

## Supporting Information

### **Harnessing of Spatially Confined Perovskite Nanocrystals using Polysaccharide-based Block Copolymer Systems**

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## MATERIALS AND METHODS

### Synthesis and characterization of the MH-*b*-PI-*b*-MH triblock Copolymer

*N*-maltoheptaosyl-3-acetamido-1-propyne (MH-C≡CH)<sup>1</sup> and 6-Azidohexanoic acid<sup>2</sup> were synthesized following the reported methods.  $\alpha$ ,  $\omega$ -dihydroxyl-terminated polyisoprenes (1,2 and 3,4-addition) (HO-PI-OH), with molecular weights ( $M_n$ ) of 8500 g mol<sup>-1</sup> and dispersity ( $\mathcal{D}$ ) of 1.14 (data from supplier), were purchased from Polymer Source, Inc (Montreal, Quebec, Canada). 6-bromohexanoic acid (Aldrich, 97%), sodium azide (NaN<sub>3</sub>, Alfa Aesar, 99%), 4-(dimethylamino)pyridine (DMAP, Aldrich, ≥99%), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC, TCI Europe, >98%) and copper nanopowder (Cu(core)/CuO(shell), Alfa Aesar, 99.9%) were used as received. Dry dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>, ≥99.8%, water content ≤0.001%) was purchased, from Aldrich and used as received. CupriSorb resin was purchased from Seachem (Madison, Georgia, USA) and used as received. Other reagents and solvents were used without further purification.

### Synthesis of $\alpha$ , $\omega$ -di-azido-terminated polyisoprene (N<sub>3</sub>-PI<sub>8.5k</sub>-N<sub>3</sub>)

The synthesis was adapted from the procedure described by Isono *et al.*<sup>3</sup> In a three-necked flask equipped with a magnetic stir bar, a solution of 6-azidohexanoic acid (349 mg, 2.22 mmol) in dry

CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added dropwise to a solution of HO-PI<sub>8.5k</sub>-OH (M<sub>n</sub> = 9000 g/mol, <sup>1</sup>H NMR) (2.0 g, 0.222 mmol), DMAP (380 mg, 3.11 mmol) and EDC (596 mg, 3.11 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (50 mL) under an argon atmosphere. The reaction vessel was cooled with an ice bath during the addition and the reaction mixture was left stirring for 36 h at 35 °C. The reaction mixture was then concentrated. Hexane was added and the solution was washed three times with a saturated solution of K<sub>2</sub>CO<sub>3</sub> and two times with water. The solution was dried with MgSO<sub>4</sub>, filtrated and concentrated to give N<sub>3</sub>-PI<sub>8.5k</sub>-N<sub>3</sub> as a sticky white solid. Yield 85%. M<sub>n</sub> (<sup>1</sup>H NMR = 9300 g/mol.

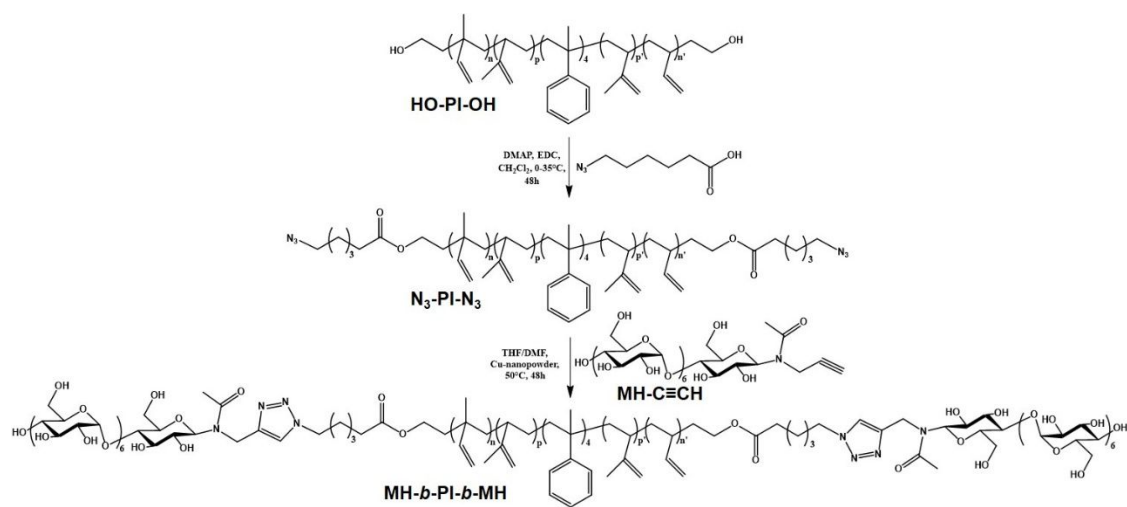
#### **Synthesis of Maltoheptaose-*block*-polyisoprene-*block*-maltoheptaose (MH-*b*-PI<sub>8.5k</sub>-*b*-MH) by click-chemistry**

A solution of (N<sub>3</sub>-PI<sub>8.5k</sub>-N<sub>3</sub>) (2.00 g, 0.215 mmol) in tetrahydrofuran (THF) (24 mL) was degassed by high-purity argon for 10 min. The solution was then cannulated to a similarly degassed solution of MH-C≡CH (636 mg, 0.516 mmol) in dimethylformamide (DMF) (15 mL) and copper nanopowder (66 mg, 1.03 mmol) was added under an argon atmosphere. The mixture was stirred at 64 °C until the infrared (IR) spectrum shows complete disappearance of the signal due to the azido group of N<sub>3</sub>-PI<sub>8.5k</sub>-N<sub>3</sub> precursor (~48h). The reaction mixture was then filtered through celite and concentrated. To completely remove copper, the concentrate was redissolved in an excess of THF together with a few milliliter of water and charged with Cuprisorb resin. The mixture was stirred at 50 °C, filtered

