2018).
 382 33 Sun, S., Yuan, D., Xu, Y., Wang, A., Deng, Z. Ligand-mediated synthesis of shape-controlled
 383 cesium lead halide perovskite nanocrystals via reprecipitation process at room temperature. *ACS*
 384 *Nano*. **10** (3), 3648-3657, (2016).
 385 34 Zhang, D., Eaton, S. W., Yu, Y., Dou, L., Yang, P. Solution-phase synthesis of cesium lead
 386 halide perovskite nanowires. *Journal of the American Chemical Society*. **137** (29), 9230-9233,
 387 (2015).
 388 35 Weidman, M. C., Goodman, A. J., Tisdale, W. A. Colloidal halide perovskite nanoplatelets:
 389 An exciting new class of semiconductor nanomaterials. *Chemistry of Materials*. **29** (12), 5019-
 390 5030, (2017).
 391 36 Sichert, J. A. *et al.* Quantum Size Effect in Organometal Halide Perovskite Nanoplatelets.
 392 *Nano Letters*. **15** (10), 6521-6527, (2015).
 393 37 Bohn, B. J. *et al.* Boosting Tunable Blue Luminescence of Halide Perovskite Nanoplatelets
 394 through Postsynthetic Surface Trap Repair. *Nano Letters*. **18** (8), 5231-5238, (2018).
 395 38 Weidman, M. C., Seitz, M., Stranks, S. D., Tisdale, W. A. Highly Tunable Colloidal Perovskite
 396 Nanoplatelets Through Variable Cation, Metal, and Halide Composition. *ACS Nano*. **10** (8), 7830-

7839, (2016).

39 Bekenstein, Y., Koscher, B. A., Eaton, S. W., Yang, P., Alivisatos, A. P. Highly Luminescent Colloidal Nanoplates of Perovskite Cesium Lead Halide and Their Oriented Assemblies. *Journal of the American Chemical Society*. **137** (51), 16008-16011, (2015).

40 Shamsi, J. *et al.* Colloidal synthesis of quantum confined single crystal CsPbBr₃ nanosheets with lateral size control up to the micrometer range. *Journal of the American Chemical Society*. **138** (23), 7240-7243, (2016).

41 Vybornyi, O., Yakunin, S., Kovalenko, M. V. Polar-solvent-free colloidal synthesis of highly luminescent alkylammonium lead halide perovskite nanocrystals. *Nanoscale*. **8** (12), 6278-6283, (2016).

42 Huang, H. *et al.* Colloidal lead halide perovskite nanocrystals: synthesis, optical properties and applications. *NPG Asia Materials*. **8** (11), e328, (2016).

43 Tyagi, P., Arveson, S. M., Tisdale, W. A. Colloidal Organohalide Perovskite Nanoplatelets Exhibiting Quantum Confinement. *J Phys Chem Lett*. **6** (10), 1911-1916, (2015).

44 Saidaminov, M. I., Mohammed, O. F., Bakr, O. M. Low-Dimensional-Networked Metal Halide Perovskites: The Next Big Thing. *ACS Energy Letters*. **2** (4), 889-896, (2017).

45 Zheng, K. *et al.* Exciton binding energy and the nature of emissive states in organometal halide perovskites. *The Journal of Physical Chemistry Letters*. **6** (15), 2969-2975, (2015).

46 Jurow, M. J. *et al.* Manipulating the Transition Dipole Moment of CsPbBr₃ Perovskite Nanocrystals for Superior Optical Properties. *Nano Letters*. 10.1021/acs.nanolett.9b00122, (2019).

47 Gao, Y., Weidman, M. C., Tisdale, W. A. CdSe Nanoplatelet Films with Controlled Orientation of their Transition Dipole Moment. *Nano Letters*. **17** (6), 3837-3843, (2017).

48 Schuller, J. A. *et al.* Orientation of luminescent excitons in layered nanomaterials. *Nature Nanotechnology*. **8** (4), 271-276, (2013).

49 Ha, S. K., Mauck, C. M., Tisdale, W. A. Towards Stable Deep-Blue Luminescent Colloidal Lead Halide Perovskite Nanoplatelets: Systematic Photostability Investigation. *Chemistry of Materials*. **31** (7), 2486-2496, (2019).

50 Paritmongkol, W., Dahod, N., Mao, N., Zheng, S.-L., Tisdale, W. Synthetic Variation and Structural Trends in Layered Two-Dimensional Alkylammonium Lead Halide Perovskites. *ChemRxiv*. 10.26434/chemrxiv.7942628.v1, (2019).

51 Stoumpos, C. C. *et al.* Ruddlesden–Popper hybrid lead iodide perovskite 2D homologous semiconductors. *Chemistry of Materials*. **28** (8), 2852-2867, (2016).

52 Akkerman, Q. A. *et al.* Solution Synthesis Approach to Colloidal Cesium Lead Halide Perovskite Nanoplatelets with Monolayer-Level Thickness Control. *Journal of the American Chemical Society*. **138** (3), 1010-1016, (2016).

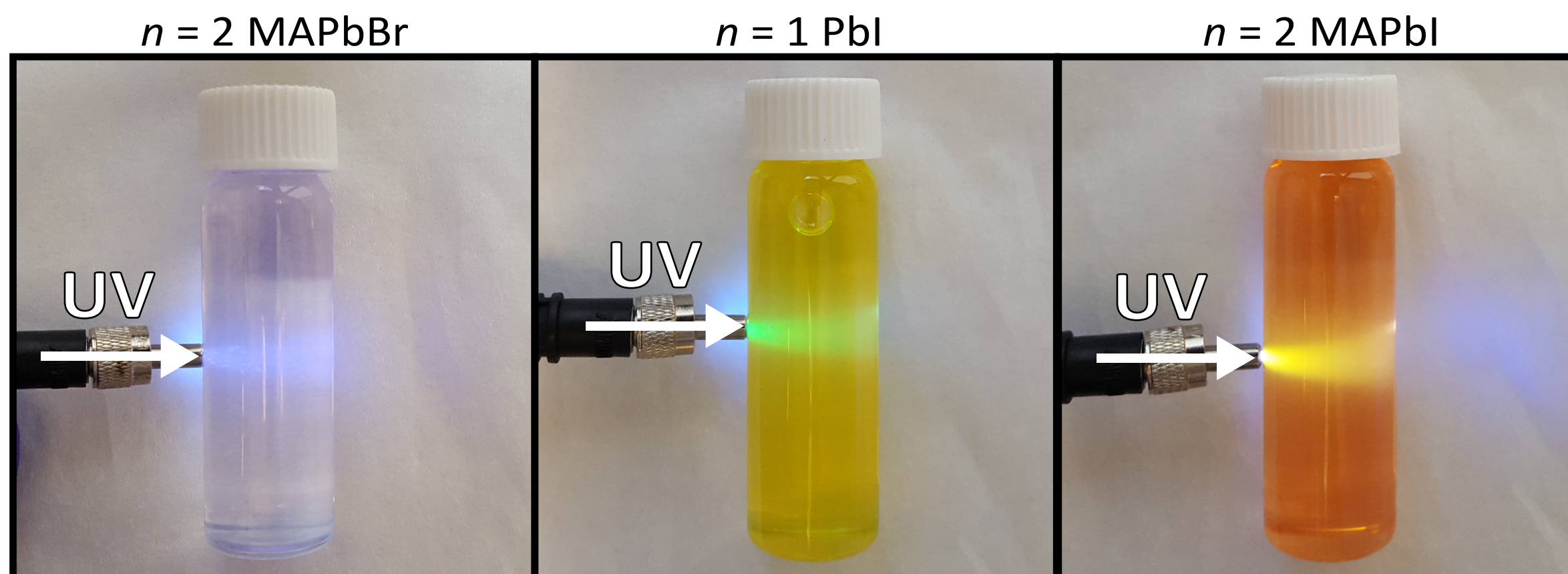
53 Kojima, A., Teshima, K., Shirai, Y., Miyasaka, T. Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. *Journal of the American Chemical Society*. **131** (17), 6050-6051, (2009).

