Ultrafast direct electron transfer at organic semiconductor and metal interfaces

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The ability to control direct electron transfer can facilitate the development of new molecular electronics, light-harvesting materials, and photocatalysis. However, control of direct electron transfer has been rarely reported, and the molecular conformation–electron dynamics relationships remain unclear. We describe direct electron transfer at buried interfaces between an organic polymer semiconductor film and a gold substrate by observing the first dynamical electric field–induced vibrational sum frequency generation (VSFG). In transient electric field–induced VSFG measurements on this system, we observe dynamical responses (<150 fs) that depend on photon energy and polarization, demonstrating that electrons are directly transferred from the Fermi level of gold to the lowest unoccupied molecular orbital of organic semiconductor. Transient spectra further reveal that, although the interfaces are prepared without deliberate alignment control, a subensemble of surface molecules can adopt conformations for direct electron transfer. Density functional theory calculations support the experimental results and ascribe the observed electron transfer to a flat-lying polymer configuration in which electronic orbitals are found to be delocalized across the interface. The present observation of direct electron transfer at complex interfaces and the insights gained into the relationship between molecular conformations and electron dynamics will have implications for implementing novel direct electron transfer in energy materials.

INTRODUCTION

Electron transfer is of heightened interest in many energy materials, such as molecular electronics, light harvesting, and photocatalysis (1–13). At an interface between two materials, electron transfer can be stimulated by incident light or electrons in one step or multiple steps (2–11, 14). Most electron transfer events involve intermediate states and multiple steps, including initial excitation, charge or exciton migration, and charge separation. As opposed to this multistep scenario, a direct interfacial electron transfer can vertically excite charges from their initial electronic states at donor molecules to the unoccupied electronic states of acceptors, such as charge transfer states, in a single step (7, 13, 15–20). Direct interfacial electron transfer is similar to an intramolecular electronic transition, such as metal-to-ligand charge transfer in organometallic compounds, but direct interfacial electron transfer occurs between molecules. Because direct interfacial electron transfer is a one-step light-matter interaction, which avoids charges propagating in space before separating at interfaces, it is more advantageous in catalysis (21, 22), solar energy materials (8, 12, 23, 24), and molecular electronics (25). For example, by using light at a certain wavelength to excite electrons directly from substrates to specific electronic states of surface adsorbates, chemical groups and reactions can be selectively activated in photocatalysis (21). In another example, by directly promoting charges to acceptor molecules in solar cells, unwanted competing processes, such as charge recombination and relaxation in bulk phases (2, 5, 15, 26, 27), can be mitigated.

To the best of our knowledge, direct electron transfer was first reported at the interface of metal adatoms and semiconductor electrodes by Gerischer and co-workers (17). Subsequent studies over the next two decades have extended to CO and metal interfaces (16, 18), C₆F₆ and metal interfaces (28), and type II quantum dots (15). It remains an open question to determine the extent of direct electron transfer at complex interfaces of energy materials (8, 12, 21, 23, 24), which consist of molecules that are not optimized for interfacial electronic coupling. In addition, a deep understanding of molecular conformation–charge dynamics relationships is necessary for applying this novel charge transfer pathway broadly in energy applications. The challenges of detecting direct interfacial charge transfer in complex interfaces are twofold: First, complex interfaces where direct charge transfer might occur are hidden in bulk materials. It is difficult to selectively probe these hidden interfaces using techniques such as two-photon photoemission (2PPE) spectroscopy. Second, strong electronic coupling at interfaces is necessary for facilitating direct interfacial charge transfer. Thus, direct interfacial charge transfer has been only experimentally demonstrated on interfaces between small atoms/molecules and metals (16–18). These systems require careful preparations of molecular monolayers to optimize the interfacial electronic interaction and thus have limited application to real energy materials. One recent novel exception was shown by Wu, Lian et al. (7) and Long and Prezhdo (13), who demonstrated a plasmon-induced metal–semiconductor interfacial charge transfer transition pathway by taking advantage of surface plasmonic resonance. This new pathway relies on synthesized nanoplasmonic materials. Ideally, to implement direct interfacial charge transfer in energy materials, it is critical to understand whether direct charge transfer exists broadly in complex interfaces of energy materials, even if without the aid of well-controlled surface plasmon or interfacial electronic coupling.