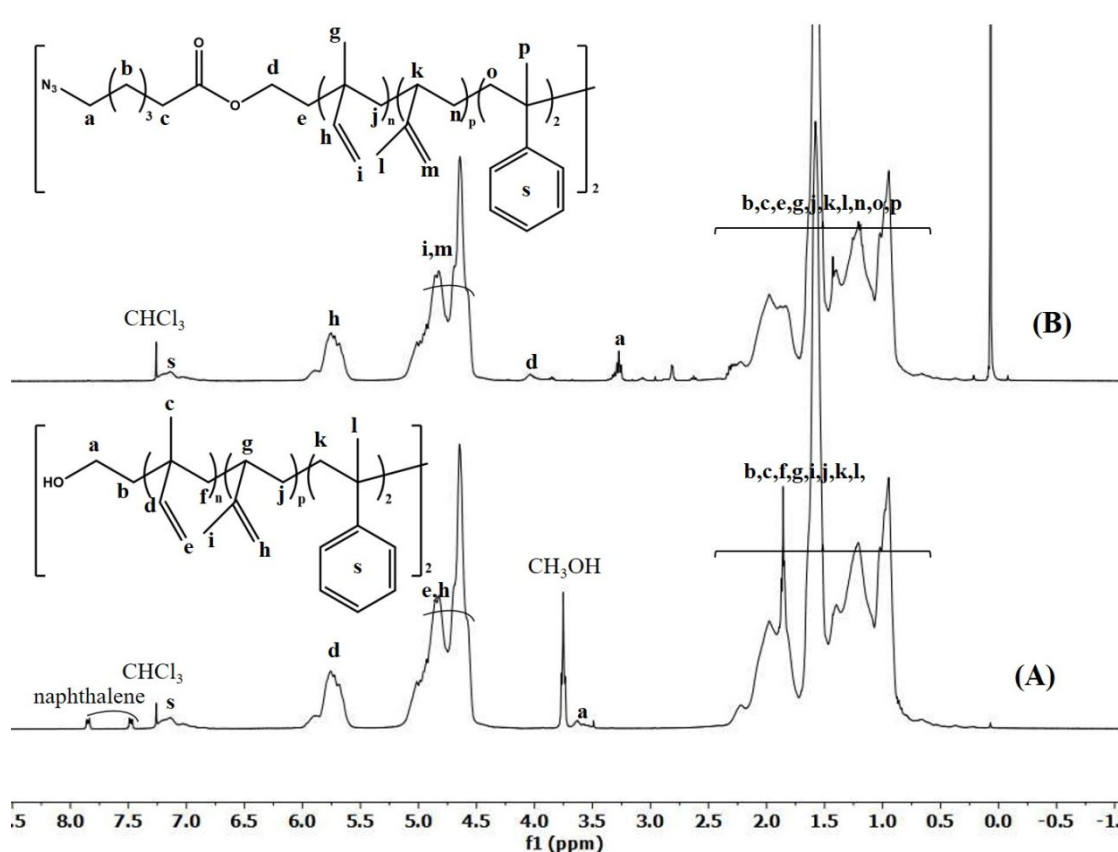
through celite and concentrated by evaporation. The crude product was then purified by precipitation in cold CH<sub>3</sub>OH. The copolymer was collected by filtration and dried under vacuum to give MH-*b*-PI<sub>8.5k</sub>-*b*-MH triblock copolymer as a white solid, with 75% yield.

