Supporting Information

Functional Polymers for Growth and Stabilization of

CsPbBr₃ Perovskite Nanoparticles

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Materials. Anisole (99.7%), mesitylene (98%), oleylamine (98%), oleic acid (90%), octadecene (90%), cesium carbonate (Cs₂CO₃, 99%), styrene (99%), azobisisobutyronitrile (AIBN, 98%), 48 bromobenzene (99%), (HBr. wt.%), hydrobromic acid 1,1,4,7,10,10hexamethyltriethylenetetramine (HMTETA, 97%), copper (I) bromide (98%) and 4-(tertbutoxycarbonylaminomethyl) phenylboronic acid, pinacol ester (Boc-Ph-Bpin) were purchased from Sigma Aldrich. Lead oxide (PbO, 99.9995%) was purchased from Alfa Aesar. Hexanes (98.5%) was purchased from EMD Millipore, acetone from Mallinckrodt, and toluene (99.5%) 99.9%) and tetrahydrofuran (THF. from Fisher Scientific. Tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) and was purchased from Strem. Styrene was passed through a plug of basic alumina before use and AIBN was recrystallized from methanol. N-(tert-butoxycarbonyl)aminoethyl methacrylate¹ (BocMA), 2-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-7-bromo-9,9-dioctylfluorene² (Br-F8-Bpin), and N-(tertbutoxycarbonyl)aminoethyl 2-bromoisobutyrate³ (BocBiB) were synthesized by following the respective literature procedures.

Characterization. ¹H NMR spectroscopy was performed on a Bruker AscendTM 500 or 400 equipped with a Prodigy cryoprobe. For diffusion ordered ¹H NMR spectroscopy (DOSY), a Bruker AscendTM 400 was used with a bipolar gradient pulse pair (ledbpgp2s) sequence and NMR tube of 3 mm diameter. The diffusion time was 0.3 s and duration of gradient was 3 ms. The gradient was calibrated by D_2O and the diffusion coefficient was calculated by fitting the attenuation plot with the equation

$$\ln \frac{I}{I_0} = -D\gamma^2 G^2 \delta^2 (\Delta - \frac{\delta}{3})$$

where I is the observed intensity, I_0 is the un-attenuated intensity, γ is proton gyromagnetic ratio, δ is the length of pulse sequence, G is the gradient strength, Δ is the diffusion time, and D is the diffusion coefficient. A JEOL JEM-2200FX transmission electron microscope was used for HR-TEM analysis, tomography, and EDS mapping. Gel permeation chromatography (GPC), using THF as mobile phase was performed on an Agilent 1260 infinity system with a refractive index detector and calibrated against polystyrene standards. A PerkinElmer TGS-2 was used for TGA analysis (under nitrogen atmosphere with a heating rate of 10 °C/min). A Shimadzu UV 3600 spectrophotometer was used for UV-Vis analysis and photoluminescence (PL) spectroscopy was performed on a fluorimeter from Photon Technology. Quantum yield was measured by comparing the PL and absorbance with the reference dye (rhodamine 123). Small-angle X-ray scattering (SAXS) analysis was performed using a GANESHA 300 XL instrument with samples of dried nanocomposite powders having concentration below 10 vol.%, assuming that all of the precursors were reacted to NPs. Powder x-ray diffraction (XRD) was performed using a PANalytical X'Pert Material Research Diffractometer with Cu Ka1 radiation. Matrix assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry utilized a Brüker Microflex spectrometer with 2-(4-hydroxyphenylazo)-benzoic acid as a matrix.



Figure S1. Synthesis of PS-NH₃Br by free-radical polymerization and Boc-deprotection. **Experimental details**

Preparation of polystyrene-co-poly(*N*-(*tert*-butoxycarbonyl)aminoethyl methacrylate) (PS-NHBoc) by free-radical polymerization (n/m = 0.10). To a solution of styrene (5.0 g, 48 mmol) and BocMA (1.1g, 4.8 mmol) in anisole (5.5 mL) was added AIBN (0.17 g, 1.1 mmol) in anisole (2 mL) under N₂ atmosphere. The mixture was heated for 5 h at 80 °C. The product was isolated by precipitation into methanol and drying under vacuum (4.1 g, 66 %). The polymer product had a number-average molecular weight (Mn) of 11 kDa, and polydispersity index (PDI) of 1.6, as determined by GPC (THF as mobile phase). For n/m ratios of 0.20 and 0.05, styrene-to-BocMA ratios were changed accordingly, while the target degree of polymerization was kept constant. ¹H NMR (CDCl₃, 500 MHz, ppm): 7.4-6.0 (br, 5H, aromatic), 1.55 (s, 9H, (CH₃)₃), 3.5-0.1 (br, alkyl). ¹³C NMR (CDCl₃, 125 MHz, ppm): 176.7-176.0, 155.5, 144.6-144.1, 128.5-127.7, 127.7-127.1, 126.2-125.2, 79.4-79.1, 63.1-62.6, 48.5-41.2, 40.9-38.5, 31.9-31.5, 28.4, 27.9, 27.3-26.5, 19.7.

