

State-Specific Nonresonant and Resonant Plasmon-Driven Electron Transfer into Single Molecules

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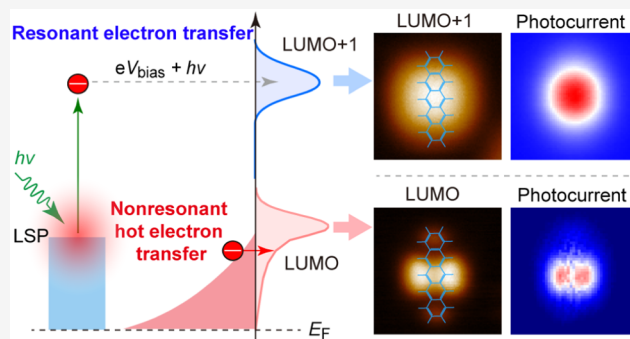


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ABSTRACT: Harnessing plasmonic energy to drive selective chemical transformations is central to photocatalysis, solar energy conversion, and molecular optoelectronics. Plasmon-driven chemistry proceeds through nonresonant plasmonic hot electron transfer or more efficient resonant charge transfer, yet cleanly disentangling these channels has remained a long-standing challenge, especially in synthetic nanoparticle systems with heterogeneous molecular environments. Here, using the nanocavity plasmon generated between an Ag tip and individual pentacene molecules on Ag(110) in a scanning tunneling microscopy (STM) junction, we directly unveil both channels with submolecular resolution. Combining chopper-modulated laser excitation with lock-in detection enables plasmon-induced current mapping at 0.3 nm resolution, allowing real-space correlation with frontier molecular orbitals. By tuning photon energy and bias voltage, we identify nonresonant hot-electron transfer via the lowest unoccupied molecular orbital (LUMO) and resonant charge transfer via LUMO + 1, where the resonant pathway markedly accelerates C–H bond breaking.



■ INTRODUCTION

Understanding the mechanism of converting light into chemical energy at the molecular scale underpins some of the most consequential challenges in modern chemistry, including solar fuel generation, heterogeneous photocatalysis, artificial photosynthesis, and molecular optoelectronics.^{1–4} Localized surface plasmons (LSPs) of metal nanostructures offer a uniquely powerful route toward this goal. LSPs concentrate light into deep-subwavelength “hot-spots”, dramatically intensifying light–matter interactions and unlocking chemistries inaccessible under conventional photoexcitation.^{5–14} A long-standing fundamental question in this field—one that directly determines how plasmonic energy is harnessed for chemistry—is whether plasmon-driven electron or energy transfer proceeds via indirect/nonresonant or direct/resonant pathways.^{15–17} The rapid, nonradiative Landau damping of LSPs (occurring within a few to tens of femtoseconds) generates energetic electrons and holes that thermalize into a quasi-Fermi–Dirac distribution near the Fermi level (E_F) (Figure 1a).^{11,18,19} The subsequent transfer of these carriers to adjacent molecules or semiconductors lies at the heart of plasmon-enhanced chemical transformations. Yet, this nonresonant, thermalized pathway is inherently inefficient, as hot-carrier transfer must compete with subpicosecond relaxation.^{10,20–22} Overcoming this fundamental bottleneck has motivated an intense global effort to engineer “direct” and

“resonant” charge transfer pathways that bypass thermalization (Figure 1b).^{23–27} Notably, LSP-driven charge transfer transitions from metal into unoccupied orbitals across the interface represent a more efficient route for plasmonic charge separation.^{28–30} Despite its fundamental importance, cleanly separating indirect/nonresonant and direct/resonant channels has remained elusive, as the two pathways coexist with overlapping spectral signatures. This difficulty is further exacerbated in realistic synthetic nanoparticle systems, where molecular heterogeneity, solvent fluctuations, and ensemble averaging obscure the underlying mechanisms.^{16,31,32} This ambiguity is not merely a technical issue; it is a core obstacle to the rational design of plasmonic photocatalysts because the identity of active orbitals ultimately dictates reaction selectivity, efficiency, and bond-cleavage specificity. Resolving this question therefore has implications far beyond plasmonics itself, reaching into catalyst design, single-molecule chemistry, and energy materials.

