Supporting Information

Synthesis of Large Two-Dimensional Lead-Free Bismuth-Silver Double Perovskites Microplatelets and Application for Field-Effect Transistors

Xiaoyu Wang, Kai Li, Hanlun Xu, Nasir Ali, Yao Wang, Qibin Shen and Huizhen Wu*

Experimental Section

Materials

Phenylethylamine (PEA, 98%), silver bromide (AgBr, 99.9%) and dimethyl sulfoxide (DMSO, anhydrous, ≥99.9%), N,N-Dimethylformamide (DMF, ≥99.9%) were purchased from Aladdin. Bismuth bromide ($BiBr_3$, 99%) was purchased from Alfa Aesar. Hydrobromic acid (HBr, ≥40 wt % in water), Hydroiodic acid (HI, ≥45 wt % in water), diethyl ether (≥99.5%), isopropanol (≥99.7%), ethanol (≥95.0%), chloroform (≥99.5%), dichloromethane (≥99.5%) and chlorobenzene (≥99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All these materials were used as received without any further purification.

PEAX synthesis

12mL HBr was dropwise added into a mixture of 10 mL PEA and 20 mL ethanol and the mixture was kept stirring in an ice bath for 1 h until complete reaction. The PEABr solution was then evaporated in a rotary evaporator at 50 ℃ to remove the solvent. The precipitate was washed with diethyl ether three times and recrystallized in ethanol. The final product was obtained after drying in a vacuum oven at 50 ℃ overnight. For PEAI synthesis, all the procedures were same except the amount of HI is 11mL.

Synthesis of $(PEA)_4BiAgX_8$

For the synthesis of $(PEA)_4BiAgBr_8$, 2 mmol PEABr, 0.5 mmol $BiBr_3$ and 0.5 mmol AgBr were dissolved in 1 mL DMSO with stirring for 10 min to form a transparent yellow precursor solution. 100μL precursor solution was quickly injected into 5 mL chloroform under vigorous stirring for 3 min. The final products were obtained after centrifuging at 4000rpm for 5 min. For the synthesis of $(PEA)_4BiAgBr_4I_4$ and $(PEA)_4BiAgBr_8$, procedures were similar to the synthesis of $(PEA)_4BiAgBr_8$, except precursor solution was changed to DMF.

Fabrication of single $(PEA)_4BiAgBr_8$ MP FETs

heavily p-type Si substrates with 100 nm SiO_2 layer were cleaned by sonication in isopropanol, ethanol and ultrapure water for 5 min, respectively, and dried by nitrogen. The electrodes were fabricated by lithography and thermal evaporation. The channel length (L) is 2μm and channel width (W) is 15μm. Single $(PEA)_4BiAgBr_8$ MP was dry-transferred onto the pre-patterned electrodes. Firstly, the $(PEA)_4BiAgBr_8$ MPs were separated by spin-coating its colloidal solution onto a cleaned SiO_2/Si substrate and dried at a low temperature (**Figure S9a**). Polydimethylsiloxane (PDMS) then covered with pressure onto the SiO_2/Si substrate, adhering $(PEA)_4BiAgBr_8$ MPs tightly. Second, PDMS with MPs was transferred onto pre-patterned electrodes. Finally, after heating at 80℃ for 10 min, with the decrease of viscidity, PDMS was peeled off and MPs were successfully transferred onto electrodes (**Figure S9b**). All the fabrication procedures were finished in ambient conditions.