Synthesis of poly(styrene-*co***-polymethacrylethylammonium-bromide) (PS-NH₃Br).** To a solution of PS-NHBoc (2 g) in dichloromethane (100 mL) was added HBr (1 mL) at room temperature, followed by stirring for 2 h. The polymers were precipitated by addition to an excess

of an ether/hexane mixture, the polymers were dried under vacuum. (1.8 g, 90%). ¹H NMR (CDCl₃, 500 MHz, ppm): 8.0-7.8 (s, 3H, NH₃), 7.4-6.0 (br, 5H, aromatic), 3.5-0.1 (br, alkyl).



Figure S2. Synthesis scheme of PS-ω-NH₃Br polymer ligand.

Polymerization of PS-\omega-NHBoc. CuBr (0.68 g, 4.8 mmol) and BocBiB (7.4 g, 24 mmol) were added to a round bottom flask, which was purged under vacuum and back-filled with nitrogen. Styrene (150 g, 1.44 mol), HMTETA (1.1 g, 4.8 mmol), and anisole (165 mL) were added, and the systems was degassed using three freeze-pump-thaw cycles. The flask was immersed in the oil bath and heated to 100 °C with stirring. The polymerization was stopped after 20 h and the polymer isolated by precipitation into hexane. The polymer was dissolved in THF and passed through a plug of basic alumina. The recovered solution was precipitated in hexane and dried under vacuum to yield 117 g (78%) of polymer product. The Mn of the polymer was estimated to be 6.4 kDa PDI 1.1, by GPC. ¹H NMR (CDCl₃, 500 MHz, ppm): 7.4-6.0 (br, 5H, aromatic), 4.6-4.3, (br, NH), 3.7-3.2 (br, 2H, CH₂), 3.2-3 (br, 2H, CH₂), 2.5-0.8 (br, 3H and 9H of Boc, alkyl). ¹³C NMR (CDCl₃, 125 MHz, ppm): 177.2, 155.6, 144.6-144.5, 128.5-127.8, 127.7-127.0, 126.0-125.3, 79.4, 63.1, 46.5-41.2, 40.9-40.0, 28.4.

Synthesis of PS-ω-NH₃Br. To a solution of PS-ω-NHBoc (30 g) in dichloromethane (200 mL) was added HBr (2.8 mL) and the mixture was stirred at room temperature for 20 h. The polymer was isolated by precipitation into methanol and dried under vacuum (30 g, 100%). The isolated polymer has a number-average molecular weight of 4.2 kDa and PDI of 1.3, as estimated by GPC with THF as eluent and polystyrene calibration standards. ¹H NMR: 8.0-7.8 (s, 3H, NH₃⁺), 7.4-6.0 (br, 5H, aromatic), 4.6-4.3, (br, NH, small fraction of residual protected group), 3.7-3.2 (br, 2H, CH₂), 3.2-3 (br, 2H, CH₂) 2.5-0.8 (br, 3H, alkyl). ¹³C NMR (CDCl₃, 100 MHz, ppm): 177.6, 146.3-144.7, 128.3-127.8, 127.7-127.2, 125.8-125.3, 60.1, 46.6-41.3, 40.8-40.0, 36.4, 28.4 (residual Boc group).



Figure S3. Synthesis of PF-NH₃Br.

