

Supporting Information

Surface-enhanced Raman scattering on organic-inorganic hybrid perovskite

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Experimental section

Materials. Lead (II) bromide (PbBr_2 , 99%), methylamine (CH_3NH_2 , 30-33 wt% in methanol), hydrobromic acid (HBr, 40%), 6-Mercaptopurine (6-MP) were obtained from Aladdin Industrial Corporation. Acetone (CH_3COCH_3 , 99.5%), ethyl alcohol ($\text{CH}_3\text{CH}_2\text{OH}$), diethyl ether ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$), N, N-dimethylformamide (DMF) were purchased from Beijing Chemical Works. 4-Mercaptopyridine (4-Mpy) was purchased from Sigma-Aldrich. All chemicals were used without any further purification.

Preparation of organic amine salt $\text{CH}_3\text{NH}_3\text{Br}$. 29 mL HBr and 13.9 mL CH_3NH_2 were added into a round-bottom flask and stirred for 2 h at 0 °C. Afterwards, the precipitates were obtained by rotary evaporation at 50 °C. And then the precipitates were washed several times by diethyl ether, and recrystallized from ethyl alcohol. Finally, the precipitates were dried in vacuum at 60 °C for later use.

Preparation of $\text{CH}_3\text{NH}_3\text{PbBr}_3$. 0.5595 g $\text{CH}_3\text{NH}_3\text{Br}$ and 1.8340 g PbBr_2 were dissolved in 30 mL of DMF. The solution was refluxed at 75 °C for 6 h. And then the solvent was removed by rotary evaporation. The mixture was washed by diethyl ether and ethyl alcohol for several times, and subsequently dried in vacuum at 60 °C.

Preparation of organic-inorganic hybrid perovskite-assembled substrate. 1 cm × 2.5 cm glass slides were washed with deionized water, ethyl alcohol, acetone, chloroform, acetone, ethyl alcohol, deionized water successively by ultrasonic cleaner. Residual organic solvents were flushed with deionized water for several times. The glass slides were then immersed in a boiling solution prepared by mixing 30% H_2O_2 and 98% H_2SO_4 with a volume ratio of 3: 7. After cooling, the glass slides

were rinsed repeatedly with deionized water. As a result, the glass slide surface was covered with hydroxyl. Finally they were immersed in an acetone solution of $\text{CH}_3\text{NH}_3\text{PbBr}_3$. After the acetone was evaporated, we got the substrates modified with $\text{CH}_3\text{NH}_3\text{PbBr}_3$.

As for 4-Mpy modified $\text{CH}_3\text{NH}_3\text{PbBr}_3$ substrate, the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ substrate was soaked in 2 mL 4-Mpy solution (1×10^{-3} M) overnight for further measurements.

The Ag colloid used in this work was prepared according to the methods described in the literature.¹

Instruments and measurements

The UV-vis spectra were recorded on a Shimadzu UV-2550 spectrophotometer. TEM images were taken using a JEOL JSM-6700F field-emission scanning electron microscope (FE-SEM) operating at 3.0 kV. Raman spectra were recorded on a LabRam Aramis Raman Microscope system (Horiba-Jobin Yvon), excited by 633 nm line of a HeNe narrow bandwidth laser (Melles Griot). The typical acquisition time was 10 s with twice accumulation. Powder X-ray diffraction (XRD) was obtained using a Siemens D5005 X-ray powder diffractometer with a Cu K α radiation source at 40 kV and 30 mA. The elemental composition and chemical state of samples were analyzed by X-ray photoelectron spectroscopy (XPS) with a VG ESCALAB MKII X-ray photoelectron energy spectrometer.

Table S1. Raman/SERS shifts (cm^{-1}) and band assignments of 4-Mpy on the Ag and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ substrates.

4-Mpy solution	Ag colloid	$\text{CH}_3\text{NH}_3\text{PbBr}_3$	Assignments
431	428	429	$7a_1$ $\delta(\text{C-S})/\gamma(\text{CCC})$
653	663	642	$6b_2$ $\beta(\text{CCC})$
724	709	716	$6a_1$ $\beta(\text{C-C})/\nu(\text{C-S})$
1002	1009	1002	a_1 ring breathing
1054	1063	1047	a_1 ring breathing/ $\beta(\text{CH})$
1114	1096	1106	$12a_1$ ring breathing/ $\nu(\text{C-S})$
1198	1200	1200	$9a_1$ $\beta(\text{CH})/\delta(\text{NH})$
1205	1221	1236	$9a_1$ $\beta(\text{CH})$
1285	1289	1283	$3b_2$ C-N stretching
1486	1474	1479	$19a_1$ $\nu(\text{C=C/C=N})$
1579	1578	1573	$8b_2$ $\nu(\text{C=C/C=N})$
1620	1607	1605	$8a_1$ $\nu(\text{C=C})$

