

Charge Transfer Effects on Resonance-Enhanced Raman Scattering for Molecules Adsorbed on Single-Crystalline Perovskite

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S Supporting Information

ABSTRACT: Single-crystalline hybrid perovskites have important photoelectronic properties for advanced semiconductor devices, such as solar cells and photodetectors. However, neither the surface-enhanced Raman scattering (SERS) property nor the correlation between SERS and photoelectronic properties for single-crystalline perovskites have ever been studied. Here, for the first time, we observed a 10⁵ enhancement in SERS for 4-mercaptopyridine (MPY) adsorbed on a methylamine lead chlorine (MAPbCl₃) single crystal. Compared to the Raman spectrum of bulk MPY molecules, the b₂ mode of the MPY molecule was selectively enhanced. This is attributed to the charge transfer (CT)



resonance mechanism at the interface between the single crystal and the adsorbed molecules, which benefit from the Herzberg-Teller contribution. UV-vis spectra demonstrated that the modification with the MPY molecules leads to the formation of a new interfacial transition state, which matches the excitation laser photon energy and results in a CT resonance process under 532 nm laser excitation. The MPY-modified MAPbCl₃ single crystal was further applied to a photoelectronic device, and the device I-Vcurve was collected under 532 nm laser irradiation. The results indicate that the MPY-modified MAPbCl₃ shows a clear photoelectronic response to the 532 nm light. This study establishes a correlation between the CT resonance-enhanced Raman and the photoelectronic responses of perovskite materials and provides guidance for future molecule-sensitized perovskite photoelectronic device studies.

KEYWORDS: SERS, charge transfer, perovskite, single crystal, $CH_3NH_3PbCl_3$, photoelectronic detection

n recent years, organo-lead halide perovskites, such as methylamino lead halide perovskites (MAPbX₃, MA = $CH_3NH_3^+$, X = Cl⁻, Br⁻, or I⁻), have attracted widespread attention due to their attractive optical and low-temperature solution processability. The perovskites have become one of the most remarkable advanced materials for photoelectronic devices, such as solar cells, photodetectors, and phototransistors.¹⁻⁶ MAPbBr₃ and MAPbI₃ used for high-efficiency solar cells or optoelectronic devices have been widely studied due to their narrow band gap and wide adsorption range located at the visible or even near-IR range.⁷⁻¹¹ Compared to those two materials, MAPbCl₃ was rarely studied due to its wide band gap and specific adsorption properties. Most research on MAPbCl₃ was mainly focused on the growth of single crystals, the structural characterization, and phase transitions with the change of the environment. Only a few papers reported the studies of MAPbCl₃ single crystals in photodetectors under UV excitation.^{12–15} Meanwhile, the single-crystal MAPbCl₃ demonstrates its attractiveness due to its intrinsic structural features. Until recently, the study of perovskite materials by the Raman method mainly focused on its structure properties or phase transitions, and Raman

spectroscopy plays a role only in the structure characterization of the perovskite materials.¹⁶⁻²⁰ However, the Raman technique is a very significant method in the interfacial charge transfer property studies, and the intensive exploration of the correlation between the interfacial optical or photoelectronic and Raman properties of the perovskite materials is crucial for applying perovskite materials in photoelectronic devices.

Surface-enhanced Raman scattering (SERS) has been a widely used spectroscopic technique since it was first discovered on silver electrodes in the mid-1970s due to its unique characteristics, such as its nondestructive nature, ultrahigh sensitivity, and abundant molecular fingerprint information.²¹⁻²⁵ The early materials for SERS studies were mainly focused on noble metals (Au, Ag, and Cu) and gradually extended to other materials, such as some alkali metals (Na, K, and Li), transition metals, semiconductor materials, and organic semiconductors.²⁶⁻³⁰ Most of the observed semiconductorenhanced Raman scattering phenomena have been explained by the charge transfer (CT) mechanism, which inspired the

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Figure 1. (A) Optical image, (B) SEM, (C) EDS analysis, and XRD spectra of the single crystal. Inset shows the enhanced spectrum of XRD in the range of 50° to 60° .

