

Supplementary Materials for

Unconventional route to dual-shelled organolead halide perovskite nanocrystals with controlled dimensions, surface chemistry, and stabilities

Yanjie He, Young Jun Yoon, Yeu Wei Harn, Gill V. Biesold-McGee, Shuang Liang, Chun Hao Lin, Vladimir V. Tsukruk, Naresh Thadhani, Zhitao Kang, Zhiqun Lin*

*Corresponding author. Email: zhiqun.lin@mse.gatech.edu

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Experimental Section

Synthesis of Heptakis[2,4,6-tri-O-(2-bromo-2-methylpropionyl)- β -cyclodextrin] (i.e., 21Br- β -CD).

β -CD (5.683 g, 5 mmol) was dried through azeotropic distillation and dissolved in 100 ml anhydrous NMP. α -bromoisobutyryl bromide (48.279 g, 210 mmol) was added drop-wise at 0°C to the mixture solution noted above under magnetic stirring using a dropping funnel. The reaction temperature was kept at 0°C for 2 h, and then gradually increased to ambient temperature. The reaction solution was maintained at ambient temperature for 22 h for complete bromination reaction. The brown solution was transferred to separation funnel and diluted with 200 ml dichloromethane. The resulting solution was washed sequentially with saturated NaHCO₃ aqueous solution and DI water until the pH was above 4.5 to remove HBr produced in bromination reaction. The product was retrieved from the resulting solution by rotary evaporation, re-dissolved in dichloromethane, and dried with anhydrous MgSO₄. The final product was obtained by removing solvent using rotary evaporation, yielding a light-yellow precipitate (12.89 g, yield = 60.5%).

Synthesis of Star-like Poly(4-vinylpyridine) Homopolymer (i.e., Star-like P4VP) Using 21Br- β -CD as Macroinitiator.

Polymerization of 4-vinyl pyridine (4VP) was performed using standard Schlenk line. A mixture solution consisting of 21Br- β -CD (0.02 mmol), CuX (0.42 mmol, X=Cl or Br), CuX₂ (0.042 mmol), Me₆TREN (1.1 mmol), anhydrous 2-propanol (40 mL), and 4VP (40 mL) was undergone five freeze-pump-thaw cycles in a 350 mL ampoule to remove dissolved oxygen in solution and then placed in an oil bath preheated to 40°C for a desired time. The 4VP homopolymerization was

stopped by quenching in liquid N₂ and exposed to air. The brown red solution was diluted with DMF and passed through an activated neutral alumina column to remove copper catalyst. The resulting solution was dried by rotary evaporation to remove excess 4VP monomer and solvent. The resulting dark brown solid was re-dissolved in 2-propanol and precipitated in cold hexane, yielding a yellow-red powder. The products were further purified by repeating the dissolution/precipitation process using 2-propanol as a solvent and cold hexane as a precipitator until a white powder was obtained. This white product was dried over vacuum and stored in dark at 0°C prior to the following chain extension reaction.

Synthesis of Star-Like Poly (4-vinylpyridine)-*block*-Poly (*tert*-butyl acrylate) (i.e., Star-like P4VP-*b*-PtBA) by ATRP Using Star-Like P4VP as Macroinitiators.

All chain extension reactions performed in an ampoule were conducted by using well-defined chlorine-terminated star-like P4VP synthesized above as macroinitiator. The solution consisting of *t*BA, star-like P4VP, CuCl, CuCl₂, and Me₆TREN (molar ratio=8000:10:10:1:11) in anhydrous DMF (1 mL *t*BA in 2 mL solvent) were degassed by three freeze-pump-thaw cycles in liquid N₂ and then placed in oil bath preheated to 60°C for a desired time. The polymerization was quenched by immersing in liquid N₂ and then exposed to air. The crude product was diluted with DMF and passed through a neutral activated alumina column to remove copper catalyst. The raw product was obtained by removing the excess *t*BA and solvent (DMF) by rotary evaporation. The resulting product was further purified by fractional precipitation using cold hexane as precipitator to remove residual *t*BA monomer and oligomer. The resulting white powder-like star-like PS-*b*-PtBA was dried at 40°C under vacuum to obtain pure star-like PS-*b*-PtBA. The final white product was stored at 0°C for the following chain extension reaction.

Synthesis of Azide-Functionalized Star-Like Poly(4-vinylpyridine)-*block*-Poly(*tert*-butyl acrylate) (i.e., Star-like P4VP-*b*-PtBA-N₃)

Purified star-like PS-*b*-PtBA (0.5 g) was dissolved in anhydrous DMF (10 mL) and sonicated for the complete dissolution of star-like diblock copolymers in DMF. Sodium azide (the molar ratio of Cl in star-like PS-*b*-PtBA : sodium azide = 1:100) was added to the reaction solution and kept stirring for 24 h at ambient temperature. After that, the original reaction solution was diluted with DMF. The product was obtained by precipitating in the mixture solution consisting of water/methanol at 0°C (the volume ratio of water to methanol = 1:1). This dissolution/precipitation process was repeated three times to remove the excess NaN₃. The purified product was dried at ambient temperature under vacuum to remove any residual solvent and stored at 0°C prior to click reaction.

Synthesis of Alkyne-Terminated Polyethylene Oxide (PEO)

Briefly, 200 mL freshly dried THF and 15.4 g (120 mmol) naphthalene were added into 500 mL three-neck flask under argon protection. Freshly cleaned potassium (4.68 g, 120 mmol) was added into the mixture solution and kept stirring for 4 h, followed by addition of 22.2 g (132 mmol) diphenylmethane. The reaction temperature was gradually increased to the refluxing temperature for 36 h. The mixture solution was titrated with 0.1 M HCl and the final concentration of Diphenylmethylpotassium is 0.5 M.

Alkyne-terminated PEO was prepared by nucleophilic substitution of the hydroxyl group on poly(ethylene glycol) methyl ether (mPEO) into the alkyne group. Typically, 10 g poly(ethylene glycol) methyl ether (2 mmol) and 60 mL dry THF was added into 250 mL flask. The DPMK solution

was introduced to the mixture solution above under the protection of argon at 0°C. The solution was kept stirring at this temperature for 1h before 10 mmol propargyl bromide was added using a syringe pump for 2 h. The reaction temperature was gradually increased to ambient temperature and allowed the reaction for 24 h. After that, the solution was removed by rotary evaporation and alkyne-terminated PEO was obtained by separation of the formed salts and precipitation in diethyl ether. The pure product was obtained by washing the raw product using diethyl ether twice, yielding a white powder like sample. ¹H-NMR (CDCl₃) δ ppm: 2.44 (t, 1H, -OCH₂C≡CH), 4.20 (d, 2H, -OCH₂C≡CH), 3.38 (s, 3H, CH₃-O-PEO), 3.60-3.70 (m, -CH₂CH₂O- of PEO main chain).

Synthesis of Star-Like Poly(4-vinylpyridine)-*block*-Poly(*tert*-butyl acrylate)-*block*-Poly(ethylene Oxide) by Click Reaction (i.e., Star-Like P4VP-*b*-PtBA-*b*-PEO)

Star-like P4VP-*b*-PtBA-*b*-PEO was prepared by grafting alkyne-terminated PEO onto star-like P4VP-*b*-PtBA-N₃ via the copper (I)-catalyzed alkyne-azide cycloaddition reaction. Briefly, 1 g star-like P4VP-*b*-PtBA-N₃ was dissolved into 40 mL anhydrous DMF, followed by addition of 0.5 g alkyne terminated PEO and the system was purged by argon for 30 min before CuCl and Me₆TREN (molar ratio=1:1.1:1:2) were added into the reaction solution. The dissolved oxygen was removed by three freeze-pump-thaw cycles in liquid N₂ and then placed in oil bath preheated to 40°C for 24 h. After that, the crude product was diluted with 60 mL DMF and passed through a neutral activated alumina column to remove copper catalyst. The raw product was obtained by removing DMF by rotary evaporation and purified by washing with diethyl ether, yielding a white powder. The final product was dried under vacuum and stored at 0°C prior to perovskite nanoparticle (PNCs) synthesis.

Synthesis Linear P4VP-*b*-PtBA-*b*-PEO Triblock Copolymer as Control

Linear P4VP-*b*-PtBA-*b*-PEO triblock copolymer was synthesized in a similar way to star-like P4VP-*b*-PtBA-*b*-PEO. The only difference is that 21Br- β -CD was replaced by α -bromoisobutyryl bromide as the initiator.

Synthesis of Star-Like Poly(4-vinylpyridine)-*block*-Poly(*tert*-butyl acrylate)-*block*-Polystyrene (i.e., Star-like P4VP-*b*-PtBA-*b*-PS) by ATRP Using Star-Like P4VP-*b*-PtBA as Macroinitiator.