Characterization

The surface morphology of the $(PEA)_4BiAgX_8$ MPs film was examined by a scanning electronic microscope (SEM, Hitachi S4800) coupled with an energy-dispersive X-ray spectroscopy (EDS) part (EDAX TEAM EDS System), as well as transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN). The $(PEA)_4BiAgX_8$ MPs crystal property was characterized by X-ray diffraction (XRD) on a PANalytical X-ray diffractometer (Model EMPYREAN) with a monochromatic Cu Ka1 radiation (λ=1.54 Å). The surface smoothness and thickness were measured by a scanning probe microscope (SPM9700) from Shimadzu. The Raman spectrum was measured under 532 nm continuous-wave laser excitation using an Andor SR-500i-B1 spectrograph. The absorbance spectra were collected by Carry 5000 UV-VIS-NIR spectrometer from Agilent Technologies. The film samples of $(PEA)_4BiAgX_8$ MPs for XRD, Raman and SEM were obtained by dropping colloidal $(PEA)_4BiAgX_8$ MPs solution on cleaned glass or ITO-plated glass with drying in ambient condition. The colloidal solutions for absorption were tested in 1×1 cm^2 path length quartz cuvettes. The FET characteristics were measured in ambient conditions by Agilent B1500A semiconductor device analyzer with the Keysight EasyExpert software.
ain Text Paragraph.

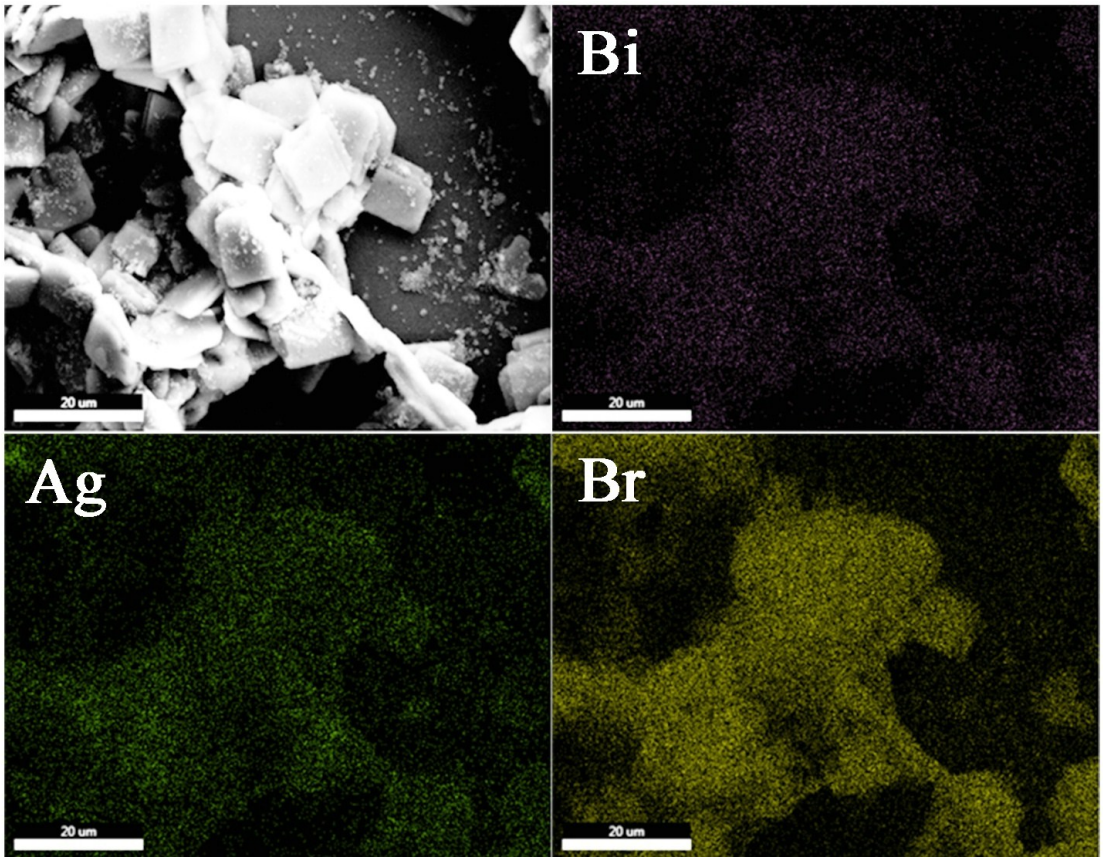
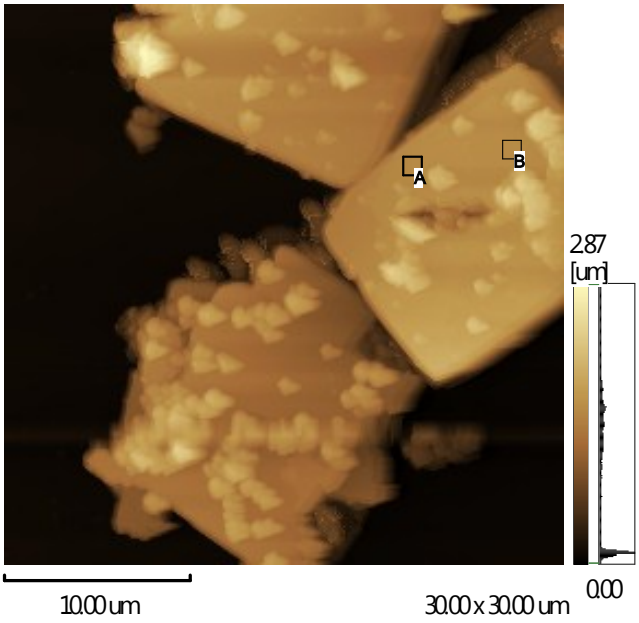