development of a novel field in exploring chemical mechanisms of SERS.³¹⁻³⁴ Compared to metals, semiconductor materials possess more controllable properties that are beneficial for SERS mechanism studies, such as tunable band gap and photoluminescence properties, high stability, and resistance to degradation.^{35,36} Until recently, a large amount of semiconductor materials have been discovered for CT-induced SERS studies, including metallic oxides, metal sulfides, silver compounds, and semiconductor nanomaterials.^{37,38} Under certain conditions, the chemical binding takes place between the adsorbed molecules and the atomic sites of the semiconductor substrates, and the adsorbent-adsorbate interaction rebuilds the band gap at the interface between the adsorbed molecules and the semiconductor materials.^{38–40} Under these conditions, the band energy at the interface will become closer to the photon energy of the excitation laser, which leads to the occurrence of a resonance Raman scattering-like effect.^{32,41} Previous studies of some molecule-modified metal oxides have shown this kind of resonance Raman scattering-like effect in SERS studies using semiconductors, such as pyridine-modified TiO_{v} NiO, and Ru-bpy dye modified mesoporous films.³⁸⁻⁴⁰ In these cases, the CT enhancement mechanism is believed to have a major contribution to the observed high SERS signals. With continued development of SERS, the semiconductor materials used have expanded from metal oxides to other nanomaterials, including single-elemental semiconductors (such as graphene, Si, and Ge) and some 2D materials (such as MoS_2), which have been proven to be capable of providing Raman enhancement based on the CT mechanism. 42-45 Until now, the SERS property based on perovskites materials as a substrate has never been studied.

Here, we report a molecule–single-crystal interface SERS study based on 4-mercaptopyridines (MPY) and a MAPbCl₃ single-crystal system. For the first time, we observed a strong SERS signal of the MPY molecules adsorbed on this single-crystal surface. The mechanism of this SERS enhancement is attributed to the charge transfer resonance at the interface of the MPY-modified single crystal. Additionally, an obviously photoelectronic response effect under 532 nm irradiation was found for this MPY-modified single-crystal system. This new phenomenon extends the CT-induced SERS study to the single-crystalline materials, and it demonstrates a great advantage for practical application in photodetectors based on single-crystal perovskites.

EXPERIMENTAL SECTION

Chemicals. 4-Mercaptopyridine, dichloromethane, *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and lead chloride (PbCl₂) were purchased from Sigma-Aldrich. MACl was synthesized as follows:¹⁵ First, a mixed solution of 1.2 M methylamine and 1 M hydrochloride acid was stirred for 2 h in an ice bath and then dried under vacuum at 50 °C for 2 h. After that, the sample was dissolved in ethanol and then filtered using a 0.2 μ m PTFE filter. Diethyl ether was then added in the filtered solution to get the MACl powder followed by vacuum drying at 60 °C.

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Synthesis of an MAPbCl₃ Single Crystal and an MPY-Modified Single Crystal, and Deposition of Au Electrodes on Its Surface. A 1 M MAPbCl₃ solution in DMSO– DMF (1:1 by volume) was prepared by dissolving equimolar amounts of MACl and PbCl₂. The solution was then filtered using a PTFE filter with a 0.2 μ m pore size. Then the precursor solution was kept in an oil bath at a temperature of 50 °C for 6 h.¹⁵

The single-crystal MAPbCl₃ surface modified with MPY molecules was achieved as follows: the single crystal was immersed in 10^{-3} mol/L MPY solutions (dissolved in CH₂Cl₂), and 6 h later, the sample was cleaned by CH₂Cl₂ and dried by N₂ flow. The 100 nm Au electrodes were deposited on the bulk single crystal and MPY-modified single-crystal surfaces by thermal evaporation.

Sample Characterization. Raman spectra were collected using a LabRAM HR Evolution Raman spectrometer (Horiba Jobin Yvon). The UV–vis spectral measurements were carried out using a Cary 5000 UV–vis–NIR spectrometer (Agilent). XRD spectra were collected using a Bruker D8 FOCUS. Scanning electron miscroscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) analysis were carried out by the scanning electron microscope (Phenom ProX). The I-V curves were collected by a 4200A-SCS Parameter Analysis (Keithley, USA). The photoelectronic detection system was constructed with 532 and 633 nm irradiation light.