Chain extension reaction with St was similar to the synthesis of star-like P4VP-*b*-PtBA. Briefly, the solution containing St, star-like P4VP-*b*-PtBA, CuCl, CuCl₂, and Me₆TREN (molar ratio=8000:10:10:1:11) in anhydrous DMF (1 mL St in 2 mL solvent) were charged into an ampoule, degassed by three freeze-pump-thaw cycles in liquid N₂ and then placed in oil bath preheated to 80°C for desired time. The polymerization was stopped by immersing in liquid N₂ and then exposed to air. The crude product was diluted with DMF and passed through a neutral activated alumina column to remove copper catalyst. The raw product was obtained by removing the excess St and DMF by rotary evaporation. The resulting product was further purified by fractional precipitation using cold methanol/water (volume ratio = 1:1) as the precipitator and DMF as the solvent to remove residual St monomer and oligomer. The resulting white powder-like star-like PS-*b*-PtBA-*b*-PS was dried at 40°C under vacuum to yield a white powder-like sample. The final white product was stored at 0°C prior to the perovskite nanocrystal (PNC) synthesis.

Synthesis of Star-like Poly(*tert*-butyl acrylate) Homopolymer (i.e., Star-like PtBA) Using 21Br- β -CD as Macroinitiator

Polymerization of *tert*-butyl acrylate (*t*BA) was performed in a way similar to star-like P4VP. A mixture solution consisting of 21Br- β -CD (0.04 mmol), CuBr (0.84 mmol), PMDETA (1.68 mmol), anisole (40 mL), and *t*BA (40 mL) was undergone three freeze-pump-thaw cycles in a 350 mL ampoule to remove dissolved oxygen in solution and then placed in an oil bath preheated to 60°C for desired time. The homopolymerization was stopped by quenching in liquid N₂ and exposed to air. The resulting solution was diluted with chloroform and passed through an activated neutral alumina column to remove copper catalyst. The resulting solution was dried by rotary evaporation to remove excess *t*BA monomer and solvent. The raw product was re-dissolved in acetone and precipitated in cold methanol/water (a volume ratio of methanol/water = 1:1), yielding a white powder. The product was further purified by repeating the dissolution/precipitation process using acetone as a solvent and cold methanol/water as a precipitator to remove linear homopolymer PtBA generated as side product during the ATRP.

Synthesis of Azide-Functionalized Star-like Poly(*tert*-butyl acrylate) (i.e., Star-like PtBA-N₃).

Synthesis of star-like PtBA-N₃ was followed the similar procedure as that of star-like P4VP-*b*-PtBA-N₃.

Synthesis of Star-like Poly(*tert*-butyl acrylate)-*block*-Polyethylene Oxide by Click Reaction (i.e., Star-like PtBA-*b*-PEO)

Synthesis of star-like PtBA-*b*-PEO was followed the similar procedure as that of star-like P4VP-*b*-PtBA-*b*-PEO via copper(I)-catalyzed alkyne-azide cycloaddition except that the ligand was changed from Me₆TREN to PMDETA.

Synthesis of Star-like Poly(acrylic acid)-*block*-Poly(ethylene oxide) (i.e., Star-like PAA-*b*-PEO) by *in-situ* Hydrolysis of Poly(*tert*-butyl acrylate) Block to Poly(acrylic acid) Block.

In-situ conversion of PtBA into PAA was catalyzed by TFA. Typically, 400 mg star-like PtBA-*b*-PEO was dissolved in 20 mL DCM, followed by addition of 1 mL TFA. The system was kept stirring at ambient temperature for 24 h before the solvent and the excess TFA were removed by rotary evaporation. The raw product was purified by washing with the mixture solution containing DCM/ethanol (the volume ratio of DCM/ethanol = 1:1), yielding a white product. The purified star-like PAA-*b*-PEO was stored at 0°C prior to PNCs synthesis.

Preparation of Methylammonium Halide (CH₃NH₃X, X=Br or I)

Methylammonium halide (CH₃NH₃X; MAX) was synthesized by reacting methylamine with the corresponding acid. First, methylamine in absolute ethanol was cooled to 0°C and stirred at this temperature with the addition of HBr or HI using a dropping funnel. The molar ratio of CH₃NH₂ to the corresponding acid is 1:1.2 for the complete consumption of CH₃NH₂. The mixture solution was kept stirring at 0°C for 2 h before the solvent was removed by rotary evaporation. The resulting

product was recrystallized in ethanol twice and washed by anhydrous diethyl ether to yield white powder-like product. The residual solvent was removed by drying under vacuum prior to use.

Synthesis of Oleylamine and Oleic Acid-Co-Capped MAPbX₃ (X=Br or I) PNCs as Control

All octylamine- or oleic acid-capped MAPbX₃ PNCs were prepared by the LARP method (8). In a typical synthesis of MAPbBr₃ PNCs, a mixture solution containing MABr (0.16 mmol), PbBr₂ (0.2 mmol), octylamine (20 μ L), oleic acid (0.5 mL), and DMF (5 mL) was dropped into 10 mL toluene which was a poor solvent for organic-inorganic hybrid perovskite. Small short-chain ligand-capped MAPbBr₃ PNCs were formed instantaneously with vigorous stirring, displaying a bright green color. The resulting PNCs were purified by centrifuge at 8500 rpm for 5 min. The supernatant was obtained, yielding a yellow-green solution with strong green emission. To maintain the colloidal stability of as-synthesized PNC solution, no further purification step was performed. To preserve the structural integrity of MAPbI₃ PNCs without decomposition, the LARP procedure was conducted both in glove box and at ambient condition as control. The purification step was performed once and the resulting MAPbI₃ PNCs colloidal solution was used as control.

Characterization

The molecular weight of hydrophobic star-like copolymers was measured by an agilent-1100 gel permeation chromatography (GPC) equipped with a G1362A refractive detector and a G1314A variable wavelength detector with one 5 μ m LP gel column (500 \AA , molecular range: 500 ~ 2 \times 10⁴ g/mol) and 5 μ m LP gel mixed bed columns (molecular range: 200 ~ 3 \times 10⁶ g/mol) with THF as the mobile phase. The molecular weight of amphiphilic star-like copolymers was measured by a

Shimadzu system (CTO-20A column oven, LC-20A pump and RID-10A refractive index detector) with DMF (stabilized with LiBr) as the mobile phase. Both THF and DMF GPCs were calibrated with PS standard samples. As one type of size exclusion chromatography, GPC was employed to measure the number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity (PDI) of star-like polymers. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ characterizations were performed using a Varian VXR-300 nuclear magnetic resonance spectroscopy. FT-IR spectra were obtained by a Magna-550 Fourier transform infrared spectrometer. The hydrodynamic size of analysis of star-like P4VP-*b*-PtBA-*b*-PS and P4VP-*b*-PtBA-*b*-PS triblock copolymers in DMF was conducted using a DynaPro Nanostar (Wyatt Technology). For the purpose of accuracy, each dynamic light scattering measurement was performed under condition that a good correlation function was obtained. The X-ray diffraction (XRD) pattern was collected by a PANalytical X'Pert PRO X-ray diffractometer using Cu $K\alpha_1$ radiation ($\lambda=1.541 \text{ \AA}$) operating at 40 kV and 40 mA. The morphology of MAPbBr₃/SiO₂ core/shell NCs was imaged using JEOL 100CX transmission electron microscopy (TEM) operating at 100 keV.

UV-Vis spectra were recorded by Shimadzu UV-Vis spectrophotometer (UV-2600) with slit width=5.0 nm. Photoluminescence (PL) spectra of PNCs solutions were collected using a Shimadzu RF-5301PC spectrofluorophotometer with the excitation wavelength of 380 nm. PL quantum yield was measured by using rhodamine 6G as a reference.

PL lifetimes of MAPbBr₃ NC before and after the SiO₂ coating were acquired by time-correlated single-photon counting technique (Hamamatsu, C10627). The excitation was provided by a femtosecond mode-locked Ti: sapphire laser (MAITAI XF-IMW) at 365 nm with an average power of 0.4mW. The time-resolved PL decay curves were fitted using a bi-exponential decay

function: $A(t) = A_0 + A_1 \exp(-\frac{t}{\tau_1}) + A_2 \exp(-\frac{t}{\tau_2})$, where A_0 , A_1 and A_2 are constants, t is the decay

time, and τ_1 and τ_2 are the PL decay lifetimes. The average PL decay lifetime was calculated using

$$\tau_{\text{ave}} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}$$

The photostability measurement of PS-capped MAPbBr₃/SiO₂ core/shell NC toluene solution was performed using all-transparent quartz cuvette with a total volume fixed at 1.5 mL. Prior to illumination, the colloidal solution was examined to ensure that the maximum of the PL intensity was below the highest value that the instrument can measure.

