

1 **Optical Gating Electron Transport through Nonphotoresponisive**
2 **Molecular Junctions**

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1 **Abstract:** The manipulation of electron transport through single-molecule junctions *via*
2 light illumination is a critical step towards molecular hybrid devices. However, most
3 kinds of molecules are nonphotoresponsive without photo absorption upon a specific
4 light illumination. Here, a strategy for high efficiently gating electron transport through
5 a nonphotoresponsive molecular junction with a general light source is provided by
6 introducing nanogap plasmons and molecular design. It is found the conductance of the
7 triphenylamine-based molecules, a nonphotoresponsive molecule with buried
8 anchoring groups, can be enhanced by two orders of magnitude under a general light
9 illumination, which should be the greatest enhancement in the family of
10 nonphotoresponsive molecules. It is further revealed that the giant conductance
11 modulation originates from the coupling of the buried anchoring groups and plasmon-
12 excited hot electrons. This work would contribute to the understanding of the
13 interaction mechanisms between light and bridged molecules, assisting the
14 development of the molecule-based hybrid optoelectronic devices.

1 The ability to control the electrical current through a molecule is a critical step to realize
2 functional molecular devices¹⁻³. A typical method to control the electronic transport
3 through single molecules is to employ the strategy of a field-effect transistor, in which
4 the molecular orbitals are energetically shifted by the gate voltage and thus the charge
5 transport through the molecule is modulated⁴. Using light as an external stimulation to
6 modulate electron transport through single molecules, like a solid field-effect transistor,
7 have attracted growing intensive interests due to its potential applications in the
8 fabrication of miniaturized hybrid optoelectronic devices. Furthermore, it provides a
9 platform to investigate the interaction between light and matter at the molecular level^{5,6}.
10 However, the mismatch between the scale of optical waves and that of individual
11 molecules presents an obstacle for achieving a high-efficiency modulation/strong
12 interaction. Luckily, surface plasmon polaritons (SPPs), which merge electronics and
13 photonics and can be confined to far subwavelength dimensions with high energy
14 intensity, may offer a solution to this size-compatibility problem^{7,8}.

15 Regarding how the electron transport through single-molecule junctions is
16 modulated by light, several mechanisms have been proposed, including photo-induced
17 intramolecular structural change⁹⁻¹⁴, photo-induced proton transfer (PIPT)¹⁵, photo-
18 assisted tunneling (PAT)¹⁶⁻¹⁸, resonant optical transitions^{19,20}, and exciton binding²¹. A
19 well-known mechanism is the conversion from photon energy to mechanical energy
20 based on photochromic molecules, such as azobenzene^{22,23}, diarylethene^{9,24}, and
21 spiropyran¹², which can be interconverted between bistable or multiple conformational
22 states under illumination. The structural transformation induced by optical absorption

1 may result in a giant conductance change, making it feasible to fabricate molecular
2 switches. PIPT can achieve photo responsiveness based on some special molecules and
3 a photoacid solvent in which the molecule isomerizes and releases a proton upon
4 illumination^{15,25}. In this way, the conductance of the molecular junctions can be
5 modulated by one order of magnitude¹⁵. The PAT mechanism (or Tien-Gordon theory)
6 explains how a periodic voltage $V_{ac}(t)$ from the electric field of the light wave drives a
7 periodic shift of the energies in the electron transmission function, *i.e.*, the photon
8 energy is transferred to individual electrons^{26,27}. It has been reported that the
9 conductance of single-molecule junctions can be enhanced up to a factor of two by
10 PAT⁵. Other mechanisms include, for example, the opening of additional conduction
11 channels resulting from an inherent asymmetry in the molecular junction under a
12 resonant optical illumination²⁰, and molecular orbitals reconstruction based on the
13 formation of bound excitons under the resonance carriers' excitation^{21,28}. These
14 previously reports promote the understanding of the interaction of light and single
15 molecules, and step forward to realize functional devices. One of the remaining
16 challenges for optical controlling electron transport through single molecules is that
17 most molecules are nonphotoresponsive, *i.e.*, they neither absorb the photon energy nor
18 undergo a structural transformation upon specific light illumination. Therefore, it is
19 greatly difficult to control electron transport through these kinds of molecules with a
20 general light source. SPPs, which can be easily excited by scattered light in the nanogap
21 without specific requirement for the incident light^{29,30}, combined with an appropriate
22 anchoring group design may solve this knotty problem.

1 To date, anchoring groups such as thiol (-SH), amine (-NH₂), pyridine, and
2 carboxylic acid (-COOH) have been extensively used because of their stable electrical
3 coupling when in contact with metal leads. Normally, the stronger the bonding group,
4 the larger the molecular conductance if the bonding group can achieve direct contact
5 with the electrodes. However, there is also a large variety of molecules that possess
6 strong anchoring groups buried in the molecule backbone (*i.e.*, the direct coupling
7 between the anchoring group and electrodes is spatially blocked by, *e.g.*, the molecular
8 branches), which will result in poor conductance of the junctions. We anticipate that
9 the poor conductance of such molecular junctions might be dramatically improved
10 under illumination if a strong coupling between the buried anchoring groups and
11 electrodes can be established *via* tunneling plasmonics³¹.

