

In Situ Detection of Interfacial lons at the Single-Bond Level

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ACCESSImage: Metrics & MoreImage: Article RecommendationsImage: Supporting InformationABSTRACT: Detecting the ionic state at the solid-liquid
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processes that accurate the interface. In this study, the adsamptionImage: GLImage: GL

interface is essential to reveal the various chemical and physical processes that occur at the interface. In this study, the adsorption states of the highly electronegative ions F^- and OH^- at the solid–liquid interface are detected by using the scanning tunneling microscopy break junction technique. With the active hydrogen atom of the amino group as a probe, the formed ionic hydrogen bonds are successfully detected, thereby enabling in situ monitoring of the ionic state at the solid–liquid interface. Through noise power spectral density analysis and theoretical simulations, we reveal the mechanism by which ionic hydrogen bonds at the interface affect the charge transport properties. In addition, we discover that the ionic state at the solid–liquid interface can be



effectively manipulated by electric fields. Under high electric fields, the concentration of the anion near the electrode is higher, and the proportion of hydrogen bonds formed is greater than that under low electric fields. This study of the interfacial ionic state at the single-bond level provides guidance for the design of high-performance materials for energy conversion and environmental purification.

INTRODUCTION

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Interface chemistry is a scientific discipline that studies the characteristics of surfaces in multiphase systems, as well as the physical and chemical processes and laws occurring on these surfaces.^{1–3} This discipline has extensive applications and profound effects across various fields, including energy conversion,^{4,5} materials science,^{6,7} electrostatic catalysis,^{8–10} electrochemistry,^{11–13}surface modification techniques,^{14,15} and environmental protection.^{16,17} Ion adsorption is a key branch of interface chemistry, and it can alter the properties of electrode surfaces through the adsorption of ions at the solid–liquid interface, thereby affecting the electron transfer and reaction kinetics at the interface.^{18,19} Understanding the state of interfacial ions and manipulating the adsorption behavior of ions at the solid–liquid interface are of great importance for its application in chemical synthesis, energy conversion, environmental protection and other fields.

In the field of interfacial chemistry, various surface analysis techniques and spectroscopic methods have been developed to observe the kinetic behavior of ions at interfaces. Scanning electrochemical microscopy monitors the variations in the electrochemical current to ascertain the distribution and concentration of ions at interfaces.^{20,21} Surface-enhanced infrared absorption spectroscopy identifies the specific chemical and physical states of ions at interfaces by recognizing particular absorption peaks and their enhancements and shifts.^{22,23} Surface-enhanced Raman spectroscopy can detect subtle changes in the structure and properties of ions at interfaces

through the interaction strength between the interface and ions.^{24,25} Nevertheless, capturing the intricate adsorption behaviors and chemical reactions of ions at the solid–liquid interface at the single-bond level remains a significant challenge. Single-molecule techniques^{26–28} are expected to detect and analyze the adsorption behavior of individual ions at the solid–liquid interface at the single-bond level, thereby avoiding interference from ensemble averaging,²⁹ which is crucial for a comprehensive understanding of the interfacial ion state.

Hydrogen bonds are one of the main intermolecular forces. A special class of hydrogen bonds is ionic hydrogen bonds. Ionic hydrogen bonds are formed between an ion and a molecule, and they have a bond strength of 5-35 kcal/mol, reaching one-third of the strength of covalent bonds.³⁰ In this study, F⁻ and OH⁻ in tetrabutylammonium fluoride (TBAF) and tetrabutylammonium hydroxide (TBAOH) are used as anion sources for adsorption to the solid–liquid interface, and molecules with amino anchoring groups are used as probes with active hydrogen sources. Utilizing the formation of ionic hydrogen bonds, we use the scanning tunneling microscopy break junction (STM-BJ) technique to perform in situ monitoring of the ionic state at the

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Figure 1. Overview of ionic hydrogen bonds at the solid-liquid interface. (a) Binding energy at the interface for different groups. (b) Schematic diagram of interfacial hydrogen bond formation process.

solid-liquid interface. Furthermore, we investigate the influence of high electric fields on the ionic state at the solid-liquid interface.

