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Zwitterionic Block Copolymers for the Synthesis and Stabilization of Perovskite Nanocrystals

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Abstract: Traditional hot injection methods for the preparation of cesium lead halide perovskite nanocrystals ($CsPbX_3$ PNCs, where X=Cl, Br, or I) rely on small molecule surfactants to produce PNCs with cube, plate, or rod-like morphologies. Here, we describe a new method whereby zwitterionic block copolymers are employed as macromolecular ligands in PNC synthesis, affording PNCs with excellent colloidal stability, high photoluminescence quantum yield, and in some cases distinctly non-cubic shapes. The block copolymers used in this study – composed of a poly(*n*-butyl methacrylate) hydrophobic block and zwitterionic methacrylate hydrophilic blocks – dissolve in useful solvents for PNC growth despite containing large mole percentages of zwitterionic groups. PNCs prepared with block copolymer ligands were found to disperse and retain their fluorescence in a range of polar organic solvents and were amenable to direct integration into optically transparent nanocomposite thin films with high PNC content.

Introduction

All-inorganic lead halide perovskite nanocrystals ($CsPbX_3$, where X = Cl, Br, I or mixtures thereof) are an emerging class of semiconductor nanomaterials that exhibit intense, narrow-band photoluminescence (PL) over the entire visible spectrum. In contrast to metal chalcogenide quantum dots (QDs), $CsPbX_3$ nanocrystals have a low lattice energy and ionic crystal structure.[1] These features open routes to room-temperature synthesis and reprecipitation, simplifying the preparation of perovskite nanocrystals (PNCs) on larger scales. However, their weakly-bound ionic lattice gives rise to PNC lability and temporal instability. Despite their large number of cesium and halide vacancies, and the presence of a soft, dynamically disordered lattice, $CsPbX_3$ PNCs are exceptionally luminescent owing to 1) the perovskite framework, which precludes formation of interstitial and anti-site defects that would otherwise lead to deep trap states, and 2) antibonding character in the valence band (VB) and spin-orbit coupling in the conduction band (CB), which places the vacancy-induced traps in the VB, CB, or at gap edges.[2] These features obviate the need for surface passivation steps, such as those frequently employed for stabilizing transition metal chalcogenide QDs, and thus reflect significant potential advantages of PNCs.[2]

While $CsPbX_3$ PNCs are exciting candidates for luminescent displays, optical information processing, and lasing technologies, their relative instability hinders progress in these areas. Most notably, their ionic bonding leads to degradation in polar solvents and dramatically alters their surface chemistry. PNCs synthesized with oleylammonium salts as capping agents have a dynamic, weakly bound ligand shell,[3] which limits their stability against sintering and PL reduction during purification. Much like prior scenarios with CdSe or InP QDs, robust schemes for PNC stabilization are needed to realize their full potential. To this end, several strategies have been described, including atomic layer deposition and sol-gel methods to encapsulate $CsPbX_3$ PNCs within a thin dielectric layer;[4,5] embedding PNCs within a gas/moisture-impermeable polymer;[6,7] or modifying the PNC surface and/or ligand chemistry.[8] Recently, Kreig, et al. reported that zwitterionic capping ligands are more tightly bound to the PNC surface relative to conventional oleyl amine (OLA) and oleic acid (OA) surfactant pairs.[9] Our group embedded PNCs into random copolymers containing pendant zwitterions, combining the film-forming and barrier properties of polymeric alkyl methacrylates with the strong, static ligand-binding of sulfobetaine (SB) and phosphorylcholine (PC) groups.[10] This afforded highly luminescent, well-dispersed, and optically transparent PNC-polymer nanocomposites, but was limited to polymers containing small amounts of zwitterion (i.e., <5 mol%), above which the polymers did not dissolve in useful solvents for PNC growth. Nevertheless, it is increasingly evident that zwitterions, in the form of both polymers and small molecule surfactants, hold potential to hone the surface chemistry and stability of nanoscale perovskites and broaden their application range.

While the above-cited work entailed post-synthetic polymer-PNC ligand exchange, polymers have also been used directly for PNC growth. For example, we utilized ammonium bromide-terminated polystyrene and polyfluorene ligands in hot injection syntheses of $CsPbBr_3$ PNCs,[11] while Meyns, et al.