Assignments from Refs. ^{2,3}

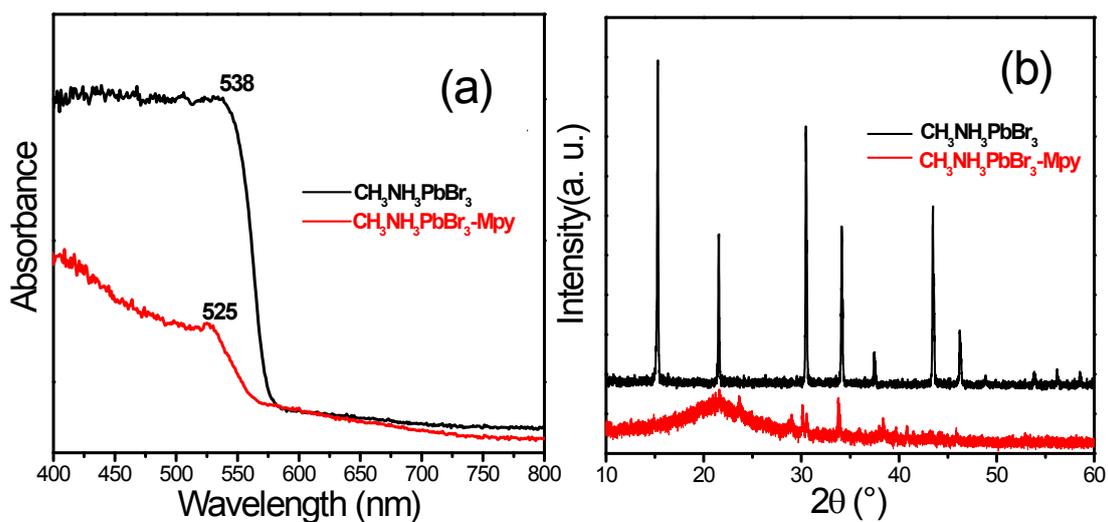


Figure S1. UV-Vis spectra (a), XRD patterns of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3\text{-Mpy}$ (b).

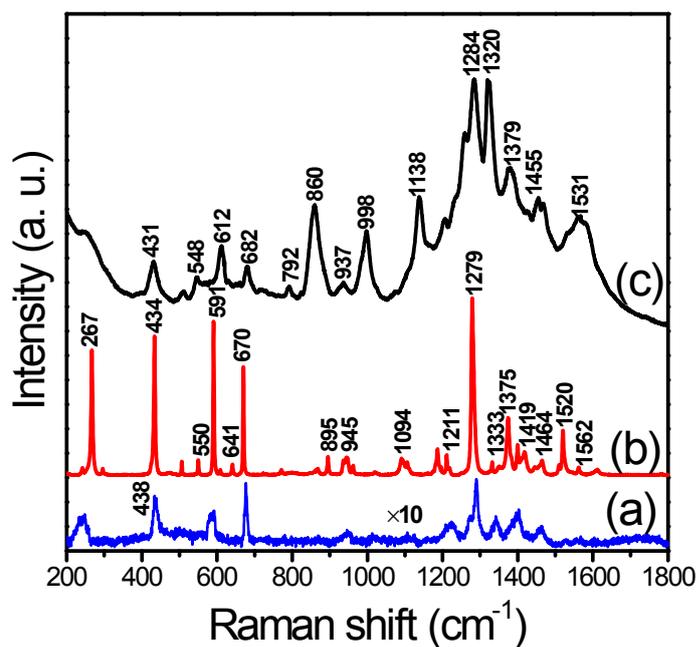


Figure S2. SERS spectra of 6-MP adsorbed on Ag colloid (c), $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (b), and normal Raman spectrum of 6-MP solution (a).