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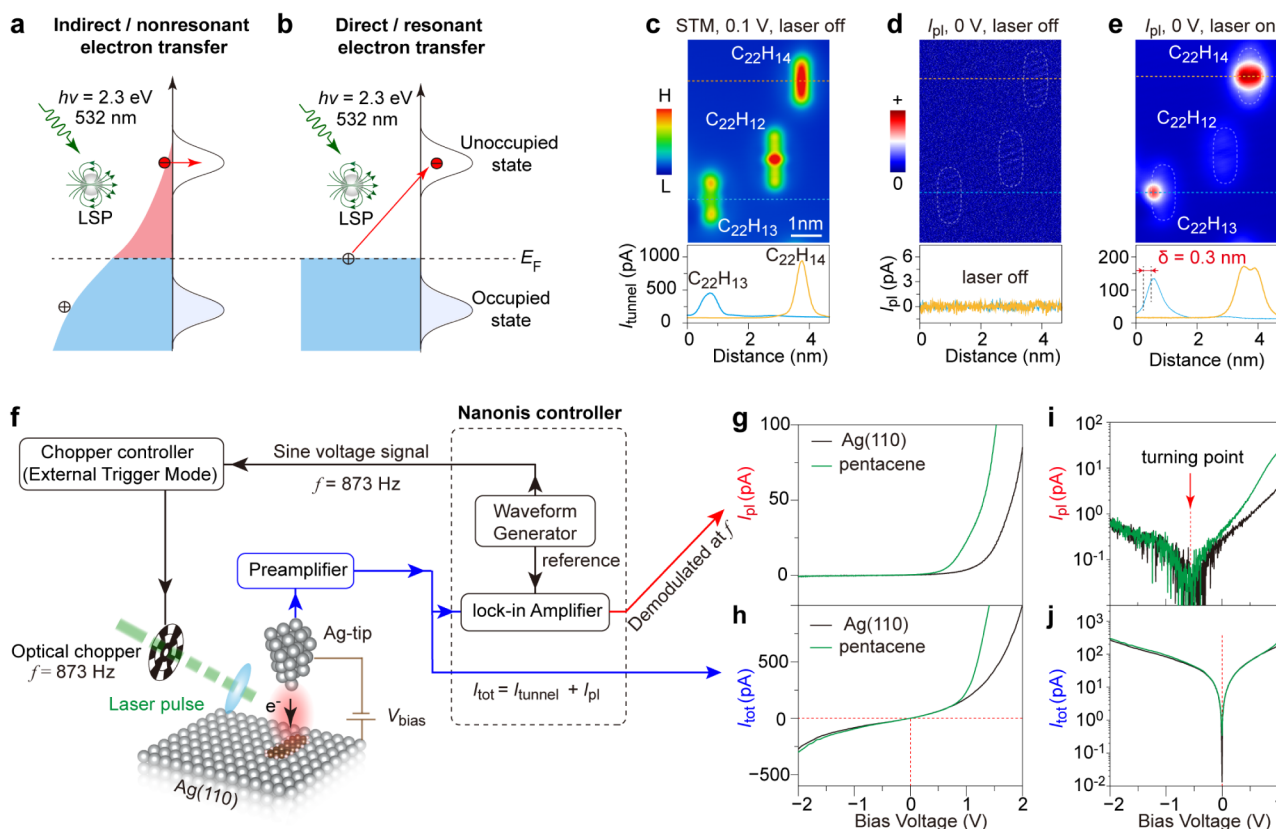


Figure 1. Schematic drawings of plasmon-driven electron transfer pathways and the lock-in detection setup. (a) Indirect/nonresonant transfer process of plasmon-induced hot electrons into an unoccupied state of molecules nearby. The nonradiative decay of LSPs generates hot carriers with a quasi-Fermi–Dirac distribution. (b) Direct/resonant electron transition driven by LSPs from metal into an unoccupied state of molecules nearby without the generation of hot electrons. (c) STM image of a pentacene molecule and its derivatives on Ag(110) taken at $V_{\text{bias}} = 0.1$ V in constant-height mode with the laser off, showing distinct features for three pentacene species. (d, e) I_{pl} images within the same frame as in (c), recorded at $V_{\text{bias}} = 0$ V in constant-height mode with the laser off and on, respectively, excited by the laser wavelength $\lambda = 532$ nm and light irradiance of 28.3 W/cm². The lower panels show the line profiles along the colored dotted line in (c)–(e). $\delta = 0.3$ nm defines the spatial resolution of the I_{pl} image, which is extracted between the lateral positions of 10%–90% peak intensities from the line profile. (f) Sketch of the experimental setup using a lock-in detection method under optical-chopper-modulated laser illumination. The frequency for the optical chopper was 873 Hz. (g, h) The recorded $I_{\text{tot}}-V$ and $I_{\text{pl}}-V$ curves in constant-height mode at the Ag(110) surface and a pentacene molecule. (i, j) The log plot of $|I_{\text{pl}}|$ and $|I_{\text{tot}}|$ in the range of -2.0 to 1.0 V from the data in (g, h), showing the positions of the turning point.

Addressing this challenge demands experimental access to plasmon–molecule interactions at the ultimate single-molecule and single-orbital limit, free from ensemble averaging. The atomically sharp apex of an STM tip acts as a nanoscale optical antenna, focusing light into intense nanocavity and picocavity^{33,34} plasmon fields, providing an ideal platform for this purpose. In parallel with ultrahigh-vacuum tip-enhanced Raman spectroscopy (TERS), nanocavity plasmons have been shown to drive chemical reactions in diverse model systems at single-chemical-bond resolution.^{34–39} Recent advances have further extended capabilities through enhanced optical spectroscopy^{39–42} and photocurrent signals.^{43–48} However, the central mechanistic question remains open: do nanocavity plasmons directly excite adsorbed molecules, or do they drive electron transfer through distinct orbital-specific pathways? Combining multimodal tip-enhanced imaging with orbital-level energy control provides a state-of-the-art platform uniquely suited to answer this question.

Here, by integrating the lock-in detection with a chopper-modulated laser-STM, we directly record the plasmon-driven photocurrent between the tip and single pentacene molecules on an Ag(110) substrate through the vacuum barrier. The well-defined single-barrier junction allows us to focus on the

nonresonant and resonant plasmonic electron transfer channels by examining the net photocurrent with characteristic energy and spatial fingerprints. Real-space correlations between the photocurrent and the molecule's electronic states reveal bias-tunable, state-specific electron injection channels into individual pentacene species, providing submolecular, orbital-resolved insight into plasmon-driven charge transfer. This single-molecule, single-orbital strategy establishes an experimental framework for disentangling and quantifying nonresonant vs resonant plasmonic pathways in a wide range of adsorbate–metal systems.