Here, using a combination of advanced transient vibrational sum frequency generation (tr-VSFG) spectroscopy (29, 30) and theoretical calculations, we present the first spectroscopic evidence of direct electron transfer at complex polymer/metal interfaces under realistic conditions and further understand molecular conformation–charge dynamics relationships. We focus on interfaces between an organic polymer semiconductor and a metal, in which the interfaces are fabricated by a simple solution-phase spin-coating process. Using tr-VSFG, we selectively probe molecular conformation and dynamics at hidden interfaces between an organic semiconductor and a metal. We observe the first dynamical electric field–induced VSFG signals, corresponding to direct
interfacial electron transfer from metal to organic semiconductor. Furthermore, we resolve two simultaneous interfacial electron dynamics with distinct VSFG spectra: One corresponds to fast charge relaxation, whereas the other reflects interfacial charge transfer. This suggests that a subensemble of molecules at the interface undergoes direct electron transfer. The experimental observations are supported by density functional theory (DFT) calculations that demonstrate that electron delocalization exists when organic semiconductors lie parallel to metal surfaces. This result indicates that although organic semiconductor molecules are deposited without controlling alignments, a portion of the molecules still adopts conformations that make the delocalized π orbitals interact strongly with metal substrates and facilitates direct interfacial electron transfer. The present result shows that it is not necessary to have perfectly controlled alignment for direct interfacial charge transfer, which implies that such a charge transfer mechanism is a viable pathway in many solution-phase processed materials, such as organic photovoltaics and flexible optoelectronics.

RESULTS
The interfaces between the organic semiconductor poly(3-hexylthiophene-2,5-diyl) (P3HT) and gold are studied by spin-coating P3HT solution onto a sputter-coated gold substrate. P3HT is an organic polymer material in which electron orbitals are delocalized through thiophene units, with a band gap of 2 eV. P3HT/gold interfaces are frequently used in molecular electronics (31, 32), organic light-emitting diodes (33, 34), organic field-effect transistors (35), and solar materials (12). When P3HT and gold are in contact, the Fermi level of gold is 0.5 eV above the highest occupied molecular orbital (HOMO) and 1.5 eV below the lowest unoccupied molecular orbital (LUMO) of P3HT (Fig. 1B), as determined by ultraviolet photoelectron spectroscopy (section S1), and it is consistent with previous results (36–40). The band energy level rearrangement maintains charge neutrality on both sides of the interface (25, 38–40). Theoretically, this band alignment should create new charge transitions between the Fermi level of gold and electronic states of P3HT, thereby promoting electrons from gold to the LUMO of P3HT or from the HOMO of P3HT to gold.

To investigate any new interfacial electron transfer transitions, and to understand molecular conformation–charge dynamics relationships, we implement tr-VSFG spectroscopy on P3HT/gold interfaces. Tr-VSFG spectroscopy is sensitive to interfacial charge dynamics and molecular conformations. It is composed of a 50-fs, 790-nm (1.57 eV) pump pulse for initiating electron excitation and a VSFG pulse sequence for probing molecules and charges at interfaces (Fig. 1A). The pump

