

Supporting Information

Continuous Manufacturing of Highly Stable Lead Halide Perovskite Nanocrystals via a Dual-Reactor Strategy

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Experimental Section

Materials

Toluene (ACS, VWR), dichloromethane (ACS, VWR), chlorobenzene (ACS, Beantown Chemical), chloroform (ACS, VWR), hexane (ACS, VWR), anhydrous dimethylformamide (DMF, Millipore), lead bromide (99.99%, TCI), cesium bromide (99.9%, STREM Chemicals), oleic acid (90%, Alfa Aesar), oleylamine (Technical grade, Sigma Aldrich), dichloromethane (>99.5%), α -bromoisobutyryl bromide (BiBB, 98%), anisole (99%), 2-butanone (99.0%), anhydrous dimethylformamide (DMF, >99.8%) anhydrous 1-methyl-2-pyrrolidinone (NMP, 99.5%), N,N,N',N',N''-pentamethyldiethylene triamine (PMDETA, 99%), trifluoroacetic acid (TFA, 99.9%), aluminum oxide powder (activated, neutral, ~325 mesh), tetrahydrofuran (THF, 99.0%), acetone (99.5%), deuterated chloroform (CDCl₃, 99.96%), and deuterated dimethylformamide (DMF-d₇, 99.5%) were purchased from Sigma-Aldrich and used as received.

Before bromination the β -cyclodextrin (β -CD, >97.0%, Sigma-Aldrich) were dried under vacuum for 48 hours at 60°C and azeotropically distilled in toluene for 2 hr at 120°C. Copper (I) bromide (CuBr, 98%, Sigma-Aldrich) was stirred in acetic acid for 2 hr, filtered, washed with ethanol and diethyl ether, and dried in vacuum at room temperature overnight. Styrene (St, 99.9%, Sigma-Aldrich), *tert*-butyl acrylate (*t*BA, 98%, Sigma-Aldrich) were distilled over CaH₂ under reduced pressure prior to use.

Methods

Synthesis of Heptakis[2,4,6-tri-O-(2-bromo-2-methylpropionyl)]- β -cyclodextrin (i.e., Br- β -CD macroinitiator): Purified β -CD (2.5 mmol) was first dissolved in 40 ml anhydrous NMP at 0°C. BiBB (105 mmol) was then added dropwise to the β -CD NMP solution and stirred for 1 hr. The reaction solution was then stirred at room temperature for an additional 24 hr to ensure completion. Next, the solution was diluted with 100 ml dichloromethane and washed with saturated NaHCO₃ aqueous solution and deionized water for at least three times, respectively. The product was recovered from the solution via rotary evaporation. The product was then re-dissolved in acetone, and the Br- β -CD acetone solution was added into water for crystallization to remove impurities. The precipitant was then dissolved in dichloromethane, dried with anhydrous MgSO₄, and filtered. All solvents were then removed via rotary evaporation to yield the final solid product.

Synthesis of hydrophobic star-like poly(*tert*-butyl acrylate) (star-like PtBA): The Br- β -CD was then used as a macroinitiator for atom transfer radical polymerization (ATRP) of *t*BA. Specifically, Br- β -CD, CuBr, PMDETA, 2-butanone, purified *t*BA (in the molar ratio= 1:1:1.5:1500:1500) were mixed in an ampoule, degassed by three freeze-pump-thaw cycles in liquid nitrogen, and placed in oil bath preheated at 60°C for a desired time. The polymerization was stopped by quenching in liquid nitrogen and exposure to ambient air. The reaction solution was then diluted with acetone, passed through a neutral activated aluminum oxide column to remove the copper catalyst, and precipitated with a methanol/water (volume ratio= 1:1) mixture to obtain the final product. The completed star-like PtBA was then dried in a vacuum at room temperature for 48 hr.