## Characterization

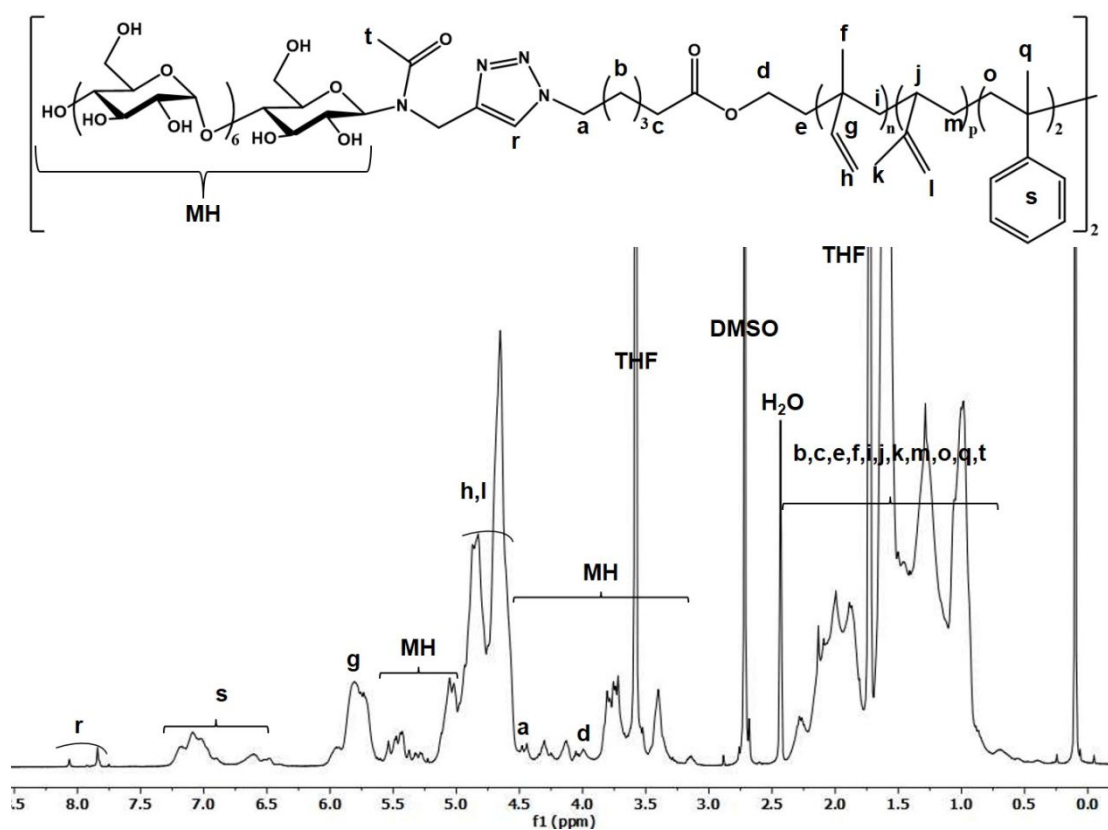
<sup>1</sup>H nuclear magnetic resonance (NMR) spectra were recorded at room temperature on a 400 MHz Bruker Avance DRX400 in CDCl<sub>3</sub> or a mixture of THF-*d*<sup>8</sup> with six drops of dimethyl sulfoxide-*d*<sup>6</sup> (DMSO-*d*<sup>6</sup>). Chemical shifts (<sup>1</sup>H NMR) were referenced to the peak of residual CHCl<sub>3</sub> at  $\delta$  = 7.26 ppm or to the peaks of residual THF at  $\delta$  = 3.60 and 1.75 ppm. Size exclusion chromatography (SEC) with THF as eluent, calibrated with polystyrene standards from Polymer Laboratories, was run with a Varian Prostar (model 210) pump at a flow rate of 1 mL min<sup>-1</sup> using two 300 mm long, mixed-D PL-gel 5  $\mu$ m columns (molecular weight range:  $2 \times 10^2 - 4 \times 10^5$  g mol/mol from Polymer Laboratories) thermostated at 30 °C, connected to a Shodex (model RI-101) refractometer detector. The infrared (IR) spectra were recorded using a Perkin-Elmer Spectrum RXI FTIR spectrometer.



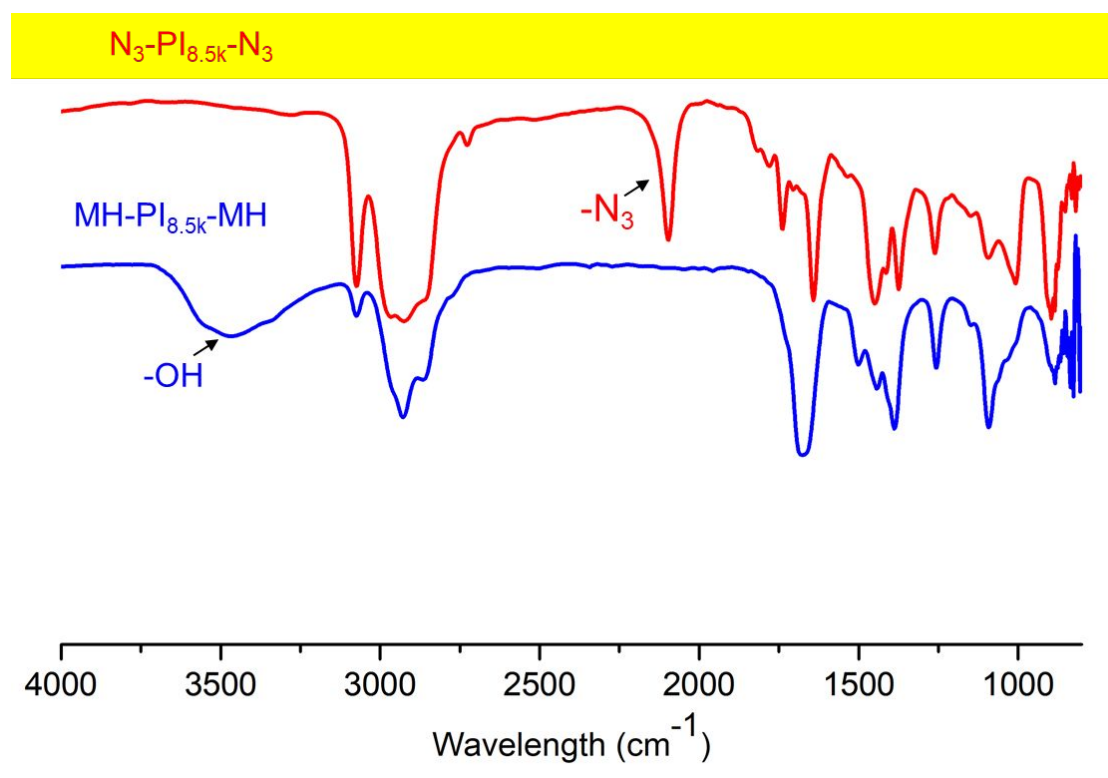
**Scheme S1:** Synthesis of MH-*b*-PI<sub>8.5k</sub>-*b*-MH triblock copolymer.