![Fig. 1. Tr-VSFG spectroscopy on P3HT/gold interfaces. (A) Experimental setup. (B) Band alignment between P3HT and gold when they are in contact with each other. The blue arrow indicates the direct charge transfer pathway. (C) Pseudocolor 2D tr-VSFG spectrum. 2D, two-dimensional. A negative signal is observed at t = 0, which recovers very fast and becomes a positive peak at t > 0. Peak maximum shifts from high frequency to low frequency. Top: Integrated tr-VSFG signal (blue) and response function (dashed red). Right: Linear VSFG spectrum. (D) Global analysis results. Two simultaneous charge dynamics are observed as shown in the lower panel. a and b in the upper panel represent the two spectral components corresponding to the two dynamics in the lower panel (for details, refer to the “Frequency-resolved tr-VSFG and DFT reveal conformation-dynamics relationship” section). a.u., arbitrary units.](image-url)
pulse fluence is set low enough that only one-photon absorption occurs (<20% of interfacial molecules are excited; section S3G). VSFG is intrinsically sensitive to molecules at noncentrosymmetric systems, such as interfaces (35, 41–43). Furthermore, like second harmonic generation (SHG) (2, 34, 44–47), VSFG should be sensitive to interfacial charge dynamics through the “electric field–induced effect” (35, 41, 43). In this experiment, the infrared (IR) frequency is set to ~3,000 cm⁻¹ to probe the CH2 and CH3 stretches of P3HT side chains. These vibrational modes are probed (instead of the thiophene ring modes) because the C–H stretches are not part of the conjugated π systems and, therefore, should only be influenced by electric fields at interfaces and not by electronic structure modifications associated with charge excitation. Each tr-VSFG spectrum is obtained by taking the difference of VSFG spectra when the pump pulse is switched on and off, which removes any intrinsic dipole electric field effects (36). To avoid sample damage, all samples are studied in a sealed sample cell and purged with N2 gas, and the samples are rastered between each scan.

**Dynamical electrical field–induced VSFG reveals interfacial electron transfer**

The tr-VSFG spectrum of P3HT/gold interfaces shows distinct time-dependent dynamics (Fig. 1C). First, the tr-VSFG spectrum becomes negative at \( t = 0 \) and recovers to a positive signal within 1 ps. It stays positive and decays slowly (~2 ns). Second, the tr-VSFG spectra have different spectral shapes at early (<200 fs) and larger (>1,000 fs) time delays. Both features encode information of ultrafast electron transfer dynamics and molecular conformations at interfaces. In the following discussion, we first focus on understanding the origin of overall dynamics and then further analyze the physical process associated with spectral shifts (Fig. 1D).

To understand the nature of this dynamic signal, we performed tr-VSFG spectroscopy on two control samples, bare gold surface and P3HT/SiO2/gold, at the same pump fluence used for P3HT/gold interfaces. We find that both control experiments show dynamics that are very different from the dynamics of P3HT/gold interfaces (Fig. 2A). The dynamic trace of gold surface is featureless, indicating that there is no strong change in the refractive index of gold surface that can result in tr-VSFG signals. The dynamic scan of P3HT/SiO2/gold also shows a flat trace within noise levels, consistent with two conclusions. First, because SiO2 is an insulator that prevents electron transfer between P3HT and gold, this result confirms that the transient signal of P3HT/gold requires P3HT to be in electrical contact with gold. Second, the fact that no dynamics in P3HT/SiO2/gold systems are observed at low pump power indicates that multiphoton excitation processes, such as a band-gap excitation of P3HT through two-photon absorption, does not occur at low pump fluence. We confirm that the P3HT in the P3HT/SiO2/gold sample can be excited through multiphoton absorption by increasing pump pulse power to 3 \( \mu \)J and above; the dynamics of P3HT/SiO2/gold at high pump fluence are very different from any dynamics discussed above, in which a negative signal with a fast hot exciton relaxation component (1.5 ps) and a slow charge recombination component are observed (fig. S6C) (48, 49). Thus, excitons can be created in bulk P3HT through multiphoton absorption. Conversely, at 1.4 \( \mu \)J or lower pump energy, multiphoton excitation is not observed, which indicates that the 790-nm pulse interacts with samples at one-photon absorption limit when pump energy is set lower than 1.4 \( \mu \)J. In addition to the control experiments discussed above, we also rule out thermal heating effects by measuring tr-VSFG signals on polymethyl methacrylate (PMMA)/gold systems. If thermal effects on gold substrate cause the observed tr-VSFG signal, then a similar signal should be obtained on PMMA/gold systems under the same pump fluence; however, it is not observed (fig. S6A).