RESULT AND DISCUSSION

Characterization of X-ray Diffraction (XRD) and SEM. Figure 1A shows a cubic single crystal as we synthesized, while Figure 1B exhibits the surface state of the crystal by SEM. EDS confirmed the elemental contents of this crystal (Figure 1C). The as-prepared single-crystal MAPbCl₃ was then characterized



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Figure 2. (A) UV–vis spectra of the MPY molecule, single-crystal MAPbCl₃, and the MPY-modified single crystal. The inset image shows the MPY-modified single crystal. (B) Time-resolved PL decay curves for the MAPbCl₃ single crystal before (black curve) and after (red curve) the modification with MPY molecules under excitation at 481 nm.

by powder X-ray diffraction (Figure 1D), which confirmed that the crystal possessed the single-phase cubic structure with the lattice parameter a = 5.68 Å.⁴⁶ Meanwhile, the MPY-modified single crystal showed the same characteristic peaks compared to the pure single-crystal MAPbCl₃. This indicates that the adsorption of MPY did not destroy the lattice structure of the material substrate and maintained the intrinsic property of the single crystal.

Measurement of UV-Vis Spectra and Photoluminescence Lifetime Characterization. UV-vis spectroscopy was used to analyze the optical properties of the MAPbCl₃ single crystal after the adsorption of MPY molecules. Figure 2A shows the UV-vis spectra of MPY (dissolved in CH₂Cl₂) and singlecrystal MAPbCl₃ before and after the adsorption of MPY molecules. The single-crystal MAPbCl₃ is transparent close to 428 nm, and its color changes from colorless (Figure 1A) to yellow (Figure 2A) after the adsorption of MPY molecule. The latter process leads to the formation of a new interfacial transition state. The bulk crystal showed a quite steep slope at 428 nm, which indicated that the band energy of the crystal is about 2.89 eV. After the adsorption of MPY, a notable longer wavelength absorbance occurred compared with that of the unmodified crystal and the band energy decreased to 2.32 eV. This interfacial photoabsorption can be attributed to the interaction between the adsorbed molecule and the single crystal.

To further demonstrate the formation of the new interfacial transition state, we studied the recombination property of the single crystal under excitation at 481 nm. Figure 2B shows the PL lifetime results for the MAPbCl₃ single crystal before and after the modification with MPY molecules. The MPY-modified single crystal exhibits double components of the carrier dynamics ($t_1 = 6$ ns and $t_2 = 1.9$ ns) with a biexponential fit of the curve. These two components are likely attributed to the interface and the bulk of the crystal, respectively. As for the MAPbCl₃ single crystal, there is no PL response under 481 nm excitation. We can thus conclude that the modification with the MPY molecule results in the formation of a new interfacial transition state.

SERS Spectra of the MPY Adsorbed on MAPbCl₃. Figure 3 shows the Raman spectra of (a) an MPY molecule adsorbed on the single-crystal surface, (b) an MAPbCl₃ single



Figure 3. Raman spectra of an MPY molecule adsorbed on the single crystal (a), single-crystal MAPbCl₃ (b), an MPY molecule adsorbed on Ag (c), and MPY powder (d). The spectra were collected under 532 nm laser excitation. Raman spectra are shifted compared with each other along the *y*-axis for better viewing.

crystal, (c) an MPY molecule adsorbed on a Ag surface, and (d) MPY powder under 532 nm laser excitation. Figure S1 shows the Raman spectra of a single crystal compared with MACl and PbCl₂. In Figure 3a, several observable bands located at 488 and 977 cm⁻¹ are attributed to the crystal mode (Figure 3b), while the 621 cm⁻¹ (C-C-C/N-C=C out-of-plane bend), 1001 cm⁻¹ (ring breathing), 1031 cm⁻¹ (C-H in-plane bend), 1182 cm⁻¹ (C-H in-plane symmetric bend), 1200 cm⁻¹ (C-H in-plane antisymmetric bend), 1582 cm⁻¹ (C-C stretch with deprotonated nitrogen), and 1602 cm⁻¹ (C-C stretch with protonated nitrogen) are intrinsic to MPY. A more detailed assignment for Raman bands of MPY under different conditions is shown in Table 1.⁴⁶⁻⁵¹