**Figure S1:** <sup>1</sup>H NMR of HO-PI<sub>8.5k</sub>-OH (A) and N<sub>3</sub>-PI<sub>8.5k</sub>-N<sub>3</sub> (B) in CDCl<sub>3</sub> (400 MHz, RT). The complete disappearance of signals at 3.63 ppm due to  $-\text{CH}_2\text{OH}$  of the HO-PI<sub>8.5k</sub>-OH and appearance of new signals at 4.04 ppm dedicated to  $-\text{CH}_2\text{N}_3$ , indicates complete azido functionalization.

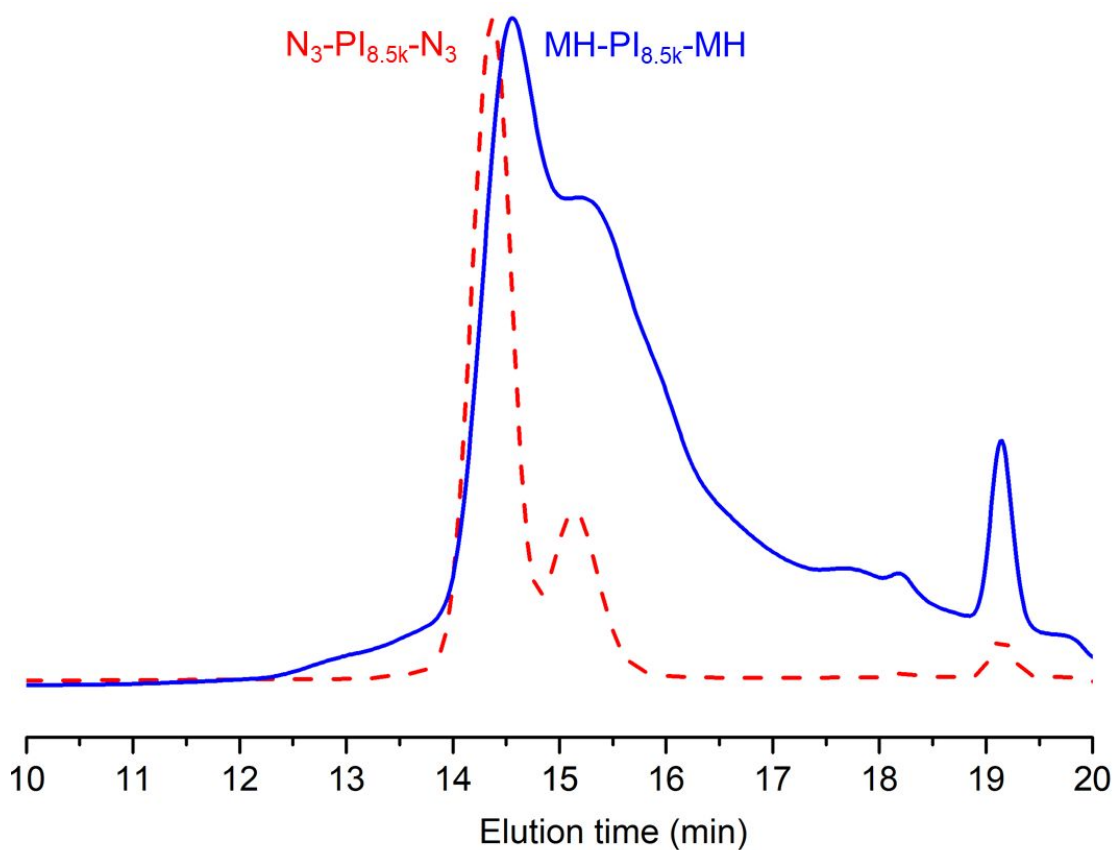


**Figure S2:**  $^1\text{H}$  NMR of MH-*b*-PI<sub>8.5k</sub>-*b*-MH tri block copolymer. The presence of signals dedicated to both PI and MH along with the appearance of new peaks positioned at 7.75 – 8.07 ppm due to triazole ring, confirms the successful formation of MH-*b*-PI<sub>8.5k</sub>-*b*-MH triblock copolymer.

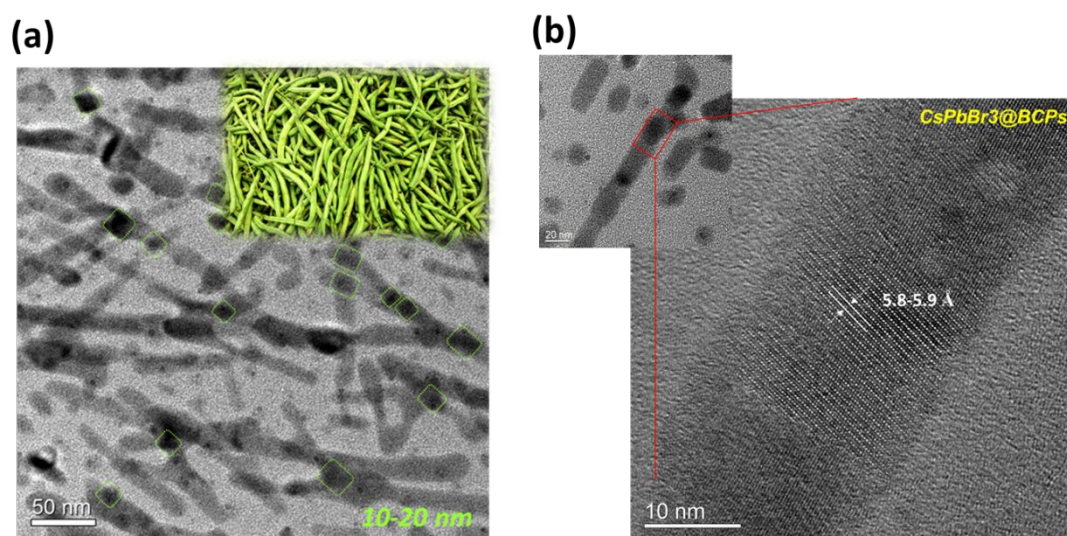


**Figure S3:** FTIR spectra of  $N_3\text{-PI}_{8.5k}\text{-N}_3$  and  $\text{MH-}b\text{-PI}_{8.5k}\text{-}b\text{-MH}$ . The complete disappearance of the signals at  $2196\text{ cm}^{-1}$  due to azido group in FTIR spectrum of  $\text{MH-}b\text{-PI}_{8.5k}\text{-}b\text{-MH}$ , indicates its full consumption during click reaction.