Under the one-photon absorption limit, the only charge dynamic that can be initiated is interfacial electron transfer between the Fermi level of gold and P3HT. The origin of this charge dynamics is similar to the interfacial electric field–induced effect, a phenomenon widely observed in SHG (2, 34, 35, 41, 43–47). Zhu and co-workers (2) and Goodman and Tisdale (50) have recently observed the ultrafast interfacial electric field–induced effect in time-resolved SHG spectra. When charges with opposite signs separate from each other at interfaces and become free charge carriers, a dc field is generated at interfaces. The dc field at interfaces can introduce additional \( \chi^{(3)} \) signals to modulate second-order optical signals, such as SHG and VSFG, as described in Eq. 1

\[
I_{\text{VSFG}} \propto |\chi^{(2)} E_{\text{IR}} E_{\text{up}} + \chi^{(3)} E_{\text{IR}} E_{\text{up}} E_{\text{dc}}|^2
\]

where \( \chi^{(n)} \) is the \( n \)-th-order nonlinear susceptibility and \( E_{\text{IR}} \), \( E_{\text{up}} \), and \( E_{\text{dc}} \) are the electric fields of mid-IR, upconversion, and dc fields, respectively. After charge separation, the interfacial electric field only exists within
very few layers near interfaces; thereby, the modulated signal is still sensitive to interfaces. The interfacial electric field effects in tr-VSFG are confirmed by the fact that the same tr-VSFG dynamics are observed, independent of whether the IR pulse frequency is tuned to be on and off from vibrational resonances of P3HT (fig. S6D), because the electric field effect should not be specific to vibrational resonance. Because electron transfer occurs only on hidden interfaces between P3HT and gold, tr-VSFG spectra can be used to exclusively probe this hidden interface. The sensitivity to hidden interfaces is further confirmed by checking the VSFG intensity at different P3HT thicknesses (section S3C) (51, 52). In contrast with SHG, when VSFG is on resonance with vibrational modes, it probes both electronic transitions through non-resonance background and vibrational modes and molecular conformations through resonance peaks. Hence, tr-VSFG is able to resolve charge dynamics with conformation specificities, as discussed below. The electric field–induced effect has been used in VSFG under electrostatic conditions (35, 41, 43) to study charge accumulations of field-effect transistors and other semiconductor devices. However, this report is the first experimental observation of a dynamical electric field–induced effect of VSFG.

The electron transfer pathway is further determined by performing tr-VSFG at a different pump photon energy. In principle, when using a 790-nm pulse to initiate electron transfer, an electron can be lifted from either the HOMO of P3HT to an unoccupied conduction band of gold or from the Fermi level of gold to the LUMO of P3HT. To differentiate these processes, an experiment is performed using a 1300-nm pulse as the pump, instead of the 790-nm pulse. In this scenario, there are no tr-VSFG dynamics observed. Only when the power of the 1300-nm pulse is increased to as high as 30 μJ to enable multiphoton absorption do similar positive dynamics appear (Fig. 2B). Because the photon energy of 1300-nm light is 0.95 eV, it can only promote electrons from the HOMO of P3HT to gold. Thus, the absence of dynamics in this 1300-nm pump VSFG probe control experiment indicates that the tr-VSFG signal in Fig. 1 is solely due to electron injection from the Fermi level of gold to the LUMO of P3HT and has no contributions from electron promotion from the HOMO of P3HT to unoccupied bands of gold.

Polarization dependence confirms direct interfacial electron transfer mechanism

Electrons can transfer from the Fermi level of gold to the LUMO of P3HT through two possible mechanisms: First, hot electrons can be created on gold surfaces and subsequently transferred to the LUMO of P3HT in competition with other relaxation pathways, such as electron-electron or electron-phonon scattering. Second, electron transfer states can be directly excited across the interface of P3HT and gold (19, 27, 53). Direct electron transfer transition can avoid relaxation pathways in bulk phases. In addition, direct electron transfer can selectively excite molecular orbitals, which can be used to improve selectivity in photocatalysis. Thus, understanding the mechanisms is critical for further engineering of this interfacial electron transfer process.