The UV light source employed in the photostability investigation was provided by UVGL-25 UV lamp with a 365-nm wavelength and power intensity of 720 $\mu\text{W}/\text{cm}^2$. The PS-capped MAPbBr₃/SiO₂ core/shell NC toluene solution was directly in contact with UV light source during the continuous illumination. The evaporation of toluene due to the heat generated by UV lamp was replenished to ensure the constant concentration of colloidal solution. Thus, the variation of PL intensity was independent on the solution concentration. The PL spectra of core/shell NC toluene solution after a 365-nm UV light illumination were recorded at a periodic interval. The moisture stability of PS-capped MAPbBr₃/SiO₂ core/shell NCs was measured in a similar way by which the colloidal toluene solution was intentionally exposed to a certain level of humidity under room light. The PL spectra of the colloidal toluene solution were recorded. The photostability and moisture stability of thin film comprising PS-capped MAPbBr₃/SiO₂ core/shell NCs were measured in a similar way. The thin film was prepared by spin coating its toluene solution at 1600 rpm for 60 s.

Table S1. Dipole moment and normalized polarity of common organic solvents.

Organic Solvent	Dipole Moment (D)^a	Normalized Polarity^b
Cyclohexane	0	0.0006
n-Hexane	0.08	0.0009
Toluene	0.31	0.099
n-Heptane	N/A	0.0012
Dichloromethane	1.14	0.309
Chloroform	1.15	0.259
Ethyl Ether	1.15	0.117
Chlorobenzene	1.54	0.188
Ethyl Alcohol	1.66	0.654
Isopropyl Alcohol	1.66	0.546
Tetrahydrofuran	1.75	0.207
Ethyl Acetate	1.88	0.228
Acetone	2.69	0.355
Methanol	2.87	0.762
Acetonitrile	3.44	0.46
N,N-Dimethylformamide	3.86	0.386
Tert-butyl Alcohol	3.9	0.389
Dimethyl Sulfoxide	4.1	0.444

a. The values of dipole moment are collected from the following online source:

<http://murov.info/orgsolvents.htm> and http://www1.biologie.uni-hamburg.de/b-online/library/newton/Chy251_253/Lectures/Solvents/Solvents.html

b. The value is collected from (37).

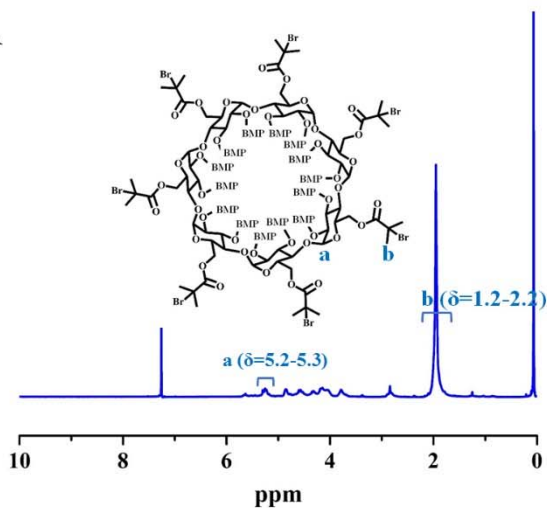
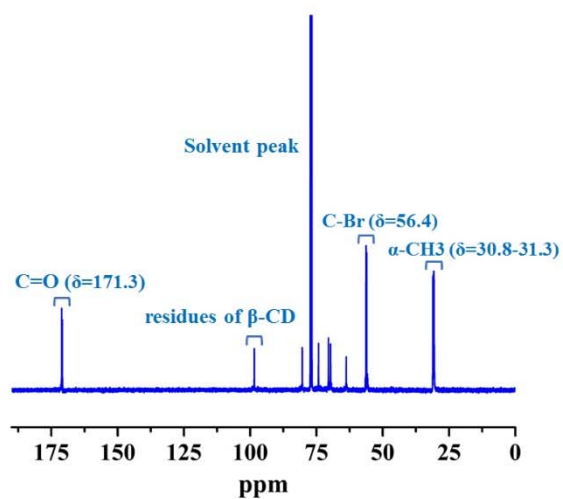
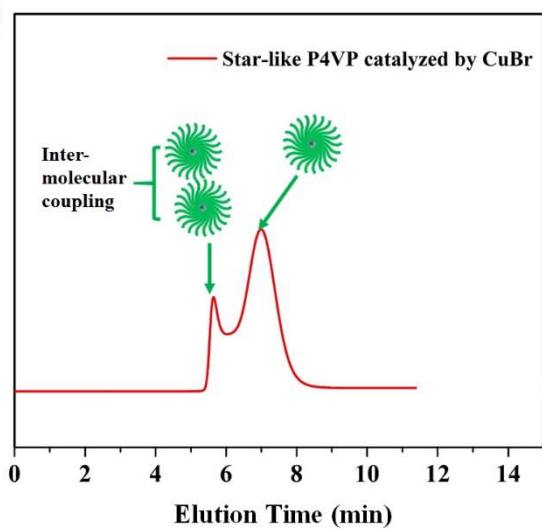
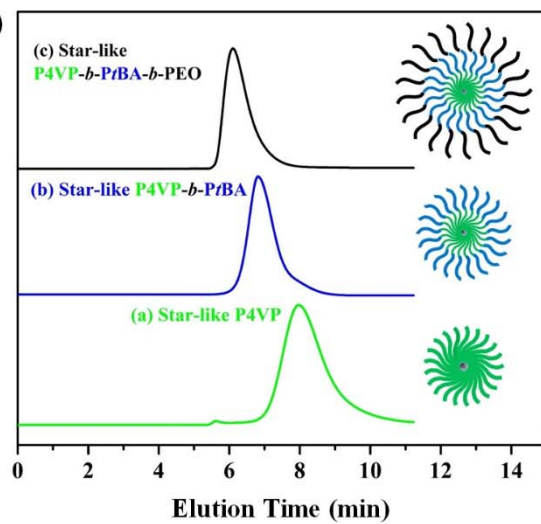
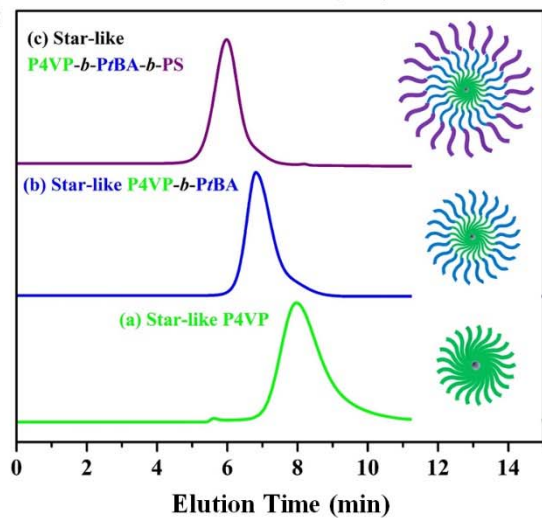
A**B****C****D****D**

Fig. S1. Characterization of macroinitiator and various 21-armed star-like homopolymer and copolymers. (A) ^1H NMR spectrum of macroinitiator heptakis[2,3,6-tri-O-(2-bromo-2-methylpropionyl)]- β -cyclodextrin (denoted 21Br- β -CD). (B) ^{13}C NMR spectrum of macroinitiator 21Br- β -CD (δ 30.8–31.3 (a- CH_3), 56.4 (C-Br), 64.0, 69.9–73.6, 74.4, 80.5, 98.6 (residues of β -CD), 171.3 (C=O)). (C) GPC trace of star-like P4VP-Br homopolymer prepared by utilizing CuBr as a catalyst and Me_6TREN as a ligand. DMF was used as the mobile phase for GPC of star-like P4VP-Br homopolymer. The shoulder appeared in high molecular weight range suggests the intermolecular coupling among star-like P4VP homopolymers. GPC traces of (D) star-like P4VP-*b*-PtBA-*b*-PEO and (E) star-like P4VP-*b*-PtBA-*b*-PS block copolymers synthesized using CuCl and CuCl_2 as the catalysts and Me_6TREN as a ligand using DMF as the mobile phase.