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/chem.202200409 employed poly(maleic anhydride-alt-1-octadecene).[12] In contrast, while block copolymers (BCPs) may template the synthesis of transition metal chalcogenide QDs and other NPs,[13] only a few accounts describe BCPs in all-inorganic $CsPbX_3$ PNC syntheses, including star-like poly(acrylic acid-b-styrene)[14–16] and linear PS-*b*-P2VP copolymers.[17] Here, we use BCPs *directly in the synthesis* of $CsPbBr_3$ PNCs, in which the copolymers contain a poly(n-butyl methacrylate) (PBMA) hydrophobic block, and a poly(sulfobetaine methacrylate) (PSBMA) or poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) zwitterionic block. This strategy merges the strong affinity of zwitterions for PNCs with BCP structures that allow inclusion of high zwitterion contents (*up to 21 mol%*) while remaining soluble in useful solvents for high temperature PNC synthesis. As will be described, we found that injection of a tri-*n*-octylphosphine-bromine complex ($TOP{\cdot}Br_2$) into a hot solution containing the BCP and cesium and lead oleate salts produced strongly luminescent $CsPbBr_3$ PNCs. PNCs prepared in this manner exhibited morphological differences relative to those synthesized in the presence of small molecule ligands. Moreover, the BCP "additive" enabled PNC dispersion in a wide range of organic solvents, including polar solvents such as isopropanol and tetrahydrofuran, which would irreversibly precipitate or dissolve small molecule-capped PNCs.

Results and Discussion

As shown in Figure 1, PBMA-*b*-PSBMA and PBMA-*b*-PMPC BCPs were prepared by reversible addition-fragmentation chain-transfer (RAFT) polymerization to yield polymers with a range of block ratios and molecular weights. The PBMA block ($PBMA_n$) was prepared first, using 4-cyano-4-dodecylthiocarbonothioyl thiopentanoic acid as the chain-transfer agent. Two PBMA macroRAFT agents (Table 1, Entries 1 and 2) were prepared with number-average molecular weights (M_n) of 13.6 and 21.0 kDa, and these polymers were used to access PBMA-*b*-PSBMA with similar block ratios and different overall chain lengths. Chain-extension to yield the zwitterionic block was best performed in a solution of hexafluoroisopropanol (HFIP), initiating with 2,2'-azobis(2-(2-imidazolin-2-yl)propane)dihydrochloride (VA-044). For the lower molecular weight BCPs, zwitterion contents ranging from 4.1 to 18.0 mol% were achieved by adjusting the SBMA feed ratio. Notably, when the initial SBMA concentration exceeded 0.5 M (>0.77 : 1 mol ratio SB:BMA feed), significant broadening of the molecular weight distribution was observed, and the resulting polymers failed to form homogeneous solutions in TFE. Nonetheless, all the BCPs in Table 1 dissolved in $CHCl_3$ and toluene at room temperature, and the disappearance of resonances associated with the PSBMA block at 4.51 and 3.72-2.33 ppm in ^1H NMR spectra of $PBMA_{13.6}SB_{2.8}$, recorded consecutively in d_3-TFE and $CDCl_3$ (Figure S6), suggests inverse micelle formation in the latter solution environment (i.e., where the zwitterionic block is insoluble). Additional characterization by dynamic light scattering (DLS) revealed a consistent increase in *Z*-average hydrodynamic diameter (d_Z) with zwitterion block length (Figure 1). Thus, compared to PBMA-*r*-PSBMA copolymers, which have limited solubility in $CHCl_3$ or toluene at low SBMA content (≤5.5 mol%), reorganization of the polymer microstructure into blocks greatly enhances solubility and allows at least 3 times greater zwitterion content to be introduced to PNC solutions.