Preperation PF-NHBoc. Br-F8-Bpin (3.3 g, 5.6 mmol), Boc-Ph-Bpin (0.37 g, 1.1 mmol), Pd(PPh₃)₄ (76 mg, 0.066 mmol), toluene (36 mL), and aliquat 336 (9 drops) were mixed in a Schlenk flask inside the glove box. The flask was removed from the glove box and 3M K₂CO₃ solution (27 mL) was added by syringe through septum. The solution was heated to 80 °C for 14 h. Then, bromobenzene (2.52 mL, 24 mmol) was added, and the mixture was stirred for an additional 6 h, then cooled to room temperature. The crude solution was separated from the aqueous phase and extracted using 10% citric acid and brine. The product was isolated by precipitation into methanol, then dried under vacuum to afford 1.6 grams of polymer (73% yield). The polymer showed a value of $M_n = 3.9$ kDa, and PDI 1.6, estimated by GPC against polystyrene

standards with THF as eluent. ¹H NMR (CDCl₃, 500 MHz, ppm): 7.9-7.75 (br, 2H), 7.75-7.54 (m, 4H), 7.48 (t, 3H), 7.4 (d, 2H), 7.37 (dd, 2H), 5.0-4.8 (br, 1H, NH), 4.4 (d, 2H), 2.1 (br, 4H), 1.5 (s, 9H, -(CH₃)₃), 1.33-0.95 (m, 20H), 0.9-0.6 (m, 10H). ¹³C NMR (CDCl₃, 125 MHz, ppm): 155.9, 151.8-151.7, 141.7, 140.8-140.5, 140.2-139.9, 128.8 (CH of Ph, end group), 128.0, 127.4, 127.2 (CH of Ph, end group), 126.3-125.9 121.6-121.4, 120.0, 79.6, 55.4-55.3, 44.4, 40.4, 31.8, 30.3, 29.2, 28.4 (CH₃ of Boc, end group), 23.9, 23.8, 22.6, 14.1.

Synthesis of PF-NH₃Br. To a solution of PF-NHBoc (1.0 g) in dichloromethane (14 mL) was added HBr (1 mL) and the mixture was stirred overnight at room temperature. The solvent was evaporated by sweeping $N_{2(g)}$ through the system, then pulling vacuum, affording the product in nearly quantitative yield. ¹H NMR (CDCl₃, 500 MHz, ppm): 8.4-8.0 (br, 3H, NH₃) 7.9-7.75 (br, 2H), 7.75-7.54 (m, 4H), 7.48 (t, 3H), 7.37 (dd, 2H), , 4.3 (d, 2H), 2.1 (br, 4H), 1.5 (br), 1.33-0.95 (m, 20H) 0.9-0.6 (m, 10H). ¹³C NMR (CDCl₃, 100 MHz, ppm): 151.8-151.7, 142.9, 141.7, 140.8-140.7, 140.5-139.5, 130.1, 128.8 (CH of Ph, end group), 128.0, 127.4, 127.0 (CH of Ph, end group), 126.2-125.9 121.6-121.4, 120.0, 55.4-55.3, 40.4, 31.8, 30.0, 29.7, 29.2, 24.0-23.7, 22.6, 14.0.

Synthesis of oleyl-functionalized CsPbBr₃ NPs. The NPs were synthesized using a slightly modified literature procedure.⁴ To a solution of Cs₂CO₃ (0.814 g) in octadecene (40 mL) was added oleic acid (2.5 mL), followed by drying under vacuum for 20 min at 120 °C. Heating the mixture to 150 °C under N_{2(g)} flow afforded a homogenous solution. Separately, a solution of PbBr₂ (0.276 g) in octadecene (20 mL) was heated under vacuum at 120 °C for 10 min. Under N_{2(g)} flow, oleic acid (2 mL) and oleylamine (2 mL) were injected and the solution was heated to 170 °C, and the Cs-oleate solution in octadecene (1.6 mL) was injected and reacted for 15 s. The resulting solution was cooled to room temperature using a water bath. For purification, 1 mL of the crude solution

and 3 mL of toluene were mixed, followed by addition of 2 mL or 4 mL of acetone as described in Figure 2A. After centrifugation (5000 rpm, 2 min), the precipitates were re-dispersed in toluene (2 mL).

Synthesis of CsPbBr₃ NPs by using PS-NH₃Br. A solution of Cs₂CO₃ (0.814 g) in mesitylene (40 mL) and oleic acid (2.5 mL) was purged with N_{2(g)} and heated to 150 °C under N_{2(g)} flow to yield a transparent solution. Separately, a solution of PbO (0.022 g, 0.10 mmol) and oleic acid (0.25 mL, 0.8 mmol) in mesitylene (10 mL) was purged with N_{2(g)} and heated to 160 °C. When the PbO solution reached 160 °C, the Cs-oleate solution in mesitylene (0.2 mL) was injected into it. Then, a solution of PS-NH₃Br (0.213 g, 0.322 g, 0.476 g for n/m= 0.2, 0.1, 0.05 respectively) in mesitylene (2 mL) and dimethylformamide (1 mL) was injected and reacted for 15 s. The solution was cooled to room temperature using a water bath, and 0.5 mL of the solution was mixed with hexane (5 mL). After centrifugation (4000 rpm, 1 min), the precipitate was redispersed in toluene (0.5 mL), and the dissolution/precipitation procedure was repeated.