12 To prove this anticipation, we experimentally measured the conductance of
13 triphenylamine-based molecular junctions, in which the direct coupling of the
14 anchoring group and electrodes is unavailable under dark conditions. As expected, a
15 poor conductance of the molecular junction is determined by analyzing the conductance
16 histograms. Interestingly, upon light illumination, two additional dramatically
17 enhanced conductance peaks appear in the conductance histogram for this
18 nonphotoresponsive molecular junction. The three conductance peaks, in total, follow
19 a log-linear relationship. We attribute these features to the interaction between surface
20 plasmons and the molecules. Assisted by density functional theory (DFT) calculations,
21 we demonstrate that the coupling of plasmon-excited hot electron and the buried
22 anchoring groups is the reason for the dramatic conductance modulation.

Results and discussion

Experimentally, we employed a custom-designed MCBJ setup integrated with a laser source for addressing the charge transport properties of molecules. In brief, a notched pure gold wire (100 μm in diameter, approximately 10 mm in length) was fixed on top of a polyimide coated substrate and the substrate was subsequently mounted in a three-point bending configuration. The gold wire was elongated and then broken by mechanical bending of the substrate, and cleanly fractured surfaces of the gold wire were exposed. The bending could also be relaxed to form atomic-scale contacts again by the control of a piezo-element, see supplementary Fig. S1. A *p*-polarized He-Ne laser ($\lambda = 632.8$ nm), in which the electric field of the incident light is parallel to the electrode axis, was used as a light source to excite strong SPPs in the nanogap as described in our previous report³².

By taking advantage of the knowledge of plasmon-induced transport properties of metal point contacts^{27,32,33}, we first investigated the electrical characteristics of bare gold electrodes with and without illumination in a shielding box. Figure 1a shows the statistical histograms with both linear coordinates and logarithmic coordinates in dark conditions. Figure 1b shows the corresponding results upon illumination. It can be found that the bare gold conductance displayed integer-multiple G_0 peaks in the histograms regardless of the illumination condition. The individual conductance traces show the same feature as well, see supplementary Fig. S2. Meanwhile, no extra peak below $1G_0$ was observed in the histograms irrespective of whether the bare metal junctions were illuminated or not (see logarithmic coordinates).

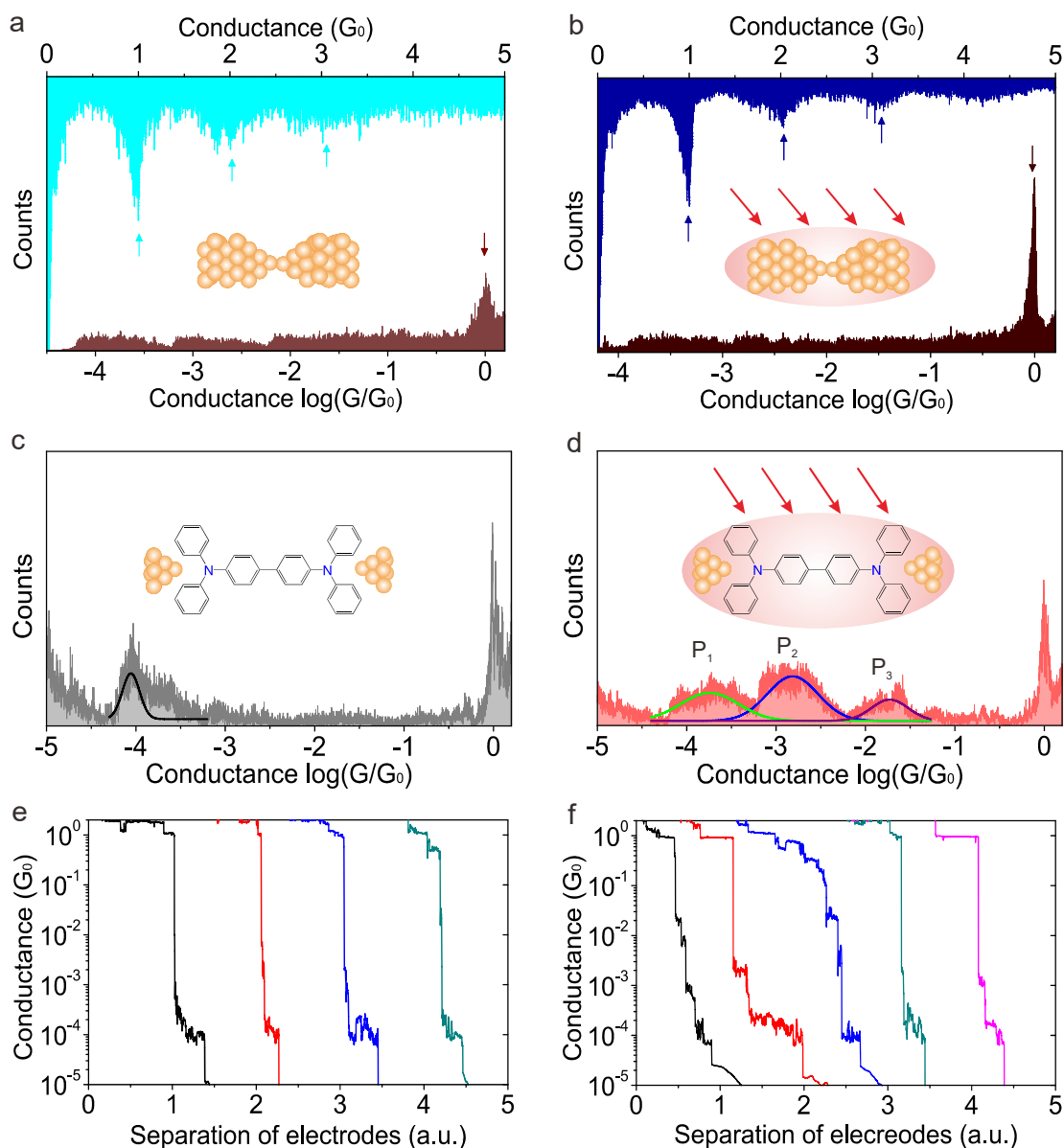


Fig. 1 | Conductance traces and histograms of the junctions with and without light illumination. (a-b) Linear and logarithm conductance histograms of bare gold wire (a) in dark and (b) upon illumination. **c** Conductance histogram of TPB molecules sandwiched between two electrodes in the absence of illumination with a Gaussian-fitted peak at approximately $8.8 \times 10^{-5} G_0$. Inset: Schematic of the molecular structure sandwiched between two separated electrodes. **d** Conductance histogram of TPB molecules in the presence of illumination, with three Gaussian-fitted peaks (P_1 , P_2 , and