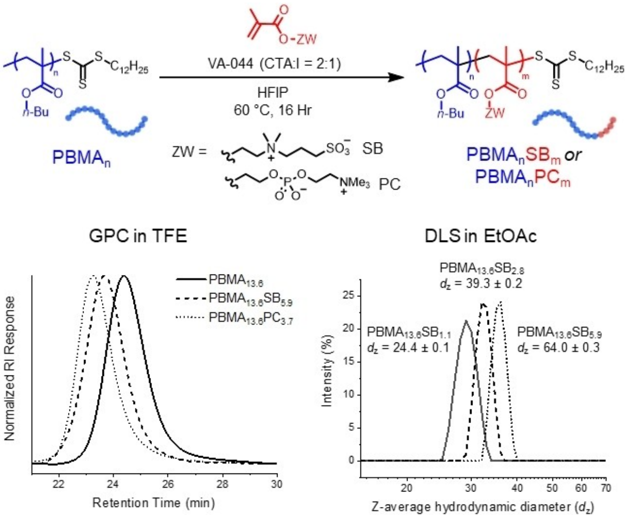

Figure 1. Synthesis of BCPs starting from a PBMA macroRAFT agent ($PBMA_n$). GPC shows narrow, uniform molecular weight distributions and DLS performed on 5 mg/mL solutions in ethyl acetate indicates the presence of nanoscale structures with *Z*-average hydrodynamic diameters that trend with zwitterion block length.

As outlined in Figure 2, the zwitterion-containing BCPs were employed in place of small molecule surfactants in the synthesis of $CsPbBr_3$ PNCs. In initial experiments using $PBMA_{13.6}SB_{2.8}$ (Table 1, *Entry 4*), the SB content was adjusted to ensure the presence of sufficient zwitterionic functionality for effective PNC growth and stabilization. In a typical procedure, the BCP was dissolved at a concentration of ~1 mM in a mesitylene solution of cesium and lead oleate salts at room temperature and heated to 130 °C, followed by rapid injection of a $TOP{\cdot}Br_2$ slurry in toluene. This yielded $CsPbBr_3$ PNCs that dispersed as a clear, fluorescent green solution, without visible aggregates or precipitated solids; PNCs prepared in this way remained colloidally stable for several months when stored under a $N_{2(g)}$

Table 1. Summary of BCPs prepared from the PBMA MacroRAFT agents in Entries 1 and 2 to yield copolymers with different block lengths and zwitterion compositions.

Entry	Description	Yield[a]	mol% zwitterion	M_n[b]	PDI[b]
1	$PBMA_{13.6}$	88%	–	13.6 kDa	1.08
2	$PBMA_{21.0}$	72%	–	21.0 kDa	1.13
3	$PBMA_{13.6}SB_{1.1}$	72%	4.1%	15.1 kDa	1.08
4	$PBMA_{13.6}SB_{2.8}$	80%	9.4%	15.1 kDa	1.06
5	$PBMA_{13.6}SB_{5.9}$	78%	18.0%	17.3 kDa	1.10
6	$PBMA_{13.6}PC_{1.5}$	79%	5.4%	18.1 kDa	1.11
7	$PBMA_{21.0}SB_{3.9}$	66%	8.7%	23.4 kDa	1.17
8	$PBMA_{21.0}SB_{10.8}$	74%	20.7%	32.1 kDa	1.24

[a] Yields for entries 3–8 were calculated based on % zwitterion content measured by ^1H NMR spectroscopy. [b] Molecular weight and PDI values were estimated by GPC in TFE relative to poly(methyl methacrylate) standards.