**Figure S4:** SEC traces of  $N_3$ -PI<sub>8.5k</sub>- $N_3$  and MH-*b*-PI<sub>8.5k</sub>-*b*-MH. The presence of a small peak in lower molecular weight side of  $N_3$ -PI<sub>8.5k</sub>- $N_3$  attributed to mono-functional starting material (PI-OH) with half molecular weight. The retention volumes of MH-*b*-PI<sub>8.5k</sub>-*b*-MH are slightly larger than those of their precursors  $N_3$ -PI<sub>8.5k</sub>- $N_3$ , which apparently indicates a decrease of molecular weights. In addition, a high molecular weight shoulder peak appears in the case of MH-*b*-PI<sub>8.5k</sub>-*b*-MH. Even though we assume that the copolymers seem to be sufficiently soluble in THF for SEC analyses, the latter is not a good solvent for maltoheptaose block. Thus, the two phenomena observed on SEC traces may be due to aggregation or self-assembly of the amphiphilic copolymers in THF. Similar observations have already been reported in the literature<sup>4,5</sup>.



**Figure S5.** a. TEM image and b. HR-TEM of the quantum-confined CsPbBr<sub>3</sub>@BCPs for MH-*b*-PI-*b*-MH-B sample.

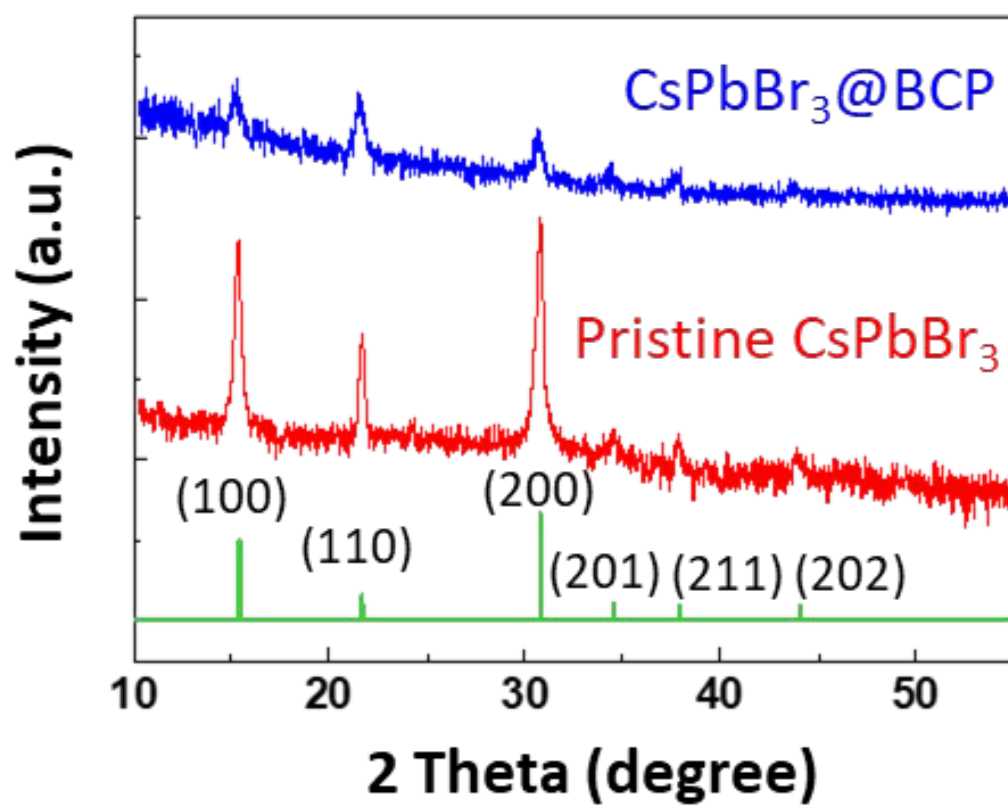
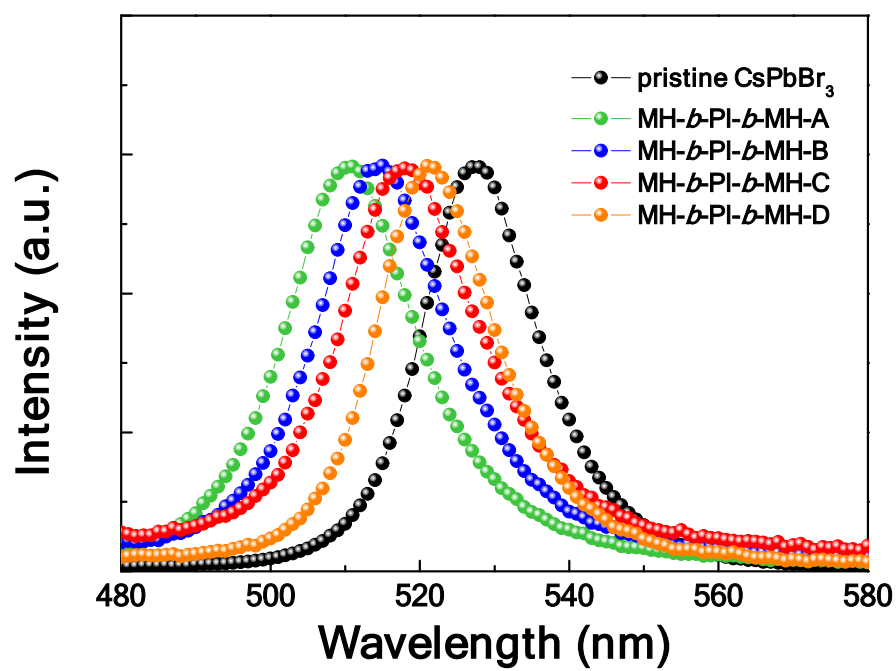
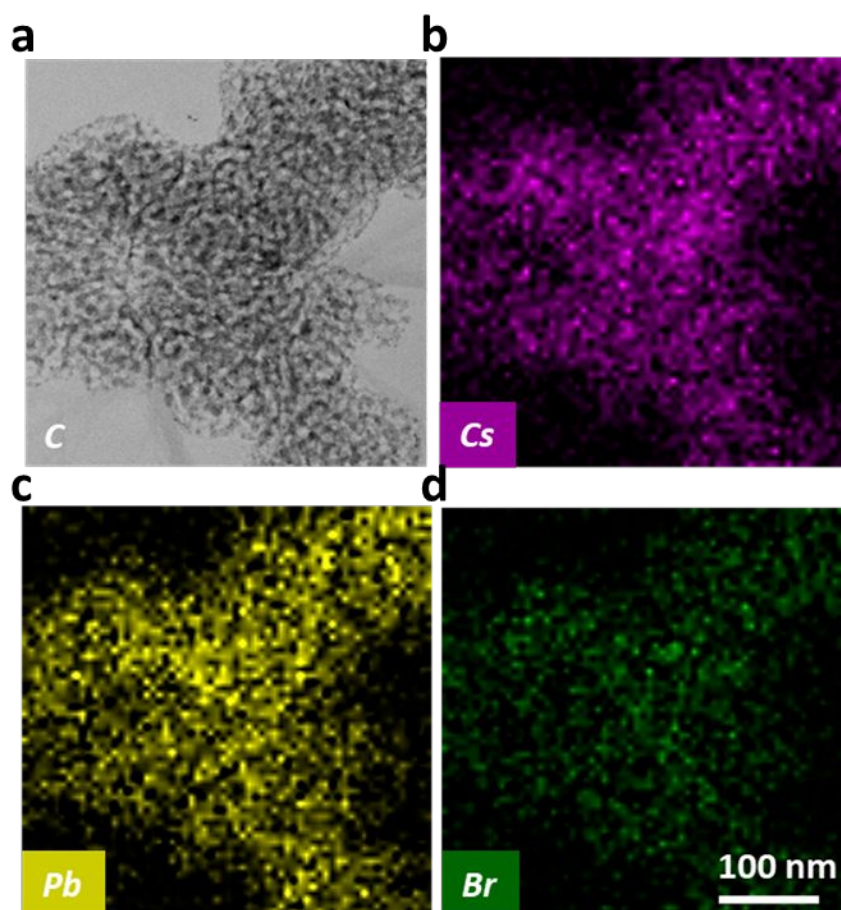