To determine the electron transfer pathway at interfaces, we examine the tr-VSFG signal’s dependence on the pump pulse’s polarization, a predominant method used for this purpose (18, 19, 53). In hot electron mechanisms, electron transfer dynamics depend only on the absorption cross section of gold. On the basis of the Fresnel equations, the 790-nm, p-polarized (perpendicular to the interfaces) pulse’s absorption by gold is four times that of s-polarized light (section S3E) (53). Therefore, if electron transfer is mediated through hot electrons, then it is expected that the tr-VSFG signal will be reduced four times when pump polarization is switched from p to s polarization. On the contrary, in direct electron transfer transition mechanisms, the transition should strongly depend on polarization, because under dipole transitions, only a p-polarized pump pulse can efficiently promote electrons directly across interfaces from gold to the P3HT layer, whereas s-polarized light can only move electrons within gold layers.

The polarization-dependent results indicate that the direct electron transfer transition mechanism dominates (Fig. 3). When P3HT/gold interfaces are pumped by s-polarized pulses at 1.4 μJ, there are no measurable dynamics, but when the same interfaces are pumped by p-polarized pulses at only 0.36 μJ, distinct electron transfer dynamics are observed. Because the s-polarized light used in this experiment is approximately four times that of p-polarized light, it compensates for the differences in absorption cross sections. However, the tr-VSFG signal intensity ratio between pumping using p- and s-polarized pulses is above 6, which is much larger than the ratio of 1 that would be expected for hot electron mechanism. Hence, this experimental result shows that a direct electron transfer occurs at interfaces; the p-polarized pump pulse promotes electrons directly from the Fermi level of gold to the LUMO of P3HT.

Frequency-resolved tr-VSFG and DFT reveal conformation-dynamics relationship

Further insights into the excitation mechanisms are observed in the spectral shifts in tr-VSFG spectra. Using global analysis (details in section S3B), the overall dynamics can be broken down into two components (Fig. 1D). Component a has a negative spectral signature at t = 0, and it recovers back to zero in 480 fs. Component b rises to a positive spectral signal in a time frame that is faster than the instrumental response and slowly decays (>2 ns). These two dynamics are simultaneous and parallel processes, rather than sequential, because as component b rises, component a has not decayed. Since the dynamics of both components a and b happen exclusively when P3HT and gold are in contact with each other, these two spectral components must represent two simultaneously different electron dynamic pathways at interfaces. The decay dynamics of component a are close to 500 fs, which is longer than a coherent artifact (150 fs) (54). Therefore, it results from a combination of coherent artifacts and other dynamics processes. These dynamics are
very similar to the dynamics observed in PMMA/gold interfaces when pumped at high fluence (fig. S6A), in which excited electrons at interfaces can only relax quickly through electron-electron and electron-phonon scatterings (55), because the gaps between the Fermi level of gold to the HOMO or LUMO of PMMA are too large for electron transfer. Thus, on the basis of the similarity, we assign the additional dynamics of component a to be a fast relaxation pathway at interfaces, which does not lead to charge separation. Excited electrons at P3HT/gold interfaces transiently modulate the electron density of interfacial molecules and, therefore, alter the second-order molecular susceptibility, which causes the negative signal (2).

The spectral dynamic of component b is unique because it only exists on P3HT/gold interfaces. It reflects direct interfacial electron transfer. The tr-VSFG intensity rises so fast that it is beyond the time resolution of our instrument (150 fs). This agrees with the direct electron transfer mechanism; a vertical excitation occurs, and no exciton migration is involved in this process. After excitation, this set of electron-hole pairs quickly separates and forms free charge carriers within 150 fs. The free charge carriers generate interfacial dc electric fields, which induces a positive signal in tr-VSFG. After charge separation, the tr-VSFG signal relaxes in about 2 ns, confirming that interfacial charge recombination is slow. This slow recombination could be due to subsequent polaron formation (56) or screening effects (57). The spectral shifts in component b are due to a preferred electric field-induced signal on specific conformations, as discussed below and in section S7 (35). On the basis of the percentage of tr-VSFG signal, it is estimated that the transition dipole moment of this interfacial electron transfer transition is on the order of a few debyes (section S3F), similar to many organic dyes (58). Thus, the probability of interfacial electron transfer is not as low as previously believed.