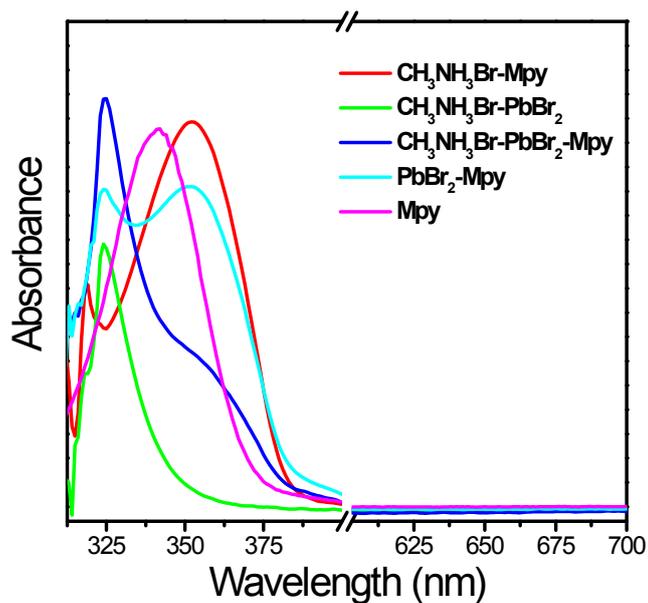
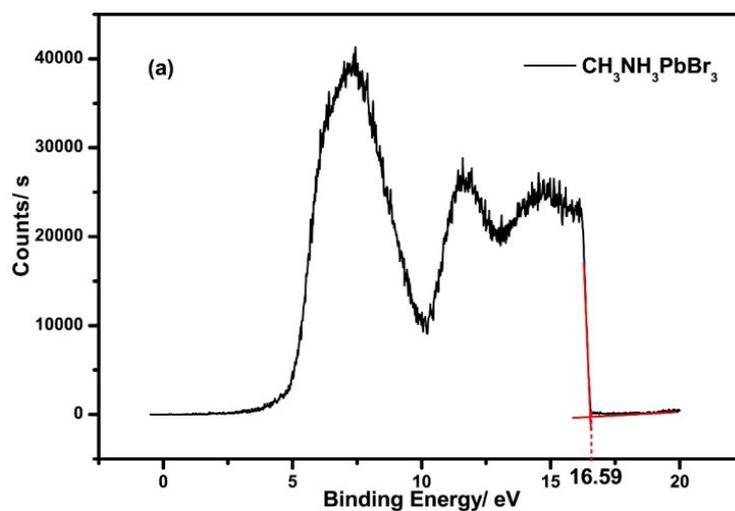


Figure S3. UV-Vis spectra of the assemblies of $\text{CH}_3\text{NH}_3\text{Br-Mpy}$ (red line), $\text{CH}_3\text{NH}_3\text{Br-PbBr}_2$ (green line), $\text{CH}_3\text{NH}_3\text{Br-PbBr}_2\text{-Mpy}$ (blue line), $\text{PbBr}_2\text{-Mpy}$ (light blue line), and bulk Mpy (pink line).

According to Figure S4, the work function of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ is 4.63 eV and the VB of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ is situated at 5.97 eV. As the UV-vis absorption band is located at 538 nm, and thus the band gap of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ between VB and CB is 2.31 eV. The CB of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ is situated at 3.66 eV.



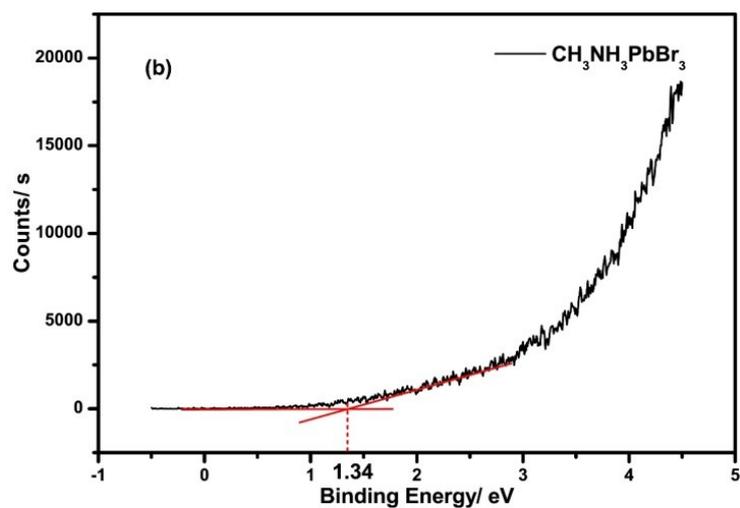


Figure S4. The UPS of $\text{CH}_3\text{NH}_3\text{PbBr}_3$.

As shown in Figure S5, the UV-Vis absorption maximum is located at 341 nm, and thus the band gap of 4-Mpy between HOMO and LUMO is 3.64 eV. According to Figure S6, the work function of 4-Mpy is 4.52 eV and the HOMO of 4-Mpy is situated at 7.98 eV. The LUMO of 4-Mpy is situated at 4.34 eV.