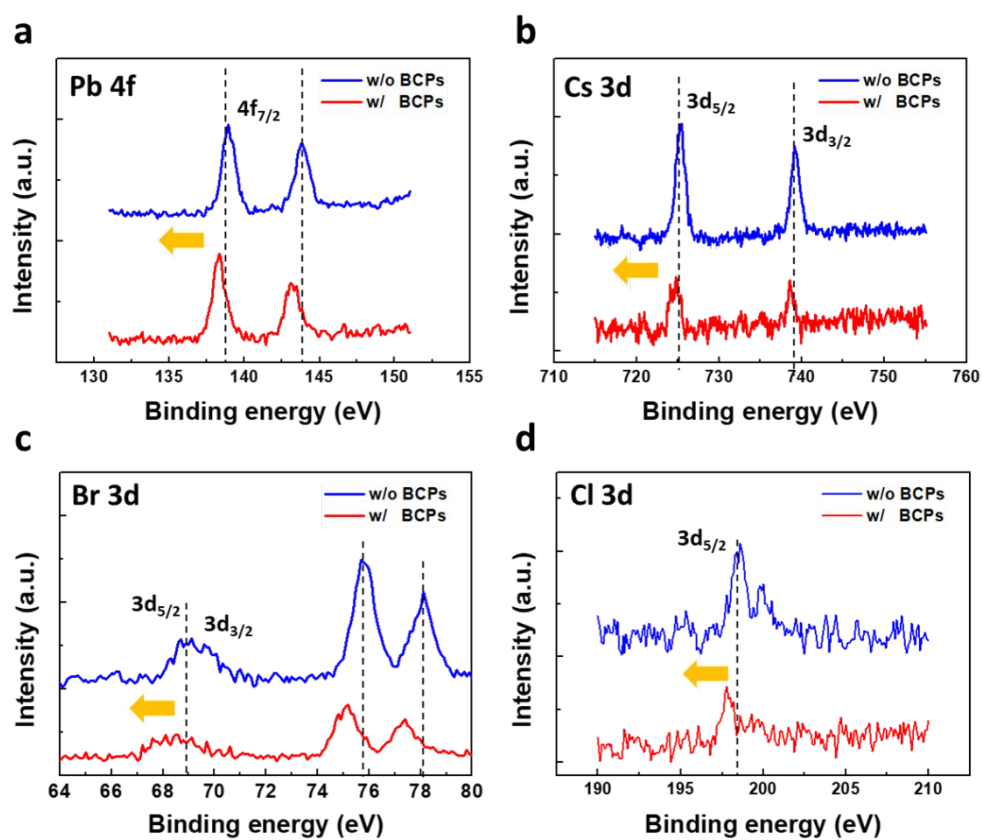
Figure S6. XRD patterns of pristine  $\text{CsPbBr}_3$  and  $\text{CsPbBr}_3@BCP$ .