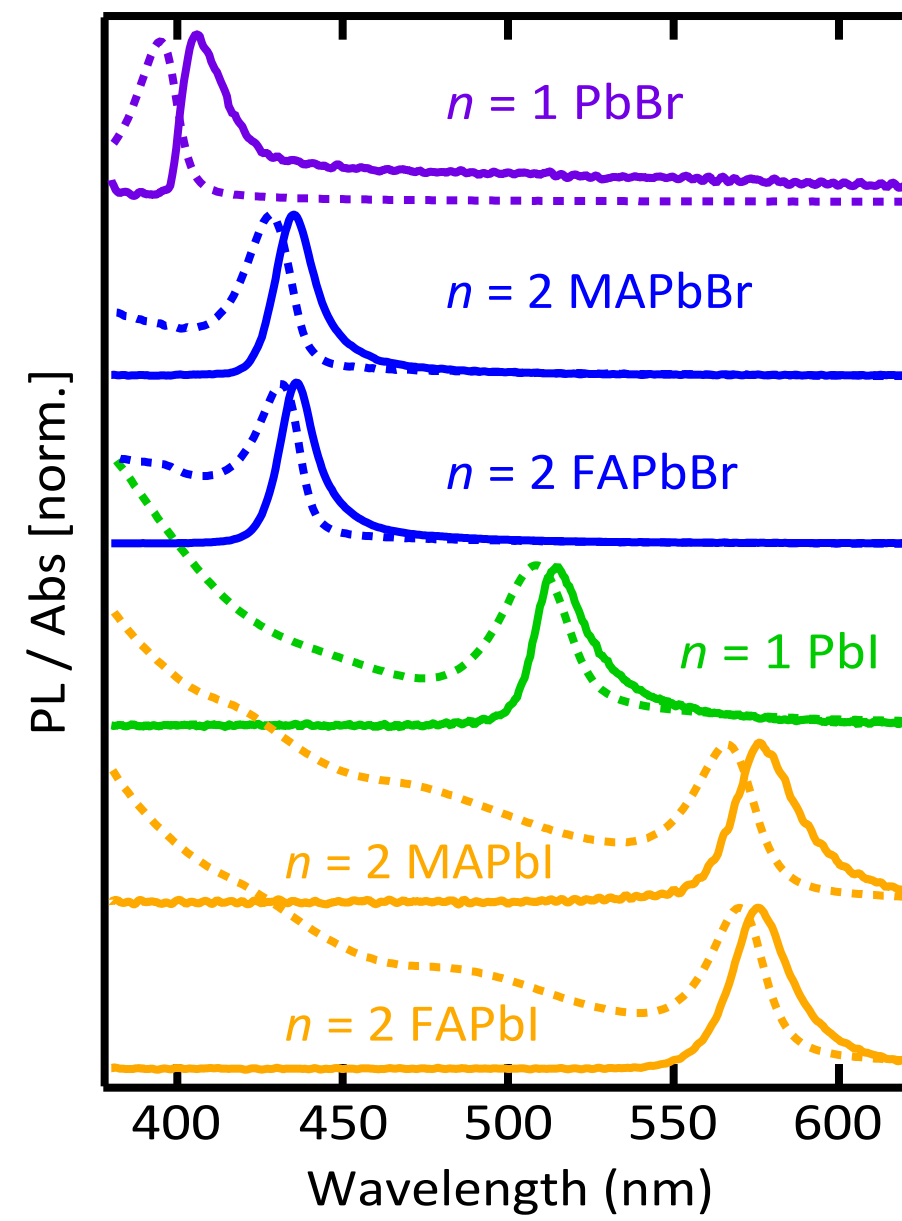
54 Bischak, C. G. *et al.* Origin of reversible photoinduced phase separation in hybrid perovskites. *Nano Letters*. **17** (2), 1028-1033, (2017).

55 Mauck, C. M., Tisdale, W. A. Excitons in 2D Organic–Inorganic Halide Perovskites. *Trends in Chemistry*. 10.1016/j.trechm.2019.04.003, (2019).