The bromination efficiency of hydroxyl groups was calculated based on the following equation

$$E_T = \frac{A_b}{18A_a} \times 100\%$$

where E_T is the conversion efficiency of hydroxyl groups on β -CD; A_b and A_a are the integral area of the methyl protons of 21Br- β -CD and the integral area of the proton shown in **fig. S1A**, respectively. An E_T value of 100% was obtained, indicating that hydroxyl groups were almost completely converted into bromoisobutyryl units.

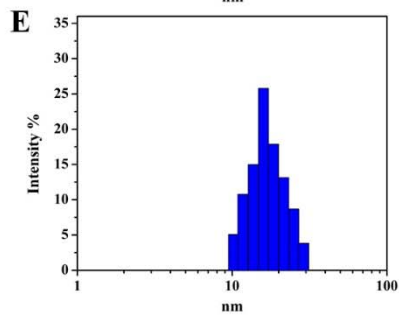
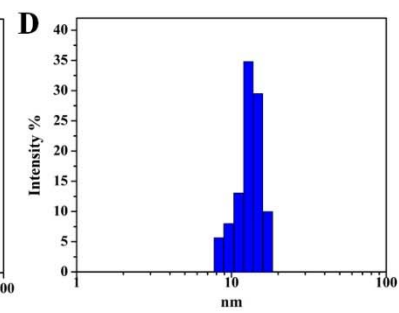
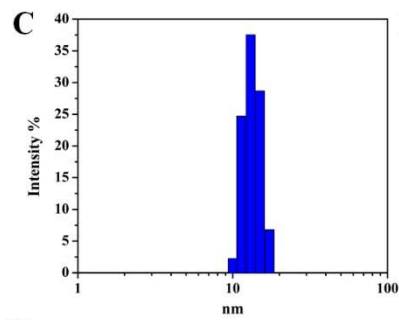
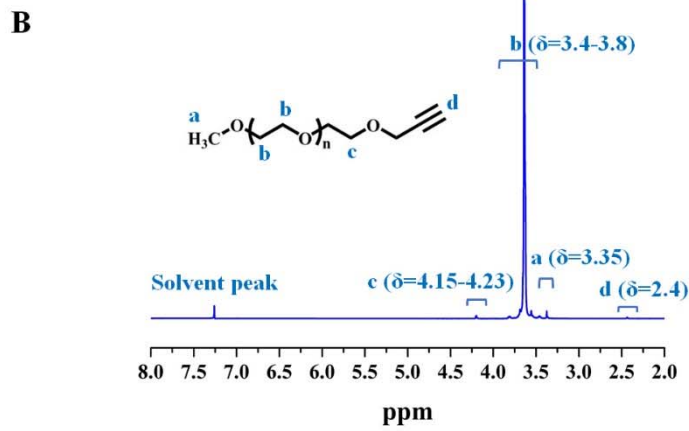
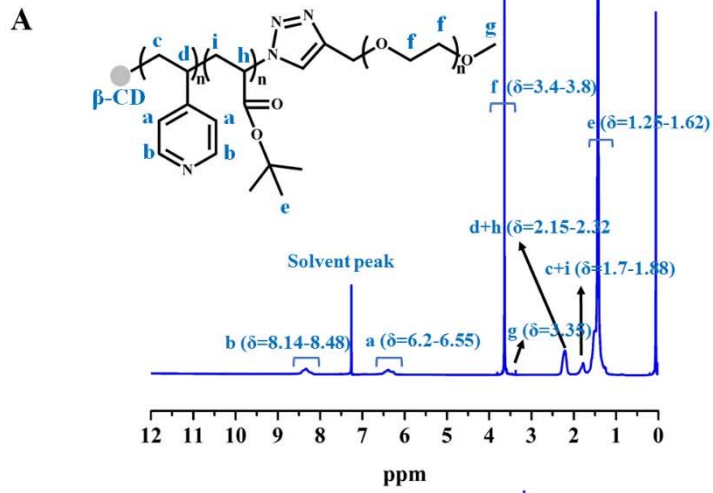


Fig. S2. NMR spectra of polymers and DLS measurements of star-like P4VP-*b*-PtBA-*b*-PEO copolymer in different solvents. (A) ^1H NMR spectrum of well-defined star-like P4VP-*b*-PtBA-*b*-PEO triblock copolymer synthesized using CuCl and CuCl₂ as the catalysts and Me₆TREN as a ligand. (B) ^1H NMR spectrum of alkyne-terminated PEO. (C) Dynamic light scattering (DLS) characterization on star-like P4VP-*b*-PtBA-*b*-PEO (Sample A in **table S1**) in pure DMF. (D) DLS characterization on star-like P4VP-*b*-PtBA-*b*-PS with the molecular weight of PS, $M_{w, \text{PS}} = 5 \text{ K}$ (Sample C in **table S1**). (E) DLS characterization on star-like P4VP-*b*-PtBA-*b*-PS with an increased molecular weight of PS, $M_{w, \text{PS}} = 10 \text{ K}$ (Sample D in **Table 1**).

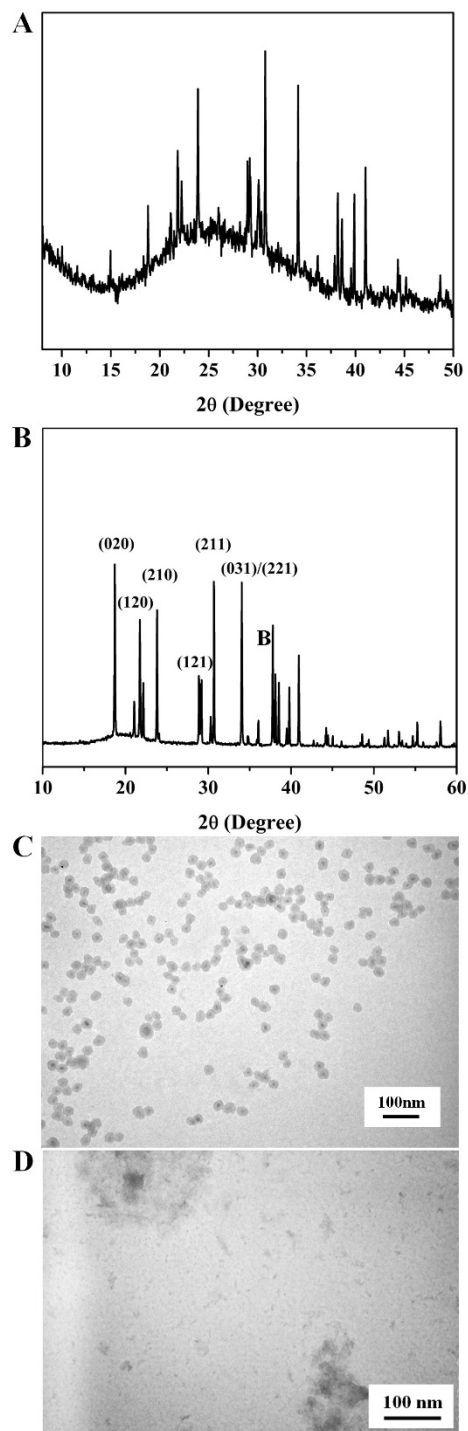


Fig. S3. Structural characterization of PNCs prepared by conventional method and star-like block copolymer nanoreactor strategy, respectively. (A) XRD pattern of MAPbBr₃ PNCs synthesized by conventional method (i.e., ligand-assisted reprecipitation with oleic acid and oleylamine as ligands, LARP) annealed in diphenyl ether at 200°C for 2 hr. MAPbBr₃ PNCs are

completely decomposed to non-perovskite material. **(B)** XRD pattern of PAA-*b*-PEO-capped PbBr₂ NCs prepared by annealing PtBA-*b*-PEO-capped PbBr₂ NCs in diphenyl ether at 200°C for 2 hr, where the peaks can be assigned to PbBr₂ NCs. **(C)** TEM images of PEO-capped MAPbBr₃/SiO₂ core/shell NCs with a MAPbBr₃ core diameter of 8.0 ± 0.3 nm and a SiO₂ shell thickness of 9.8 ± 0.4 nm, crafted by capitalizing on star-like P4VP-*b*-PtBA-*b*-PEO as nanoreactor (Sample B in **table S1**). **(D)** Synthesis of MAPbBr₃ PNCs using linear P4VP-*b*-PtBA-*b*-PEO as nanoreactor.