Synthesis of hydrophobic star-like poly(*tert*-butyl acrylate)-block-polystyrene (star-like *PtBA-b-PS*): The star-like *PtBA* was then used as a macroinitiator to grow PS via ATRP. Star-like *PtBA*, CuBr, PMDETA, St and anisole (molar ratio=1:1:1.5:1200:2000) were mixed in an ampoule, degassed by three freeze-pump-thaw cycles in liquid nitrogen, and polymerized at 90°C for specific period of time. Afterwards, the reaction was quenched by immersing in liquid nitrogen and exposing to ambient air. The reaction solution was then diluted with THF, and passed through a neutral, activated aluminum oxide column to remove the copper catalyst. Subsequently, the final product was purified by precipitation with cold methanol and dried at 40°C under vacuum for 48 hours.

Synthesis of amphiphilic star-like poly(acrylic acid)-block-polystyrene (Star-like *PAA-b-PS*): To convert the *PtBA* to PAA, 200 mg star-like *PtBA-b-PS* diblock copolymers were added into 100 ml anhydrous dichloromethane and 2 ml TFA. The solution was then stirred for 24 hr at room temperature to ensure the hydrolysis of the *PtBA*. After hydrolysis, rotary evaporation was used to remove excess TFA, and a white-powder like product was obtained. This powder was then re-dissolved in DMF, precipitated with cold methanol, filtered, and dried at room temperature in vacuum overnight.

Construction of flow reactor

To create the flow reactor, 1.6 mm inner diameter PTFE tubing (from SCAT Europe) was cut to the 15cm. It was then fitted onto one end of a polypropylene/polyethylene tapered Y connector (VWR). Two pieces of PTFE tubing with one end adapted to female Luer Lock fitting (Hamilton Company) were then attached to the other two ends of the tapered connector. The female Luer Lock fittings allowed for facile connection to the syringes that contained the precursor (10mL BD) and crystallization (50mL Chemglass borosilicate) solvents, which were dispersed by the Single Syringe Pump (Fisherbrand). A schematic diagram of the flow reactor can be seen in **Figure S1**.

The same precursor solutions were used for all trials. The templated precursor solution was created by dissolving 10mg *PAA-b-PS* nanoreactor, 0.1mmol CsBr (20mg), and 0.1mmol PbBr₂ (36mg) in 20mL DMF. The control precursor solution was created by dissolving 0.1mmol CsBr (20mg), and 0.1mmol PbBr₂ (36mg), 0.5mL oleic acid, and 50 μ L oleyamine in 20mL DMF.

Both control and templated PNCs were synthesized by loading the syringes with the solvents and flowing each at the desired rate. The completed PNCs were collected from the end of the reactor tube. The resulting CsPbBr₃ PNCs were then purified by centrifugation at 13k RPM for 10 minutes. The supernatant was collected, while any aggregates that had precipitated were discarded.

Characterization

The molecular weights and polydispersity indexes of polymers were measured by gel permeation chromatography (GPC) equipped with a G1362A refractive detector and a G1314A variable wavelength detector, one 5 μ m LP gel column (500 \AA , molecular range: 500~ 2×10^4 g/mol) and one 5 μ m LP gel mixed bed column (molecular range: 200~ 3×10^6 g/mol), and THF as mobile phase with a rate of 1.0 ml/min at 35°C. The GPC was calibrated with monodisperse linear PS as

standard. $^1\text{H-NMR}$ were measured using Varian mercury 400 nuclear magnetic resonance spectroscopy with either CDCl_3 or DMF-d_7 as solvent.

The photoluminescence (PL) spectra of the CsPbBr_3 PNCs was obtained by a PerkinElmer LS 55 fluorescence spectrometer with a 365nm excitation light. The absolute photoluminescence quantum yield (PLQY) was measured with a Hamamatsu Quantaurus QY Plus with an excitation wavelength of 365 nm. The absorbance of the PNCs from 800-300 nm was examined with a Shimadzu UV-2600. The morphologies of the PNCs were investigated with a JEOL CX-II transmission electron microscope (TEM) operated at 100 keV.