56 Gong, X. *et al.* Electron-phonon interaction in efficient perovskite blue emitters. *Nat.*

441 *Mater.* **17** (6), 550-556, (2018).
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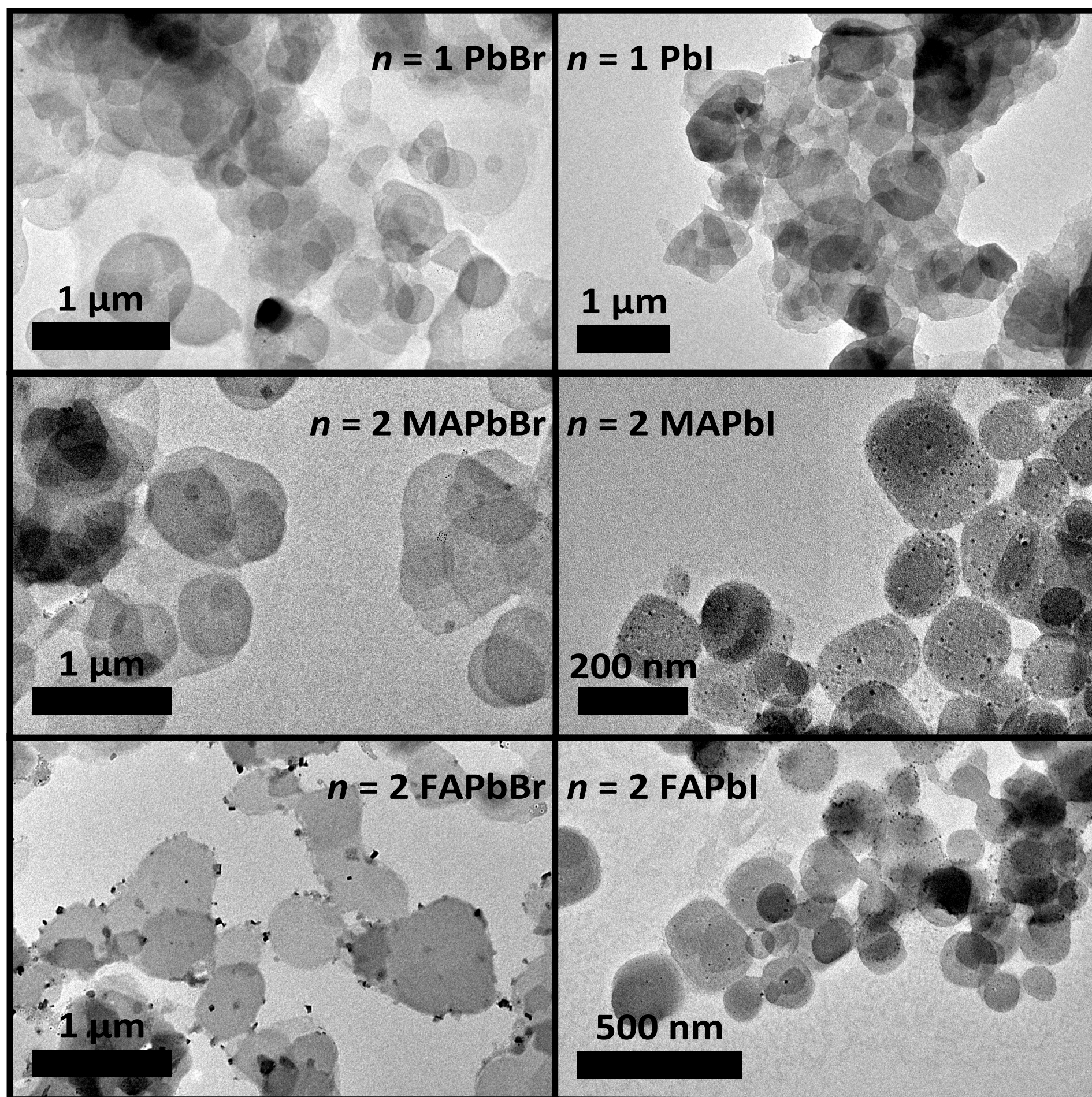
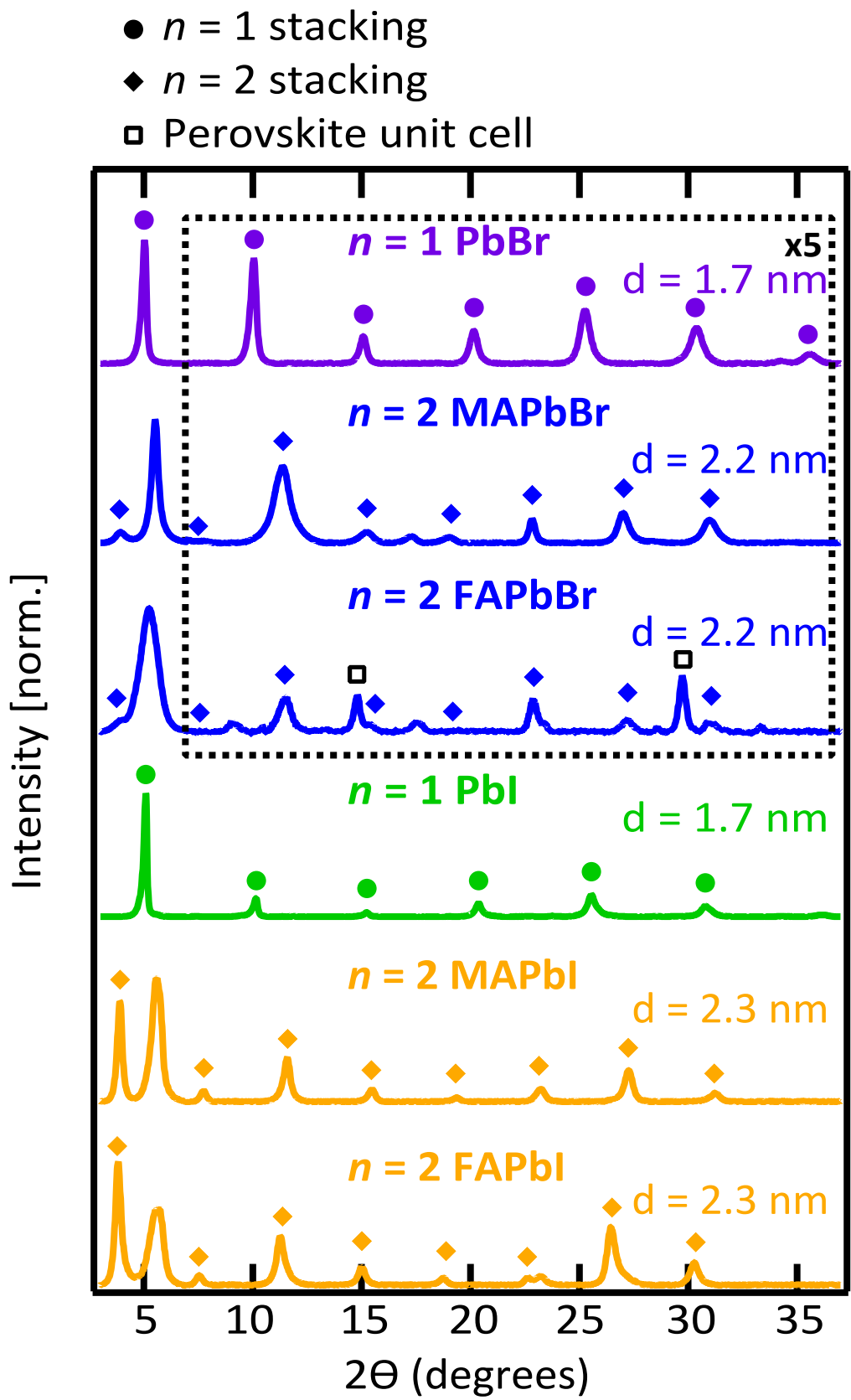
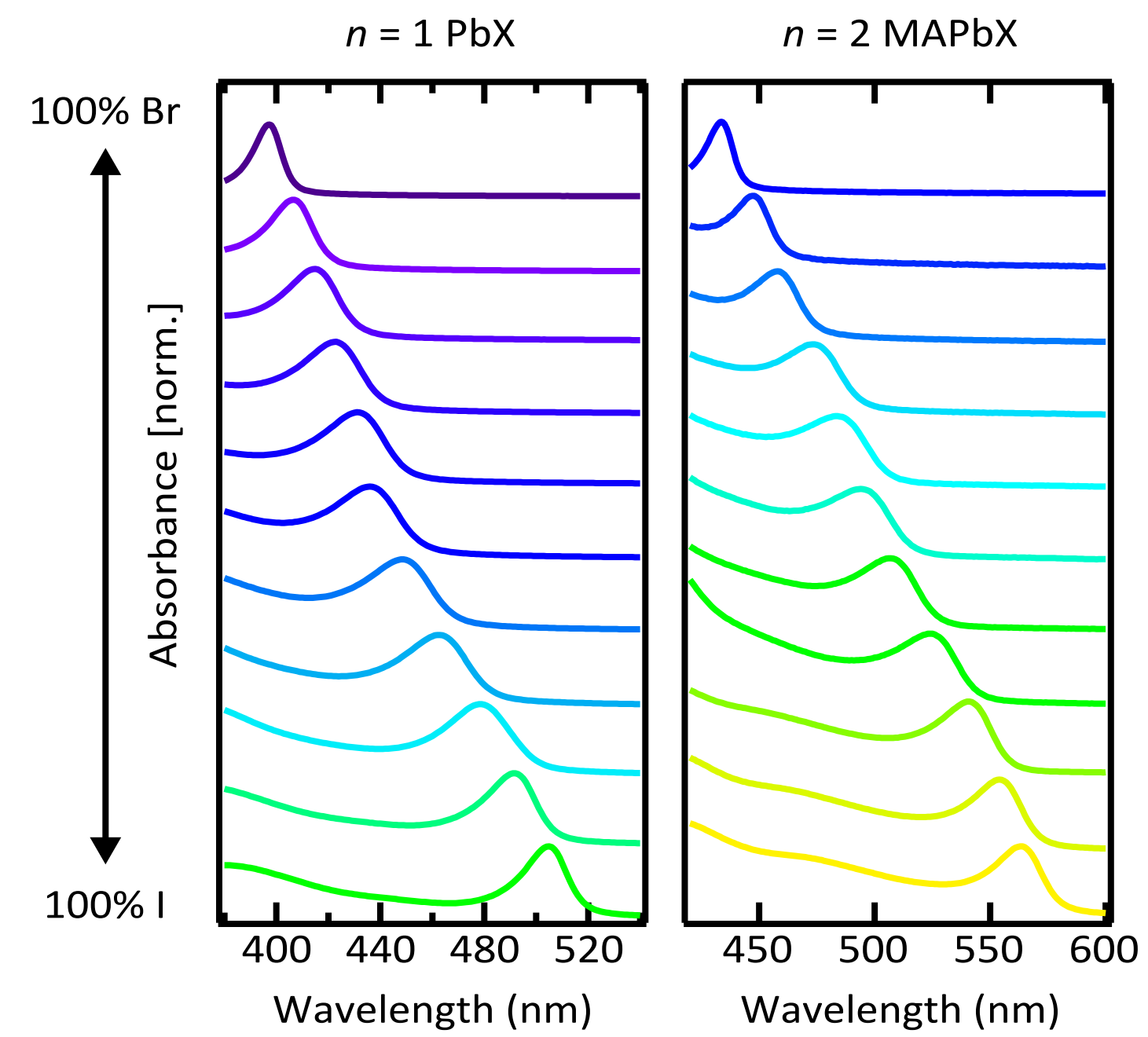
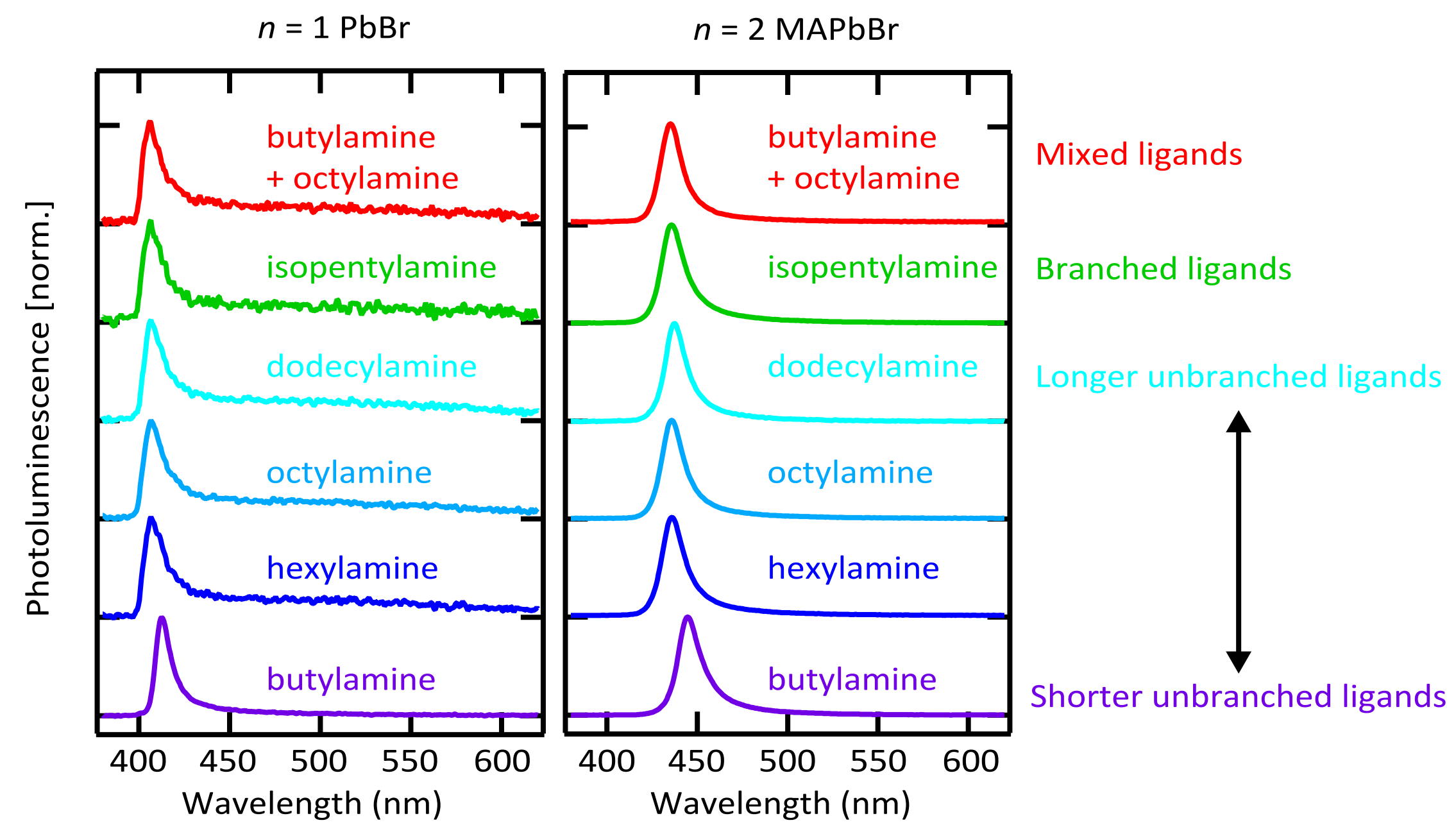


