#### CHEMICAL PHYSICS

# Single-molecule field effect and conductance switching driven by electric field and proton transfer

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Single-molecule junctions (SMJs) offer a novel strategy for miniaturization of electronic devices. In this work, we realize a graphene-porphyrin-graphene SMJ driven by electric field and proton transfer in two configurations. In the transistor configuration with ionic liquid gating, an unprecedented field-effect performance is achieved with a maximum on/off ratio of ~4800 and a gate efficiency as high as ~179 mV/decade in consistence with the theoretical prediction. In the other configuration, controllable proton transfer, tautomerization switching, is directly observed with bias dependence. Room temperature proton transfer leads to a two-state conductance switching, and more precise tautomerization is detected, showing a four-state conductance switching at high bias voltages and low temperatures. Such an SMJ in two configurations provides new insights into not only building multifunctional molecular nanocircuits toward real applications but also deciphering the intrinsic properties of matters at the molecular scale.

#### INTRODUCTION

The concept of single-molecule devices has been well verified in many examples (1), such as memories, diodes, field-effect transistors (FETs), or switches (2-10). The miniaturized FETs and switches are the keys to miniaturization and performance improvement of electronic devices. To this end, seeking multifunctional singlemolecule devices is of crucial importance to further reduce the footprint of the device and improve the integration and functionality of nanoelectronic circuits. An ideal FET with the practical application value should have the advantages of room temperature stability and high performance, which means strong gate regulation, high device on/off ratio, and low power consumption. To date, most single-molecule FETs are implemented under low temperature, and their performance is modest at room temperature (11-13). In general, the FETs controlled by solid-state or electrochemical gates have a maximum on/off ratio of about two orders of magnitude (14, 15). For switches, easy triggering, controllability, and room temperature stability are essential characteristics. Most molecular switches are based on drastic conformational changes of the molecule, which might lead to instability (6, 16, 17). Only a few molecular stochastic switches via hydrogen tautomerization, without conformational change, were realized on metal substrates under low-temperature vacuum and high bias voltages (18–22).

\*Corresponding author. Email: guoxf@pku.edu.cn (X.G.); rmwang@ustb.edu.cn (R.W.); jiacc@nankai.edu.cn (C.J.); jlyang@ustc.edu.cn (J.Y.); long.chen@tju.edu.cn (L.C.) †These authors contributed equally to this work. In this work, we present a single-molecule device with functions of high-performance field effect and controllable tautomerizationinduced switching in two different configurations. The device consists of a single porphyrin molecule in the junction comprising nanogapped graphene electrodes and robust covalent linkages (Fig. 1), and the optical images of the devices with and without ionic liquid are shown in fig. S5. Through ionic liquid gating, the single-molecule FET with a high on/off ratio has been realized. In addition, under a wide range of bias voltage and temperature, especially at room tem-

perature and a small bias voltage, multistate switching induced by pro-

ton transfer-induced tautomerization has been precisely modulated.

#### **RESULTS AND DISCUSSION**

#### Field effect through ionic liquid gating

Unlike traditional organic FETs, single-molecule FETs operate by manipulating molecular orbitals with gate (13), which can be considered from the inherent characteristics of molecular orbitals, molecule-electrode coupling, and gate control capabilities. In the ionic liquid gated single-molecule FET, an electrical double layer is formed at the interface between the ionic liquid and the singlemolecule junction. Because the thickness of the dielectric is reduced to a dimension comparable to the ionic radius, a strong gate electric field is generated to effectively manipulate the molecular orbitals, which is different from the case of electrochemical gating that accompanies redox reactions (23). In the present study, 5,15-di(4aminobiphenyl) porphyrin (fig. S6A) is designed as a functional molecule to construct a stable single-molecule junction, in which its terminal amino groups on both sides are covalently bonded with the carboxyl groups at the end of graphene electrodes. The molecular center of porphyrin has a highly delocalized electron density distribution of molecular orbitals (fig. S6B) and a moderate HOMO-LUMO (highest occupied molecular orbital-lowest unoccupied molecular orbital) energy gap (fig. S6C), which are beneficial to the response of molecular orbitals to the gate. Biphenyl is used as the spacer group, which can lead to a moderate coupling between porphyrin and graphene electrodes. The ionic liquid, N,N-diethyl-N-(2-methoxyethyl)-Nmethylammonium bis(trifluoromethyl sulfonyl) imide (DEME-TFSI)