RESULTS AND DISCUSSION

Overview of the lonic Hydrogen Bonds at the Solid– Liquid Interface. Through theoretical simulations, it can be observed that the binding energies between the gold electrode and F^-/OH^- anions are ~1.91 and ~2.48 eV, respectively, which are higher than the Au–N binding energy (~0.55 eV) (Figure 1a). This is mainly due to the strong physical electrostatic adsorption between negatively charged ions and electron-deficient gold. Based on the above experimental design and theoretical calculations, we use F^- and OH^- anions as ionic hydrogen bond acceptors and the activated hydrogen atom in the amino functional group as the ionic hydrogen bond donor. By forming new interfacial states with the anions, the behavior and reaction of the anions at the solid–liquid interface are monitored (Figure 1b).

Exploring Electronic Characteristics of the Interfacial **Ion States.** We use 4,4"-diamino-*p*-terphenyl (TP) as the target molecule, with F⁻ from TBAF and OH⁻ from TBAOH serving as the sources of the anions, to investigate the behavior of the anions at the interface using the STM-BJ technique (Figure 2a,d,g). Single-molecule junctions are formed and broken in 1,2,4-trichlorobenzene (TCB) solution containing 0.5 mM TP (Figure 2a), TP/F⁻ (Figure 2d) and TP/OH⁻ (Figure 2g), which are obtained by adding TBAF and TBAOH. At a bias voltage of 0.1 V, approximately 5000 conductance traces are used to construct two-dimensional (2D) conductancedisplacement histograms (Figure 2b,e,h). These histograms exhibit the characteristic features of integer multiples of the quantum conductance G_0 ($G_0 = 2e^2/h$, 77,500 nS) and specific molecular signals below G_0 . The corresponding one-dimensional (1D) conductance histograms are used for quantitative analysis (Figure 2c,f,i). For TP (Figure 2c), only one conductance plateau can be clearly observed, whose Gaussianfitting conductance peak is $\sim 0.35 \times 10^{-3} G_0$ (≈ 27.50 nS). In this case, the $-NH_2$ group forms an Au-N coordination bond with Au at the molecule/electrode contact, which is consistent with previously reported results.³¹ For TP/F⁻ (Figure 2f) and TP/ OH⁻ (Figure 2i), two distinct conductance peaks are evident. The Gaussian-fitted conductance peaks are $\sim 0.35 \times 10^{-3} G_0$ ($\approx 27.50 \text{ nS}$) and $\sim 0.15 \times 10^{-4} \text{ G}_0$ ($\approx 1.2 \text{ nS}$) for TP/F⁻, and ~ $0.36 \times 10^{-3} G_0 (\approx 28.14 \text{ nS}) \text{ and } \sim 0.20 \times 10^{-4} G_0 (\approx 1.55 \text{ nS})$

for TP/OH⁻. Notably, the high-conductance (G_H) states of TP/ F⁻ and TP/OH⁻ are identical to the conductance state of TP, whereas the new low-conductance (G_L) states are significantly lower than the conductance state of TP. Typical single traces of the TP, TP/F⁻, and TP/OH⁻ junctions are shown in Figure 2b,e,h, respectively. With the addition of ions, due to the weak interaction of hydrogen bonds, the G_H and G_L states can occur separately. In addition, there is a competition between the ionic hydrogen bond and the Au–N coordination bond, both of which may become the dominant factor. This dynamic equilibrium enables the single-molecule junction to transition between high and low conductance states.

To verify whether the $G_{\rm H}$ and $G_{\rm L}$ states originate from the tunneling effect through the same oligophenylene molecular skeleton and determine the source of different conductance states, we perform quantitative analysis of the statistical conductance plateau lengths (Figure 2c,f,i). The conductance plateau length for TP is approximately 0.70 nm (Figure 2c). The $G_{\rm H}$ states of TP/F⁻ and TP/OH⁻ have conductance plateau lengths of ~ 0.70 and ~ 0.66 nm, respectively, which are almost identical to that of TP, further demonstrating that the $G_{\rm H}$ states of TP/F $^-$ and TP/OH $^-$ are consistent with the conductance states of TP. However, the G_L states of TP/F⁻ and TP/OH⁻ have conductance plateau lengths of ~0.85 and ~0.79 nm, respectively, which are slightly longer than that of TP. The plateau length statistics after adding the snap-back distance of Au-Au (0.5 nm) are also consistent with the theoretically calculated plateau lengths (Figure S1). Given the molecular length of TP and these plateau lengths, the junctions for both the $G_{\rm H}$ and $G_{\rm L}$ states are formed by the TP molecular backbone bridging across two electrodes, rather than by one electrode directly coupling to the conjugated π system.³² Furthermore, the experimental results obtained by adding TBAOH to butanediamine (Figure S2), which are consistent with those of TP/OH^- , have ruled out the possibility that the $G_{\rm L}$ states originated from the $\pi - \pi$ stacking of the benzene rings within the TP molecule,³³ and the energy after anion adsorption on gold is lower (Figure S3). Therefore, we speculate that the $G_{\rm L}$ state arises from the molecular junctions formed during the anion adsorption process at the interface.