Figure S1. EDS elemental mapping of $(PEA)_4BiAgBr_8$ MPs.



All Area		A		B	
Length-X	30.000[um]	Length-X	1.000[um]	Length-X	1.000[um]
Length-Y	30.000[um]	Length-Y	1.000[um]	Length-Y	1.000[um]
Area	900.000[(um)2]	Area	1.000[(um)2]	Area	1.000[(um)2]
Ra	603.854[nm]	Ra	18.956[nm]	Ra	35.514[nm]
Rz	3.868[um]	Rz	5.494[nm]	Rz	7.231[nm]
Rzjis	1.912[um]	Rzjis	0.000[nm]	Rzjis	0.000[nm]
Rq	700.335[nm]	Rq	19.007[nm]	Rq	35.564[nm]
Rp	2.449[um]	Rp	22.275[nm]	Rp	32.423[nm]
Rv	1.419[um]	Rv	16.781[nm]	Rv	39.654[nm]

Figure S2. Surface smoothness analysis of $(PEA)_4BiAgBr_8$ MPs

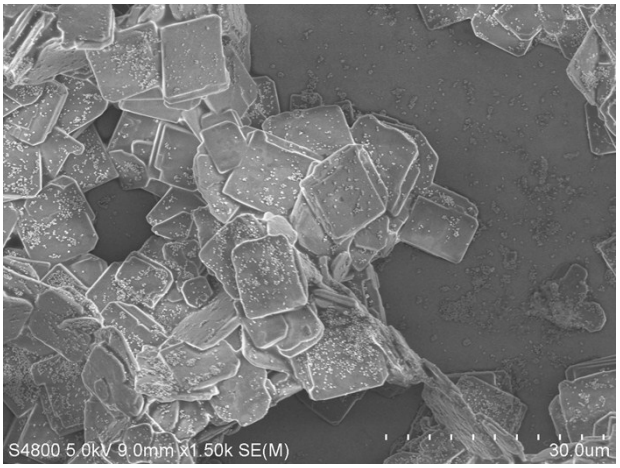


Figure S3. SEM image of $(PEA)_4BiAgBr_8$ MPs with oleic acid during synthesis.