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(fig. S7) is used as the electrolyte, which has cation and anion with the similar size of ~0.75 nm. Because of the large electrochemical window of the used ionic liquid (24) and the nonelectrochemical activity of the porphyrin molecule, the device works in a nonfaradaic regime. During the gating process, an electrical double layer with a thickness of less than 1 nm is formed on the surface of the entire junction including the single molecule and graphene electrodes. Therefore, an electric field of up to 10 MV/cm generated inside the



Fig. 1. Schematic of a graphene-porphyrin-graphene junction that highlights ionic liquid gating and hydrogen tautomerization.

electrical double layer (25) can be effectively applied to the singlemolecule junction, which can effectively manipulate the molecular orbitals. The gate electrode is placed at a distance of  $\sim$ 0.1 mm from the single-molecule junction. This distance has little effect on the formation of the electric double layer so it does not affect the generated gate electric field and the gate control ability. Details of molecular synthesis, device fabrication, and measurement conditions are provided in Materials and Methods.

Typical gate-dependent  $|I_D|$ - $V_D$  characteristics for the junction are shown in Fig. 2A and fig. S29. For both positive and negative  $V_D$ , changing  $V_G$  from -2 to 0 V notably decreases  $|I_D|$ , while changing  $V_G$ from 0 to 2 V notably increases  $|I_D|$ , clearly proving an effective gate modulation of the junction. By monitoring  $I_D$  that changes with  $V_G$  at a fixed  $V_D$ , transfer characteristics can be obtained to further evaluate the transistor performance. Transfer characteristics for the junction at  $V_D = -0.02$ , -0.1, -0.2, -0.3, and -0.4 V are shown in Fig. 2B, all exhibiting ambipolar charge transport behaviors. When  $V_D = -0.02$  V, the maximum/minimum value of  $|I_D|$ , that is, the on/off ratio acquired from the transfer characteristics is about 4800. In addition, the other six devices also exhibit similar characteristics, all with a high on/off ratio exceeding 1000, with an average of about 3100 (fig. S30).

Although the on/off ratio decreases with the increase of  $|V_D|$ , it exceeds 1000 at  $|V_D| \le 0.4$  V. The slope,  $dV_G/d(\log|I_D|)$ , which describes the gate efficiency, can reach up to ~179 mV/decade (fig. S8). Such high on/off ratio and gate efficiency indicate the high field-effect performance of the single-molecule device. To understand the field-effect mechanism of the single-molecule device, the two-dimensional visualization of dI/dV plotted versus  $V_G$  and  $V_D$ 



**Fig. 2. Field-effect properties of a porphyrin junction with ionic liquid gating. (A)**  $|I_D|$  versus  $V_D$  characteristics at  $-2 V \le V_G \le 2 V$  with a step of 1 V. (**B**) Transfer characteristics at  $V_D = -0.02$ , -0.1, -0.2, -0.3, and -0.4 V. Inset shows  $V_D$ -dependent on/off ratios. (**C**) Two-dimensional visualization of d//dV plotted versus  $V_G$  and  $V_D$ . Black dashed lines are auxiliary markers of the conductance diamond edge. (**D**) Schematic band diagram for the device when  $V_G$  is applied. (**E**) Gate-dependent transmission spectra at  $-2 V \le V_G \le 2 V$  with a step of 1 V. The *p*-HOMO and *p*-LUMO are marked with downward and upward triangles, respectively. (**F**) Theoretical transfer characteristics at  $V_D = -0.02 V$ .

is shown in Fig. 2C. The diamond-shaped low conductivity in the central area (green and blue) corresponds to off-resonant transport through the HOMO-LUMO gap. The red orange high conductance in the outer region is caused by resonant transport with the frontier molecular orbitals into the bias window (Fig. 2D). These results indicate that the energy level of molecular orbitals can be effectively regulated by electrical gating. The orbital shift for applying a 1-V gate voltage is ~0.53 eV, which can be obtained from the positive slope of the diamond in the conductance mapping (Fig. 2C). The conductance mapping test has been implemented for several cycles. Another typical two-dimensional visualization of dI/dV versus  $V_D$  and  $V_G$  of the same device is shown in fig. S28. Similar field-effect performance confirms the fatigue resistance of the single-molecule FET.