The different dynamics of components a and b can only be detected using spectrally resolved tr-VSFG data. If only the dynamics of the integrated tr-VSFG signal are measured, it is impossible to determine whether the dynamics of components a and b are simultaneous or sequential because of their similarity. Furthermore, as discussed in detail in section S5, when tr-VSFG is performed with IR frequency to be off-resonance from the vibrational modes, which is equivalent to tr-SHG, the tr-VSFG signal under the off-resonance condition cannot be dissected by either global analysis or singular-value decomposition (SVD) into two spectral/dynamical components. This significant difference is due to the fact that, when on-resonance, tr-VSFG probes both electronic and vibrational transitions, whereas tr-SHG and off-resonance tr-VSFG are only sensitive to electronic transitions. Hence, when different conformations are perturbed by charge dynamics, the different dynamics can be directly traced back to the corresponding vibrational features, which make them distinguishable through subtle differences in the VSFG spectra. By contrast, when the IR pulse is off-resonance, only the electronic transition is probed, which is less sensitive to molecular conformations and thus leads to indistinguishable spectra for the two conformations, despite exhibiting distinct charge dynamics.

Because interference between various spectral components can also, in principle, induce spectral changes, we performed spectral fittings for the two spectral components to determine whether optical interference or distinct conformations are responsible for the observed global analysis components (section S7). We considered two scenarios: In scenario 1, all parameters of resonant and nonresonant signals are allowed to vary in the fitting procedure, whereas only amplitudes and phases of the nonresonant signal are allowed to change in scenario 2, to mimic the effect associated with optical interference between resonant and nonresonant signals (35). We found that the two spectral components can only be correctly simulated in scenario 1. In scenario 2, only one component, in the best case, can be fitted reasonably well, whereas the other component one is poorly reproduced, displaying both amplitude and phase mismatches (fig. S12). We thus conclude that optical interference is the dominant effect responsible for the two observed components. It is found that, to correctly reproduce the two components, the peak positions of the vibrational modes must be slightly different in the fits to components a and b. This supports the interpretation that the two components reflect structural differences of P3HT at the interface, which, in turn, are responsible for different charge dynamics. To further determine the phase of all peaks, heterodyne detection (59–63) will need to be implemented, which is out of the scope of this work.

We note that there are two parallel electron dynamics associated with distinct VSFG spectra at interfaces, and that only one of them corresponds to direct interfacial electron transfer. This indicates that only molecules with some specific conformations at interfaces facilitate direct electron transfer. To understand how direct electron transfer happens at this interface and why only subensemble molecules participate in direct electron transfer, we perform DFT calculations to gain insights into the interaction of organic semiconductor molecules and gold. We place a sexithiophene (6T) molecule on top of a gold surface. 6T is an oligomer analog of P3HT, which has similar electronic structures and makes the calculation more affordable. Two extreme configurations of 6T are modeled (parallel and perpendicular to the gold surface), and their relative distances are optimized under these configuration constraints. After optimization, the parallel configuration energy level is slightly lower by 1.1 kcal/mol than the perpendicular configuration. Given the small energy difference, both parallel and perpendicular configurations and alignments in between these configurations are likely present at the interfaces.