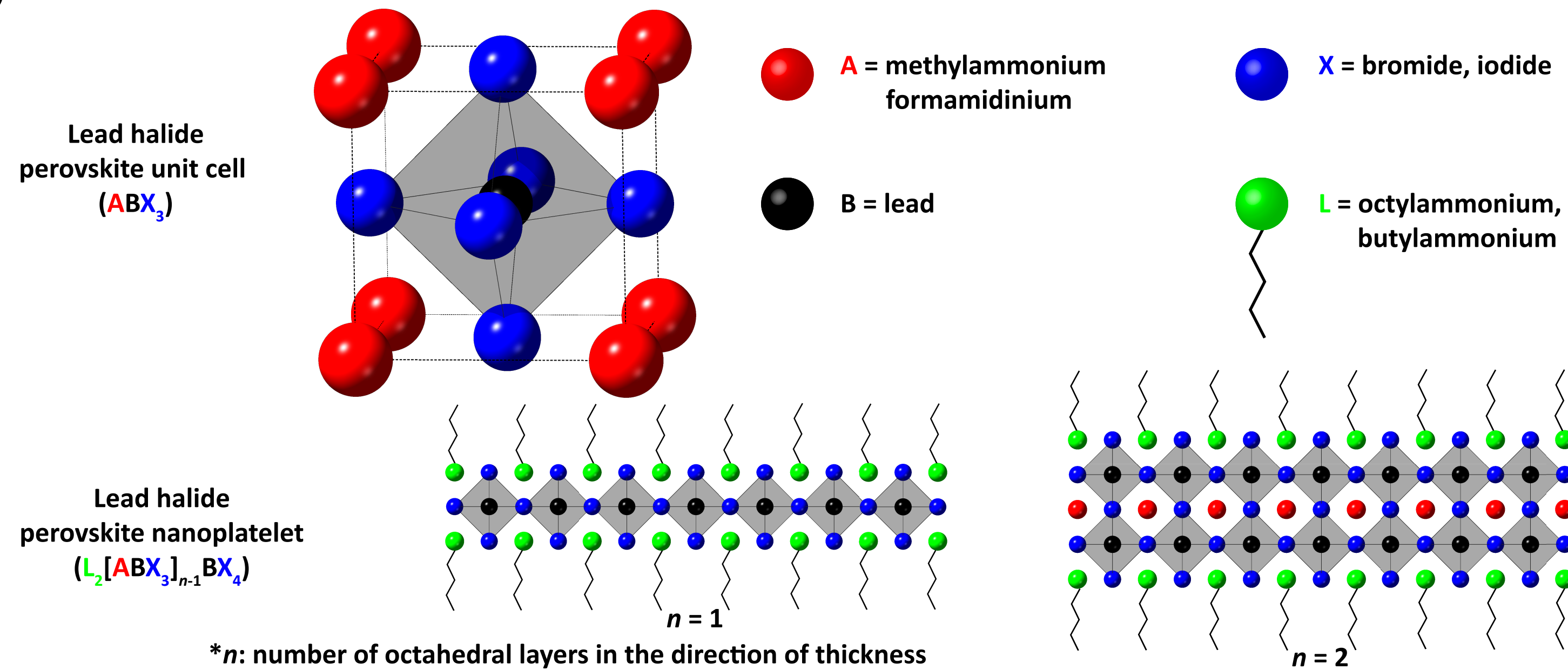
Figure 5



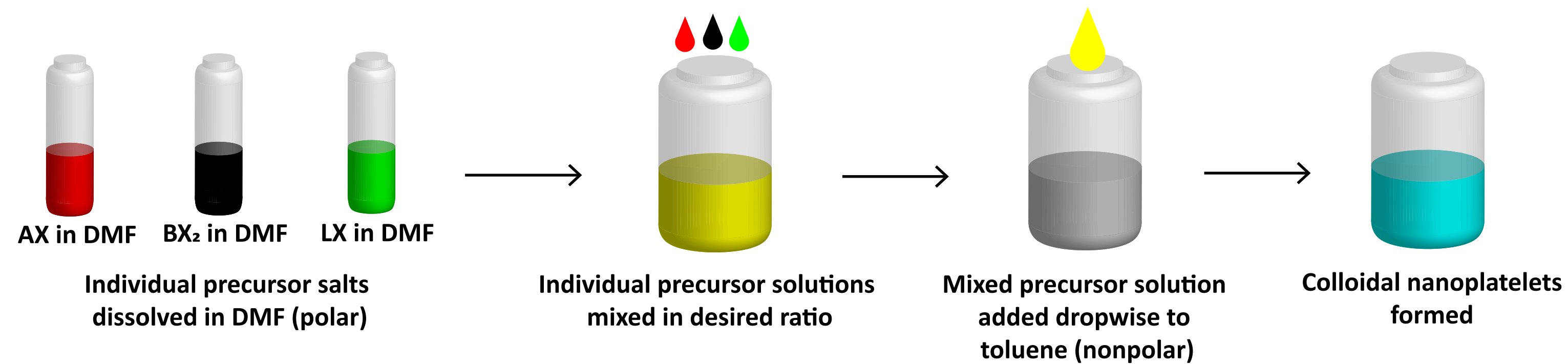




(a)



(b)



	MABr	FABr	PbBr ₂	BABr	OABr	MAI	FAI	PbI ₂
<i>n</i> = 1 PbBr	0	0	1	1	1	0	0	0
<i>n</i> = 2 FAPbBr	0	1	2	5	5	0	0	0
<i>n</i> = 2 MAPbBr	1	0	2	5	5	0	0	0
<i>n</i> = 1 PbI	0	0	0	0	0	0	0	1
<i>n</i> = 2 FAPbI	0	0	0	0	0	0	1	2
<i>n</i> = 2 MAPbI	0	0	0	0	0	1	0	2

BAI	OAI
0	0
0	0
0	0
1	1
5	5
5	5

Name of Material/ Equipment	Company	Catalog Number
Equipment		
365nm fiber-coupled LED	Thorlabs	M365FP1
Avantes fiber-optic spectrometer Cary 5000	Avantes	AvaSpec-2048XL
FEI Tecnai G2 Spirit Twin TEM	Agilent Technologies	
PANalytical X'Pert Pro MPD	FEI Company	
	Malvern Panalytical	
Materials		
n-butylammonium bromide (BABr)	GreatCell Solar	MS305000-50G
n-butylammonium chloride (BACl)	Fisher Scientific	B071025G
n-butylammonium iodide (BAI)	Sigma-Aldrich	805874-25G
N,N-dimethylforamide (DMF)	Sigma-Aldrich	227056-1L
n-dodecylammonium bromide (DDABr)	GreatCell Solar	MS300880-05
formamidinium bromide (FABr)	GreatCell Solar	MS350000-100G
formamidinium iodide (FAI)	GreatCell Solar	MS150000-100G
n-hexylammonium bromide (HABr)	GreatCell Solar	MS300860-05
lead bromide (PbBr2)	Sigma-Aldrich	398853-5G
lead chloride (PbCl2)	Sigma-Aldrich	268-690-5G
lead iodide (PbI2) solution	Sigma-Aldrich	795550-10ML
methylammonium bromide (MABr)	GreatCell Solar	MS301000-100G
methylammonium iodide (MAI)	GreatCell Solar	MS101000-100G
n-octylammonium bromide (OABr)	GreatCell Solar	MS305500-50G
n-octylammonium chloride (OACl)	Fisher Scientific	O04841G
n-octylammonium iodide (OAI)	GreatCell Solar	MS105500-50G
iso-pentylammonium bromide (i-PABr)	GreatCell Solar	MS300710-05
toluene	Sigma-Aldrich	244511-1L

Comments/Description

Excitation source (Photoluminescence)

Photoluminescence detector (Photoluminescence spectra)

UV-Vis spectrophotometer (Absorption spectra)

Transmission electron microscopy (TEM) operating at 120kV

X-ray diffraction (XRD) operating at 45 kV and 40 mA with a copper radiation source.

butylamine hydrochloride

Anhydrous, 99.8%

.99.999%

98%

0.55M in DMF

octylamine hydrochloride

Anhydrous, 99.8%



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Author(s):

Seung Kyun Ha, William A. Tisdale

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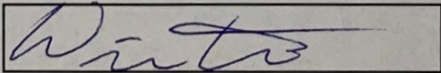
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Response to the Editor

Editorial Comments

1. Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues.

Author response: We appreciate the editor's reminder. We thoroughly proofread the manuscript. There are still some words that Microsoft Word do not recognize (red-lined words in the manuscript such as 'nanoplatelets'), but those words are widely used in the field of perovskites/semiconductor nanoparticles, and we believe that the readers will not have any difficulty in understanding the manuscript.

2. Please do not use more than one note for each step.
3. Please avoid long notes/steps (more than 4 lines)

Author response: We appreciate the suggestion and modified the protocol to make sure that no more than one note is used for each step. Also, we did our best to make notes/steps concise. There are a few steps or notes that slightly exceed 4 lines, but it was inevitable to include all the necessary information.

4. Figure 5: Please provide a short description of the figure in Figure Legend.
5. Figure 6: Please provide a short description of the figure in Figure Legend.

Author response: Thanks to the editor's suggestion, we have added a short sentence in the legends of Figure 2, 3, 4, 5, 6 and 7, describing the main point for each figure.

Supporting Information for:

Facile Synthesis of Colloidal Lead Halide Perovskite Nanoplatelets via Ligand-Assisted Reprecipitation

*Seung Kyun Ha, William A. Tisdale**

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, 02139, USA

Nanoplatelets	PLQY
$n = 1$ PbBr	< 0.1 %
$n = 2$ MAPbBr	6.8 %
$n = 2$ FAPbBr	5.8 %
$n = 1$ PbI	0.2 %
$n = 2$ MAPbI	0.9 %
$n = 2$ FAPbI	0.7 %

Table S1. Photoluminescence quantum yields (PLQY) of as-synthesized colloidal perovskite nanoplatelets in toluene.

Note: Samples were excited using a 405 nm LED (Thorlabs) except $n = 1$ PbBr. $n = 1$ PbBr nanoplatelet solution was excited using a 365 nm LED (Thorlabs), but sample emission peak was too weak and below the detection limit of the setup.