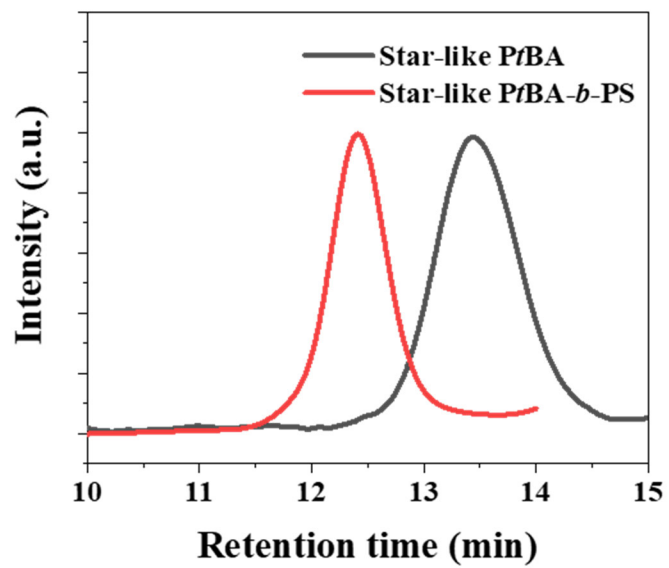


Figure S1. GPC traces for star-like PtBA and PtBA-*b*-PS.

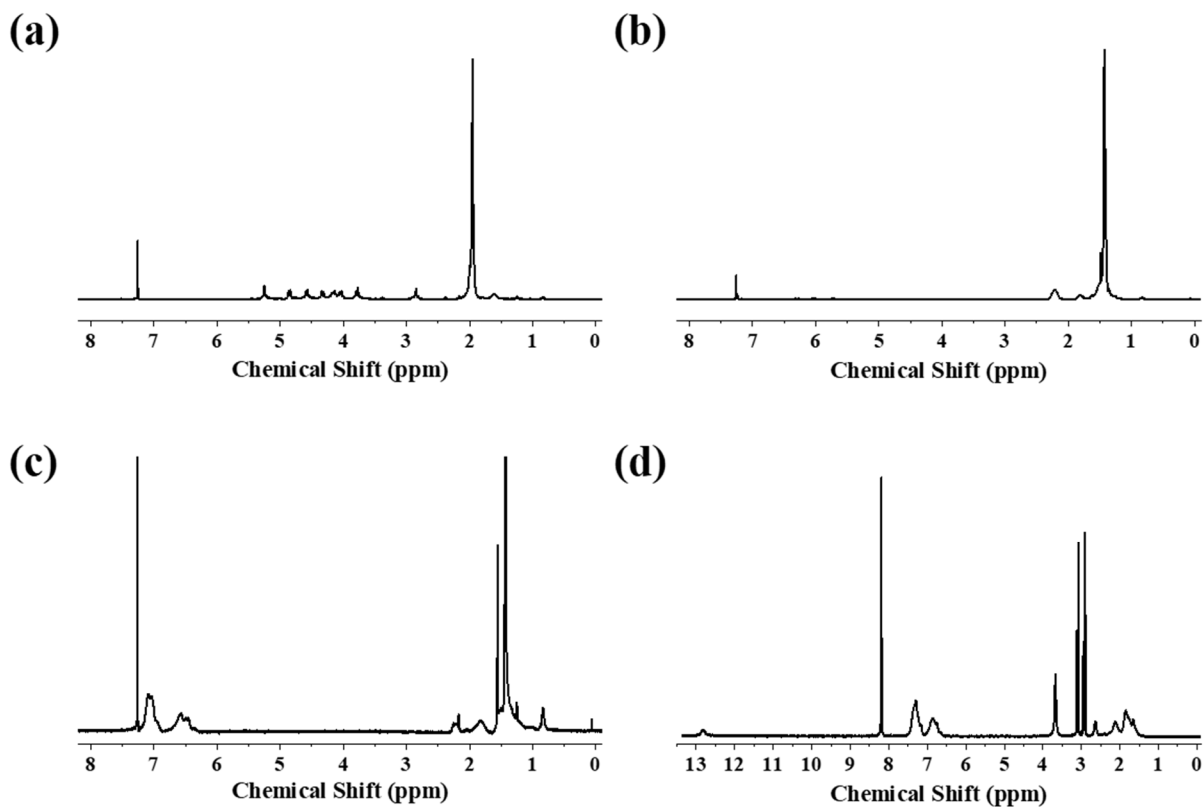


Figure S2: NMR spectra from (a) brominated β -CD, (b) star-like PtBA, (c) star-like PtBA-*b*-PS, and (d) star-like PAA-*b*-PS.