However, the parallel and perpendicular orientations have markedly different electronic interactions with gold surfaces. When aligned in parallel, the calculated LUMO and HOMO orbital structures of 6T have a significant amount of delocalization into gold substrates with an isovalue of 0.0015 e/Å³ (Fig. 4). Consequently, the electron transfer transition at the interface becomes a transition between delocalized HOMO and LUMO, which subsequently undergoes fast charge separation. This strong interaction between organic conjugated molecules and metal generally exists in molecules that have π orbitals (64). Similar direct electron transfer has been observed in molecules with small conjugation systems, such as C₆F₆ (28). Conversely, when aligned perpendicularly, no orbital delocalization is observed (section S6). Thus, when perfect control of molecular alignment is difficult to achieve, the disorder of organic semiconductor/gold interfaces serves as a practical scenario that allows the occurrence of direct interfacial electron transfer. When many orientations coexist on the interfaces, a subensemble of P3HT is parallel or close to parallel to the gold surface, allowing for strong electronic coupling between delocalized π electronic orbitals of P3HT and electronic bands of gold and thus enabling direct electron transfer transition to occur at interfaces.

**DISCUSSION**

Although the present experimental and calculation results agree with previous investigations of direct electron transfers on simple interfaces under vacuum conditions using 2PPE spectroscopy, but they also extend this phenomenon of direct interfacial electron transfer to complex
and hidden interfaces between organic semiconductors and metals (16–18). Previous studies have shown that for small molecules at metal interfaces, direct electron transfer transition can exist when strong adsorbate-substrate electronic coupling, direct chemical σ bonding, or coupling to image potential states exists at interfaces (18, 28). The present results indicate that even for complex interfaces composed by organic semiconductor polymers with various orientations, a part of surface molecules can adopt geometries that induce a substantial amount of electronic orbital delocalization into metal surfaces. Under this condition, interfacial molecules and metal atoms at the interface form delocalized HOMO and LUMO electronic orbitals, and interfacial electron transfer becomes an electronic transition between them, followed by charge separation. This picture further confirms the advantages of direct interfacial electron transfer: it only involves electron moving from one orbital to another orbital within the delocalized electronic structures and does not involve any spatial charge propagations.

Furthermore, dynamic electric field–induced effect is observed for the first time in tr-VSFG, which provides a unique way to resolve multiple electron dynamics at hidden interfaces. In combination with DFT calculations, the tr-VSFG spectra can reveal molecular conformation–charge dynamics relationships. This technique is complementary to 2PPE because it does not require vacuum conditions and can be explicitly sensitive to the interfaces where charge separation occurs. Thus, electron transfer interfaces that are close to the device working environments or at liquid/solid interfaces can be explored in the future. One caveat is that we cannot determine absolute molecular orientations directly from VSFG measurement of vibrational modes of P3HT side chains because the side chains are flexible. P3HT orientation at interfaces can be measured by probing the ring mode of thiophene backbones, but the interpretation of the corresponding tr-VSFG spectra of thiophene backbone is more complicated because besides electric field–induced effects, the tr-VSFG spectra of thiophene can also be affected by changing of oxidation states after interfacial charge transfer occurs. However, this caveat might not exist for other molecular interfaces. We notice that the observed dynamics do not involve surface plasmon polariton because the momentum-energy conservation between photon and surface plasmon polariton cannot be satisfied under our current experimental conditions (65). However, interfacial dynamics induced by surface plasmon polariton using gratings or prism geometry can be studied using the method presented here. Lastly, the overall efficiency of charge transfer of this complex interface is not as high as that observed in other nanomaterials (7, 15). Yet, it could be enhanced by optical engineering, for example, using mesoscopic framework (66) to prepare interfaces with a larger surface area or using hyperbolic metamaterials (67) to enhance charge transfer rate.

In conclusion, by detecting the first transient electric field–induced VSFG spectra, it was shown that a direct metal-to-organic molecule electron transfer can occur on complex interfaces prepared by a solution-phase spin-coating process. This observation is consistent with previous measurements on spin-coated organic semiconductor heterojunction materials, which inferred the occurrence of direct sub-band-gap transition at interfaces (9, 68, 69). In addition, the strong dependence of direct interfacial charge transfer to light polarization could enable new polarization-selective detectors. Thus, the demonstration of direct photon-initiated electron transfer at complex interfaces will open the potential to broadly apply this mechanism in artificial energy materials, selective photocatalysis, and substrate-mediated coherent control.