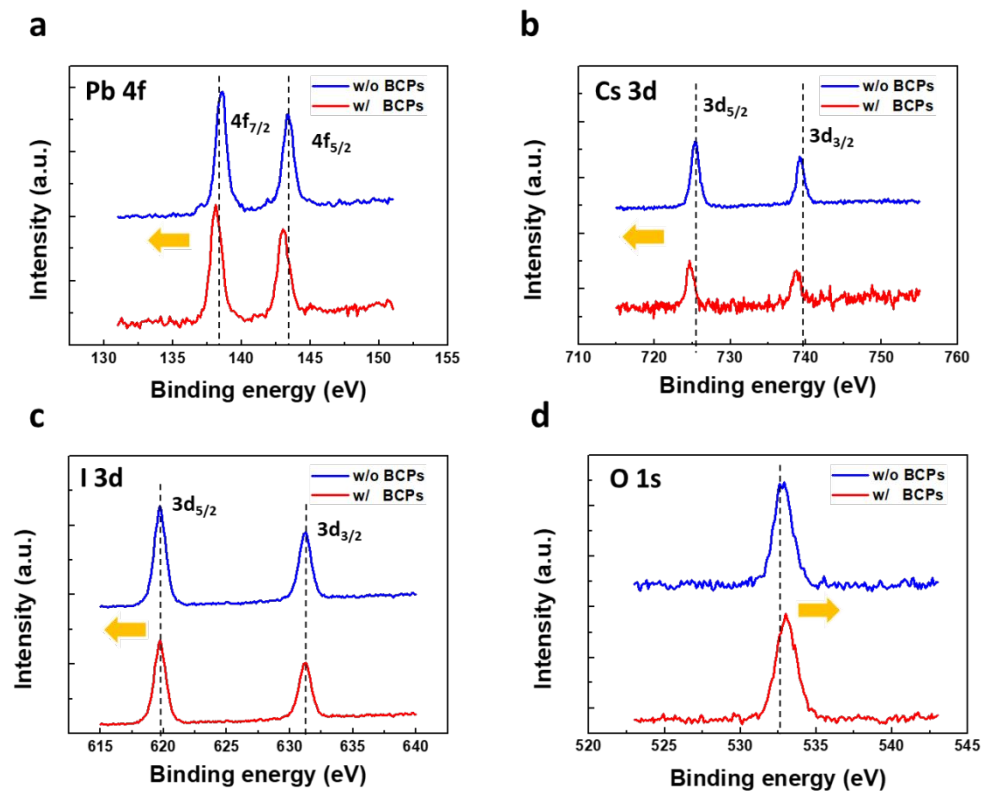
**Figure S7.** PL emission peak of the pristine CsPbBr<sub>3</sub> and MH-*b*-PI<sub>8.5k</sub>-*b*-MH-based composite films.



**Figure S8.** **a.** The bright field TEM image of MH-*b*-PI<sub>8.5k</sub>-*b*-MH/CsPbBr<sub>3</sub> nanostructured film with 100% CsPbBr<sub>3</sub>. EDS mapping images of **b.** Cs, **c.** Pb and **d.** Br atoms of the TEM image

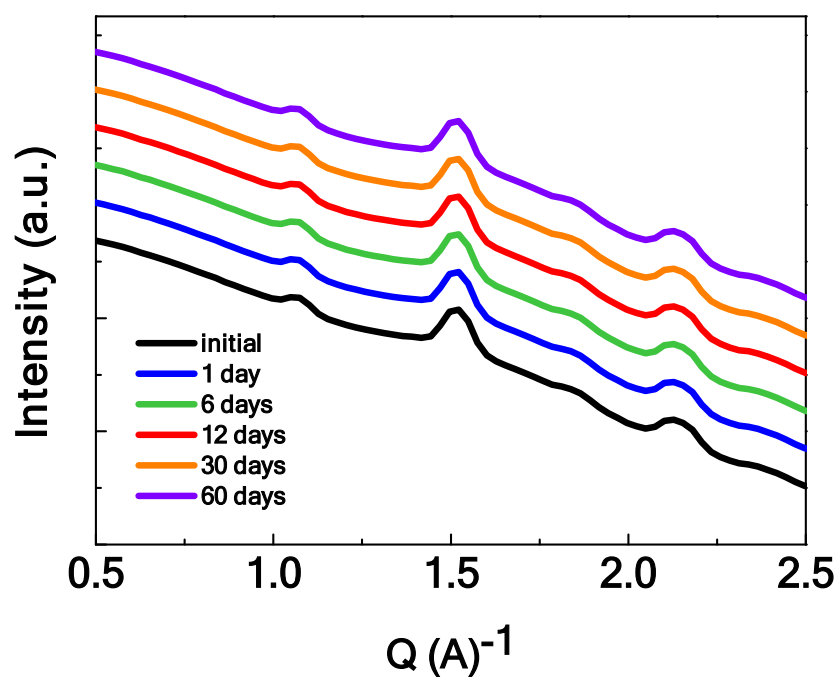


**Figure S9.** Photoelectron spectra from x-ray photoelectron spectroscopy (XPS) for **a.** Pb 4f, **b.** Cs 3d, **c.** Br 3d and **d.** Cl 3d of pristine CsPbClBr<sub>2</sub> and MH-*b*-PI<sub>8.5k</sub>-*b*-MH-based composite films.