Nanoplatelets	Ligands	MABr	PbBr ₂	BABr	HABr	OABr	DDABr	i-PABr
$n = 1$ PbBr	butylamine	0	1	2	0	0	0	0
$n = 1$ PbBr	hexylamine	0	1	0	2	0	0	0
$n = 1$ PbBr	octylamine	1	1	0	0	2	0	0
$n = 1$ PbBr	dodecylamine	0	1	0	0	0	2	0
$n = 1$ PbBr	isopentylamine	0	1	0	0	0	0	2
$n = 1$ PbBr	butylamine + octylamine	0	1	1	1	0	0	0
$n = 2$ MAPbBr	butylamine	1	2	3	0	0	0	0
$n = 2$ MAPbBr	hexylamine	1	2	0	5	0	0	0
$n = 2$ MAPbBr	octylamine	1	2	0	0	10	0	0
$n = 2$ MAPbBr	dodecylamine	1	2	0	0	0	5	0
$n = 2$ MAPbBr	isopentylamine	1	2	0	0	0	0	5
$n = 2$ MAPbBr	butylamine + octylamine	1	2	5	5	0	0	0

Table S2. Formulation guidelines for perovskite nanoplatelet precursor solutions with different ligand species. Numbers in the table indicate the volumetric equivalents of each precursor solutions (columns) that should be combined to achieve the targeted nanoplatelets (rows), according to the concentration specifications in the protocol text.

Abbreviations: MABr: methylammonium bromide, PbBr₂: lead bromide, BABr: butylammonium bromide, HABr: hexylammonium bromide, OABr: octylammonium bromide, DDABr: dodecylammonium bromide, i-PABr: isopentylammonium bromide

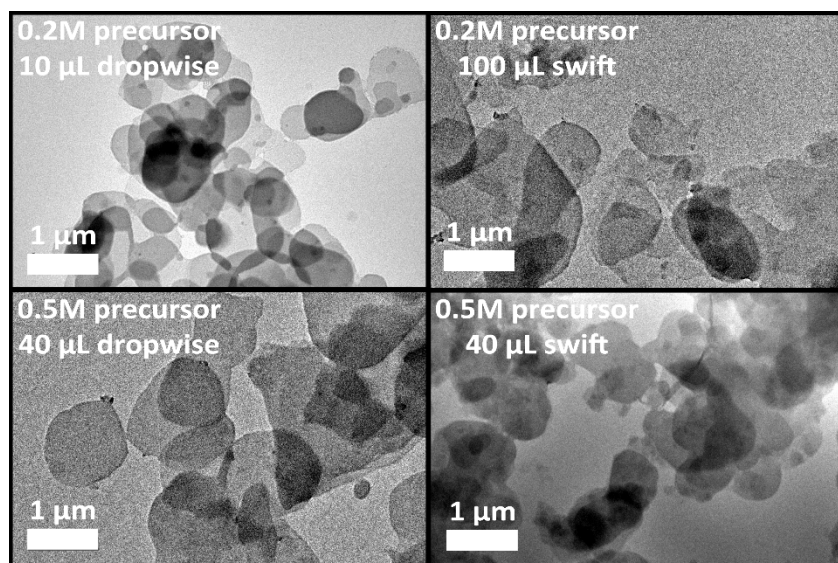


Figure S1. Transmission electron microscopy (TEM) images of $n = 2$ MAPbBr nanoplatelets synthesized by different injection methods with varying amounts of precursor solution.

- ‘0.2M and 0.5M precursor’ refer to MABr:PbBr₂:BABr:OABr = 1:2:5:5 mixture of 0.2M and 0.5M individual (MABr, PbBr₂, BABr and OABr) precursor solutions, respectively. For dropwise and swift injection of precursor solution, a pipette and a syringe was used, respectively. $n = 2$ MAPbBr nanoplatelets synthesized by different injection methods with varying amounts of precursor solutions did not show noticeable differences in their shape, size and polydispersity.

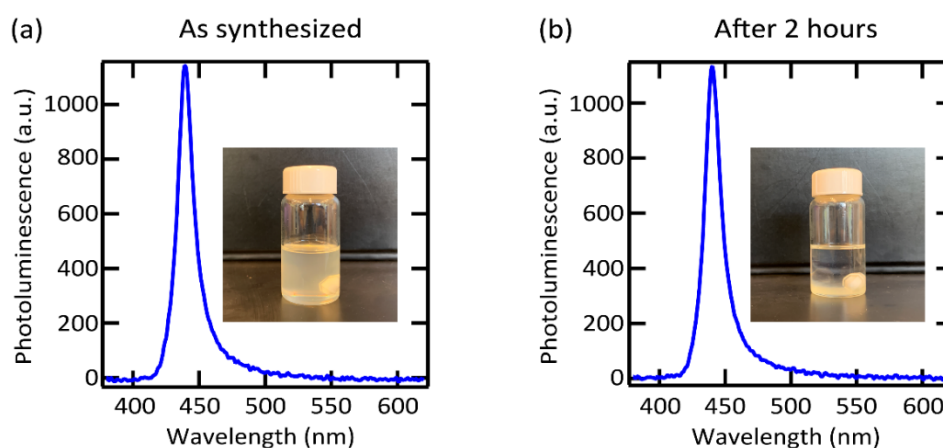


Figure S2. Photoluminescence spectra of (a) as-synthesized $n = 2$ MAPbBr nanoplatelet solution and (b) after nanoplatelet precipitation and redispersion. (Insets: Images of (a) as-synthesized and (b) precipitated perovskite nanoplatelet solutions.)

- To maximize the visibility of nanoplatelet precipitation, 100 µL of 0.2M precursor solution, instead of standard 10 µL, was injected dropwise into 10 mL toluene for this experiment. PL spectrum taken from redispersed solution after precipitation still showed quantum-confined $n = 2$ MAPbBr nanoplatelet emission with the same intensity and confirmed that precipitation occurred due to the aggregation of the nanoplatelets instead of bulk (3D) perovskite formation.

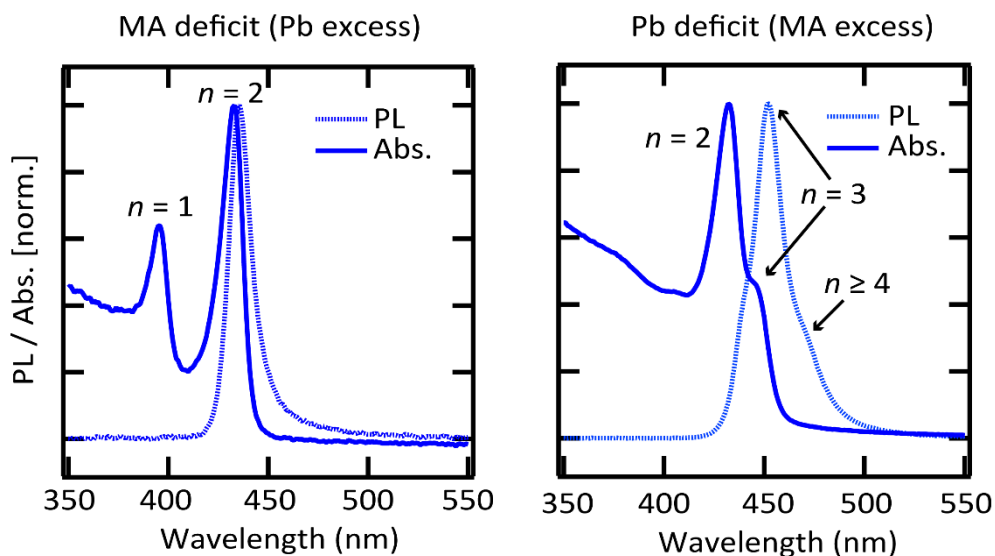


Figure S3. Example photoluminescence and absorption spectra of MA-deficit and Pb-deficit attempts on synthesizing $n = 2$ MAPbBr nanoplatelets.