1 P₃) at approximately 1.8×10^{-4} G₀, 1.5×10^{-3} G₀, and 1.9×10^{-2} G₀, respectively. (e-f)
2 Logarithm conductance traces during the separation of the electrodes (e) without laser
3 illumination and (f) in the presence of illumination.

4 Our previous work showed that the atomic-scale geometries of electrodes can tune
5 the hybridization type of amine bond groups in 4,4'-diaminobiphenyl (DBP) molecular
6 junctions³⁴. In this work, the H atoms in the anchoring groups (-NH₂) at the ends of
7 DBP were replaced by benzenes to generate the N,N,N',N'-tetraphenylbenzidine (TPB)
8 molecular junctions, as shown in Fig. 1c. In this way, the direct coupling between the
9 anchoring N atoms and electrodes is spatially hindered by the benzenes. A previous
10 study showed that a strong UV-visible absorption only appeared approximately 299-
11 351 nm for a triphenylamine-based molecule³⁵. Our target molecule TPB, as one of the
12 triphenylamine-based derivatives, shows a similar absorption peak wavelength smaller
13 than 446 nm by both density functional theory (DFT) calculation and optical
14 spectroscopy measurement, see supplementary Fig. S3. Our experiments were
15 performed under light illumination with a 623.8 nm laser far from the absorption peaks,
16 which means that the TPB molecules are unlikely to undergo an optical transition to an
17 excited state by the optical absorption.

18 The TPB molecules were dissolved in an organic solvent (≈ 1 mM in
19 tetrahydrofuran) and were self-assembled on gold contacts for 30 minutes after
20 breaking the metal wire. The conductance traces were recorded in ambient conditions
21 after drying the samples with nitrogen. The recorded conductance traces show a
22 stepwise feature during the separation process, as expected. The plateaus located far

1 below G_0 indicate that the electrodes were bridged with the target molecules, and the
2 lowest plateaus arose from the charge transport across a single TPB molecule bridged
3 junction. Several representative traces recorded in dark are shown in Fig. 1e. The
4 conductance histogram was created by five hundred conductance traces without data
5 selecting. A peak located at approximately $8.8 \times 10^{-5} G_0$ can be observed in the
6 conductance histogram, as shown in Fig. 1c.

7 We further recorded the conductance of the target molecule in the presence of
8 illumination by focusing a 632.8 nm He-Ne laser at the junction region. From the
9 analysis of the histogram presented in Fig. 1d, we obtained a completely different
10 conductance profile with three peaks (P_1 , P_2 , and P_3) approximately $1.8 \times 10^{-4} G_0$,
11 $1.5 \times 10^{-3} G_0$, and $1.9 \times 10^{-2} G_0$. Comparing these peaks with the one presented in Fig. 1c,
12 two essential features can be observed. First, the peak (P_1) in Fig. 1d shifted to a little
13 bit higher conductance value when the junction was illuminated. We attribute this
14 observation to 1) plasmon-induced hot carriers directly transfer across the nanogap
15 between electrodes^{31,33,36,37}, and 2) photo-assisted tunneling⁵. Both of them contribute
16 a small proportion of the total current. Second, two additional peaks (P_2 and P_3) with
17 much higher conductance values (up to 100 times larger) than P_1 appeared upon
18 illumination. These two additional peaks should not be caused by the hot carriers
19 transferring across the nanogap, photo-assisted tunneling, or bound excitons as
20 previously reported, since the conductance enhanced by them is rather limited, normally
21 no more than a factor of two^{5,21}.

22 Considering the specific structure of the molecule, our observations may originate

1 from two particular mechanisms: 1) The molecular conformation changes upon laser
2 illumination, which may cause dramatic conductance changes. It has been reported that
3 the conductance of a biphenyl molecular junction has a strong correlation with the
4 internal twist angle between adjacent benzene rings in the molecular backbone³⁴. If the
5 two adjacent benzene rings rotate relative to each other, the degree of the π -conjugation
6 between them will change, thereafter leading to a conductance change; 2) The coupling
7 of the molecule-electrode at the two terminals is modulated upon illumination, which
8 produces two extra peaks in the conductance histogram.

9 To determine which mechanism is responsible for the significant conductance
10 modification, a further experiment was performed with N,N,N',N'-tetraphenylbenzene-
11 1,4-diamine (TPD), whose molecular backbone includes only one benzene, as
12 illustrated in the inset of Fig. 2. With this kind of molecule, the effect arising from the
13 relative rotation of the two benzene rings along the molecule backbone can be excluded.
14 Figure 2a and Fig. 2b show the conductance histogram of the molecular junctions in
15 dark conditions and upon illumination, respectively. Figure 2a shows a peak located at
16 approximately $2.8 \times 10^{-4} G_0$. In contrast, Fig. 2b presents three peaks (P_1' , P_2' and P_3')
17 located at approximately $3.0 \times 10^{-4} G_0$, $7.2 \times 10^{-3} G_0$, and $9.8 \times 10^{-2} G_0$, respectively.
18 Figure 2c and Fig. 2d show several typical conductance traces during separation in dark
19 conditions and under illumination. It can be found that the conductance traces presented
20 in Fig. 2d show more steps compared to Fig. 2c, which is coherent with the histogram
21 as presented in Fig. 2a and Fig. 2b.