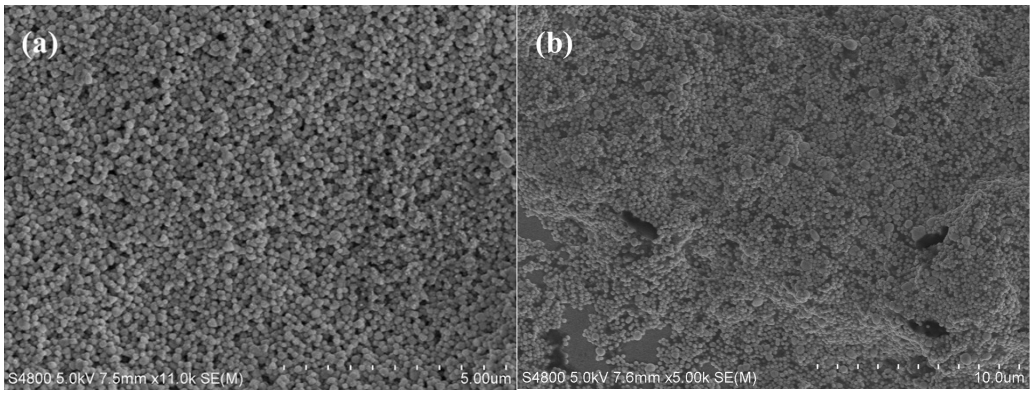


Figure S4. SEM images of products obtained by (a) dichloromethane and (b) chlorobenzene as recrystallization solvents respectively.

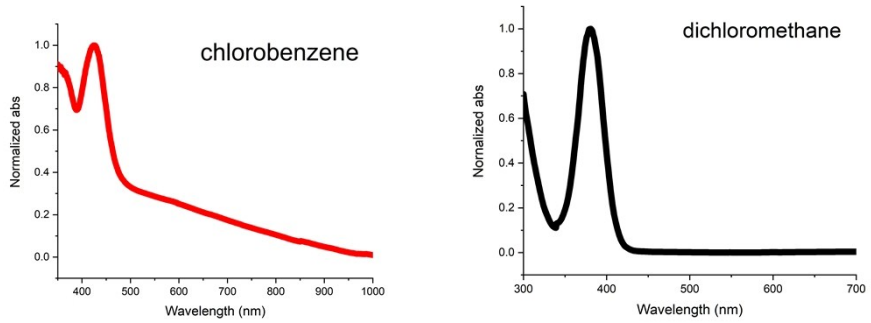


Figure S5. Absorbance spectra of products obtained by chlorobenzene and dichloromethane, respectively.

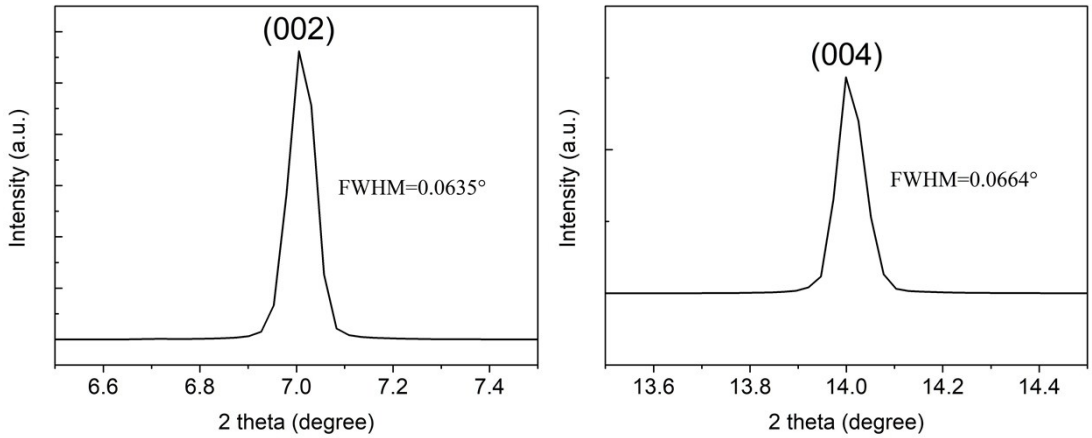


Figure S6. XRD patterns of $(PEA)_4BiAgBr_8$ MPs of (002) and (004).