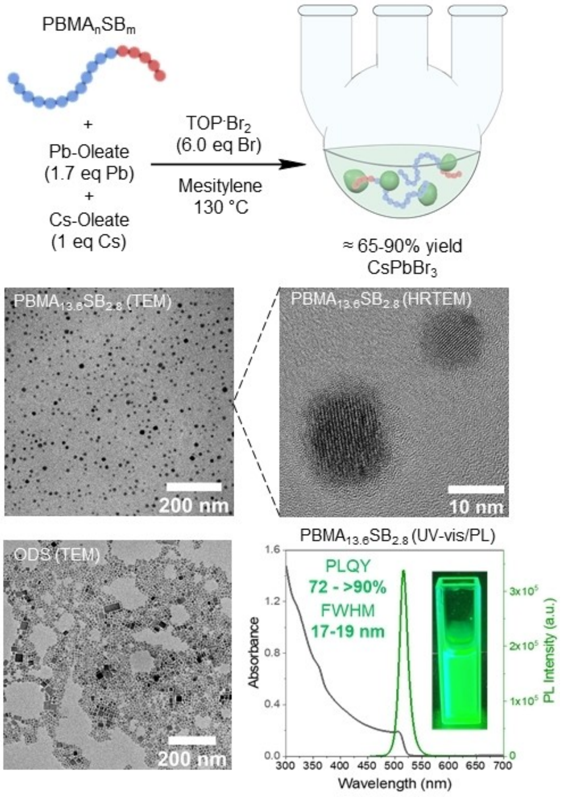

Figure 2. Zwitterion-containing BCP surfactants for synthesizing $CsPbBr_3$ PNCs. TEM and HRTEM images comparing PNCs prepared with $PBMA_{13.6}SB_{2.8}$ and ODS ligands. UV-vis and PL emission ($\lambda_{ex}=450$ nm) of PNCs with BCP ligands as solutions in toluene. Ranges for isolated yields, PLQY and FWHM refer to results for all BCP ligands including $PBMA_{13.6}SB_{2.8}$.

atmosphere with minor sedimentation. The PNCs obtained resembled those synthesized using small molecule zwitterions, with high isolated yields (~70%) and high quantum yields (PLQYs), and a slight red shift (5-10 nm) in the peak PL emission.

Interestingly, visualization of these PNCs by transmission electron microscopy (TEM) revealed non-cubic structures, typically with misshapen or rounded edges (Figure 2). To date, the most common morphologies encountered for $CsPbX_3$ nanocrystals are cubes, sheets, or wires; other shapes are observed less frequently.[14,18] In addition, the PNCs synthesized using these BCPs appear to be evenly dispersed after drop-casting onto a TEM grid, whereas the ODS-capped PNCs collect into extended, edge-on tiles (Figure 2). Using small molecule zwitterions in place of traditional amine/carboxylic acid ligands more than doubles the isolated yield of $CsPbBr_3$ PNCs but affords oblate cuboidal PNCs with a broad initial size distribution. For example, Kreig, et al., reported octadecylsulfobetaine (ODS) or lecithin as capping ligands in the PNC synthesis, followed by repeated size-selective precipitations to produce narrow size dispersity PNCs.[19,20] These prior studies also describe an acute sensitivity of the crude ODS-capped PNC reaction solution to ambient humidity, necessitating PNC isolation under inert atmosphere. In contrast, PNCs prepared in the presence of $PBMA_{13.6}SB_{2.8}$ required no special handling and gave a somewhat narrower distribution of PNC diameters ($d = 11 \pm 3$ nm) when isolated as a single fraction. Using the reported molar extinction coefficient for $CsPbBr_3$ PNCs, we calculated a yield of ≈65% (ca. 5 mg/mL $CsPbBr_3$ [see Supporting Information for calculation]), comparable to syntheses using small molecule zwitterions. EDS spectroscopy of these nanocrystals suggests a Br-rich stoichiometry with an average Cs:Pb:Br ratio of 1:0.8:3.5 (Figures S12 and S13). X-ray diffraction revealed Bragg peaks consistent with an exclusively othorhombic *Pbnm* phase (Figure S14), in agreement with previous studies that find this phase to be the stable polymorph at room temperature in both bulk and nanoparticle form.[21] Control experiments performed without added ligand, or conducted with PBMA homopolymer, failed to produce high quality PNCs, instead yielding large quantities of aggregates (Figure S10) and poorly dispersible solids with poor colloidal stability such that accurate size and PLQY determination is not possible. While changing the polymer to a random microstructure, i.e., PBMA-*r*-PSBMA, would be an insightful control experiment, these random copolymers are insoluble in hot mesitylene even at low zwitterion content (≥ 2 mol% SB), such that their use as ligands for PNCs requires an additional ligand exchange step.[10]