RESULTS

Measuring the Net Plasmon-Induced Current (I_{pl}) Using a Lock-In Technique

We carried out laser-combined STM measurements of the pentacene molecule and its derivatives on Ag(110), with an Ag tip if not specified. The three pentacene species (C₂₂H₁₄, C₂₂H₁₃, and C₂₂H₁₂) on Ag(110) have been characterized in our previous studies,^{38,49} where one and two H atoms are removed due to C–H bond breaking at the central benzene ring in pentacene derivatives of C₂₂H₁₃ and C₂₂H₁₂,

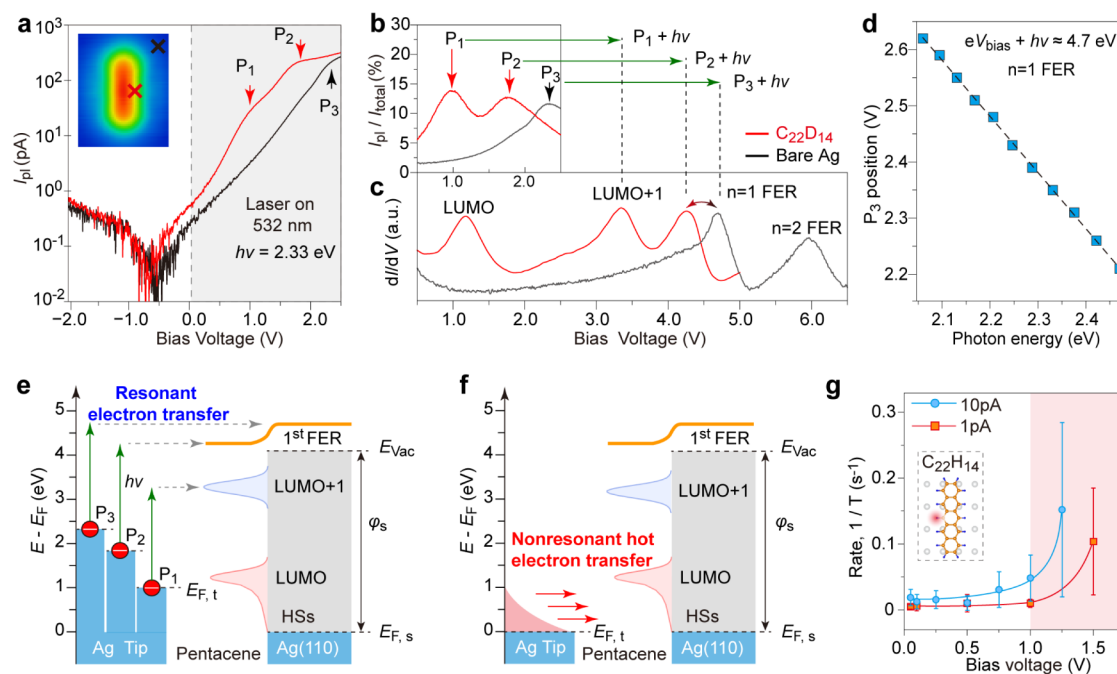


Figure 2. Resonant and nonresonant charge transfer through specific electronic states. (a) $I_{\text{pl}}-V$ spectra obtained in constant-height mode at the $\text{C}_{22}\text{D}_{14}$ molecule and $\text{Ag}(110)$ surface, as indicated by the crosses in the inset STM image. (b) The corresponding $I_{\text{pl}}/I_{\text{tot}}$ curves from (a) in the range of $V_{\text{bias}} = 0.5-2.5$ V, showing more pronounced resonance peaks of P_1 , P_2 , and P_3 . (c) Constant-current mode dI/dV spectra of $\text{C}_{22}\text{D}_{14}$ and bare $\text{Ag}(110)$ (set point: 0.5 V and 100 pA; modulation: 30 mV at 937 Hz; laser off). The green arrows from peaks in (b) to electronic states in (c) represent the photon energy ($h\nu = 2.33$ eV) of a CW 532 nm laser. (d) Negative linear relationship between the P_3 peak position and the excitation photon energy. The photon energy is changing the wavelength from 502 to 602 nm with a supercontinuum light source. The peak positions are extracted from the spectra in [supplementary Figure S10](#). (e) Energy diagram of resonant electron transfer by raising the bias voltage to match the energy level alignment with $\text{LUMO} + 1$ and $n = 1$ FER. (f) Energy diagram of nonresonant hot electron transfer to LUMO and HSs . (g) The reaction rate measured for C–H bond breaking under 532 nm ($28.3 \text{ W}/\text{cm}^2$) light irradiation recorded as a function of bias voltage. The two sets of data were obtained with different tip–sample distances, with tunneling current set points of 1 pA and 10 pA, respectively. At each bias voltage, the reaction events were averaged over 9 independent measurements, with error bars indicating the standard deviation. The red and blue solid curves serve as guides for the eyes. The inset shows the specific C–H bond breaking in the molecule.