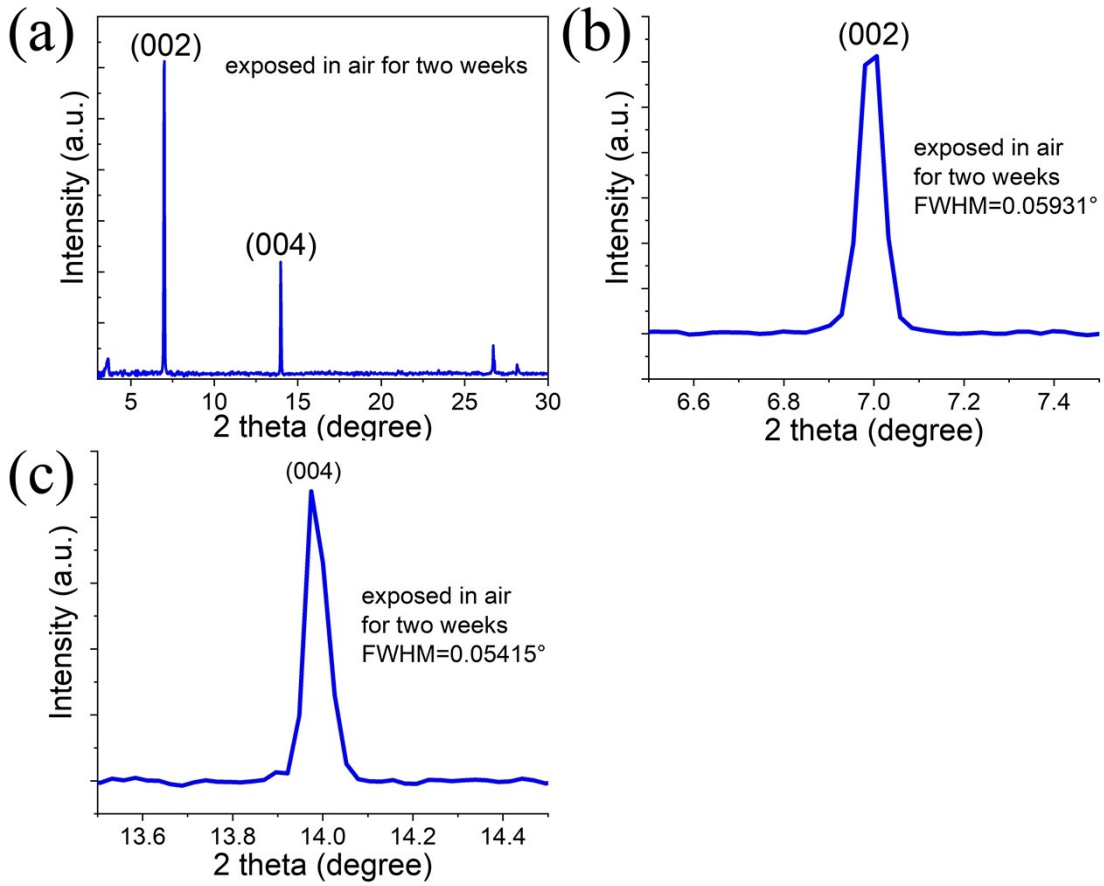


Figure S7. (a) XRD patterns of $(PEA)_4BiAgBr_8$ MPs exposed in air for two weeks. (b, c) enlarged (002) and (004) diffraction peak, respectively.