Exploring the Charge Transport Mechanism of the Interfacial Ion States. To confirm the anionic states at the interface between the electrodes and molecules, noise power spectral density (PSD) analysis is performed to gain a deeper understanding of the transport mechanisms.³⁴ The measure-



Figure 2. Single-molecule electrical measurements of TP, TP/F⁻ and TP/OH⁻. (a, d, g) STM–BJ measurement diagrams of TP (a), TP/F⁻ (d) and TP/OH⁻ (g) single-molecule junctions. (b, e, h) 2D conductance-displacement histograms of TP (b), TP/F⁻ (e) and TP/OH⁻ (h) junctions at 0.1 V bias voltage. Inset: conductance-displacement traces of molecular junctions (red, blue, green, and purple) and those of Au contacts in the pure solvent (black traces). (c, f, i) 1D conductance histograms of TP (c), TP/F⁻ (f) and TP/OH⁻ (i) junctions. Inset: corresponding plateau length statistics.

ment of the flicker noise involved suspending the molecular junction for 200 ms and extracting the conductance signals during this period. A plot is then constructed by correlating the normalized conductance variations with the normalized noise power, and a 2D histogram is constructed using thousands of conductance traces. By fitting the 2D distribution, the obtained noise power scale is normalized to $G^{1.0}$ and $G^{2.0}$, where G represents the average conductance and 1.0 and 2.0 are the scaling exponents of the PSD, indicating the transition of the conductance from through-bond to through-space, respectively.^{35,36} The through-space mechanism refers to the tunneling of charges through space, rather than through chemical bonds.³ There are two scenarios for through-space tunneling: one involves weak coupling between the electrode and molecule, and the other involves weak coupling within the molecular junction.^{34,36} The results show that the noise power scaling exponent for TP is $G^{1.03}$ (Figure S4a,b), while the $G_{\rm H}$ values of TP/F⁻ and TP/OH⁻ exhibit noise power scaling exponents of $G^{1.12}$ and $G^{1.17}$, respectively (Figures 4a,b, S4c,e). The results indicate that the electron transfer in $G_{\rm H}$ after adding ions, as well as in TP, is dominated by through-bond transmission mechanisms. In contrast, the $G_{\rm L}$ values of TP/F⁻ and TP/OH⁻ exhibit noise power scaling exponents of $G^{1.45}$ and $G^{1.42}$, respectively (Figures 4d,e, S4d,f), indicating that the electron transfer in $G_{\rm L}$ is affected by a synergistic mechanism of both through-space and through-bond transmissions. This phenomenon may stem from the formation of weak hydrogen bond interactions between the anions (F⁻ and OH⁻) and the active hydrogen atom at one end of the $-NH_2$ group, while the other end of the $-NH_2$ group maintains Au–N coordination bond coupling.



Figure 3. Noise PSD testing and theoretical analysis. (a, b, d, e) 2D histograms of normalized flicker noise power versus average conductance for TP/ F⁻ (a, d) and TP/OH⁻ (b, e) junctions corresponding to $G_{\rm H}$ states (a, b) and $G_{\rm L}$ states (d, e). (c) Calculated transmission spectra of TP, TP/F⁻ and TP/OH⁻ junctions. (f) Projected HOMO distribution of TP, TP/F⁻ and TP/OH⁻ junctions.