- MA and Pb deficit (Compared to the stoichiometric ratio of $\text{MABr}:\text{PbBr}_2 = 1:2$ for $n = 2$ MAPbBr nanoplatelets) resulted in the formation of thinner and thicker nanoplatelets, respectively, along with intended $n = 2$ MAPbBr nanoplatelets.

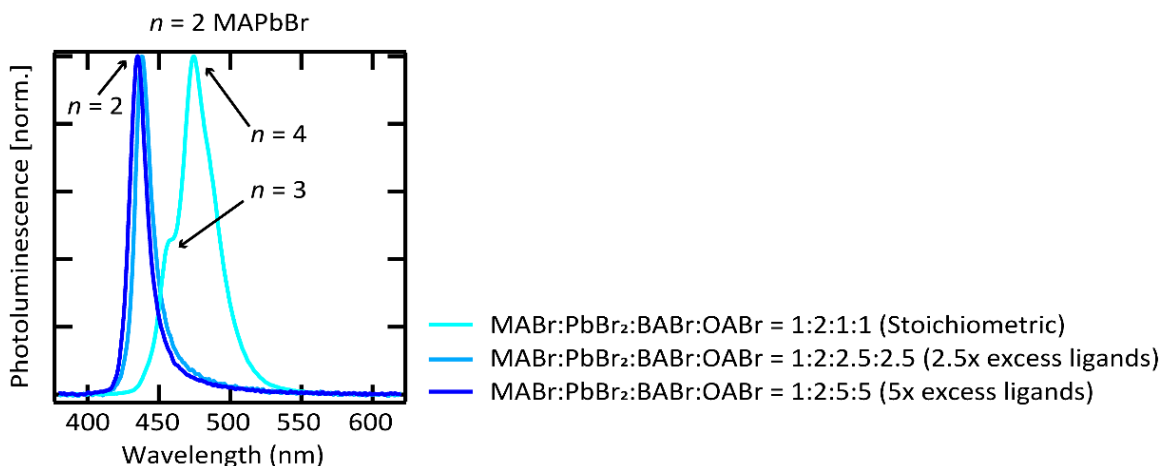


Figure S4. Necessity of adding excess ligands in the precursor solution for precise thickness control.

- Presence of excess ligands in the precursor solution was proven to be crucial to prevent the formation of thicker nanoplatelets and ensure thickness homogeneity of the system.

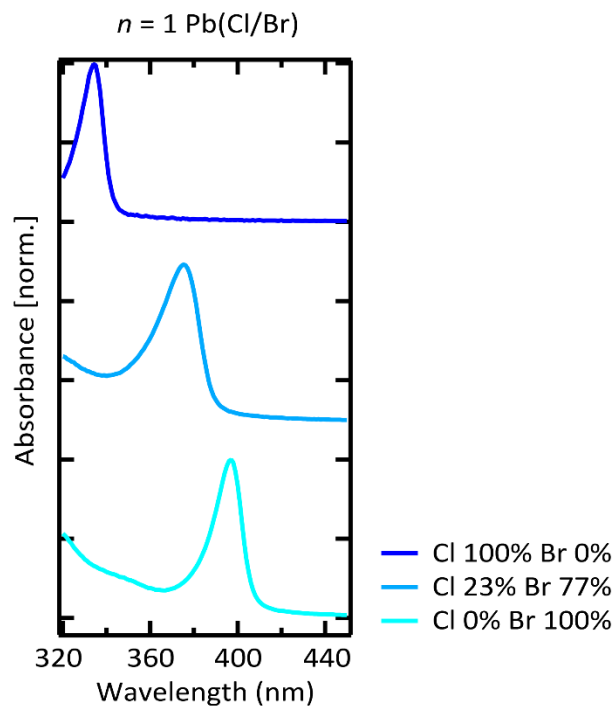


Figure S5. Normalized absorption spectra of $n = 1$ $\text{Pb}(\text{Cl}/\text{Br})$ nanoplatelet solutions.

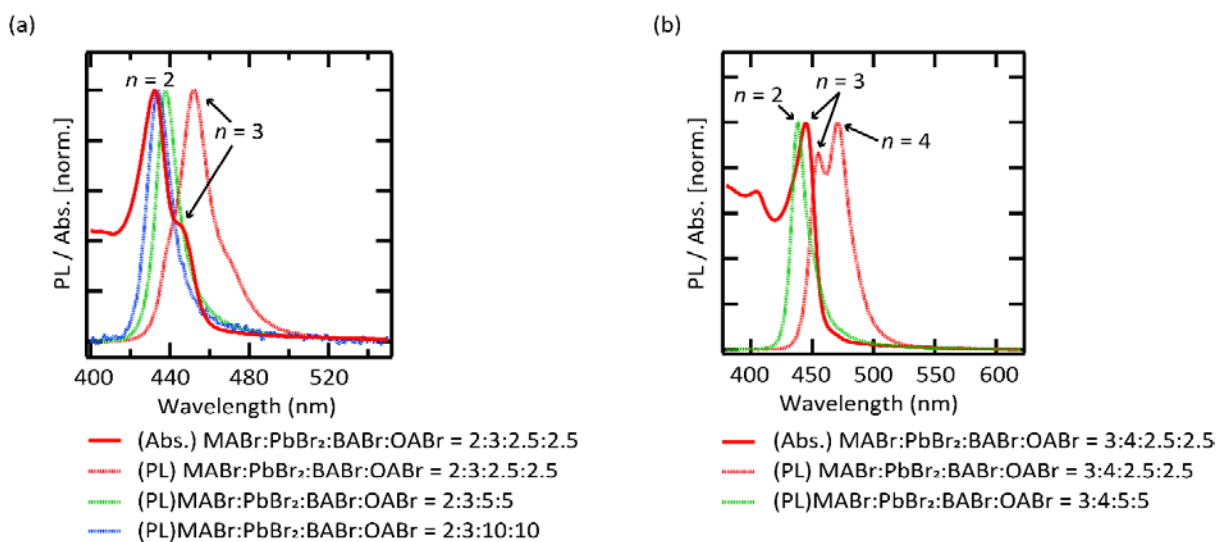


Figure S6. Unsuccessful attempts on the synthesis of (a) $n = 3$ and (b) $n = 4$ MAPbBr nanoplatelets.

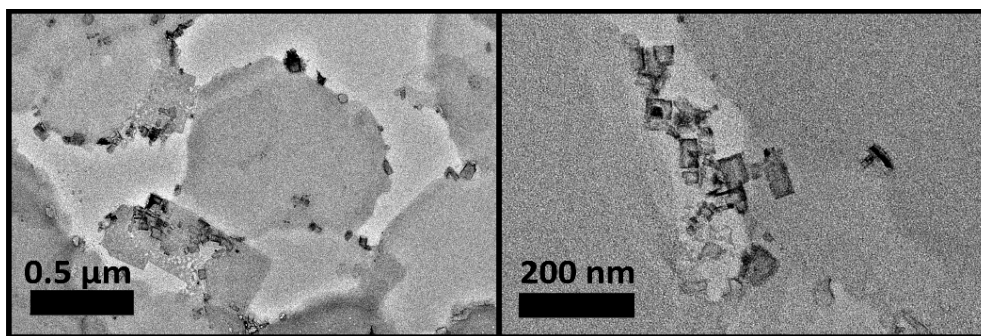


Figure S7. Transmission electron microscopy (TEM) images of $n = 2$ FAPbBr nanoplatelets.

- Dot-like structures observed in $n = 2$ FAPbBr TEM image in Figure 4 seemed to be smaller nanoplatelets.