As Figure 3c shows, the SERS spectrum of MPY adsorbed on a Ag surface exhibits several characteristic peaks located at 427, 705, 720, and 1093 cm⁻¹, which differs from the SERS spectrum of an MPY molecule adsorbed on the single-crystal MAPbCl₃. The difference of the characteristic bands of these two spectra could be attributed to different adsorption modes of the MPY molecules on the surface of different materials. As

Table 1. Raman Peak Assignment

band assignment	MPY/ MAPbCl ₃ single crystal/ cm ⁻¹	MPY/ Ag/ cm ⁻¹	MPY/ cm ⁻¹	ref
ring def with C-S/C-C-C stretch		427	430	49
C–C out-of-plane asym bend			472	49
C-C-C/N-C=C out-of-plane bend	621		646	49, 51
C-C-C/N-C=C scissor			663	49
ring def with C–C in-plane wag		705		49
C-C/C-S stretch		720	722	48, 51
ring breathing	1001	1006	990	48, 49
C–H in-plane bend	1031	1060	1044	49, 51
trigonal ring breathing with C–S		1093	1107	47, 49
C–H in-plane sym bend	1182		1199	48, 51
C–H in-plane asym bend	1200	1202		47, 49, 51
C–H in-plane wag		1221		49, 51
C–H/N–H in-plane wag	1452		1461	49
ring stretch (C=C/C=N)	1482	1475	1478	51
C–C stretch with deprotonated nitrogen	1582	1578	1604	47, 50, 51
C–C stretch with protonated nitrogen	1601	1606	1618	47, 50, 51

is well known, the -SH group can be easily combined with Ag to form a S-Ag coordinate bond. Therefore, the bands at 427 cm⁻¹ (ring re-formation with C-S/C-C-C stretch), 720 (C-C/C-S stretch), and 1093 cm⁻¹ (trigonal ring breathing with C-S), which were correlated with the C-S mode, can be clearly observed. As for the single-crystal MAPbCl₃, the MPY

molecule tends to adsorb on its surface through N atom in the pyridine ring, which results in the disappearance of these two C–S mode-related Raman peaks. Moreover, the adsorption of MPY through N atom results in the disappearance or intensity decrease of other related bands compared with the SERS spectrum of MPY on Ag surface, such as the bands at 705 cm⁻¹ (ring deformation with C–C in-plane wag).

Figure 4 shows the XPS results of the N and S atoms in the three samples: MAPbCl₃, MAPbCl₃+MPY, and MPY. As Figure 4A shows, the peak for the N atom of the MPY molecule shows a 2 eV shift after being adsorbed on the single-crystal surface, which can be attributed to the bonding formation between the N atom of MPY and the single crystal, while the peak for the N atom of MAPbCl₃ shows nearly no change. As for the S atom (Figure 4B), only the MPY molecule shows an obvious characteristic peak. We can thus conclude that the MPY molecule adsorbed on the crystal surface through the N atom.

Mechanism of the SERS Enhancement of MPY Adsorbed on a Single-Crystal Surface. As is well known, two mechanisms are widely accepted to explain the contribution to the enhancement phenomenon. First of all, the electromagnetic mechanism (EM) was believed to be the most crucial contribution to the substantial enhancement of the Raman spectrum. The most impressive example is the singlemolecule detection, which is estimated to possess an enhancement factor as large as $10^{12}-10^{15}$. 52-54 During this process, the laser-induced surface plasmon resonances on the metal cluster surface result in a strong local enhancement of the electric field, which extremely enhances the Raman signal of the molecule adsorbed on or near the metal surface. On the other hand, the so-called chemical mechanism (CM) is of equal importance in SERS studies.55,56 For this, the factor contributing to enhancement in metals or semiconductors due to the above mechanism is associated with the chemical adsorption of the probe molecule and includes either molecule-metal/semiconductor or metal/semiconductor-molecule charge transfer. The application of Herzberg-Teller theory has been the most comprehensive approach in the study of this effect. The main



Figure 4. XPS result for the N and S atoms in the three samples: CH₃NH₃PbCl₃, CH₃NH₃PbCl₃+MPY, and MPY.