The gating processes of the device were also investigated by theoretical simulations. It can be observed from Fig. 2E that when  $V_{\rm G}$ changes from –2 to 2 V, the transmission spectroscopy shifts along the positive direction. Both perturbed HOMO (*p*-HOMO) and *p*-LUMO, which are dominant conductive channels, can move in and out of the bias window, resulting in ambipolar gate modulation of the molecular device. Correspondingly, from the theoretical transfer characteristics at  $V_{\rm D} = -0.02$  V (Fig. 2F), an ambipolar behavior and a high on/off ratio of about 10<sup>7</sup> can be observed, which further proves that the high field-effect performance of the device originates from the effective regulation of molecular orbitals by electrical gating. The lower experimental ratio and the bump in Fig. 2B in the low voltage region may be attributed to the defects/ impurities of graphene electrodes and the external environment interference. It is worth mentioning that the gating mechanism is the same as the gate dielectric configuration, not the electrochemical transistor configuration. The gate dielectric configuration is used for theoretical simulation, which considers the movement of the molecular orbital energy levels during the gating. The results of the simulation can fully reproduce the experimental behavior, which helps to attribute the transistor effect to molecular orbital gating rather than some redox reaction.

#### Tautomerization-induced two-state switching

In a two-probe device structure without ionic liquid, a two-state stochastic conductance switching was observed in the current-voltage  $(I_{\rm D}-V_{\rm D})$  characteristics from 300 to 160 K (Fig. 3, A to C, and fig. S9), as the sweeping step was set as 0.5 mV with a step length of 30 ms. The conductance ratio of the stochastic switched high/low states is 3 to 4. Notably, with decreasing the temperature, the onset bias of switching increases, as shown in the representative  $I_{\rm D}$ - $V_{\rm D}$ curves at 280, 220, and 180 K. The onset bias here refers to the minimum drain-source bias required to drive the two-state conductance switching. This kind of two-state conductance switching can be further verified clearly in the real-time current  $(I_D-t)$  measurement, as shown in the insets in Fig. 3 (A to C) and figs. S10 to S17. Another reproducible device showing two-state switching is presented in figs. S31 and S32. Similar two-state conductance switching is also observed at negative biases, as shown in fig. S33. On the basis of these real-time data, the kinetic information was analyzed. The dwell times of high-conductance and low-conductance states were extracted from each  $I_{\rm D}$ -t curve (fig. S18). As the switching rate k is



**Fig. 3. Temperature- and bias-dependent switching of a porphyrin junction.** (**A** to **C**) *I*<sub>D</sub>-*V*<sub>D</sub> characteristics at different temperatures of 280, 220, and 180 K. The blue and red solid curves are visual aids for the low and high conductance states. Insets show corresponding *I*<sub>D</sub>-*t* trajectories at bias voltages marked with gray dashed lines. (**D**) Arrhenius plots of ln *k* versus 1000/T for the low and high states at 0.25 V. The activation energies were obtained by Arrhenius equation. (**E**) In *k* versus *V*<sub>D</sub> characteristics, where the round points correspond to ln *k* at 280 K and the square points correspond to ln *k* at 240 K (also see fig. S19). (**F**) Theoretical energy diagrams for the transition between H1 and H2 under different electric fields.

the reciprocal of the lifetime ( $\tau$ ), the  $\tau$  values at  $V_{\rm D} = 0.25$  V under different temperatures were used to obtain the Arrhenius activation energy for the low ( $E_{\rm Low}$ ) and high ( $E_{\rm High}$ ) conductance state as ~0.51 and ~0.38 eV, respectively (Fig. 3D). In addition, the switching rate increases with bias in an exponential way but with a kink at  $V_{\rm D} =$ ~0.55 V and  $V_{\rm D} =$  ~0.35 V for the low-conductance state and highconductance state, respectively (Fig. 3E).