Utilizing the polymers in Table 1, we examined the effect of polymer loading, block ratio, and molecular weight on PNC formation. Under hot injection conditions, zwitterionic BCPs gave PNCs with similarly high PLQY (>70%) and isolated PNC yields (65-92%, Table S2). The morphologies of the resulting PNCs varied, in some cases resembling those displayed in Figure 1, and in other cases displaying defined edges and cuboidal shapes (Figures S9). Despite some variation in PNC shape and size across experiments, PLQY values were consistently high and emission maxima were centered similarly (λ_{max} 514–518 nm). Earlier examples of zwitterion-capped PNCs employed SB and PC zwitterions interchangeably,[9] and we make the same observation here for polymers, with the highest $CsPbBr_3$ yield (≈92%) obtained using $PBMA_{13.6}PC_{1.6}$ as ligand. The PNC-stabilizing effects of the diblock copolymers appear to operate over a range of polymer and zwitterion concentrations, and all experiments were performed at a fixed mass concentration of polymer in the precursor solution (16 mg/mL). Based on our observations, the molar concentration of polymer chains appears to be more important than the overall concentration of zwitterions: examples where the concentration of polymer chains was halved ($\sim 5 \times 10^{-4}$ M; for example when doubling the molecular weight as in the case of $PBMA_{21.0}SB_{3.9}$ or $PBMA_{21.0}SB_{10.8}$) were accompanied by turbidity or sedimentation. Not only do the BCPs impart long-term colloidal stability when the PNCs are stored as crude solutions in mesitylene, at least one example ($PBMA_{13.6}SB_{2.8}$) showed essentially complete retention of PLQY (>90%) after storage under $N_{2(g)}$ for six months.

Experiments intended to isolate PNCs synthesized in the presence of BCPs revealed that solvents such as isopropanol (*i*PrOH) and ethyl acetate - common anti-solvents for precipitation of ODS or oleylammonium-capped PNCs - produce stable dispersions. To precipitate and wash the polymer-ligated PNCs we used 1-octadecene, which produced a polymer-PNC pellet that was centrifuged and washed with *n*-hexane. This BCP-modified solubility suggests BCP-PNC interactions, which were examined further by solution NMR spectroscopy, recorded before and after precipitation into 1-octadecene, by tracking the ^{1}H and ^{31}P NMR spectra of the PNCs after redispersing in $CDCl_3$. Given the size of the PNCs ($d = 11$-13 nm, estimated by TEM), tumbling in solution will broaden and obscure the resonances of surface-bound molecules - to account for this, a $PBMA_{13.6}SB_{2.8}$-$CsPbBr_3$ PNC sample was digested in a mixture of d_6-DMSO and $CDCl_3$ after one precipitation/wash cycle and then characterized. Despite repeated precipitation, PNC dispersions in toluene retained their bright PL emission, and the near absence of any signals for oleic acid (5.4 ppm, ^{1}H NMR) or TOP/TOPO (−33 or 50 ppm, ^{31}P NMR) suggests a key role of the polymer in imparting colloidal stability (Figures S7 and S8). In addition, these ^{1}H NMR spectra reveal no compositional change in the polymer before and after hot injection (Figure S15). To further confirm that the polymer does not degrade at temperatures used for PNC synthesis, a sample of the $PBMA_{13.6}SB_{2.8}$-$CsPbBr_3$ PNCs was digested in hot TFE, and the isolated polymer analyzed by GPC (Figure S16), showing the polymer molecular weight to be unchanged before and after the hot injection procedure.