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Figure 5. SERS spectra of MPY adsorbed on single-crystal MAPbCl₃ under 473, 532, and 785 nm laser excitation (A) and illustration of the mechanism under different laser illumination (B). Notice that direct transitions between the LUMO and HUMO are forbidden for these three lasers. Raman spectra shifted compared with each other along the *y*-axis for better viewing.

process could be simply described as the excitation of an electron from a filled highest occupied orbital of the molecule (HOMO) to an empty level on the metal/semiconductor band (molecule-metal/semiconductor) or from a filled level of the metal/semiconductor to the lowest unoccupied orbital of the molecule (LUMO). Such conditions are a resonance-like Raman process in which charge transfer between the substrate and the molecule constitutes the intermediate stage.

In our case, the single-crystal MAPbCl₃ does not possess surface plasmons along the excitation region of the lasers' lines used in these experiments (473, 532, and 785 nm), which indicates that the electromagnetic mechanism cannot be the dominant contribution to the surface-enhanced Raman signal of the MPY-modified single-crystal MAPbCl₃. The observed SERS signal can be explained by the CT mechanism. As described above, the adsorption of the molecule will lead to a red shift for the UV-vis spectra. The band-band transition energy of the interface between single crystal and MPY molecule can be calculated as 2.32 eV (Figure 2A). This energy excellently fits with the excitation laser energy at 532 nm wavelength. Under these conditions, when the excitation light (532 nm) irradiates the sample surface, a CT resonance will take place in the energies of the single-crystal/MPY interface. This resonance process is mainly due to modification of the energy band gap from 2.89 eV to 2.32 eV, which matches the 532 nm excitation laser well. As a result, the Raman signal of the adsorbed MPY molecule was enhanced.

The evidence for the chemical enhancement mechanism is strongly associated with individual modes of the adsorbed molecules. Compared to those in the SERS spectrum of MPY adsorbed on Ag and its bulk Raman signal, there is greater enhancement of several bands, such as 1001 and 1031 cm⁻¹ bands, in the SERS spectrum of the MPY-modified single crystal. Some weaker bands at 621, 1452, and 1582 cm⁻¹, assigned to the b₂ mode of the MPY molecules, were also observed, which can only be selectively enhanced by the CT mechanism through Herzberg–Teller contributions. The additional SERS enhancements from the MPY-single-crystal complex, particularly the enhancement of the b₂ mode, result from the new band level formation at the interface of the complex and could be ascribed to the charge transfer between the single crystal and the MPY molecules.

To further verify the CT resonance process at the interface of the MPY-modified single crystal under a 532 nm excitation wavelength, the SERS spectra of this system were analyzed under 473 and 785 nm laser irradiation (Figure 5A). The Raman spectra at 473 nm irradiation show some weak characteristic peaks of MPY as compared to the spectrum under 532 nm irradiation. The energy of the 473 nm photon is 2.62 eV, which is larger than the interface band transition energy and located far from resonance conditions. Such large excitation energy does not match the 2.32 eV band gap, and most of the photons energy acts on the interior of the singlecrystal MAPbCl₃. Thus, the 473 nm irradiation could not produce enough photon energy with excellent resonance conditions comparable to the 532 nm excitation. As a result, the SERS spectra under 473 nm irradiation does not show a resonantly enhanced Raman signal as under 532 nm laser irradiation.

A few processes can cause SERS:³¹ (1) surface plasmon induced growth of a cross section of this process, (2) resonance-enhanced processes, and (3) charge transfer between the substrate and molecule. In the case of all used lasers (473, 532, and 785 nm), none of them can be considered as the one that has contribution from the first process due to the fact that the surface plasmons in the used medium are lying at far shorter wavelength. It is difficult to estimate the relative role of the second and third processes on SERS. However, in the case of the 532 nm pump, these two processes influence SERS simultaneously, while in the case of the 473 nm pump, only the third process could be taken into account. That is why, in our opinion, the 532 nm pump has a stronger influence on the SERS compared with the 473 nm pump.

As for the 785 nm excitation conditions, we did not observe any characteristic bands on the SERS spectra, since the 785 nm photon energy (1.58 eV) is too low to excite the transitions between the band levels at the interfaces. Therefore, it can be concluded that, with the excitation of the 532 nm laser, the charge transfer resonance takes place between the interface and results in the SERS enhancement of the adsorbed MPY molecules. The difference in the schemes of the SERS spectra under illumination by three laser sources is shown in Figure 5B.