To figure out the origin of this two-state conductance switching, we first exclude the possibilities resulting from charge trapping and phenyl twisting. For charge trapping-induced conductance switching, there are usually two typical characteristics: localized frontier molecular orbital (LFMO) and sufficient bias to provide electrons with enough energy to hop from the electrode directly to the LFMO, which means that the onset bias of this kind of switching has a negligible dependence on temperature. Therefore, the conductance switching with temperature-dependent onset bias is not based on the charge trapping mechanism. For the switching effect induced by phenyl twisting, it usually happens at around 80 to 140 K and needs the intercoupling large enough between each phenyl ring (26, 27), which cannot be applied to the present porphyrin molecular system. On the basis of theoretical calculations, it can be observed that there are three different stable tautomers (H1, H2, and H3) (fig. S20) due to proton transfer (28) among different nitrogen atoms in the porphyrin ring. H1 is in the trans configuration with two hydrogens at diagonal nitrogen sites, which is the most stable. H2 and H3 are with different cis configurations, where two hydrogens occupy neighboring nitrogen sites. From Fig. 3D, it can be observed that the activation energy of the high-conductance state is lower than that of the low-conductance state. Because the activation energies are related to the theoretical calculated transition energy barriers among the three possible configurations (fig. S21), the only possibilities are that high is H2/low is H1, high is H3/low is H1, or high is H3/ low is H2. When considering the transmission spectra (fig. S22), the conductance of H3 is notably lower than that of H1 and H2. Therefore, only the case where high is H2/low is H1 can remain. Furthermore, the activation energy for H1 and H2 agrees qualitatively well with that obtained from experimental data, which further confirms that the two-state switching is caused by the transition between H1 and H2.

One effect of the applied bias voltage can be interpreted in terms of inelastic scattering. When a certain bias voltage is reached, the crossing electron can provide enough energy to activate the switching event. This corresponds to the transition point of  $\ln k$  versus  $V_{\rm D}$ characteristics shown in Fig. 3E, where the increase in slope at high biases is due to the inelastic scattering of the crossing electrons. The theoretical activation energies for H1 and H2 (Fig. 3F) agree qualitatively well with the transition voltage points, which further confirms that the two-state switching is caused by the transition between H1 and H2. However, the difference in slope after the transition point of different states can also be observed (Fig. 3E), which indicates other effects of the applied bias. The effect of the electric field is qualitatively simulated through further theoretical calculations. For the transition from H1 to H2, the activation energy decreases in a more and more obvious magnitude as the electric field is larger than 0.5 V/Å. However, the activation energy for the transition from H2 to H1 hardly changes with increasing the electric field. This is also consistent with the experimental results that  $\ln k$ for both H1 and H2 increase in a linear way with increasing bias voltages but with a transition point as the slope of  $\ln k$  relative to  $V_{\rm D}$ 

increases under large bias voltages, and the slope for H1 under large bias voltages is larger than that for H2 (Fig. 3E).

The tautomerization mechanism induced by proton transfer in porphyrin involves both vibrational excitations in the macrocycle that temporarily reduce the separation of the hydrogen from the adjacent nitrogen site and proton tunneling (29, 30). When the bias voltage is lower than the transition energy barrier, thermal excitation dominates proton transfer; when the bias voltage is higher than the transition energy barrier, the excitation caused by inelastic electron tunneling dominates proton transfer. It should be mentioned that this room temperature tautomerization in porphyrin is impressive because previously reported tautomerization of porphyrin was observed at low temperatures within scanning tunneling microscopy (18, 20, 31). In addition, for scanning tunneling microscopy-based studies, molecules are directly adsorbed on the substrates, and electrons are injected vertically from the probe to the molecular plane. In these cases, the substrate has a notable influence on the tautomerization reaction, especially when the molecule is in direct contact with the metal substrate (31). In contrast, for single-molecule junctions, single molecules are covalently bonded to nanogapped graphene electrodes. Because the molecule is suspended in the junctions, the influence of the substrate is negligible.