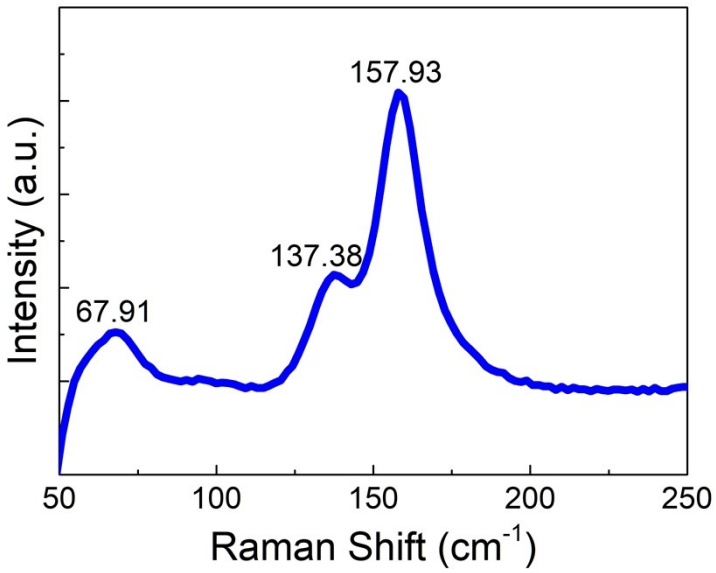


Figure S8. Raman spectra of the (PEA)4BiAgBr8 MPs.

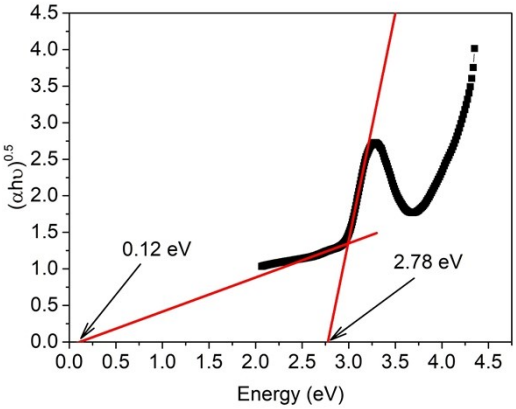


Figure S9. Tauc plot of an indirect bandgap of the absorbance spectrum of $(PEA)_4BiAgBr_8$ MPs.

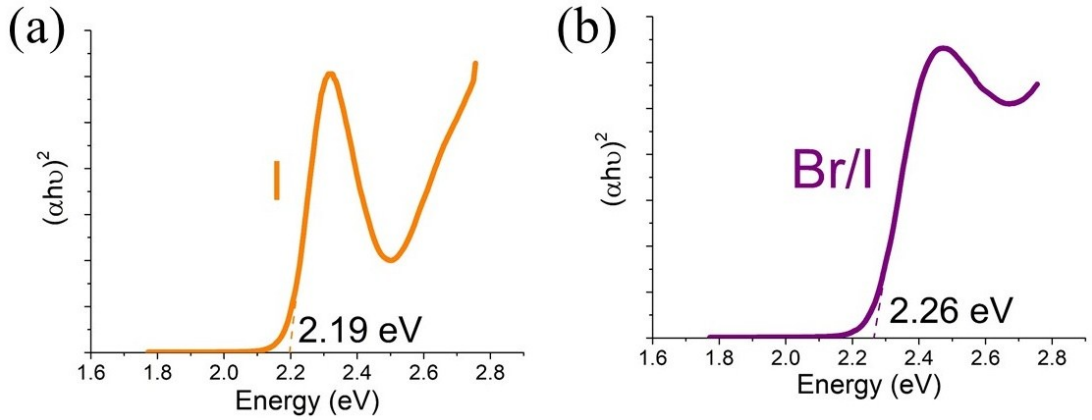


Figure S10. Tauc plots of direct bandgaps of the absorbance spectra of (a) $(PEA)_4BiAgBr_4I_4$ and (b) $(PEA)_4BiAgI_8$ MPs.