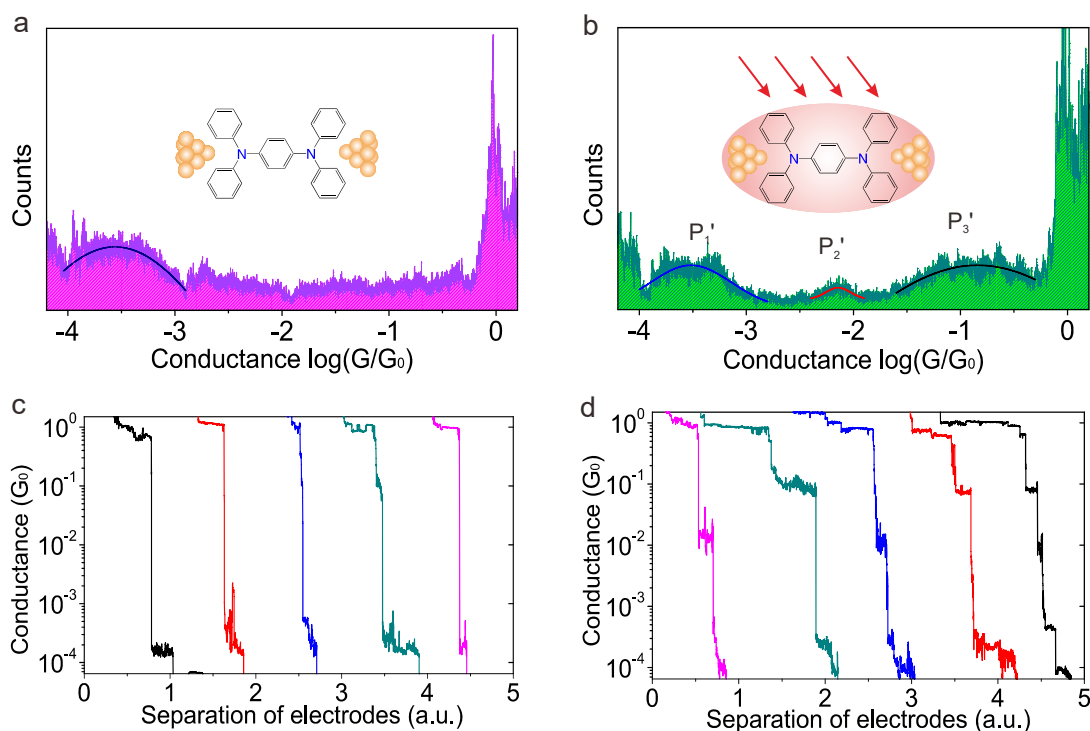


Fig. 2 | Conductance traces and histograms of the TPD junctions with and without light illumination. **a** Conductance histogram of TPD molecules in dark condition, with a Gaussian-fitted peak at approximately $2.8 \times 10^{-4} G_0$. The inset illustrates the molecular structure sandwiched between two separated electrodes. **b** Conductance histogram of TPD molecules upon illumination with three Gaussian-fitted peaks (P_1' , P_2' , and P_3') at approximately $3.0 \times 10^{-4} G_0$, $7.2 \times 10^{-3} G_0$, and $9.8 \times 10^{-2} G_0$, respectively. **(c-d)** Logarithm conductance traces during the separation of electrodes **(c)** without light illumination and **(d)** upon illumination.

Comparing these conductance histograms of TPD molecular junctions (Fig. 2a and 2b) with that of TPB molecular junctions (Fig. 1c and 1d), we found a common feature that there is only one obvious peak in the dark, while two additional peaks appear under illumination for both TPD and TPB junctions. We now turn to establish the relationship

between these peaks' values. Interestingly, we found that the conductance values for both types of molecules followed $P_2 \approx \sqrt{P_1 \times P_3}$ upon illumination, where P_1 , P_2 , and P_3 are the minimal, middle, and maximal conductance values, respectively. The charge transport across a two-terminal molecular junction follows the Breit–Wigner formula³⁸.

$$T(E, V) = 4\Gamma_1\Gamma_2 / \{[E - E_0(V)]^2 + [\Gamma_1 + \Gamma_2]^2\} \quad (1)$$

where $T(E, V)$ is the transmission coefficient of the electrons at an energy E under a bias V , and Γ_1 and Γ_2 describe the coupling of the molecular orbital to the left electrode and right electrode, respectively. E_0 is the eigenenergy of the molecular orbital which may be shifted slightly due to the coupling of the orbital to the electrodes³⁹.