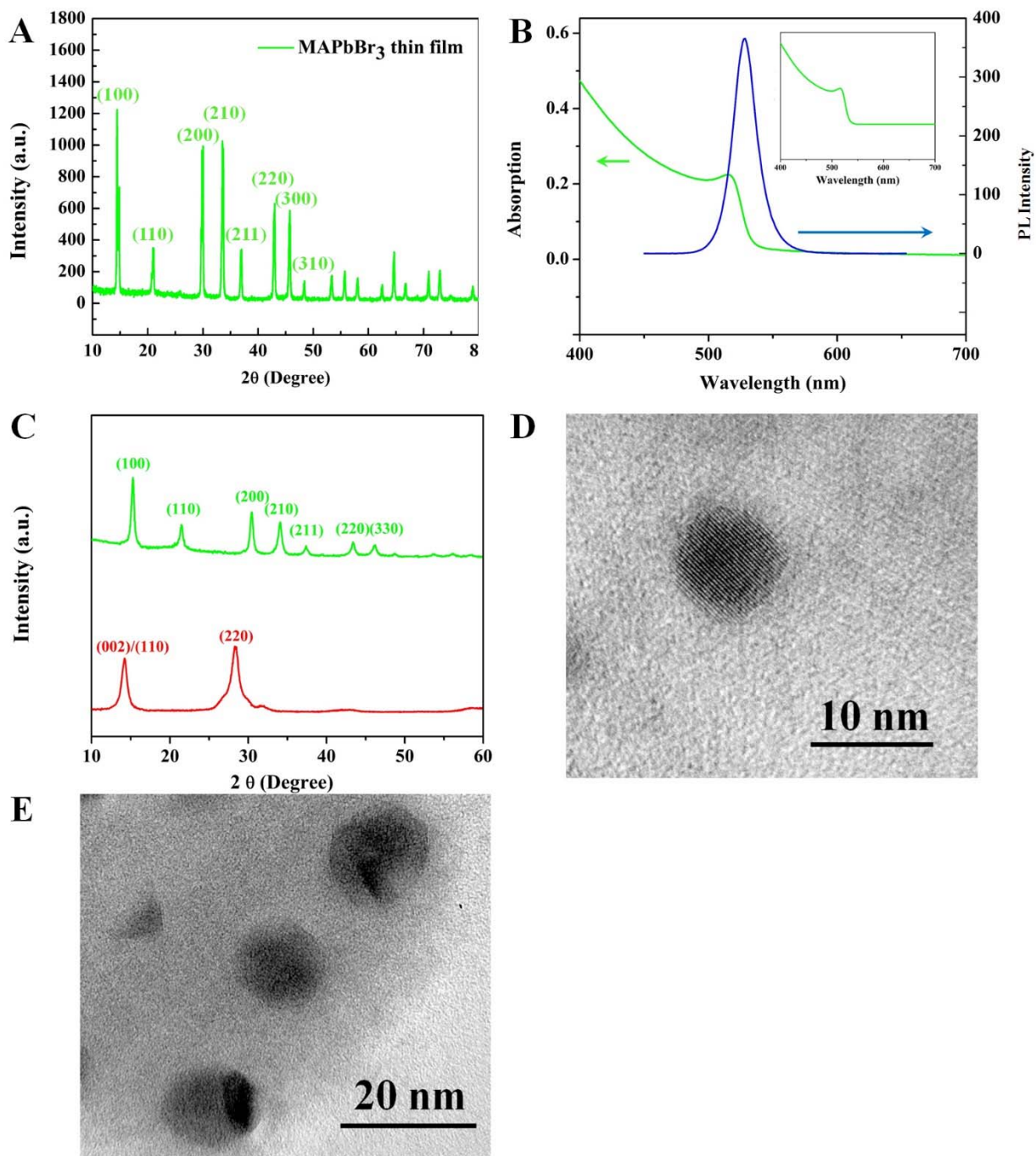


Fig. S4. XRD patterns, UV-vis absorption and PL spectra, and TEM images of perovskites. (A) XRD pattern of bulk MAPbBr₃ perovskite material prepared by dropping perovskite precursors dissolved in DMF into toluene. (B) UV-Vis absorption and PL spectra of PEO-capped MAPbBr₃/SiO₂ core/shell NCs in toluene (inset: the UV-Vis absorption of MAPbBr₃ NCs prior to the SiO₂ coating). (C) Comparison of XRD profiles of PEO-capped MAPbBr₃ and PEO-capped

MAPbI₃ PNCs prepared by using star-like PAA-*b*-PEO as nanoreactors. TEM images of (D) PEO-capped MAPbI₃ PNCs prepared by using star-like PAA-*b*-PEO as nanoreactors. (E) oleylamine- and oleic acid-co-capped MAPbI₃ PNCs.

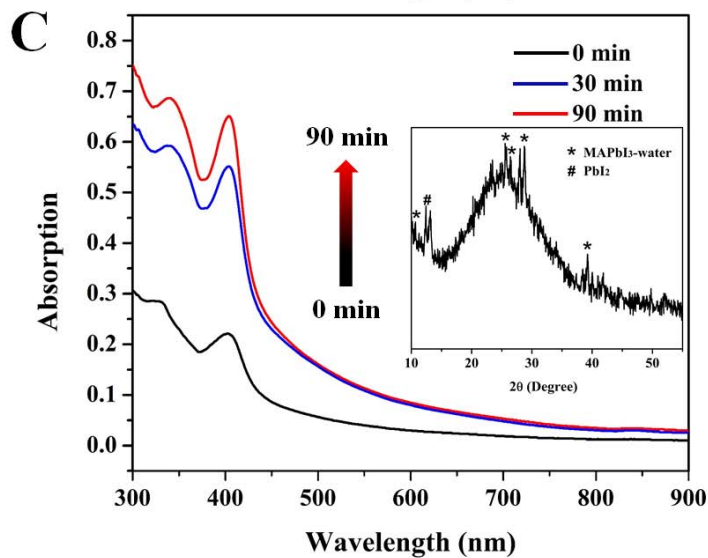
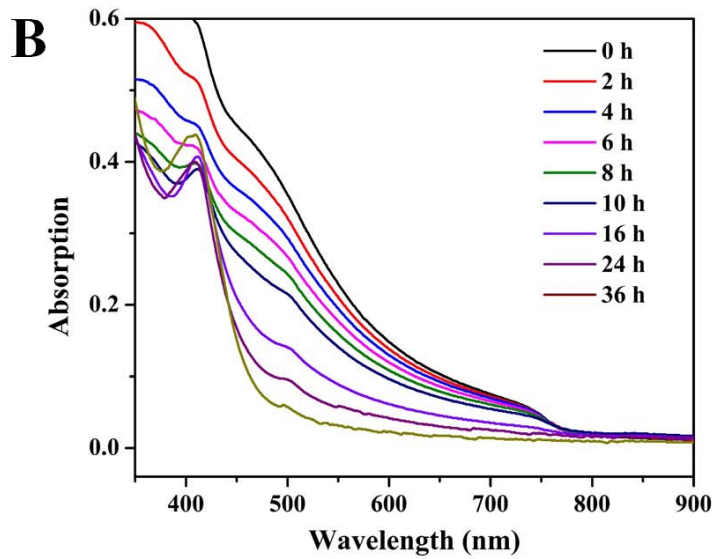
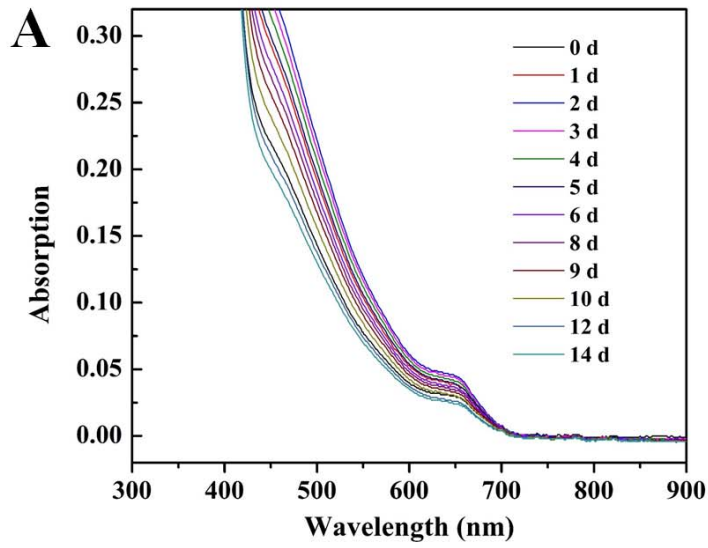


Fig. S5. UV absorption spectra of MAPbI₃ PNCs prepared by different methods. (A) Evolution of UV-Vis absorption spectra of 10 nm PEO-capped MAPbI₃ PNCs prepared using star-like PAA-*b*-PEO as nanoreactor under ambient condition. (B) Evolution of UV-Vis absorption spectra of MAPbI₃ PNCs prepared by dropping MAPbI₃ precursor DMF solution into toluene with stirring (i.e., the ligand-assisted reprecipitation (LARP) route) in glove box. The appearance of absorption peak at approximately 410 nm is due to the formation of white decomposed perovskite (i.e., non-perovskite material). The fast decrease in the absorption peak from 700-800 nm is attributed to the decomposition of MAPbI₃ PNCs. (C) Evolution of UV-Vis absorption spectra of MAPbI₃ PNCs prepared by dropping MAPbI₃ precursor DMF solution into toluene with stirring under ambient condition. The appearance of absorption peak at approximately 410 nm is due to the formation of white decomposed perovskite (i.e., non-perovskite material). The XRD pattern of this white product shown as an inset indicated it contains PbI₂ and MAPbI₃-water complexes with no clear XRD pattern from MAPbI₃. There is no absorption peak from MAPbI₃ PNCs as they are completely decomposed right after synthesis, indicating that MAPbI₃ PNCs cannot be obtained using the LARP method under ambient condition.