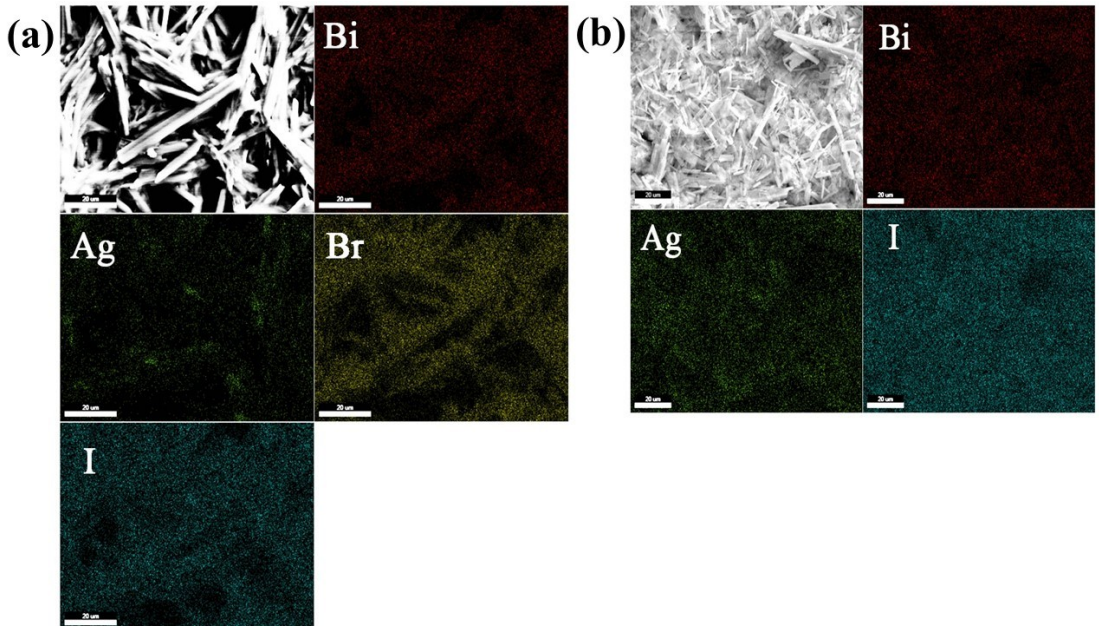


Figure S11. EDS elemental mapping of (a) $(PEA)_4BiAgBr_4I_4$ and (b) $(PEA)_4BiAgI_8$ MPs.

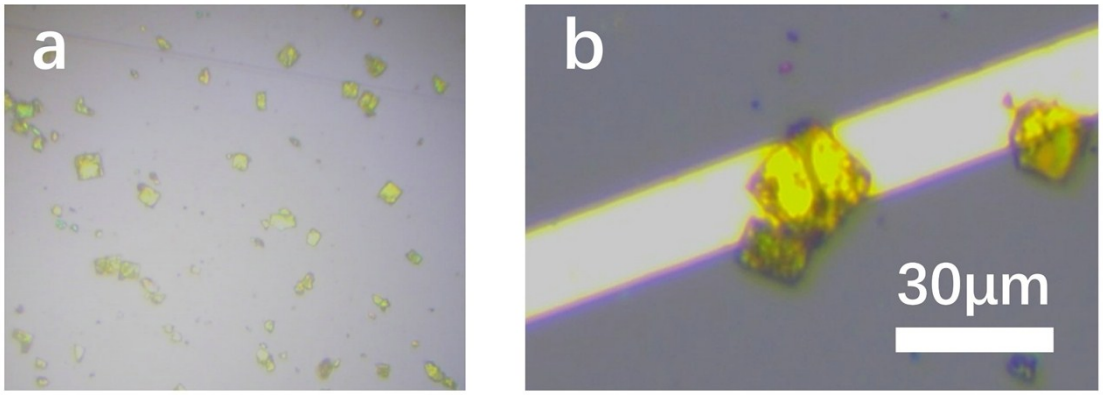


Figure S12. (a) Separated $(PEA)_4BiAgBr_8$ MPs on SiO_2/Si substrate. (b) Single $(PEA)_4BiAgBr_8$ MP FET fabricated via dry transfer procedure.

Table S1: Summary of characteristics of $(PEA)_4BiAgX_8$

	Shape	Absorption edge	Bandgap
Br	squares	412	3.05
Br/I	rods	561	2.26
I	belts	576	2.19