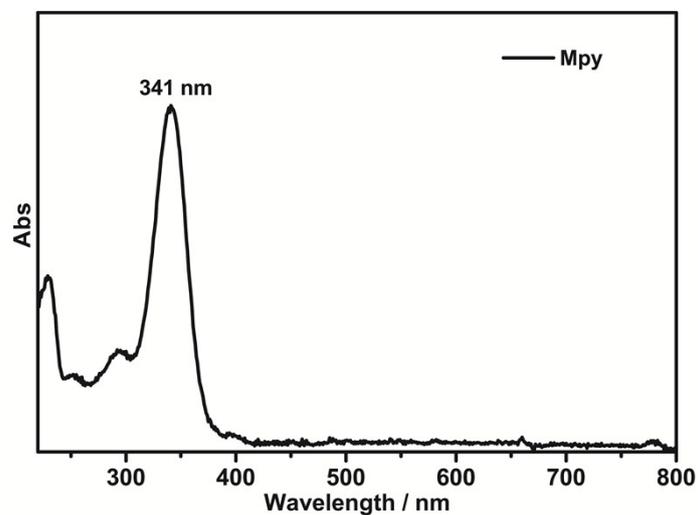


Figure S5. The UV-vis spectrum of Mpy.

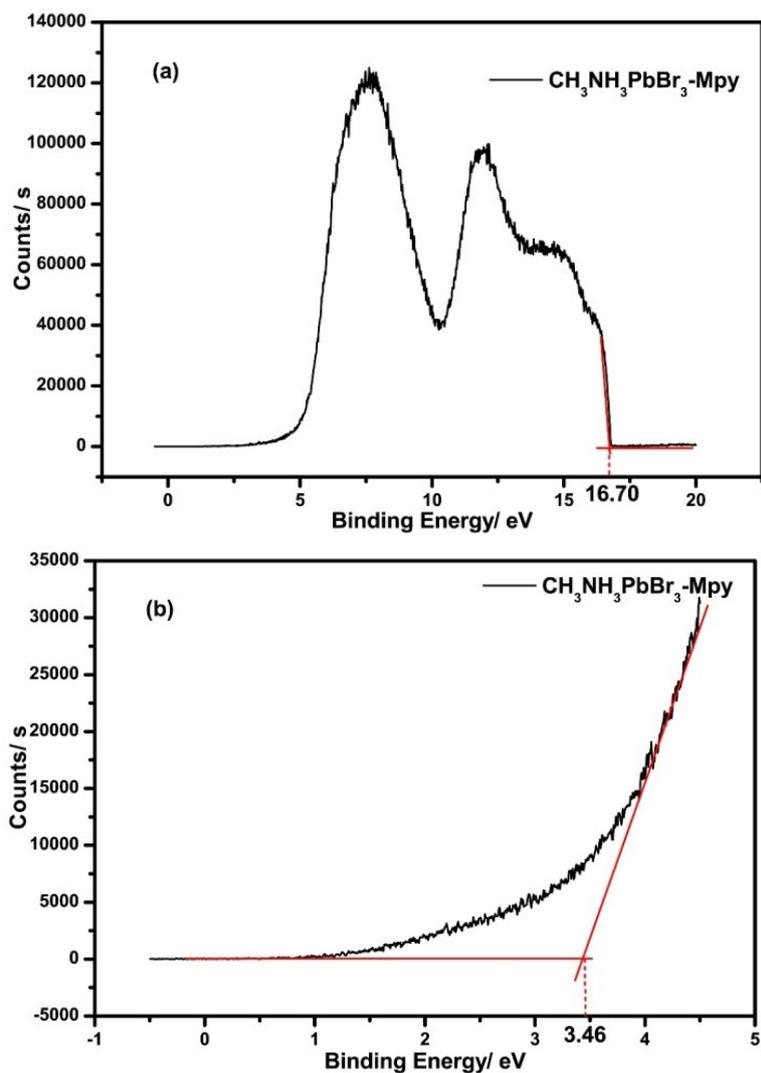


Figure S6. The UPS of $\text{CH}_3\text{NH}_3\text{PbBr}_3\text{-Mpy}$ assembly.

References

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2. Y. Wang, J. Zhang, H. Jia, M. Li, J. Zeng, B. Yang, B. Zhao and W. Xu, *J Phys. Chem. C*, 2008, **112**, 996-1000.
3. M. A. Bryant, S. L. Joa and J. E. Pemberton, *Langmuir*, 1992, **8**, 753-756.