Figure S4. (A) UV-Vis spectra of PS-NH₃Br NPs with varying n-to-m ratio; (B) UV-Vis and PL spectra of PS-NH₃Br NPs with excitation at 350 nm; (C) XRD pattern of PS-NH₃Br NPs.

Synthesis of CsPbBr₃ NPs using PS- ω -NH₃Br. A solution of PbO (0.013 g, 0.06 mmol), Cs₂CO₃ (0.01 g, 0.03 mmol) and oleic acid (0.17 mL) in mesitylene (17 mL) was purged with N_{2(g)} and heated to 160 °C. Then, a solution of PS- ω -NH₃Br (2.0 g) in mesitylene (4 mL) was injected and reacted for 10 min. The solution was allowed to cool to room temperature by immersing the flask into a water bath, followed by precipitation with hexanes. The mixture was subjected to centrifugation and the isolated solid was redispersed in toluene.

Synthesis of CsPbBr₃ NPs using PF-NH₃Br. A solution of PbO (0.008 g, 0.036 mmol), Cs₂CO₃ (0.006 g, 0.018 mmol) and oleic acid (0.12 mL, 0.34 mmol) in mesitylene (12 mL) was purged with $N_{2(g)}$ and heated to 160 °C. Then, a solution of PF-NH₃Br (0.47 g, 0.12 mmol) in mesitylene (3 mL) was injected and reacted for 10 s. The resulting mixture was cooled to room temperature by immersing the flask into a water bath and addition of pentane (13 mL pentane to 1mL of crude solution). The mixture was subjected to centrifugation and the recovered solid was redispersed in toluene.

Experiments on polymer/NP films. The PS- ω -NH₃Br NP solution from the reaction mixture (1 mL) was precipitated into hexane (3 mL) and centrifuged (5000 rpm, 2 min). The collected solid was dissolved in a 5 wt.% toluene solution of polystyrene (M_n : 6.4 kDa). Spin coating the solution onto a Si wafer (2000 rpm for 60s) produced the desired film (for TEM measurements, 0.01 g of polystyrene was used and the spin coating was performed directly onto the TEM grid). In a comparative control experiment, the crude solution of oleyl NPs (1 mL) was centrifuged (5000 rpm for 2 min) and the isolated solid was dissolved in a toluene solution of polystyrene (5 wt.%), then subjected to spin coating as described above.



Figure S5. (A) HR-TEM image the PS- ω -NH₃Br NPs; (B) EDS spectrum and atomic ratio of the NPs. (Cs : Pb : Br = 1.0 : 0.9 : 3.4)



Figure S6. (A) HR-TEM image the PS-NH₃Br NPs. The red bar indicates the lattice spacing on (100) plane; (B) 3D reconstruction by TEM tomography showing NP cubes; (C) EDS mapping image and high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) of the PS-NH₃Br NPs (scale bars = 25 nm); (D) EDS spectrum and atomic ratio of the NPs. (Cs : Pb : Br = 1 : 1 : 3)



Figure S7. (A) DLS analysis of the oleyl NPs and PS-NH₃Br NPs; From DLS analysis, hydrodynamic diameters ($D_{\rm H}$) of the oleyl NPs and PS-NH₃Br NPs were 14 nm and 40 nm; Comparing the values of the difference between D_H to the edge lengths by TEM (8.4 nm and 21.1 nm), the PS-NH₃Br NPs show a larger difference in size (19 nm) than the oleyl NPs (5.8 nm), attributed to the presence of the passivating polymers; (B) TGA results for the PS-NH₃Br NPs purified by 1-fold and 5-fold excess of hexane addition compared to the crude solution.



Figure S8. Degradation profile of normalized intensity of the oleyl NPs and PS-ω-NH₃Br NPs against 1-propanol; (A) Thin films immersed in 1-propanol; (B) Colloidal NPs in mixed solution of toluene (1 mL) and 1-propanol (0.5 mL).



Figure S9. (A) UV-Vis spectra of the PF-NH₃Br NPs in a toluene solution and a drop-cast film; (B) PL spectra of a PF-NH₃Br NP film.

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