respectively. These three pentacene species can be distinguished from the topographic STM image recorded at $V_{\text{bias}} = 0.1$ V with the laser off ([Figure 1c](#)). To examine the net plasmon-induced current (I_{pl}), $V_{\text{bias}} = 0$ V is set to make zero tunneling current ($I_{\text{tunnel}} = 0$). When the laser is off, the I_{pl} image is featureless with zero photocurrent ([Figure 1d](#)). By illuminating with the 532 nm laser, it is interesting to observe that the I_{pl} image shows distinct submolecular-resolved features for each pentacene species ([Figure 1e](#)). Intense signals of I_{pl} appear in the vicinity of the middle two C–H bonds of $\text{C}_{22}\text{H}_{14}$ and the residual middle C–H bond of $\text{C}_{22}\text{H}_{13}$, while only weak signals of I_{pl} are detected at the periphery of $\text{C}_{22}\text{H}_{12}$. From the line profiles of I_{pl} , a spatial resolution of $\delta \sim 0.12$ nm can be obtained (lower panel in [Figure 1e](#)), which is defined by the lateral distance within the 10–90% peak intensities.⁵⁰

When $V_{\text{bias}} \neq 0$ V, I_{tunnel} and I_{pl} will be together recorded by the preamplifier as the total current (I_{tot}). To extract the net I_{pl} from the $I_{\text{tot}} = I_{\text{pl}} + I_{\text{tunnel}}$, we apply the lock-in detection setup with an optical chopper modulating I_{pl} as an AC-like current ([Figure 1f](#)). In this setup, a sinusoidal reference signal is first generated at a specific frequency ($f = 873$ Hz) by the internal waveform generator of the Nanonis controller. This signal serves a dual purpose: (1) it is output to an external optical chopper controller as a TTL trigger; (2) the same signal is fed into the controller's internal lock-in amplifier module as the reference for phase-sensitive detection. Second, the optical chopper, triggered at the 873 Hz reference frequency,

modulates the laser beam before being focused onto the tip–sample tunneling junction. This modulated illumination generates AC-like I_{pl} at the same frequency $f = 873$ Hz, which is recorded by the preamplifier together with the I_{tunnel} . Third, the built-in lock-in amplifier extracts only the AC-like I_{pl} that is synchronous with the 873 Hz reference signal.

With this lock-in detection technique, I_{pl} and I_{tot} can be simultaneously recorded. [Figure 1g,h](#) shows typical $I-V$ curves from the I_{pl} and I_{tot} channels with the Ag tip over a deuterated pentacene molecule ($\text{C}_{22}\text{D}_{14}$) and the bare $\text{Ag}(110)$ surface, respectively, when illuminated with modulated laser light. Here, deuterated $\text{C}_{22}\text{D}_{14}$ was used because of its enhanced stability against high bias voltages and laser illumination compared to $\text{C}_{22}\text{H}_{14}$. The electronic equivalence of hydrogenated and deuterated pentacene species on $\text{Ag}(110)$ has been verified by measuring dI/dV spectra and maps ([Figure S1](#)). Log plots of $|I_{\text{pl}}|$ and $|I_{\text{tot}}|$ in the range of -2.0 to 1.0 V show that the zero current appears at approximately $V_{\text{bias}} = 0$ V in the $I_{\text{tot}}-V$ curves ([Figure 1j](#)), but shifts to $V_{\text{bias}} = -0.7$ V in the $I_{\text{pl}}-V$ curves ([Figure 1i](#)), which we denote as the turning point. In contrast to the zero current commonly observed at zero bias under dark conditions, this turning point at $V_{\text{bias}} = -0.7$ V can be attributed to electron tunneling resulting from the asymmetric distribution of plasmon-induced hot electrons between the Ag tip and the $\text{Ag}(110)$ substrate ([Figure S2](#)). In line with the previous study,⁵¹ the positions of the turning

point vary under different Ag tip conditions (Figure S3) due to their varied hot electron distributions.

We further confirm that the net I_{pl} dominantly originates from the plasmon-driven electron transfer rather than the photoinduced process or other artifacts based on four key observations: (1) a negligible ratio of $I_{\text{pl}}/I_{\text{tot}}$ when using a W tip (Figure S4) due to tungsten's weak plasmonic response under 532 nm light irradiation compared to the Ag tip; (2) the dependence of I_{pl} on the photon energy in the range of 502–602 nm, showing the overlapping range of Ag plasmonic response as measured by STM-induced luminescence (Figure S5); (3) the enhanced I_{pl} with increasing laser power (Figure S6); and (4) the dependence of I_{pl} on the polarization of the incident laser (Figure S7).

Identifying the Resonant and Nonresonant Pathways of Plasmon-Driven Electron Transfer

The log plot of $|I_{\text{pl}}| - V$ in Figure 2a reveals peak-like features at high bias voltage, labeled by P_1 and P_2 , measured at the adsorbed $\text{C}_{22}\text{D}_{14}$ molecule on the Ag(110) surface. The peaks become more pronounced when plotting the $I_{\text{pl}}/I_{\text{tot}}$ ratio as a function of bias voltage (Figure 2b; see more details in Figure S8), which shows voltage-dependent enhancement of I_{pl} relative to the total current I_{tot} . The reproducibility of these peaks has been verified under different tip conditions (Figure S9). Similarly, a peak (labeled by P_3) appears at a higher bias voltage in the $I_{\text{pl}}/I_{\text{tot}}$ ratio curve obtained on the bare Ag(110) surface (black curve in Figure 2a,b). To understand the origin of these peaks, we measured the electronic states at the sites of the pentacene molecule and the bare Ag(110) surface by recording dI/dV spectra in constant-current mode without laser excitation (Figure 2c). Our analysis shows that peak P_3 at the bare Ag(110) surface originates from plasmon-driven resonant electron tunneling from the Ag tip to the first-order Rydberg-like series of field emission resonant ($n = 1$ FER) states of Ag(110), which is located at 4.7 V according to the measured dI/dV spectrum (black curve in Figure 2c). By tuning the wavelength from $\lambda = 502$ to 602 nm (Figure S10), the sums of the electron energy at peak P_3 and the photon energy give a nearly constant value, that is, $eV_{\text{bias}} + h\nu = 4.7$ eV (Figure 2d), in good agreement with the energy of the $n = 1$ FER state of the Ag(110) surface. Similar plasmon-driven resonant electron tunneling from the Ag tip to the FER of the Ag(111) surface has been reported under illumination using 532 and 633 nm lasers.⁵² However, how molecular orbitals participate in such resonant processes is still highly pursued.