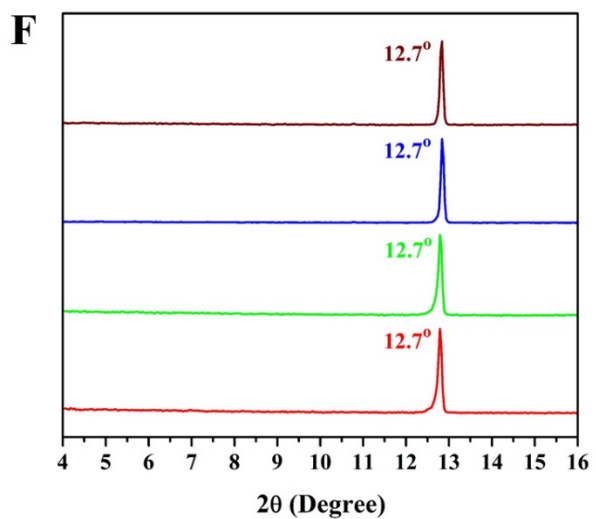
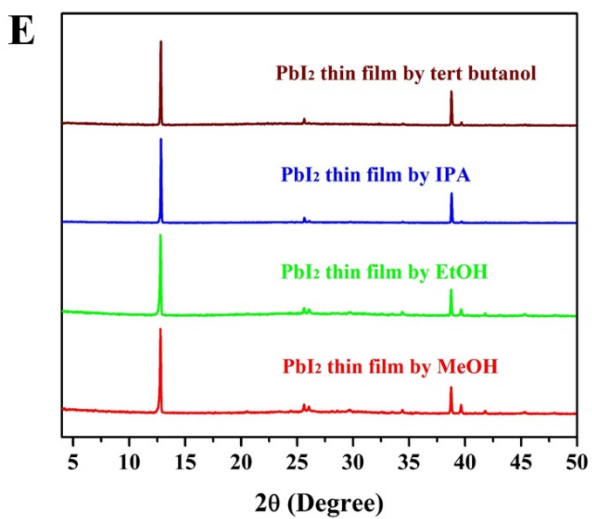
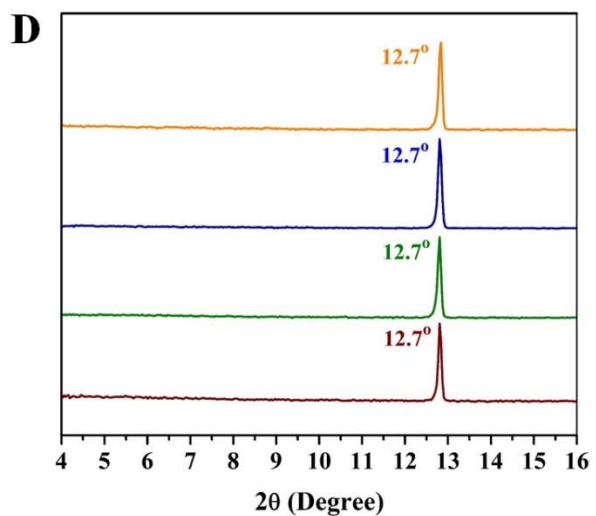
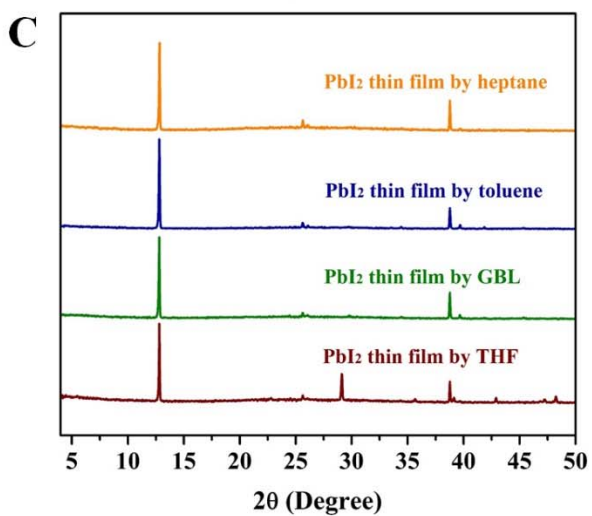
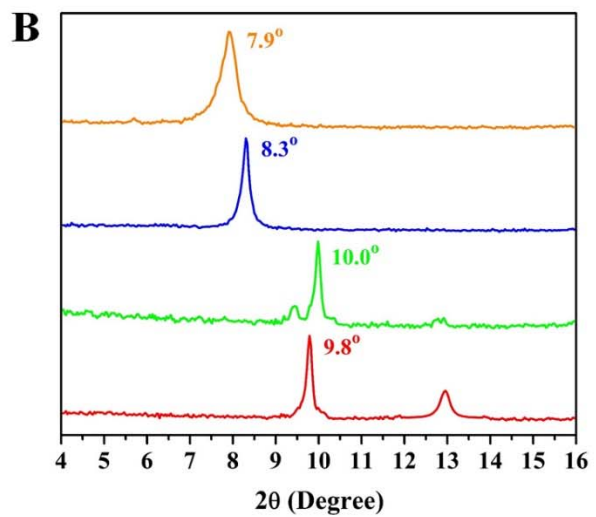
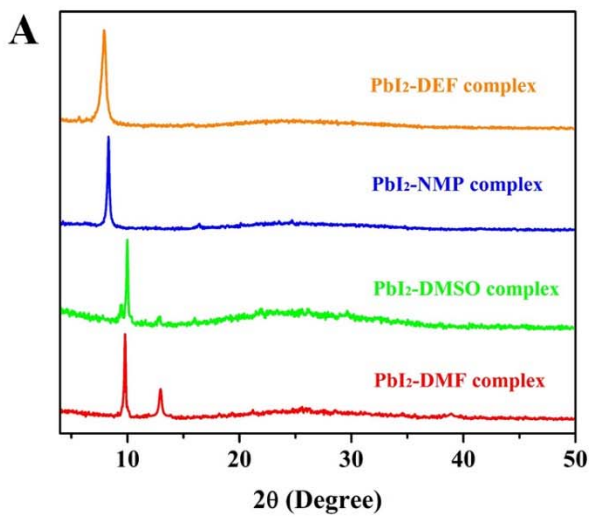


Fig. S6. XRD patterns of MAPbI₃ prepared by reacting MAI with PbI₂ dissolved in different solvents. (A) XRD patterns of PbI₂ thin films formed by spin-coating PbI₂ from various coordinate organic solvents (i.e., DEF, NMP, DMSO and DMF). (B) Close-up diffraction patterns of PbI₂ thin films in (A), suggesting the formation of PbI₂-solvent complex. (C) XRD patterns of PbI₂ thin films by spin-coating PbI₂ from various non-coordinate organic solvents (i.e., heptane, toluene, GBL and THF). (D) Zoom-in diffraction patterns of PbI₂ thin films in (C), indicating the formation of PbI₂ crystals. (E) XRD patterns of PbI₂ thin films by spin-coating PbI₂ from various non-coordinate organic solvents (i.e., *tert* butanol, IPA, EtOH and MeOH). (F) Close-up diffraction patterns of PbI₂ thin films in (E), signifying the formation of PbI₂ crystals. The full names of the following solvents, DEF, NMP, DMSO, DMF, GBL, THF, IPA, EtOH and MeOH are diethylformamide, N-Methyl-2-pyrrolidone, dimethyl sulfoxide, dimethylformamide, gamma-butyrolactone, tetrahydrofuran, isopropanol, ethanol and methanol.