#### Tautomerization-induced multiple switching

In addition to H1 and H2, there is another tautomeric state, H3, with two hydrogen atoms on the left or right side (fig. S20). For the transition from the initial state H1 to this state H3 at zero bias, it has a transition energy barrier as high as ~0.76 V (figs. S21 and S23), which means that thermal activation of this transition is forbidden. However, when the applied bias voltage is larger than 0.8 V and temperature drops below 160 K, another two new conductance states clearly appeared. Therefore, there exists four distinct conductance states (Figs. 4, A and C, and figs. S25 to S27). The four-state switching can also be observed from the current-voltage characteristics at 160 K and higher temperatures (fig. S24). Another reproducible device showing similar four-state switching is exhibited in fig. S34.

At 140 K, the thermal energy is as half as that at room temperature, which means that the lifetime of H3 could be longer. On the basis of this point, the two new conductance states should be related to H3. In the view of the whole junction architecture, it can be observed that H3 results in asymmetry throughout the molecular backbone. Therefore, the two equivalent configurations where the two hydrogens are located at the right/left two nitrogen sites (H3-R and H3-L as shown in Fig. 4B) become distinguishable under different bias electric fields. To figure out which conductance state corresponds to H3-R or H3-L, theoretical  $I_D$ - $V_D$  curves were calculated as shown in Fig. 4B. Obviously, under bias voltages where the electric field is applied from left to right through the molecular backbone, the conductance of H3-L is larger than that of H3-R. This electric field enhanced conductance of H3-L is also higher than the conductance of H1. As a result, the conductance states can be attributed clearly as shown in Fig. 4C. The detailed switching processes between each tautomer are shown in Fig. 4D, where H1 $\rightleftharpoons$ H2, H1⇒H3R, H2⇒H3L, and H3R⇒H3L undergo reversible transitions. To understand these transitions, schematic energy diagrams for all these four configurations as well as the corresponding transition states are illustrated in Fig. 4E. Note that the transition energy barriers for all these transitions can be effectively crossed under a



Fig. 4. Multiple switching at high biases. (A) Representative *I*<sub>D</sub>-*t* trajectories and corresponding statistical histograms at 0.95 V and 140 K, which clearly show four distinguishable conductance levels. (B) Theoretical *I*<sub>D</sub>-*V*<sub>D</sub> characteristics for the junctions in H3-L and H3-R states, which are electric field–induced symmetry-breaking states. a.u., arbitrary units. (C) Enlarged data in (A) to show the transitions between four states. (D) Transition statistics between each state. (E) Corresponding energy diagrams for the transitions. The solid line represents the transition through one-step proton transfer; the dashed line represents the transition through two-step proton transfer.

bias voltage higher than 0.8 V. In addition to one-step proton transfers of H1→H2 and H1→H3R, two-step proton transfers can also be effectively activated during H2→H3L and H3R→H3L transitions.

The tautomerization switching is not observed during fieldeffect measurements. This is because for the current-voltage curves of the field effect, a large scanning step of 10 mV is used, where the current tends to the average value of the conductance states. In addition, the electric field generated during the ionic liquid gating may inhibit proton transfer, thereby suppressing the tautomerization switching effect.