Based on the assignment of P_3 , we further analyze the origins of the P_1 and P_2 peaks observed at the pentacene molecular sites by taking into consideration of the molecular orbitals. The measured dI/dV spectrum of pentacene (red curve in Figure 2c) shows that the lowest unoccupied molecular orbital (LUMO) and LUMO + 1 are located at 1.25 and 3.30 V, respectively, in line with previous reports.^{38,53,54} The state located at 4.2 V derives from the $n = 1$ FER state of the Ag(110) surface that is originally located at 4.7 V on bare Ag(110), which is a result of the downward shift of the local vacuum level caused by the molecule–substrate interaction.^{55,56} As indicated by the green arrows in Figure 2b,c, the observed peaks of P_1 and P_2 reflect the plasmon-driven resonant electron transfer from the Ag tip to LUMO + 1 and the downward-shifted $n = 1$ FER state at the pentacene molecule, respectively, where the energy match still satisfies the relation of $eV_{\text{bias}} + h\nu$. Despite their different line shapes owing

to the involvement of different mechanisms in measurements, Voigt fitting shows that the line widths of peaks P_1 and P_2 reasonably match those of LUMO + 1 and $n = 1$ FER peaks, respectively (Figure S8d,e). These results demonstrate that the specific molecular orbitals and electronic states of the substrate can contribute to the resonant plasmon-driven charge transfer channels (Figure 2e). By contrast, we find that the LUMO and the lower energy hybridized states (HSs) near E_{F} may contribute to the nonresonant hot electron transfer (Figure 2f). Further validation of the energy level alignment with $eV_{\text{bias}} + h\nu$ requires determining the one-photon process for the sketched charge transfer pathways. We measured the I_{pl} curves by tuning the light power (Figure S11a). From the power-law dependence,⁵¹ the fitting exponents of $m \sim 0.9$ confirm the one-photon-driven charge transfer processes (Figure S11b).

Resolving Nonresonant and Resonant Processes of Various Pentacene Species

The plasmon-driven charge transfer is responsible for the C–H bond breaking of $\text{C}_{22}\text{H}_{14}$ at the central benzene ring, producing derivatives $\text{C}_{22}\text{H}_{13}$ and $\text{C}_{22}\text{H}_{12}$. Our previous study has shown that the C–H bond breaking involves two quanta of plasmons, measured with varied power of a 532 nm laser at $V_{\text{bias}} = 0.1$ V.³⁸ This can be attributed to the process that the first photon drives nonresonant charge transfer to the LUMO of pentacene, while the second photon promotes its energy to overcome the reaction barrier of ~ 3.0 eV. This interpretation is in line with the photoassisted C–H bond breaking of azulene on Ag(110) that the electron tunneling into the LUMO is resonantly coupled with a photon to gain enough energy to overcome the ~ 2.6 eV activation barrier.⁵⁷ In our case, due to the nonresonant nature of hot electron transfer, the observed reaction rate is very low at $V_{\text{bias}} < 1.0$ V (Figure 2g). In contrast, a rapid increase of the reaction rate is observed when $V_{\text{bias}} > 1.0$ V, at which the resonant transfer occurs from the Ag tip to LUMO + 1, providing enough energy to overcome the reaction barrier of ~ 3.0 eV.

We further compare the nonresonant and resonant charge transfer pathways for the three pentacene species. Figure 3a shows the waterfall plots of the constant-current mode dI/dV spectra, recorded along the 10-point line grids across deuterated pentacene species of $\text{C}_{22}\text{D}_{14}$, $\text{C}_{22}\text{D}_{13}$, and $\text{C}_{22}\text{D}_{12}$ on Ag(110), for direct comparison of the relative energy positions of the LUMO, LUMO + 1, and $n = 1$ FER states. For LUMO + 1, slight upward shifts of 0.15 and 0.19 V are observed for $\text{C}_{22}\text{D}_{13}$ and $\text{C}_{22}\text{D}_{12}$, respectively, relative to the position located at 3.3 V for $\text{C}_{22}\text{D}_{14}$. Meanwhile, similar shifts are observed for the $n = 1$ FER state appearing at the molecular sites. The plot of the $I_{\text{pl}}/I_{\text{tot}}$ ratio as a function of bias voltage for the three pentacene species shows distinct P_1 and P_2 resonance peaks (Figure 3b). The peaks of $\text{C}_{22}\text{D}_{13}$ and $\text{C}_{22}\text{D}_{12}$ shift toward higher bias voltages relative to $\text{C}_{22}\text{D}_{14}$. For each pentacene species, the energy positions of the LUMO + 1 and $n = 1$ FER state can be well correlated with the P_1 and P_2 peaks by considering the relation $eV_{\text{bias}} + h\nu$ under 532 nm illumination (Figure 3c), demonstrating their roles as the plasmon-driven resonant electron injection channels. This energy match is further verified by using the 633 nm ($h\nu = 1.96$ eV) illumination (Figure S12), where a 0.33 eV shift for the corresponding peaks equals the photon energy difference between 532 and 633 nm light.