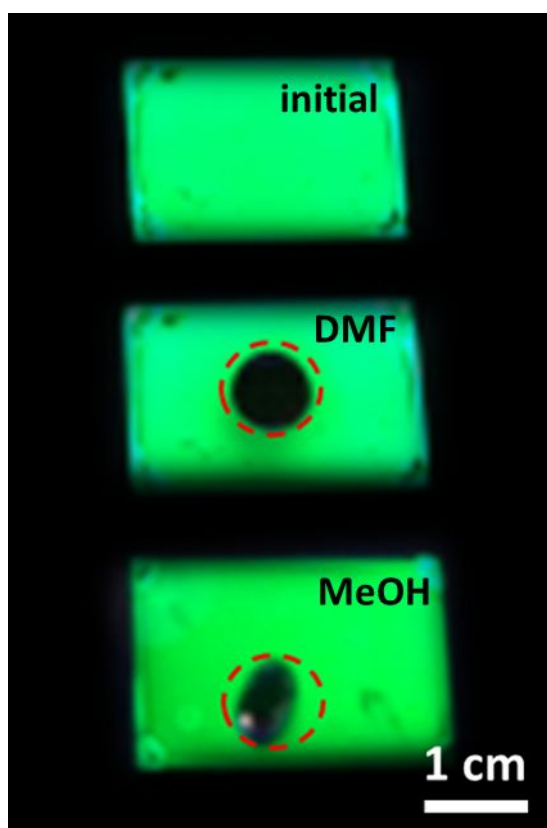
**Figure S10.** Photoelectron spectra from x-ray photoelectron spectroscopy (XPS) for **a.** Pb 4f, **b.** Cs 3d, **c.** I 3d and **d.** O 1s of pristine CsPbI<sub>3</sub> and MH-*b*-PI<sub>8.5k</sub>-*b*-MH-based composite films.



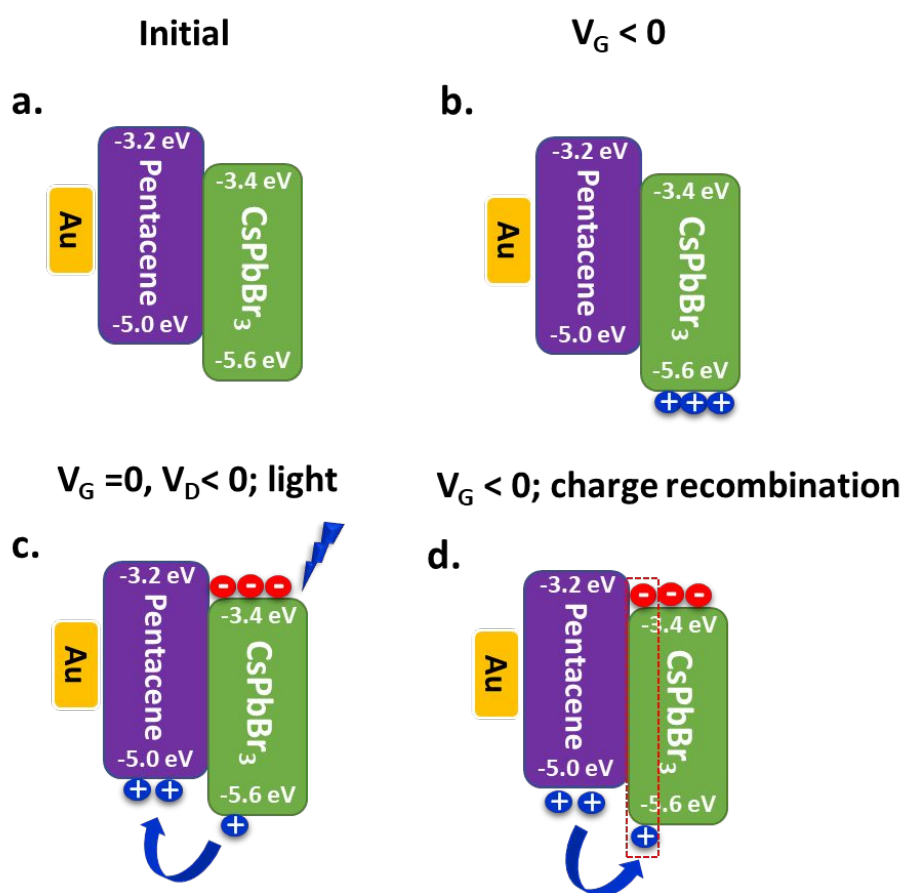


**Figure S11.** GIWAXS 1D pattern of the MH-*b*-PI<sub>8.5k</sub>-*b*-MH-B composite film upon

70% relative humidity for 60 days.



**Figure S12.** Anti-solvent characteristics of MH-*b*-PI-*b*-MH-B sample at the initial state and under DMF and MeOH drop test where red dot circle demonstrated the solvent drop.



**Figure S13.** Proposed mechanism for the studied photomemory devices. **a.** Initial state, **b.** after applying a negative  $V_G$  for 1s, **c.** after light illumination, and **d.** applying a negative  $V_G$  for 1s again.

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