In our cases, TPB and TPD molecules have a common anchoring group (triphenylamine), from which the molecule-electrode coupling strength is weak such that the last term of the denominator in the Breit-Wigner formula can be omitted. Thus, formula (1) can be simplified as:

$$T(E, V) \approx 4\Gamma_1\Gamma_2 / [E - E_0(V)]^2 \quad (2)$$

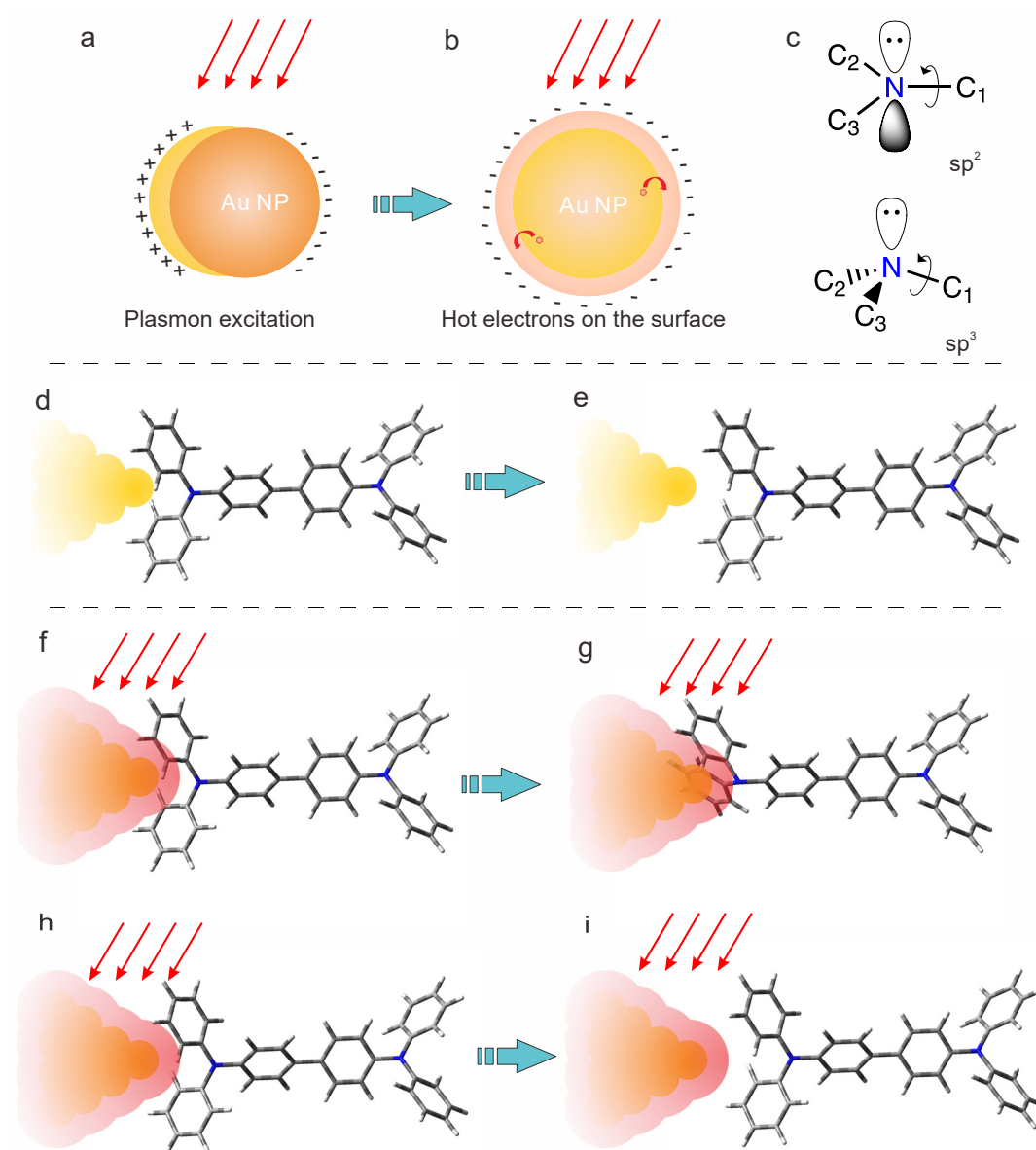
The transmission of a symmetric molecule can have three possible states ($4\tau_1^2/[E - E_0(V)]^2$, $4\tau_1\tau_2/[E - E_0(V)]^2$, $4\tau_2^2/[E - E_0(V)]^2$) in cases of the molecule-electrode coupling strength being different at two ends (τ_1 , τ_2 where $\tau_1 \neq \tau_2$) upon illumination. It can be found that these three transmission values follow the equation $T_2 \approx \sqrt{T_1 \times T_3}$, agreeing with experimental observations.

Subsequently, we try to address the coupling change between the target molecules and electrodes induced by the laser illumination. It has been reported that plasmon-excited nanoparticles or nanogaps can be an efficient source of hot electrons^{40,41}. For

1 simplicity, we used nanoparticles instead of nanoelectrodes to schematically show the
2 distribution of hot electrons. Figure 3a and 3b depict how plasmon excitation can create
3 hot electrons on gold nanoparticle (Au NP) surfaces. Following the optical excitation,
4 each plasmon quantum can decay into either a radiative photon (scattering) or a
5 nonradiative electron-hole pair. For small nanostructures, a dominant decay channel is
6 the electron-hole pair formation^{42,43}. It has also been reported that as the nanogap
7 between the electrodes decreases below a critical size, *e.g.*, less than 0.5 nm, the
8 plasmon interactions enter a quantum conductive regime where the decay of the
9 plasmons creates a distribution of hot electrons, which causes the transfer of electrons
10 between the nanoelectrodes^{31,44,45}. Weng *et al.* directly visualized hot-electron
11 distributions in the junction regions *via* shot noise by using a scanning near-field optical
12 microscope⁴⁶, which demonstrated that the hot electrons can be spatially diffused by
13 fluctuating EM evanescent fields, see supplementary Fig. S4 for more details. All these
14 reports indicate that the nanogap can host a large number of hot electrons, and hot
15 electrons can extend further away from the nanoelectrodes, which may dramatically
16 change the coupling state between electrodes and sandwiched molecules.