We noticed that common alcohols (e.g., isopropanol) used as precipitant for purifying PNCs synthesized by conventional method (i.e., LARP) tend to partially destroy the structural integrity of PNCs depending on the amount of precipitant used (**fig. S7**). For instance, even the introduction of 10% butanol by volume into the purified PNCs colloidal solution is still sufficient to trigger a complete degradation (**fig. S7D**) due to the presence of hydroxyl groups of butanol, causing the loss of emission.

The presence of outer PEO blocks in star-like P4VP-*b*-PtBA-*b*-PEO triblock copolymer (or PAA-*b*-PEO diblock copolymer) not only offers an excellent colloidal stability due to the intimate and permanent tethering to the surface of MAPbBr₃/SiO₂ core/shell NC (or MAPbI₃ PNC), as a result of original covalent bonding between the PEO blocks and the star-like P4VP-*b*-PtBA (or the star-like PAA), but also *for the first time* enables the PNC purification using solely the nonpolar solvent (i.e., n-hexane as a precipitant in our study).

Our star-like block copolymer nanoreactor route capitalizes on n-hexane as a non-polar destabilizing solvent (i.e., function as a precipitant instead of a good solvent as in copious past work noted above) for PNCs, imparting excellent colloidal stability of the resulting PNCs and sustaining their structural integrity.

In addition, we monitored the absorption peak of MAPbI₃ PNCs synthesized by the LARP method in glove box upon exposure to different alcohols by UV-Vis spectroscopy. Clearly, compared to MAPbBr₃ PNCs (**fig. S7A-D**), MAPbI₃ PNCs are much more unstable (**fig. S7E-H**) as a trace amount of alcohol was able to induce complete decomposition, signifying that a more stringent purification step should be taken during the purification of iodine-containing PNCs. It is worth noting that even the addition of ACS grade acetone into MAPbI₃ PNCs dispersed in toluene was sufficient to completely degrade PNCs, probably due to a trace amount of water in acetone, which transformed perovskite into white perovskite-water intermediate (**fig. S7H**). Nevertheless, owing to the intimate and permanent surface capping with PEO chains, PEO-capped PNCs flocculate in non-polar solvents (e.g., n-hexane). n-hexane with very low polarity and water content can be exploited as a precipitant, preserving the structural integrity of MAPbI₃ PNCs during the purification process.

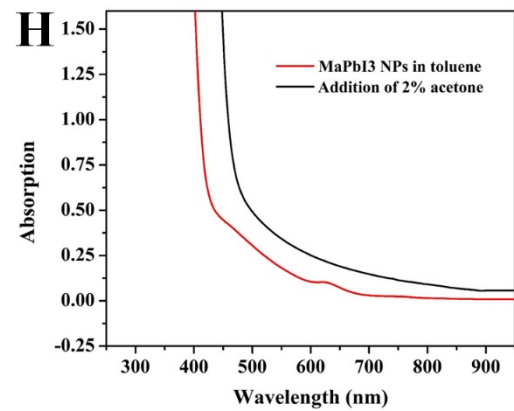
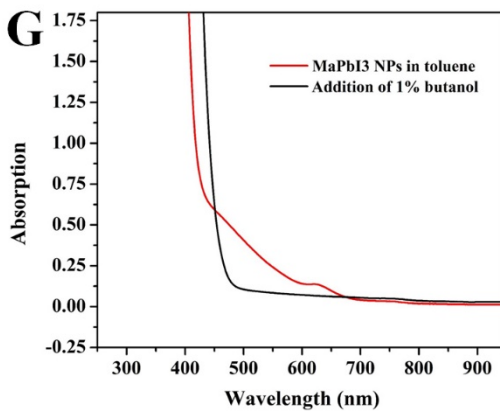
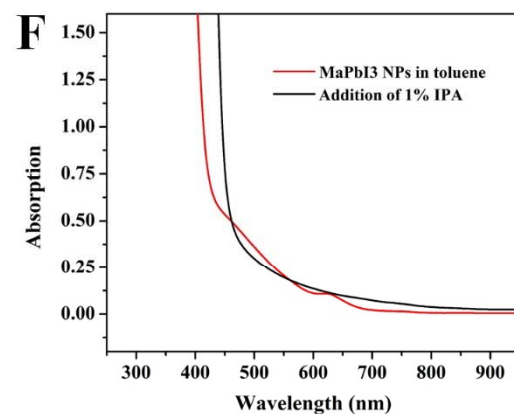
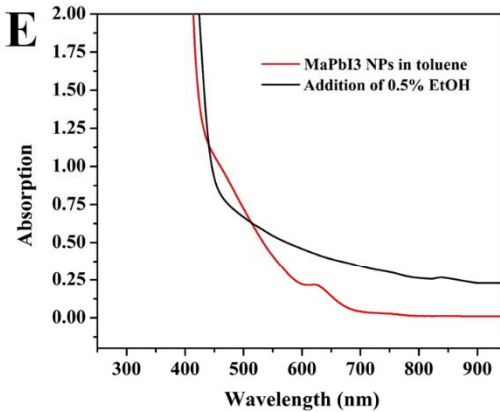
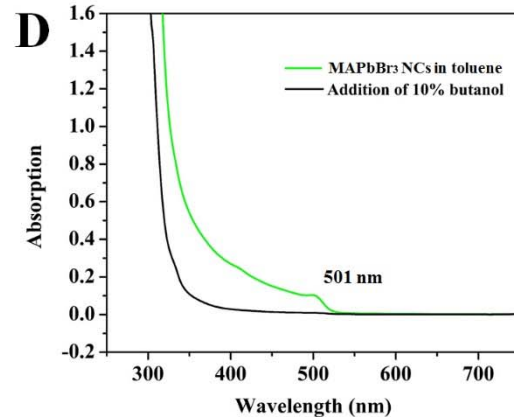
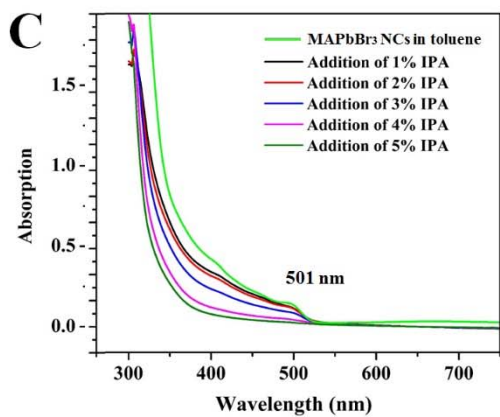
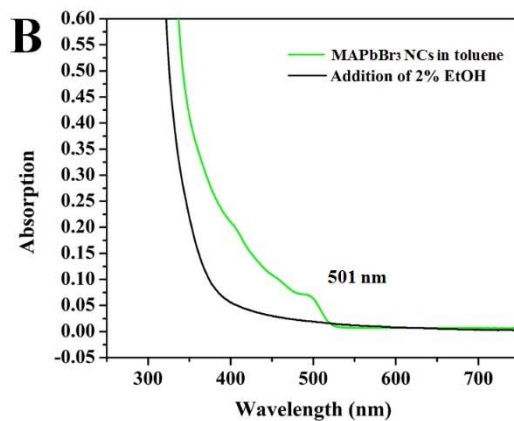
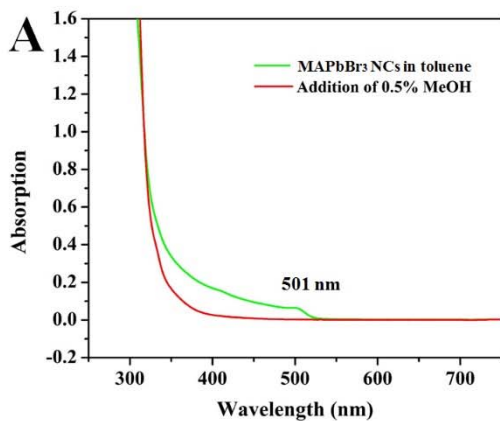


Fig. S7. Stability of MAPbX₃ PNCs synthesized by conventional method (i.e., LARP) upon exposure to various common polar organic solvents by the addition of a designated volume of these solvents into the purified PNC toluene solution. UV-Vis spectra of MAPbBr₃ NCs in contact with (A) MeOH, (B) EtOH, (C) IPA and (D) butanol. UV-Vis spectra of MAPbI₃ NCs in contact with (E) EtOH, (F) IPA, (G) butanol and (H) acetone. The disappearance of the absorption peak is due to the dissolution or decomposition of MAPbX₃ NCs in different solvents.