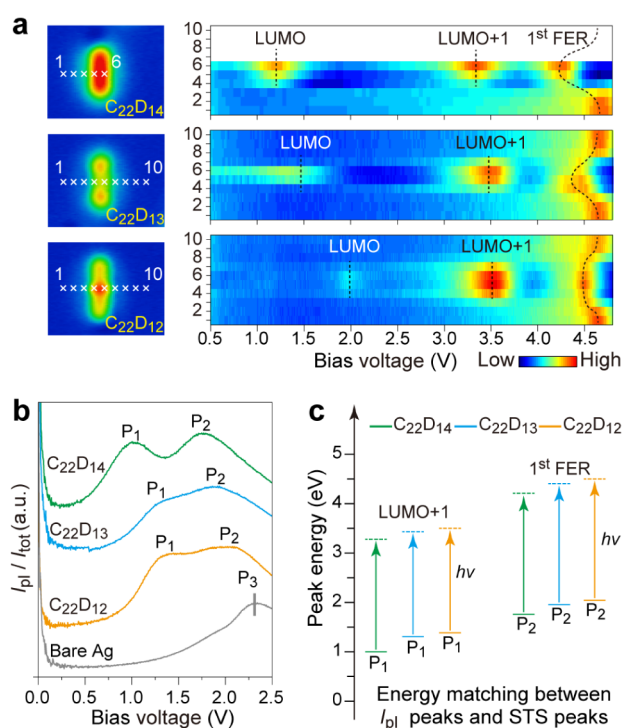


Figure 3. Comparing the charge transfer channels of three pentacene species. (a) Waterfall plots of dI/dV spectra recorded in constant-current mode without laser excitation, acquired along the short axis of the $C_{22}D_{14}$, $C_{22}D_{13}$, and $C_{22}D_{12}$, as marked by the crosses in the corresponding STM images (in the left panels). (b) I_{pl}/I_{tot} ratio as a function of bias voltage for $C_{22}D_{14}$ (green), $C_{22}D_{13}$ (blue), $C_{22}D_{12}$ (orange), and Ag(110) (gray), under 532 nm laser illumination. The curves are vertically offset for clarity. (c) The energy alignment between P_1 and LUMO + 1 and between P_2 and $n = 1$ FER, for the three pentacene species, with the peak positions extracted from (a) and (b).

Spatial Correlation between the Molecular Orbitals and the I_{pl} Images

The LUMO located at 1.3, 1.5, and 2.0 V, respectively, for $C_{22}D_{14}$, $C_{22}D_{13}$, and $C_{22}D_{12}$, is responsible for nonresonant hot electron transfer. The interaction of pentacene with the Ag(110) substrate largely modifies the intrinsic molecular orbitals and leads to the formation of strongly hybridized states (HSs), as revealed by the calculated density of states (DOSs, Figure S13). Due to rapid electron–electron scattering (tens of femtoseconds) followed by electron–phonon cooling on the ps time scale, the initially nonthermal plasmon-excited carrier population quickly thermalizes.^{19,58,59} Therefore, on the time scale relevant to our lock-in measurements, the plasmonic hot-electron distribution is well described by a thermalized, quasi-Fermi–Dirac distribution,

$$f(E, T_e) = \frac{1}{1 + \exp[(E - E_F)/k_B T_e]}$$

where T_e is the effective electron temperature and k_B is the Boltzmann constant. At a typical $T_e = 2000$ K,^{58,59} approximately 95% of hot electrons are estimated to be distributed between 0 and 0.5 eV above the tip's E_F . Near zero bias, hot electron transfer occurs predominantly through nonresonant processes to the unoccupied HSs + LUMO within this range (Figure 2f). In contrast, the fraction of hot electrons with energies more than 2.0 eV above E_F is estimated

to be smaller than $\sim 10^{-5}$. This negligible population suggests that at ~ 1.0 V bias voltage, nonresonant hot electron transfer to LUMO + 1 and the $n = 1$ FER would be highly inefficient. Thus, peaks P_1 and P_2 are not expected for nonresonant injection and instead reflect a plasmon-assisted resonant pathway, where energy matching between the plasmon and specific electronic states enables efficient electron transfer.

We measured the HSs from E_F to LUMO by recording the dI/dV spectra (Figure 4a). From the enlarged spectra (Figure 4b), it can be seen that the dI/dV signal measured at $C_{22}D_{12}$ is nearly identical to that on bare Ag(110), indicating a weak contribution from the molecule. In contrast, the spectra acquired at $C_{22}D_{13}$ and $C_{22}D_{14}$ molecules exhibit a higher density of states than the bare Ag(110) surface, suggesting a significant hybridized contribution from the molecules. The characteristic spatial distributions of HSs are systematically presented by dI/dV maps in Figure S14. For $C_{22}D_{14}$ (Figure 4c), dI/dV maps of HSs and the LUMO show two spots near the central C–D bond sites although becoming less intense at lower V_{bias} (Figure 4d). Consistently, the I_{pl} image obtained at zero bias voltage with constant-height mode shows the same location of two spots at the molecular center (Figure 4e), implying that the nonresonant hot electron transfer from the Ag tip to $C_{22}D_{14}$ mainly proceeds through its HSs + LUMO. However, the I_{pl} image obtained at 1.0 V shows a much-expanded density, giving an overall rounded square shape (Figure 4g). This rounded square shape at 1.0 V is much different from HSs + LUMO but similar to LUMO + 1 at 3.3 V (Figure 4f), supporting that LUMO + 1 is responsible for the resonant plasmon-driven electron injection into the $C_{22}D_{14}$ molecule.