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18



1
2 **Fig. 3 | Schematics of the generation of hot electrons on gold nanoparticle surface**
3 **and the change of orbital hybridization of N atom upon illumination. a** Plasmon-
4 excited gold nanoparticles as an efficient source of hot electrons. **b** The expanded
5 distribution of hot electrons on the surface of the nanoparticles. **c** The dihedral angle of
6 N atom in $sp^2(180^\circ)$ and $sp^3(120^\circ)$ hybridization state. **d** The initial junction structure
7 without laser illumination. Only one electrode is shown in the molecule junction. **e** The
8 breaking of the molecular junction during the stretching process in the dark. **f** The

1 distribution of hot electrons expanded beyond the electrode surface (marked by red
2 shadow) in the presence of illumination, and the junction structure shows sp^2
3 hybridization type before relaxation. **g** sp^3 hybridization after relaxation since the hot
4 electrons can attach to the N atom. **h** The Au-N coordinate covalent bond breaks and
5 sp^2 hybridization occurs when the N atom is stretched out of the distribution of hot
6 electrons. **i** The complete breaking of the molecular junction due to the stretching
7 process under illumination.

8 Figure 3d and 3e describe the evolution of TPB molecular junction from a
9 connected state to a disconnected state in the absence of illumination, as confirmed by
10 the following calculations. During this stretching process, the anchoring groups
11 triphenylamine remain in the sp^2 hybridization state, because the steric hindrance of the
12 two benzene rings at the end of the molecule blocks the direct coupling between Au and
13 N atoms. As previously reported, the hot electrons can extend further away from the
14 nanoelectrodes than an equilibrium electron distribution^{18,46}, and subsequently reach
15 the anchoring N atom of the TPB molecule. For a nearby electron acceptor, the hot
16 electrons can efficiently transfer from a plasmonic nanostructure state into the
17 acceptor's electronic states because of their higher energy⁴². Meanwhile, the lone pair
18 of electrons on the N atom forms a coordinate bond with the Au atom *via* the extended
19 hot electrons⁴⁷. Figure 3f-3i present the evolution of the hybridization type of N atom
20 upon illumination during the stretching process. The hot electrons near the surface of
21 the electrodes can attach to the nearby N atom when the gap size is small enough (Fig.
22 3f), which may result in hybridization switching of the N atom from sp^2 to sp^3 after a

1 suitable relaxation time (Fig. 3g). During the stretching process, the molecule moves
2 away from the electrodes on the one hand and the local field strength in the nanogap
3 decreases on the other, see supplementary Fig. S5 for more details. On condition that
4 the gap size exceeds the extended proximity range of the hot electrons, the Au-N bond
5 will break and the hybridization state consequently changes back to sp^2 (Fig. 3h).
6 Further stretching will cause the complete breaking of the molecular junction (Fig. 3i).
7 This repeatable process is most likely the reason for the observation of three statistically
8 determined conductance upon illumination, which we will further elaborate in below.

9 To have an in-depth understanding of our system, we investigated the electron
10 transport through the TPB molecular junctions by means of first-principle calculations.
11 The original structure of the isolated TPB in the absence of electrodes was investigated
12 by optimizing it in Gaussian 09 Package⁴⁸. We found that the N atoms remain in sp^2
13 hybridization, which means that the gold atoms cannot connect to the N atoms easily
14 due to the steric hindrance of the benzene rings. Therefore, there was only one peak
15 with a low conductance value in the absence of illumination during the stretching
16 processes, and this peak can be attributed to the weak coupling of the benzene rings and
17 electrodes.

18 Furthermore, quasi-static geometric optimizations with various gap sizes between
19 the electrodes were simulated, which were chosen to describe the dynamic stretching
20 process, so that one can compare geometric structures of different hybridization types.
21 To describe the effect of hot electrons upon light illumination, we set the initial
22 hybridization state of the anchoring structure to sp^3 , when the molecules were adsorbed

1 on the electrode surfaces. In this way, the gold atom on the tip of the electrode can form
2 a coordinate bond with the N atom *via* the lone pair of electrons. The models for the
3 geometric optimization consisted of two-layer Au (100) electrode units and a single
4 TPB molecule bonded to the electrodes on the top sites. The geometric optimizations
5 and electronic structure calculations were performed with the Lanl2DZ basis set in
6 Gaussian 09 package.

7 By optimizing the structures with various gap sizes, we obtained three types of
8 optimized geometric structures, as presented in Fig. 4. For each gap size in each
9 molecular junction, the dihedral angle ($C^1-N-C^2-C^3$), *i.e.*, the angle between the plane
10 (C^1-N-C^2) and plane (C^2-N-C^3) as presented in Fig. 3c, varies from 120° to 180° . The
11 trivalent nitrogen atoms could be either sp^2 - (N-torsion 180°) or sp^3 -hybridized (N-
12 torsion 120°), or could be in an intermediate hybridization state. Our target molecule
13 can connect with the gold electrodes *via* two sp^3 -hybridized terminals (dihedral angle
14 is approximately 130°) at both ends as the gap size is 13.08 \AA (Fig. 4a and 4d), or *via*
15 an sp^2 -hybridized terminal (dihedral angle $\sim 172^\circ$) at one end and an sp^3 -hybridized
16 terminal (dihedral angle approximately 128°) at the other as the gap size is
17 approximately 13.98 \AA (Fig. 4b and 4e), or *via* two sp^2 -hybridized terminals (dihedral
18 angle is approximately 169° and 174°) at both ends when the gap size is stretched to
19 16.58 \AA (Fig. 4c and 4f).