In this study, the field effect and switching functions are realized in a single porphyrin-based single-molecule junction with two different configurations. Through molecular engineering and ionic liquid gating, the constructed single-molecule transistor exhibits an excellent ambipolar field-effect performance with high on/off ratio and high gating efficiency. Because of proton transfer-induced

served in the same device. Such proton transfer can be effectively activated and well controlled in a large temperature range starting from room temperature and a large bias voltage range starting from zero bias. Both experimental results and theoretical calculation consistently reveal that the two-state switching between H1 and H2 is activated by the voltage-dependent thermal excitation and electron injection excitation mechanism. At high bias voltages, four-state switching is achieved due to the activation of electric field–induced symmetry-breaking states. Using this molecule to make a device with dual functions is attractive if one could achieve the switching behavior within the ionic liquid environment. The multifunctional single-molecule devices that take advantage of natural electronic and tautomeric properties of the molecular components will be implemented in a variety of electronic devices, thus building a bridge between hard electronics and the soft molecular world.

tautomerization of porphyrin, another switching function is ob-

#### MATERIALS AND METHODS

#### **Molecular synthesis**

The details of molecular synthesis are provided in the Supplementary Materials (scheme S1 and figs. S1 to S4).

#### Details of device fabrication molecular connection

The point-contact graphene electrodes of the single-molecule device were fabricated by the method of dash-line lithography described in detail in the previous study (*32*). For molecular connection, the graphene devices, porphyrin compounds, and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride were added into the reaction vessel with argon (Ar)-protecting atmosphere to keep water and oxygen free. Then, 10 ml of anhydrous pyridine was injected into the vessel, and the concentration of the molecule solution was about  $10^{-4}$  M. After being kept in the dark for 2 days for molecular connection, the devices were then taken out from the solution, washed with copious acetone and ultrapure water to remove residues on the surface, and rinsed with trifluoroacetic acid to ensure the pristine conformation of porphyrin. Last, the devices were dried with N<sub>2</sub> gas.

#### **Device characterization**

By using a Keysight B1500A semiconductor characterization system and a Karl Suss (PM5) manual probe station, the device was characterized at room temperature in the ambient atmosphere. The ionic liquid, DEME-TFSI, was dropped onto the center of the porphyrin device using a homemade microsyringe. The electrical characterization of the field-effect and switching characteristics of the devices were carried out on Lakeshore TTPX Cryogenic Probe Stage featuring the Model 336 Controller with the liquid nitrogen cooling system. The FET measurements were carried out from 220 to 300 K, and the hydrogen transfer measurements were carried out from 80 to 300 K, which were both in a vacuum environment.

#### **Theoretical calculations**

Theoretical simulations of isolated molecules were carried out within the Perdew-Burke-Ernzerh (PBE) of generalized gradient approximation (GGA) (33) and implemented in Vienna Ab Initio Simulation Package (VASP) (34). The van der Waals interaction was counted in by using the method of Grimme (density functional theory with long-range dispersion correction, DFT-D3) (35, 36). The projector augmented wave potential (37) and the plane-wave cutoff energy of 400 eV were used. A supercell with at least 10-Å vacuum space around the molecule and a  $\Gamma$  *k*-point were used. In the supercell, the positions of all atoms were relaxed until the force was less than 0.001 eV/Å. The criterion for the total energy was set as  $1 \times 10^{-7}$  eV. Dipole correction was considered. The climbing image nudged elastic band method (38) was used to find the minimum energy pathways and energy barriers for transformation among different isomers.

The transport device model was constructed by three parts, i.e., left electrode, central region, and right electrode. Both electrodes were semi-infinite *p*-type doped graphene. The central region consisted of the extended molecule and one electrode extension on both sides. We further placed an electrostatic gate and a dielectric region ( $\varepsilon \sim 14.5$ ) (*39*) above the central molecule. Considering that the graphene was also gated in the experiment, the carrier density of graphene electrodes was tuned according to the applied gate voltage (*40*). The structures of the transport devices were optimized by VASP package with GGA-PBE functional. The electronic transport simulations were performed using the real-space nonequilibrium Green's function techniques

(41, 42) with GGA-PBE functional, as implemented in the Quantum ATK software (version: R-2019.03). The Pseudo Dojo pseudopotential with Medium basis sets was adopted. The density mesh cut-off was set to be 100 Ha. A *k*-point mesh of  $2 \times 1 \times 111$  and  $24 \times 1$  was used for device self-consistent calculations and transmission spectra analysis, respectively.

#### SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at https://science.org/doi/10.1126/ sciadv.abm3541

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### Single-molecule field effect and conductance switching driven by electric field and proton transfer

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