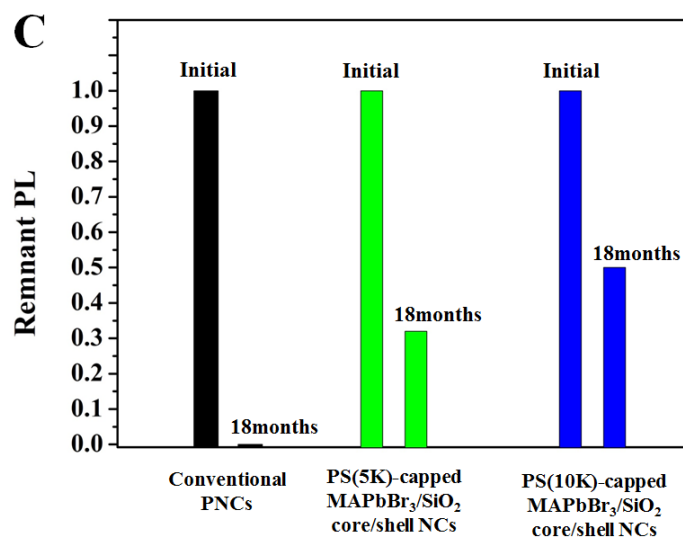
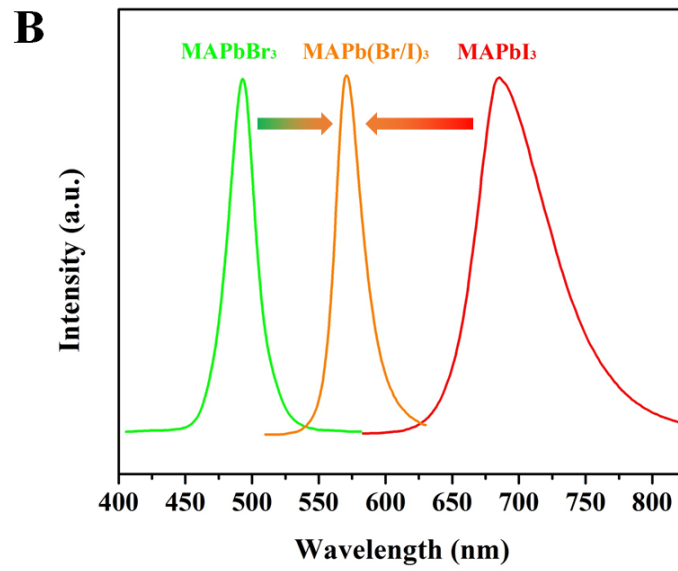
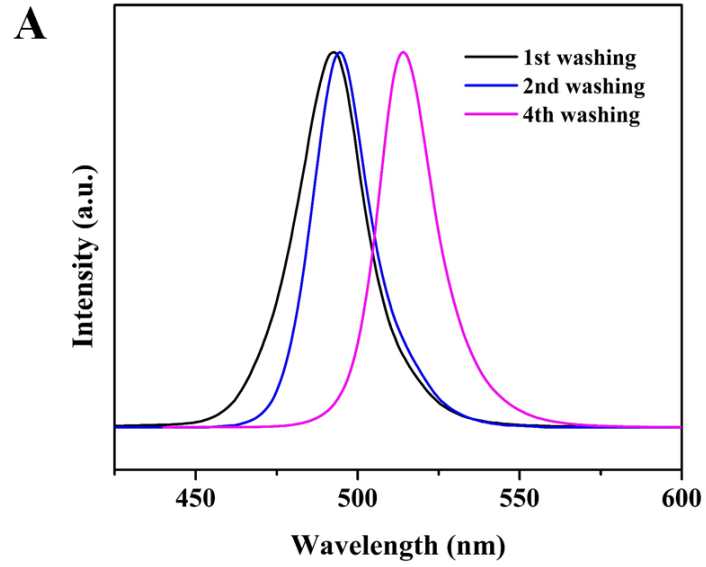


Fig. S8. MAPbBr₃ PNCs prepared by conventional method when exposed to repeated solvent washing and mixing with PNCs of different compositions. (A) Red-shift of PL peak of MAPbBr₃ PNCs prepared by the LARP method during the repeated washing process using acetone as a precipitant and hexane as a solvent. (B) Chemical composition homogenization upon the mixing of MAPbBr₃ and MAPbI₃ PNCs. Both of which are synthesized by the LARP method. (C) Stability of PS-capped MAPbBr₃/SiO₂ core/shell NCs dispersed in toluene in closed vial at ambient condition for 18 months. In sharp contrast, the remnant PL of conventionally prepared MAPbBr₃ PNCs went to zero after a 18-month storage.

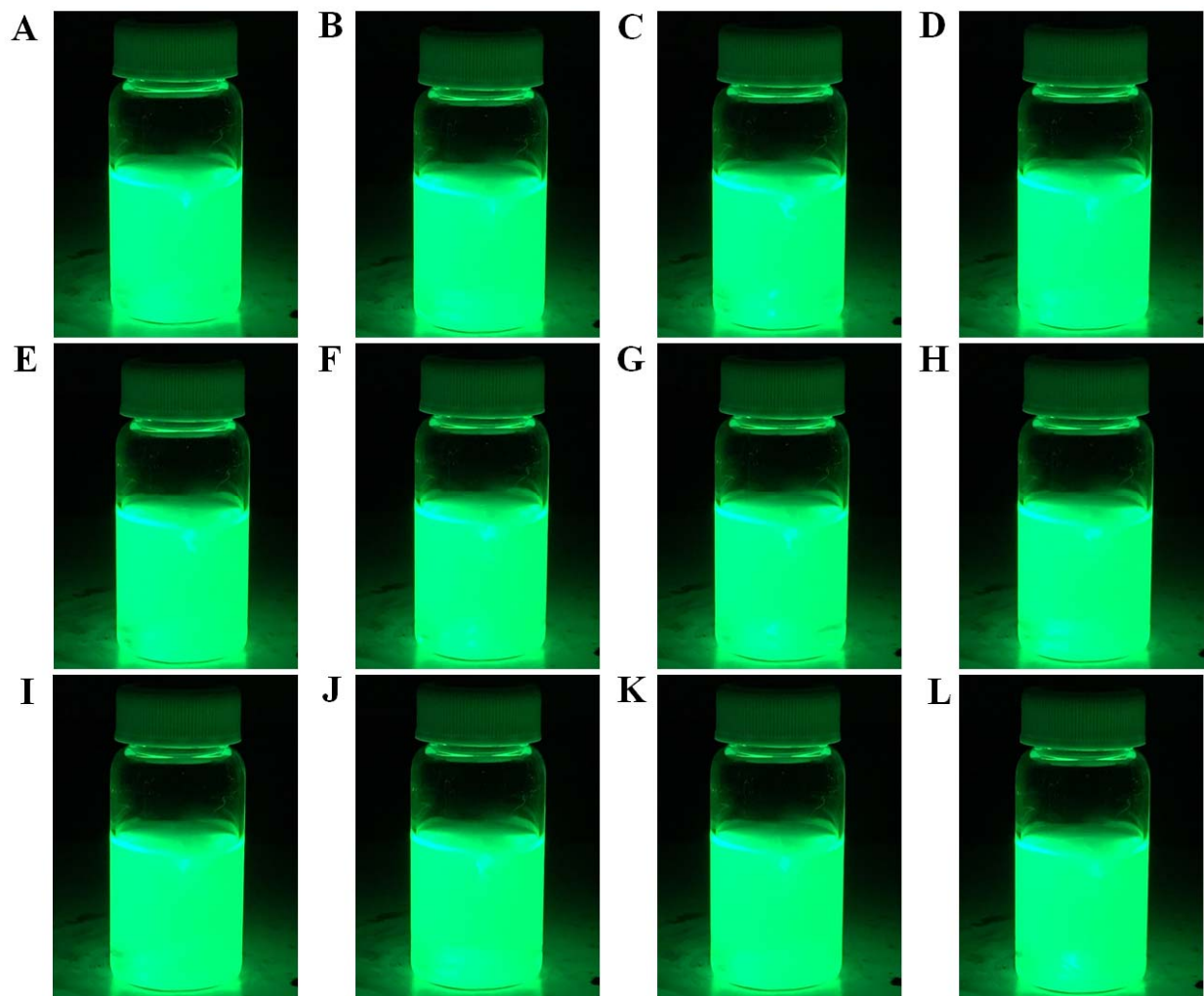


Fig. S9. Digital images of evolution of PS-capped MAPbBr₃/SiO₂ core/shell NCs dispersed in toluene with the addition of 20% water (by volume) under 365-nm UV light. (A) 1 min, (B) 3 min, (C) 10 min, (D) 30 min, (E) 60 min, (F) 90 min, (G) 120 min, (H) 150 min, (I) 180 min, (J) 210 min, (K) 240 min, and (L) 300 min. Photo Credit: Yanjie He, Georgia Institute of Technology.