PNC capping ligands with long hydrocarbon tails limit PNC solubility to all but a few solvents (e.g., toluene, hexanes). In contrast, the ability to disperse BCP-ligated PNCs in solvents such as *i*PrOH or ethanol (EtOH) without total precipitation or PL quenching represents a potential advantage of polymeric ligands. PNCs prepared with $PBMA_{13.6}SB_{2.8}$ ligands were dissolved in EtOH, *i*PrOH, tetrahydrofuran (THF) or 1,4-dioxane at concentrations of ca. 0.5 mg/mL and held at room temperature for 24 h. BCP-PNCs formed fluorescent solutions in each of these four solvents, with only slight sedimentation in THF and EtOH. For PNCs synthesized using 'normal' concentrations of $PBMA_{13.6}SB_{2.8}$ (i.e., 1 mM, 1x BCP loading, Figure 3) the solution PLQY values remained high in *i*PrOH ($64 \pm 2\%$) and EtOH ($74 \pm 1\%$). While ethers such as THF or dioxane gave lower values (43 ± 3 and $31 \pm 2\%$, respectively), doubling the $PBMA_{13.6}SB_{2.8}$ concentration used during the PNC synthesis (2x BCP loading, Figure 3) produced PNCs that retained $> 90\%$ PLQY in all four solvents tested, suggesting that the number of BCP chains associated with the PNCs is critically important. TEM images of the PNCs dispersed in EtOH (Figure S11) showed the presence of individual PNCs after 24 h, and DLS measurements confirmed that the BCP-PNCs remained well-dispersed in *i*PrOH or EtOH ($d_Z = 46$ nm). Previous work established that PNCs with zwitterion capping ligands such as ODS are resilient to *washing* with polar solvents;[9] however, long-term exposure to these solvents may sinter or dissolve the PNCs. To test this, samples of PNCs with ODS ligands were added to the same solvent series and analyzed. As expected, these PNCs precipitate from solution, and we find that after 24 h the solids are difficult to redisperse in toluene and/or are too unstable to accurately measure PLQY. From these observations, we conclude that BCPs improve on the polar solvent-tolerance of small molecule zwitterions and render PNCs dispersible in a way that exploits this solvent-resistance.

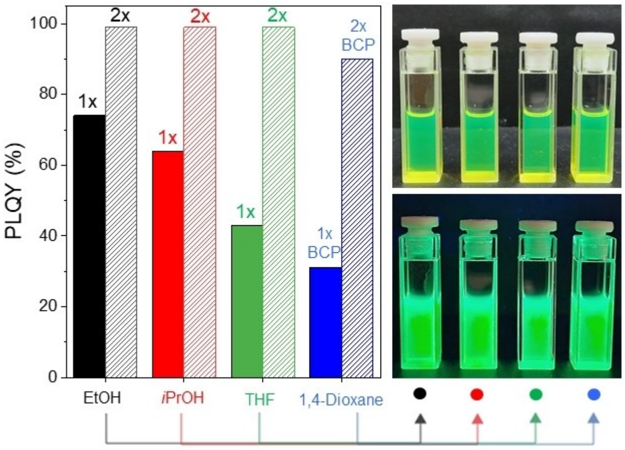

Figure 3. 24 Hour stability of PNCs prepared with $\mathbf{PBMA_{13.6}SB_{2.8}}$ as solutions in polar solvents (*left*). Photographs of cuvettes containing $\mathbf{PBMA_{13.6}SB_{2.8}}$ PNCs under ambient conditions (*upper right*) and UV-irradiation (*lower right*, $\lambda_{ex} = 365$ nm) in ethanol, isopropanol, tetrahydrofuran and 1,4-dioxane.

Notably, PNC films were amenable to casting directly into nanocomposites from solution without assistance from additional polymer. These films exhibited bright PL and a shift in emission wavelength from solution to the solid state depending on whether the films were cast in a glovebox ($\lambda_{em} = 516 \rightarrow 507$ nm) or under ambient conditions ($\lambda_{em} = 516 \rightarrow 522$ nm, Figure S17). The $CsPbBr_3$ content of these films was estimated to be ~35% w/w by thermal gravimetric analysis, or more than double the maximum loading (15 wt%) reported for random copolymer-based nanocomposites in our previous work;[10] the films remained optically transparent on drying and storage. While the PNC films are air and moisture-sensitive (Figure 4), there is almost no change in integrated PL intensity when storing the films for one month in a benchtop desiccator. The absence of any redshift or PL decay over this period suggests that the BCP effectively prevents PNC sintering in the solid state. The AFM topographic image of a spin-coated PNC film with $PBMA_{13.6}SB_{2.8}$ ligand, displayed in Figure 4, confirms the high density of PNCs embedded within the polymer matrix, with surface features representing PNC clusters of somewhat larger lateral dimensions than revealed by TEM. While the ability to directly cast BCP-PNCs into robust films is a useful property by itself, we also find that the BCP-PNCs can be dispersed in PBMA homopolymer ($M_n = 42$ kDa, $Đ = 2.10$). The resulting transparent films have improved PL stability under ambient conditions, retaining 67% of their initial PL intensity after two weeks. Similar to our previous work with PBMA-*r*-PSBMA random copolymers,[10] the PNC films prepared with added PBMA remained fluorescent after fully submerging in water for 12 h, whereas films prepared from ODS-capped PNCs and PBMA lost nearly all of their fluorescence emission characteristics.