**MATERIALS AND METHODS**

**Tr-VSFG spectroscopy**

A tr-VSFG spectrometer with a pump probe pulse sequence was used (Fig. 1A). Briefly, a 50 fs, 790-nm pulse served as the pump beam, and the probe was a VSFG signal that was generated by the mid-IR beam and the 790-nm up-conversion pulse (full width at half maximum, 9.5 cm$^{-1}$) at the sample surface. The time delay between the pump and the probe was controlled by a motorized stage. The center wavelength of the mid-IR was tuned to 3.3 mm to be on resonance with the C–H vibrational modes of P3HT. All beams were focused by an f = 10 cm parabolic mirror onto the sample at about 60°, and they were spatially and temporally overlapped. The signal was collected by another parabolic mirror and was collimated. After being collimated, the signal passed through band-pass filters to remove residual 790-nm beams, entered the monochromator, and was detected by a charge-coupled device camera (400 × 1340, Andor). A pair of waveplates and a polarizer were used in each beam path to control both beam intensity and polarization.

**Electronic structure calculation**

The initial structures were created by putting the organic semiconductor molecule in parallel (structure 1) and perpendicular (structure 2) with the Au(100) surface. Then, the geometry optimizations were performed using the Perdew-Burke-Ernzerhof (PBE) (70) functionals, as implemented in the Quantum ESPRESSO package (71). A kinetic energy cutoff of 30 Ry and a charge density cutoff of 300 Ry were used. Ultrasoft pseudopotentials were taken from the Quantum ESPRESSO pseudopotential download page (www.quantum-espresso.org/pseudopotentials; files: Au.pbe-nd-van.UPF, C.pbe-van ak.UPF, H.pbe-van ak.UPF, and S.pbe-van bm.UPF). Because of the large size of the unit cell, calculations were carried out using the Γ point in the Brillouin zone. All structures were fully relaxed within a convergence of less than 0.1 mRy for the total energy and 0.5 mRy/a.u. for the forces on atoms. The density of states and charge distribution were calculated at the optimized geometry.
SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/11/e1701508/DC1

section S1. Sample preparation and band characterization

section S2. Transient SFG spectrometer

section S3. Data acquisition, analysis, and calculations

section S4. Supplementary figures and tables

section S5. Frequency-resolved spectra of tr-VSFG under on- and off-resonance conditions

section S6. DFT calculation

section S7. Optical interference

fig. S1. Ultraviolet photoelectron spectroscopy on bare gold and P3HT/Au interfaces.

fig. S2. Band alignment between P3HT and gold, when they are in contact with each other.

fig. S3. a1, a2, and a3 correspond to singular values of components a (red), b (blue), and c (black).

fig. S4. Simulation results of the two-interface model.

fig. S5. Fitting results of the pump-off and pump-on SFG spectra at both time zero and positive time delay.

fig. S6. Tr-VSFG dynamics of the control experiments.

fig. S7. Static VSF of P3HT/Au, P3HT/SiO2/Au, and bare Au samples.

fig. S8. SVD and global analysis results comparison of tr-VSFG under on and off-resonant conditions.

fig. S9. Density of states for structure 1 (left) and structure 2 (right).

fig. S10. Electronic orbital of LUMO (left) and HOMO (right) bands of P3HT/Au interfaces in structure 1.

fig. S11. Electronic orbital of LUMO (left) and HOMO (right) bands of P3HT/Au interfaces in structure 2.

fig. S12. Comparison between two fitting scenarios for SVD components.

table S1. Peak positions of scenario 1 for a and b.

table S2. Peak intensity of scenario 1 for a and b.

table S3. Peak width of scenario 1 for a and b.

table S4. Parameters for nonresonance signal of scenario 1 for components a and b.

table S5. Parameters for scenario 2.

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