Table S1. Optical properties of CsPbBr₃ PNCs synthesized via conventional LARP using various antisolvents.

Solvent	Solvent Polarity	PLQY (%)	Emission Peak (nm)
Toluene	9.9	51.3	507
Chlorobenzene	18.8	9.4	502
Dichloromethane	30.9	0.5	515
Chloroform	25.9	0.5	507
Hexane	0.9	0	-

Table S2. The Reynolds number (Re) for all flowrates calculated using the equation below.

Total Flow ($Q_{\text{precursor}}+Q_{\text{tol}}$) (mL/hr)	Re
5060	1662
4060	1334
3060	1005
2060	677
1060	348

Reynolds Number Calculation:

$$Re = \frac{\rho Q D}{\mu A}$$

ρ = Density of fluid [kg/m³] = **867 kg/m³**

Q = Flowrate [m³/s]

D = Inner diameter of tube [m] = **0.0016 m**

μ = Dynamic viscosity of liquid [Pa*s] = **5.83E-4 Pa s**

A = Cross sectional area of tube [m²] = $\pi (D/2)^2 = \pi (0.0008)^2 =$ **2.01E-6 m²**

Conversion of Variable Flowrates:

$Q = 5060 \text{ mL/hr} =$ **1.41E-6 m³/s**

$Q = 4060 \text{ mL/hr} =$ 1.13E-6 m³/s

$Q = 3060 \text{ mL/hr} =$ 8.50E-7 m³/s

$Q = 2060 \text{ mL/hr} =$ 5.72E-7 m³/s

$Q = 1060 \text{ mL/hr} =$ 2.94E-7 m³/s

As an example, Re for total flowrate of 5060 mL/hr is given as follows:

$$Re = (870 \text{ kg/m}^3)(1.41\text{E-6 m}^3/\text{s})(0.0016 \text{ m})/(5.60\text{E-4 Pa}\cdot\text{s})(2.01\text{E-6 m}^2) = 1662$$

Calculation of radius of gyration of PAA block¹

$$\langle Rg^2 \rangle = \frac{Nb^2}{6} \left(\frac{3-\frac{2}{f}}{f} \right) \quad (\text{Equation S1})$$

N is degree of polymerization of star-like PAA calculated from M_n f is the number of arms.
 b is Kuhn length (0.69nm for PAA).²

$$N = \frac{273,000 \frac{g}{mol}}{72.06 \frac{g}{mol}} = 3788$$

$$\langle Rg^2 \rangle = \frac{3788 * (0.69nm)^2}{6} * \frac{3 - \frac{2}{21}}{21}$$

$$\langle Rg \rangle = 6.45 \text{ nm}$$

$$D = 12.9 \text{ nm}$$

Calculation of yield of (mass/time) of the dual-reactor system

The amount of synthesized CsPbBr₃ PNCs is calculated by determining the volume of all PNCs synthesized within the nanoreactor and then converting to mass using the density of CsPbBr₃. An explanation of each value is given below.

$$0.010g * \frac{mol}{651,000g} * \frac{1}{20mL} * \frac{60mL}{hr} * \frac{6.02*10^{23}}{mol} * \frac{4}{3} \pi (6.4 * 10^{-9}m)^3 * \left(\frac{4.55g}{cm^3}\right) * \left(\frac{100cm}{m}\right)^3 = \underline{0.139}$$

g/hr

Mass of nanoreactor added / molar mass of PAA-*b*-PS nanoreactor / added volume of DMF * antisolvent flowrate * Avogadro's number * expected volume of each CsPbBr₃ PNC * density of CsPbBr₃ * unit conversion = expected yield (Equation S2)

Note: Density of CsPbBr₃ is reported as 4.42 g/cm³.³

References

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