Estimation of the Enhancement Factor. The enhancement factor is a powerful method for evaluation of the contribution of the single crystal on the Raman spectra of the

(B) (A) MPY+MAPbCl, 8000 0.2 M MPY in CH,Cl, Raman Intensity / Arbitr. Unit 6000 **Raman Intensity** 4000 2000 1588 8 3 -20 ò 20 -140 -120 -100 -80 -60 -40 40 60 80 100 120 140 1000 1200 400 800 1400 1600 1800 600 Z/µm Raman Shift / cm⁻¹

Figure 6. (A) Depth-dependent Raman intensity of the single Si wafer at the 520.7 cm⁻¹ band under 532 nm laser excitation. A pinhole size of 100 μ m and a 50× working-length objective were used. (B) Comparison of Raman spectra of MPY molecules adsorbed on single-crystal perovskite and in CH₂Cl₂ solutions. The peaks labeled by stars are the characteristic peaks of CH₂Cl₂ (Figure S2).



Figure 7. (A) Device schematic of the MPY-modified MAPbCl₃ single-crystal-based photodetector device. (B) I-V curves of the MPY-modified MAPbCl₃ single crystal under 532 nm, 633 nm illumination and in dark conditions.

adsorbed MPY molecules. The enhancement factor (EF) for an MPY-modified single crystal was calculated according to the following equation:

$$EF = \frac{I_{SERS}}{I_{Raman}} \frac{N_{b}}{N_{ads}}$$
(1)

Here, $N_{\rm b}$ is the number of molecules on the bulk samples and $N_{\rm ads}$ is the number of adsorbed molecules, while $I_{\rm SERS}$ and $I_{\rm Raman}$ are the intensity of the SERS and original Raman spectra of MPY, respectively. The spectra of the adsorbed and free molecules were measured under identical conditions. To obtain a quantitative evaluation of the enhancement factor, the Raman spectrum of an MPY molecule adsorbed on the single-crystal surface and the Raman spectrum of the 0.2 M MPY solotion were measured to obtain the information on the peak intensities of the adsorbed and bulk molecules under similar conditions.

The number of MPY molecules adsorbed on the singlecrystal surface and the powder effectively excited by the laser beam constitute other necessary parameters used in the determination of the EF in this system. We assume that all the MPY molecules are vertically adsorbed on the single-crystal surface with a closed-pack array. It has already been reported that the area occupied by one MPY molecule is approximately 0.7 nm^{2.48} The surface concentration value of the MPY can be estimated to be approximately 1 to 2 nm⁻², and the number of MPY molecules adsorbed on the single-crystal surface within the focus area is approximately 2×10^6 . Thus, the number of those MPY molecules located under the laser beam should be $S_{\rm B}/S_{\rm M}$:

$$N_{\rm ads} = \frac{S_{\rm B}}{S_{\rm M}} \tag{2}$$

Here $S_{\rm B}$ is the area of the laser beam and $S_{\rm M}$ is the area of one MPY molecule. The collection efficiency of scattered photons from MPY molecules in the solution of the MPY molecules varies with the focus depth. Therefore, the effective range near the focus point of the laser is a key point in determining the number of MPY molecules. The effective range of our laser irradiation was measured with a 50× lens microscope under a 532 nm laser. The silicon wafer was used to investigate the focus depth profile. The intensity of the characteristic band for Si at 520.7 cm⁻¹ was measured by a depth-dependent Raman analysis from $-500 \ \mu m$ to 500 $\ \mu m$ with steps of 1 $\ \mu m$ (Figure 6A). We determined that the effective area contains a band intensity higher than 25% of the maximum intensity of the Si wafer at the focus point. So the effective distance (h) near the focus point is 40 $\ \mu m$. Then the volume (ν) of the MPY solution

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under the effective distance can be calculated as $S_{\rm B} \times h$. Therefore, the number of MPY molecules in the solution under the effective beam range can be obtained by the following equations:

$$N_{\rm B} = c \times S_{\rm B} \times h \times N_{\rm A} \tag{3}$$

Correspondingly,

$$\frac{N_{\rm B}}{N_{\rm ads}} = \frac{c \times S_{\rm B} \times h \times N_{\rm A}}{S_{\rm B}/S_{\rm M}} \tag{4}$$

This parameter was defined as $N_B/N_{ads} = 3.36 \times 10^4$. As obtained from the spectra, the relative intensity of the MPY molecule is 265 at 990 cm⁻¹, while the SERS intensity of the band at 1001 cm⁻¹ of the MPY-modified single crystal is 2043 (Figure 6B). Therefore, the EF was estimated to be 2.6×10^5 . It should be mentioned that during this calculation the number of MPY molecules adsorbed on the single crystal was determined as an upper limit, and thus the EF represents a lower limit.