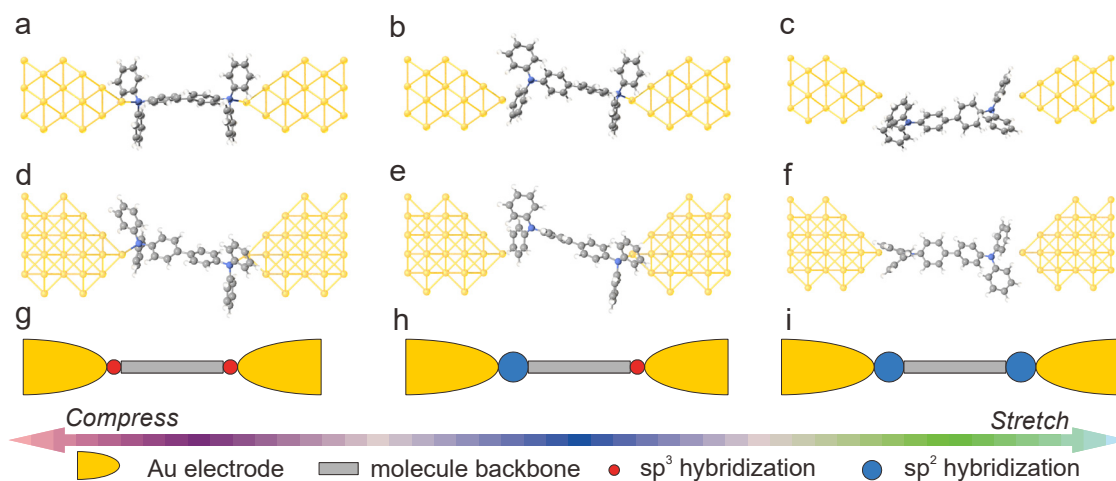


Fig. 4 | Three types of optimized geometric structures with different electrodes gap sizes. (a-c) present the front view of the optimized geometric structures with 13.08 Å, 13.98 Å and 16.58 Å gap sizes between electrodes, respectively. The N atoms are marked by blue color. (d-f) show the top-front view of the optimized geometric structures with the different gap sizes as presented in (a-c). (g-i) illustrate the different types of hybridization with different gap sizes, which correspond to the structures presented in (a-c).

For convenience, we named these three structures of molecule junction as sp^3 - sp^3 , sp^3 - sp^2 and sp^2 - sp^2 . Notably, the gold electrode couples with the molecule directly by Au-N bond for the sp^3 -hybridized terminals, while the electrode weakly couples with the molecule by π electron *via* the benzene ring for the sp^2 -hybridized terminals. When the electrode tip couples with the N atom rather than the benzene ring, the electrons transport across a shorter molecular backbone. The shorter transport path together with a stronger coupling will result in a much larger conductance value, see supplementary Fig. S6.

The transport characteristics of modeled single-molecule junctions were investigated by employing nonequilibrium Green's function (NEGF) method in conjugation with density functional theory (DFT) in TranSIESTA electronic transport package^{49,50}. The simulations were performed with the Perdew-Burke-Ernzerhof (PBE) functional in the generalized gradient approximation (PBE-GGA) for exchange-correlation⁵¹. The current under a finite bias voltage was calculated according to the Landauer-Büttiker formula⁵².

$$I = 2e/h \int T(E, V) [f(E - \mu_L) - f(E - \mu_R)] dE \quad (3)$$

where $T(E, V)$ is the transmission coefficient of the electrons at an energy E under a bias voltage V . $f(E - \mu_{L/R})$ is the Fermi-Dirac distribution for electrons at energy E in the left/right electrode with chemical potential $\mu_{L/R}$.

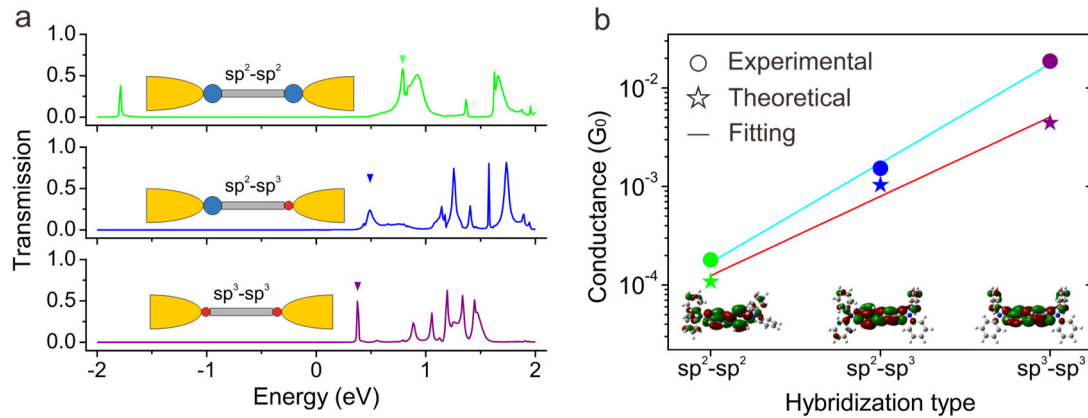


Fig. 5 | Transmission spectra and conductance of TPB molecular junctions. a

Transmission spectra of TPB molecular junctions at 0.8 V for sp^2-sp^2 (green), sp^2-sp^3 (blue) and sp^3-sp^3 (purple) structures, respectively. The arrows indicate the shift of the LUMO-dominated transmission peak for different types of junctions. Inset: Schematic of the different types of junctions. **b** Conductance with the logarithm scale as a function

of the hybridization type of molecular junctions. The circles represent experimental data and stars show the data extracted from the theoretical simulations. Inset show the wave function of LUMO with three different type of molecule junctions.