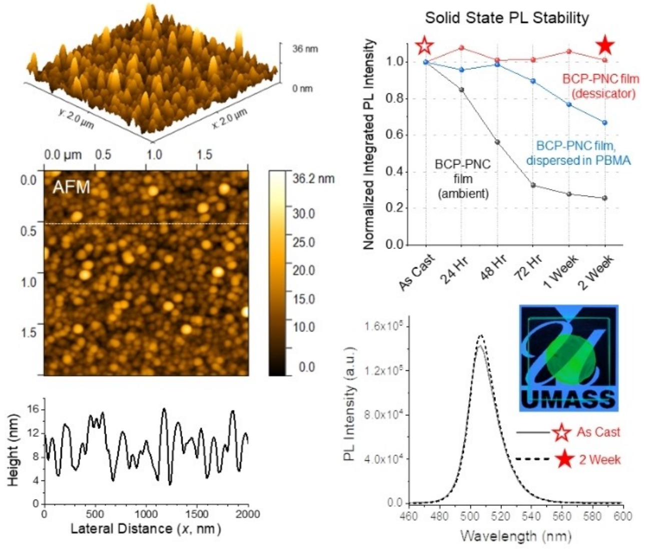

Figure 4. AFM height image of surface of a spin-coated PBMA$_{13.6}$SB$_{2.8}$ film. The height profile of a 2D slice, marked by a white line on the topograph, is shown below. Solid state PL stability of PBMA$_{13.}$SB$_{2.8}$ PNC films with and without added PBMA stored under ambient or dry conditions. Integrated PL Intensities were normalized to the initial value 'as cast' for each sample. PL emssion spectra for the BCP-PNC film before and after holding two weeks in a desiccator.

Conclusion

By arranging *n*-butyl methacrylate and zwitterionic methacrylates into amphiphilic block copolymers, we described the first example of a zwitterion-based macromolecular ligand used directly in PNC synthesis. The block polymer architecture has a profound effect on polymer solubility in hydrophobic solvents, accommodating zwitterion concentrations of up to 21 mol% while dissolving at room temperature in mesitylene and toluene. This feature enables the use of BCPs under hot-injection conditions, resulting in PNCs with reproducibly high PLQYs and good-to-excellent isolated PNC yields. The BCP has an unmistakable role in stabilizing the resulting PNCs, as without it large amounts of poorly dispersible aggregates form. The PNCs thus prepared can be handled as solutions and nanocomposites in ways inaccessible to PNCs with more traditional capping ligands - for example forming stable dispersions in alcohol solvents or casting directly into nanocomposite films. Fundamental advances of this nature, expanding the methods and means by which PNCs can be synthesized and processed, are needed for integration into electronic materials and devices.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: nanocomposite · nanocrystal · perovskite · polymer zwitterion

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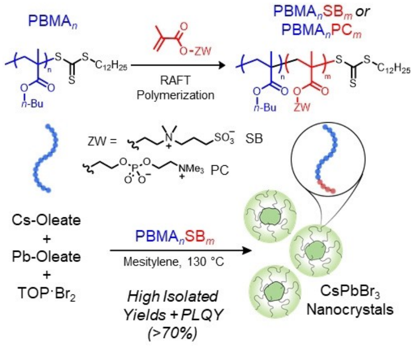
A novel synthesis of cesium lead halide perovskite nanocrystals (PNCs) is enabled by replacing conventional small molecule ligands with zwitterion-containing block copolymers (BCPs) that are soluble in liquid phases useful for hot injection PNC syntheses. PNCs prepared in this manner are obtained in high yields with bright photoluminescence, with the zwitterionic BCPs facilitating efficient PNC isolation, long-term stability, and direct conversion to nanocomposite films.



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Zwitterionic Block Copolymers for the Synthesis and Stabilization of Perovskite Nanocrystals