Practical Application of the 4-MPY-Modified MAPbCl₃ Single-Crystal Perovskite in Photoelectronic Detection. The MAPbCl₃ single crystal shows a photoelectronic response only in the UV region due to its intrinsic optical properties. However, as illustrated above, the MPY-modified MAPbCl₃ single crystal possesses resonance effects under 532 nm irradiation. So, one can expect that the modification of MPY will tune the photoelectronic response of the MAPbCl₃ single crystal to the visible region (532 nm) and promote its application in photoelectronic detection.

To evaluate the photoelectronic response of the MPYmodified single crystal to a 532 nm laser, we constructed a photodetector device based on the MPY-modified MAPbCl₃ (Figure 7A). The 100 nm thick Au layers were deposited on the material surface as two electrodes. The photoelectronic response of the materials was investigated by current–voltage (I-V) curves measured under illumination with 532 nm light and compared with the illumination under 633 nm light and in dark conditions.

The result is shown in Figure 7B. The MPY-MAPbCl₃, at 2 V, shows nearly no current response under dark conditions, while a significant growth of current up to 6×10^{-8} A was observed under 532 nm light. Under dark conditions, the MPY molecule layer acts as an insulating layer, which restricts the electric transition between the Au electrode and the single crystal. Under the 532 nm illumination conditions, the MPYmodified single crystal possesses a 2.32 eV band gap, which matches the energy of the light source and leads to a CT resonance between the MPY molecule and the single crystal. As a result, the MPY-modified single crystal shows a photoelectronic response under 532 nm irradiation, which elucidates the interfacial CT-resonance process in this system. We also studied the photoresponse property for the MAPbCl₃ single crystal and MPY molecule separately, and the results do not show any photoresponse under 532 nm irradiation (Figures S3 and S4). Meanwhile, the MPY-MAPbCl₃ system does not show any photoelectronic response to 633 nm laser irradiation, since the photon energy of 633 nm light does not match the interface band gap of this system. It should be mentioned that the bulk MAPbCl₃ single crystal and MPY molecules were separately analyzed by inserting similar Au electrodes for comparison with the MPY-MAPbCl₃ structure shown in Figure 6A. These two separated configurations did not have a similar response to the MPY-MAPbCl₃ structure. It can be thus concluded that the

photoelectronic response of the MPY-modified single crystal to 532 nm light was caused by CT resonance with 532 nm light excitation. This phenomenon can be used for further exploration of the molecule-sensitized perovskite materials in different studies, and it is expected to further improve the photoelectronic properties of perovskite single crystals.

CONCLUSION

We have observed an enhancement of the Raman signal from MPY-modified single-crystal MAPbCl₃ for the first time. The enhancement factor is estimated to be on the order of 10⁵. The UV-vis spectrum studies were used to corroborate that a resonance process occurs at the interface between the MPY molecules and the single-crystal surface under 532 nm laser excitation. The selective enhancement of the MPY signal at the b₂ mode on the crystal surface further proves the CT mechanism at the interface through the Hertzberg-Teller contribution. We show that charge transfer is the most likely mechanism responsible for the observed enhancement, as the plasmon resonances are ruled out. In addition, the MPYmodified single crystal was found to show a clear photoelectronic response under 532 nm excitation light. This novel study on the CT-induced SERS enhancement on a singlecrystal surface not only provides a new direction in SERS studies but also builds a connection between CT-resonanceenhanced Raman scattering and photoelectronic effects. This phenomenon also provides a new molecule-sensitized singlecrystal perovskite used for a photoelectronic detection study combined with a Raman technique.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsphotonics.8b00152.

Additional Raman spectra and the I-V curves of MAPbCl₃ and MPY molecules as a contrast experiment

(PDF)(PDF)(PDF)(PDF)(PDF)

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Notes

The authors declare no competing financial interest.

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