To confirm the correlation between the anion state at the interface and the conductance, molecular junctions are constructed based on the interfacial anion states. The transmission coefficient is then calculated using a combination of the nonequilibrium Green's function and density functional theory with Quantum ATK version 2022.03. The transmission spectrum shows that the charge transport of TP, TP/F⁻, and TP/OH⁻ is dominated by the highest occupied molecular orbital (HOMO). The transmission coefficients of TP/F⁻ and TP/OH^{-} at $E - E_{F} = 0$ are similar and significantly lower than that of TP (Figure 3c), which is consistent with the experimental results. In addition, the possibility that anions may affect molecular conductance through other means has also been ruled out (Figure S5). Because we cannot exclude the possibility of anion adsorption and hydrogen bond formation at both ends of the electrodes, we also construct molecular junctions with hydrogen bonds at both ends (Figure S6). The transmission spectrum values calculated for the double-ended junction are very low, below the detection threshold of the instrument. Thus, the double-ended junction cannot be observed in the experiment. To investigate the effect of the hydrogen bond connections at the interface on the charge transport orbitals, we analyze the transmission eigenstates and the molecular projected self-consistent Hamiltonians of the three molecular junctions (Figure 3f, see Figures S7 and S8 for more information). For TP, the transmission eigenstates at the interface of the HOMO and lowest unoccupied molecular orbital molecular junctions have a large distribution on both the electrodes and molecules (Figures S7a and S8a). Compared with TP, the HOMO-dominated orbital transmission is significantly weakened owing to the weak hydrogen bond interactions in TP/F⁻ and TP/OH⁻ (Figure 3f, see Figures S7b,c, S8b,c for more information), leading to a decrease in the

conductance. Furthermore, the cations do not affect the HOMO transmission process, further indicating that the weak hydrogen bonding interaction between the anion at the interface and the $-NH_2$ group reduces the molecular conductance. It should be noted that previous STM conductance measurements of TP in tetrabutylammonium perchlorate (TBAClO₄) did not observe the G_L states.³⁸ We performed similar tests by adding TBAClO₄, and no G_L state was observed (Figure S9). This may be because the weak hydrogen bonding between ClO_4^- and the amino groups makes it undetectable. However, at low biases, the observed experimental results are consistent.

Electric-Field Manipulation of the Interfacial Ion States. To better understand the anion state at the interface and control the hydrogen bond interaction at the interface, the interfacial ion states under different electric fields are investigated, with the applied bias voltage ranging from 80 to 160 mV. The 1D and 2D single-molecule conductancedisplacement histograms for TP/OH⁻ are shown in Figures 4a and S10, respectively. As the bias voltage increases, both $G_{\rm H}$ and $G_{\rm L}$ persist, but the proportion of $G_{\rm L}$ gradually increases. Specifically, as the bias voltage increased from 80 to 160 mV, the proportion of $G_{\rm L}$ increases from ~48.0 to ~62.8% (Figure 4b). This may originate from the high charge density on the gold electrode under a high electric field, resulting in stronger electrostatic adsorption of the anion, higher anion concentration near the electrode, and a greater proportion of hydrogen bond formation (Figure 4c). By measuring the formation probability of interfacial ionic hydrogen bonds, this technique can be used to detect the ion density at the solid-liquid interface.

CONCLUSIONS

Using the active hydrogen atom of the amino group as a probe, the ionic states of the highly electronegative ions F^- and OH^- at



Figure 4. Electric field regulated interfacial ion states. (a) 1D conductance histograms of TP/OH⁻ junction under a bias voltage increasing from 80 to 160 mV. (b) The ratio of G_L states in TP/OH⁻ junctions under different bias voltages. (c) Schematic diagram of changes in ion concentration at the interface under the action of an electric field.

the solid—liquid interfaces are successfully detected in situ at the single-bond level by the STM-BJ technique. By noise PSD analysis and theoretical simulation, we find that the interfacial ion state has a significant influence on the charge transport characteristics within the molecular junction, and the probability of ion hydrogen bond formation can be improved by manipulating the ion state at the solid—liquid interface using an electric field. This work not only improves the understanding of interfacial chemistry but also provides guidance for the design of high-performance materials for energy conversion and environmental purification.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.4c06738.

Experimental methods, theoretical calculation of the plateau length, STM-BJ test results of butanediamine and butanediamine/OH⁻, configuration of anion before and

after connection with gold, flicker noise analysis, theoretical results, STM-BJ test results of TP/ClO_4^- , and bias-dependent test results of TP/OH^- (PDF)

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Notes

The authors declare no competing financial interest.

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