Similar spatial correlations between molecular orbitals and the I_{pl} images have been made for pentacene derivatives $C_{22}D_{13}$ (Figure 4h–l) and $C_{22}D_{12}$ (Figure 4m–q). The HSs + LUMO of $C_{22}D_{13}$ is mainly located around the residual central C–D bond on one side, while the HSs + LUMO of $C_{22}D_{12}$ becomes much weaker and is located at the periphery of the molecule. Clearly, the I_{pl} images at $V_{bias} = 0$ V are in good agreement with the distributions of the HSs + LUMO for both $C_{22}D_{13}$ and $C_{22}D_{12}$ species. Similarly, the I_{pl} images at $V_{bias} = 1.2$ or 1.3 V correspond to the spatial distributions of LUMO + 1 of $C_{22}D_{13}$ and $C_{22}D_{12}$ molecules. To further validate our assignments, the characteristics of LUMO and LUMO + 1 are simulated by plotting the local DOS maps (Figure S15). In addition, the characteristics of I_{pl} images are verified under both the constant-height and constant-current modes with different set points to confirm the same physical origin rather than imaging artifacts (Figure S16). These bias-tunable and state-specific features demonstrate that the HSs + LUMO and LUMO + 1 are responsible for distinct plasmon-driven electron-transfer pathways into pentacene species.

DISCUSSION

Determining nonresonant/indirect or resonant/direct charge transfer between plasmonic metal nanostructures and the adjacent molecules has been a long-standing task in plasmonic chemistry.^{16,60} A common solution is to insert a thin insulating spacer between the plasmonic nanoparticle and the molecules.^{31,61} This spacer physically isolates the two, thereby suppressing nonresonant hot electron transfer and emphasizing the role of plasmon-driven resonant energy transfer across the insulating layer. Different from such physical isolation, the well-controlled vacuum gap between an Ag tip and pentacene

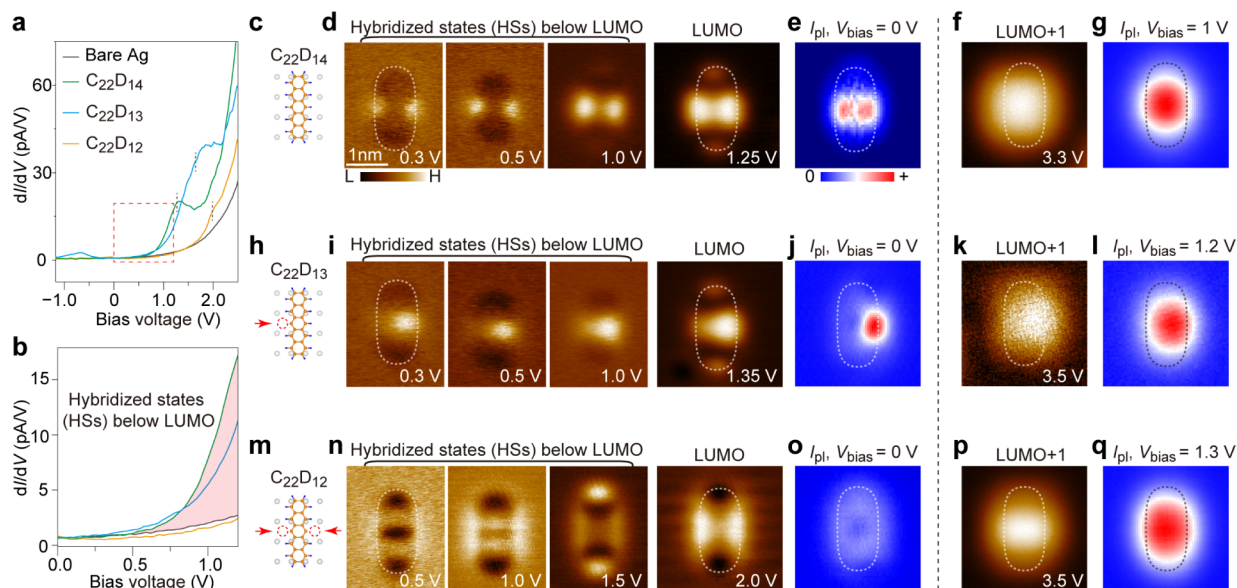


Figure 4. Orbital-resolved I_{pl} images of the three pentacene derivatives. (a, b) dI/dV spectra recorded in constant-height mode for the three pentacene species and the bare Ag(110) surface. The area marked by the dashed rectangle is enlarged in (b), showing the intensity of HSs between E_F and the LUMO. (c) Molecular structure of $\text{C}_{22}\text{D}_{14}$. (d) Constant-current mode dI/dV maps for the HSs ($V_{\text{bias}} = 0.3, 0.5, 1.0$ V) and LUMO ($V_{\text{bias}} = 1.25$ V) of $\text{C}_{22}\text{D}_{14}$. Scale bar: 1 nm. (e) Constant-height mode I_{pl} image of $\text{C}_{22}\text{D}_{14}$ at $V_{\text{bias}} = 0$ V for hot electron transfer (tip stabilized on Ag at 0.1 V, 100 pA; then feedback off, bias set to 0 V for constant-height scanning). (f) dI/dV map of LUMO + 1 ($V_{\text{bias}} = 3.3$ V) of $\text{C}_{22}\text{D}_{14}$. (g) Constant-height mode I_{pl} image at $V_{\text{bias}} = 1$ V for resonant electron transfer to LUMO + 1. (h–l) Similar data obtained for $\text{C}_{22}\text{D}_{13}$. (m–q) Similar data obtained for $\text{C}_{22}\text{D}_{12}$. All dI/dV spectra and maps were obtained in dark conditions with the laser off, and the I_{pl} images were obtained with a 532 nm laser at 28.3 W/cm^2 .