For comparison, we calculated the transmission spectra and the corresponding conductance in the TPB molecular junctions at 0.8 V bias voltage for these three structures. Figure 5a presents the transmission spectra of sp^2-sp^2 , sp^2-sp^3 and sp^3-sp^3 structures, respectively. The LUMO-dominated transmission peak of the sp^3-sp^3 structure is the closest to the Fermi level, followed by the transmission peak of the sp^2-sp^3 structure, and finally the transmission peak of the sp^2-sp^2 structure. The conductance of the TPB molecular junctions of sp^2-sp^2 , sp^2-sp^3 and sp^3-sp^3 configurations was calculated to be $1.1 \times 10^{-4} G_0$, $1.0 \times 10^{-3} G_0$, and $4.4 \times 10^{-3} G_0$, respectively, as shown in Fig. 5b. The logarithm values of the theoretical conductance exhibit a linear relationship, which means that the calculated molecular conductance values also follow $G_2 \approx \sqrt{G_1 \times G_3}$, in agreement with the experimental results. Notably, the measured conductance data are higher than the theoretically calculated data, and we attribute it to 1) direct transport of plasmon-induced hot carriers through the nanogap or photo-assisted tunneling, which contributes as additional tunneling current^{33,36}; 2) as long as stable coordinate bonds between Au and N atoms are established, the hot carriers can extend into the benzene ring and envelop the N atom, thus enhancing the electron transmission¹⁸, which is not taken into consideration in the theoretical calculation. It can also be found that the wave functions for all the three kinds of junction are located on the molecular backbone instead of anchoring groups despite the fact that sp^2

1 hybridization shows a better conjugated effect, which indicates the anchoring groups
2 contribute a poor conductivity. As mention above, for an sp^3 hybridization anchoring
3 group, the electrode atoms couple with N atom directly, which decreases the length of
4 the scattering region and thus enhances the conductance of the molecule junctions. This
5 abservation agree well with the calculated condutance.

6 **Conclusion**

7 In conclusion, a giant photo-induced conductance enhancement is revealed in TPB and
8 TPD molecular junctions by extending our laser-integrated MCBJ setup. Accordingly,
9 a concept that a strong coupling between molecules (with buried anchoring groups) and
10 electrodes may be established *via* plasmon-induced hot electrons is put forward. The
11 large number of hot electrons generated by plasmon excitation broad the spatial
12 distribution of electrons. This effect causes the electrodes to interact with the buried
13 anchoring atoms in the molecules, resulting the changing of the hybridization state. The
14 experimental results agree well with the theoretical predictions calculated by employing
15 density functional theory (DFT) combined with nonequilibrium Green's function
16 (NEGF) method. This work provides a method to modulate molecular conductance by
17 two orders of magnitude *via* light illumination and may promote the development of
18 single molecule-based hybrid optoelectronic devices.

19 **Methods**

20 **Chemicals:** Poly (pyromellitic dianhydride-co-4,4'-oxydianiline), amic acid solution (PAA) was
21 purchased from Signa-Aldrich, used as a precursor for polyimide coatings. N-methyl-pyrrolidinone
22 (>99% purity) was purchased from Aladdin to dilute PAA for better fluidity. N,N,N',N' -

tetraphenylbenzidine (98% purity) was purchased from Meryer Technologies and used without further purification. Tetrahydrofuran (99% purity) was purchased from Aladdin.

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Author contributions

D. X., T. L. and B. X. initiated the project. Z. Z., T. L. and D. X. designed the experiments. Z. Z. and C. G. performed the electrical measurement. F. S. and Z. L. executed the optimization simulations and measured the UV-Vis spectra. Z. Z. and T. N. performed the finite-element simulations for field strengthen in the nanogaps. X. Z. and L. N. helped to prepare the samples for electrical investigations. Q. W. and K. K. contributed to the key comments for upgrading the paper. All authors were involved in the writing of the paper.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information is available for this paper at xxxxx

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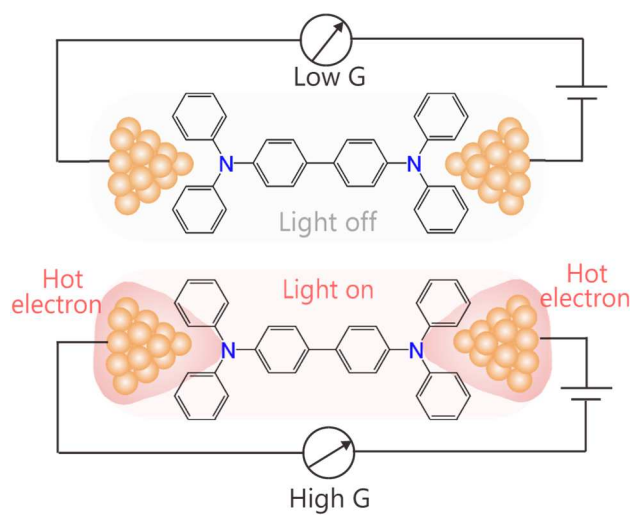
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1 **Table of Contents:**



2

3 **A giant conductance enhancement:** the conductance of nonphotoresponsive molecules can be
4 enhanced by two orders of magnitudes *via* light illumination, which results from the coupling of
5 plasmon-excited hot electrons and the buried anchoring group.