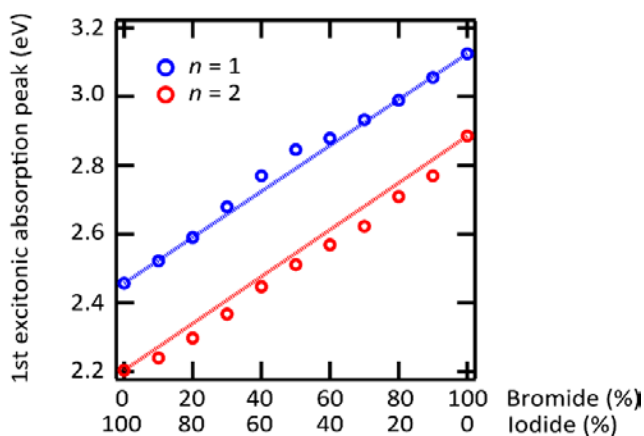


Figure S8. First excitonic absorption peak energy as a function of halide composition in the precursor solution for $n = 1$ PbX and $n = 2$ MAPbX nanoplatelets. Dotted lines show the straight line between bromide-only and iodide-only nanoplatelet excitonic absorption energies.

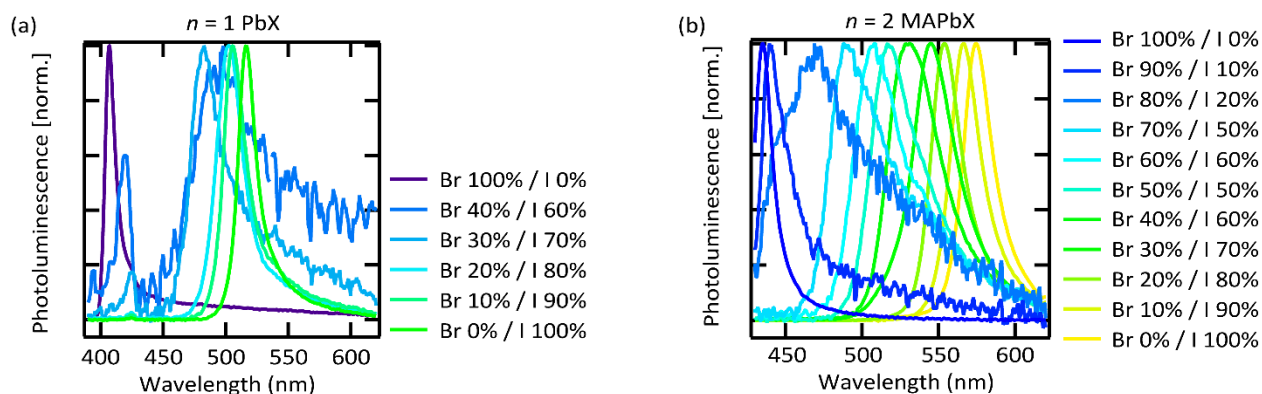


Figure S9. Normalized photoluminescence spectra of colloidal (a) $n = 1$ PbX and (b) $n = 2$ MAPbX perovskite nanoplatelet solutions with mixed halides.

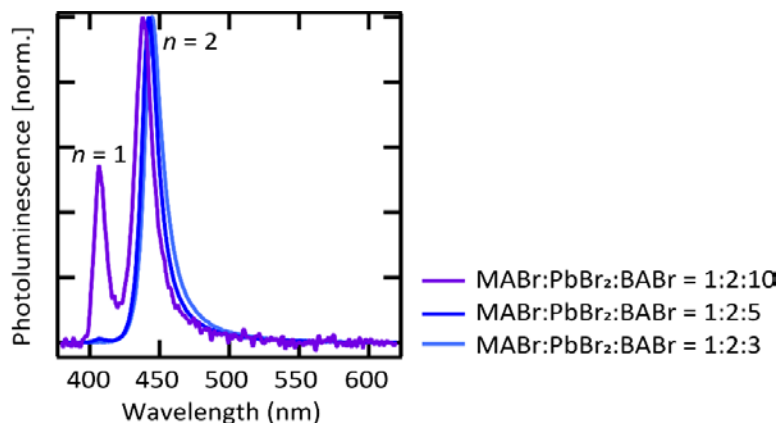


Figure S10. Normalized photoluminescence spectra of colloidal lead bromide perovskite nanoplatelet solution with varying amounts of butylammonium bromide ligands added in the precursor solution.

- When butylammonium was employed as the only ligand species in the system, standard ratio of MABr:PbBr₂:LBr = 1:2:10 (L: ligands) resulted in the formation of both $n = 1$ and $n = 2$ nanoplatelets. Ratio had to be modified to MABr:PbBr₂:LBr = 1:2:3 to retain the thickness purity in the system. In general, when new ligand species is employed, it is likely that the relative amount of ligands in the precursor solution may need to be slightly adjusted for precise thickness control.

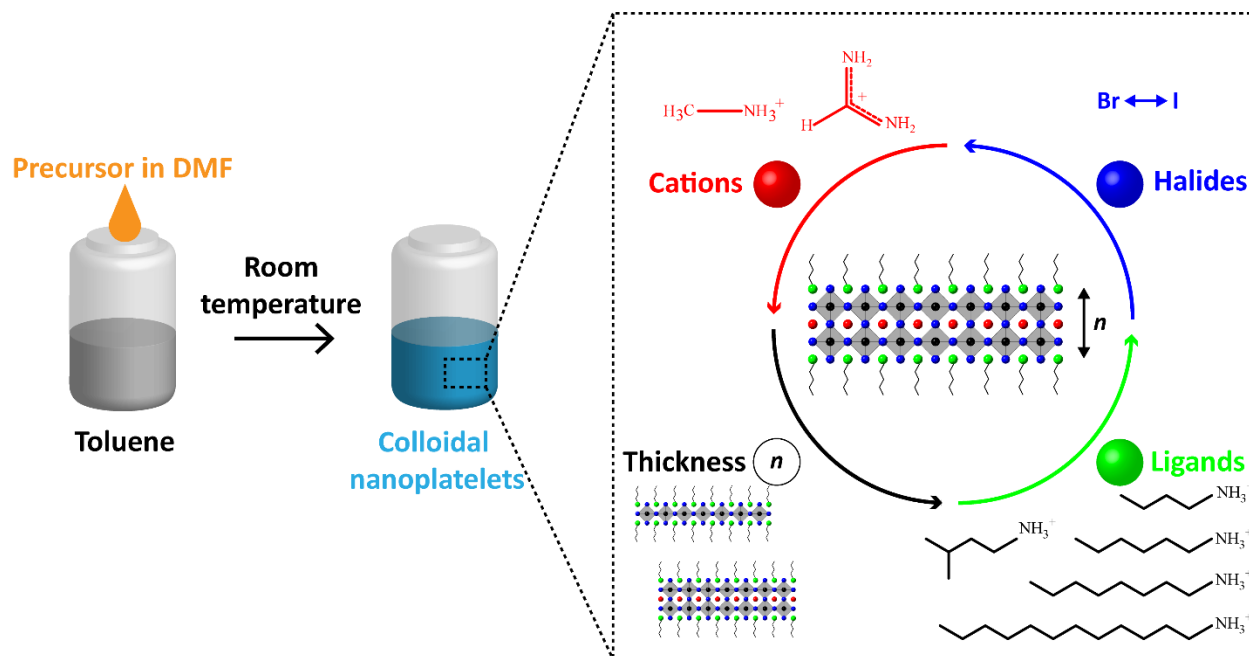


Figure S11. Schematic illustration of the synthetic protocol and its universal applicability in synthesizing colloidal lead halide perovskite nanoplatelets with various thicknesses and compositions.



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