molecules forms a natural isolation with a precisely controllable distance of 0–20 Å, which not only supports nonresonant charge transfer through quantum tunneling but also acts as a vacuum isolation to interrogate resonant processes. This advantage makes the tip–vacuum–molecule junction an ideal platform to study nonresonant/resonant plasmonic processes under one plasmonic nanostructure and one molecule configuration. The vacuum isolation also makes it possible to use bias voltage to tune the relative energy match between the Ag tip and molecules for plasmonic charge transfer, in addition to the photon energy transfer strategy.

This tip–vacuum–molecule single-barrier junction differs from the double-barrier junction, which incorporates an additional NaCl insulating layer.^{45,47} In the double-barrier configuration, bidirectional electron transfer occurs, with competing electron flows from both the metal tip and the metal substrate into the decoupled molecule. This can result in the charging of the molecule into anionic or cationic states. Consequently, the NaCl-based architecture is ideal for investigating intrinsic molecular excited states with minimal perturbation from the substrate. In contrast, the single-barrier junction, where the molecule interacts directly with the metal substrate, enables the interrogation of resonant and nonresonant transport channels under unidirectional electron injection from the tip into the molecule. More broadly, in applications such as plasmon-enhanced electrochemistry and photochemistry, metal electrodes (e.g., Pt, Au) are widely employed—not only to support plasmonic nanoparticles and molecular adsorbates but also to direct charge flow and facilitate redox reactions. As a result, molecule–metal interactions are unavoidable in realistic electrochemical environments. In this context, the adsorption of pentacene on an Ag(110) substrate in our study serves as a model system for mimicking a realistic molecule/electrode interface.

Submolecule-resolved I_{pl} images directly indicate the plasmonic electron injection positions inside a single molecule. This exceptional real-space resolution benefits from the atomically sharp protrusions at the tip apex to make a highly confined plasmonic field, much smaller than in the case of synthetic nanoparticle systems. The spatial and energy correlations of I_{pl} images with the molecular frontier orbitals enable us to assign state-specific charge transfer channels. This highly localized molecule–plasmon interaction has potential implications for inducing bond-selective chemical reactions under plasmonic fields,⁶² such as the observed C–H bond breaking solely in the central benzene ring of pentacene.

CONCLUSIONS

In summary, by using the lock-in technique to extract the net I_{pl} with a laser-STM, we resolve distinct nonresonant hot electron transfer and resonant electron transfer channels from the Ag tip to pentacene molecules. Bias-tunable resonances and orbital-resolved I_{pl} images confirm that the HSs + LUMO contribute to the nonresonant hot electron transfer, while LUMO + 1 and the shifted $n = 1$ FER are responsible for the resonant charge transfer. The I_{pl} images certainly indicate the nonequilibrium charge states, rather than the ground state, of molecules under plasmonic fields. Future integration of the I_{pl} measurements with a femtosecond laser provides an opportunity to study the nonequilibrium carrier dynamics and other excited states, such as excitons, with joint spatial-temporal-energy resolutions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.Sc21031>.

Experiment details of sample preparation, STM-AFM experiments, DFT calculations, and photocurrent experiments; supplementary figures for comparable electronic structures of hydrogenated and deuterated pentacene on Ag(110) (S1), hot electron tunneling pathways in the tip-sample junction under different bias voltages (S2), varied turning points in $I_{\text{pl}}-V$ curves under different tip conditions (S3), photocurrent on the Ag(110) surface measured using tungsten and silver tips (S4), photon-energy dependence of I_{pl} and the plasmonic response on Ag(110) (S5), power-dependent photocurrents obtained on bare Ag(110) (S6), polarization-dependent photocurrents obtained on bare Ag(110) (S7), measuring $I_{\text{tot}}-V$ and $I_{\text{pl}}-V$ curves, and the plot of $I_{\text{pl}}/I_{\text{tot}}$ ratio curves (S8), consistency of the $I_{\text{pl}}-V$ resonance peaks on $\text{C}_{22}\text{D}_{14}$ under different tip conditions (S9), the resonance peak P_3 on bare Ag(110) measured with increasing laser fluxes and photon energies (S10), verification of the one-photon process in photocurrent measurements (S11), energy match between P_1 and LUMO + 1 under 633 nm excitation (S12), density of states (DOS) and projected density of states (PDOS) of pentacene derivatives on Ag(110) (S13), HSs between E_F and the LUMO of pentacene derivatives on Ag(110) (S14), DFT-experiment comparison of LUMO/LUMO + 1 spatial maps for pentacene derivatives on Ag(110) (S15), and reproducibility of I_{pl} imaging in constant-height and constant-current modes (S16) (PDF)

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Notes

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