Emergent complexity of quantum rotation tunneling

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Conformational isomerism determines the performance of materials and the activity of biomolecules. However, a complete dynamic study of conformational isomerization is still a formidable challenge at the single-molecule level. In this work, we present real-time in situ electrical monitoring of the full rotation dynamics of a single aromatic chain covalently embedded in graphene electrodes with single-event resolution. We reveal that the dynamic process of phenyl ring rotations at low temperature is dominated by quantum rotation tunneling rather than the guasi-free rotation process. The emergent complexity of different intramolecular rotations in a single aromatic molecule is demonstrated, including the alternating unidirectional rotation with multi-, single-, and half-circle delays driven by inelastic electron tunneling, which has not been previously adequately considered at the macroscopic level. This work builds a bridge between macroscopic and microscopic worlds and improves our understanding of structure-activity relationships, potentially bringing different functions to ordinary materials.

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INTRODUCTION

As the consensus among chemists, the concept that "structure determines properties" has guided the design and preparation of various functional materials (1, 2), including the editing of molecular skeletons and the regulation of molecular arrangements. For example, the conformational isomerism induced by the chemical bond arrangement notably affects the reactivity (e.g., the cis-addition in the Diels-Alder reaction), selectivity (3-5), electron transport (6, 7), and photophysical properties (8-10). In general, the molecular conformation is difficult to control, which is usually considered to be in thermal equilibrium, i.e., rapid switching among different conformations. A unique example is the molecular motor (10-12). To simplify the rotation mode, the unidirectional rotation can be approached by the introduction of chiral steric hindrance moiety and alternating external stimuli. However, for the most commonly used multiphenyl system, the conformational isomerization triggered by σ bond rotations between different phenyl rings is rapid and complicated, involving the multiple rotation modes. The characterization of these detailed dynamic processes necessitates the adequate consideration of individual differences, especially the emergent complexity of intramolecular twisting with increasing number of σ bonds (13–15). A comprehensive understanding and the manipulation of intramolecular many-body rotations, including the direction, the coupling with the external energy, and the emergent complexity, is the key step toward the precise preparation of high-performance molecular materials.

Single-molecule detection provides the capability to focus on only one individual molecule (16) and its intramolecular conformational change (17, 18). In particular, single-molecule electrical detection enables the high-sensitivity characterization of the stereoelectronic effect, that is, the close relationship between the molecular conductance

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and π - π overlap of phenyl rings (6, 7, 19, 20). The integration of an individual molecule into electrode pairs meets the requirements for the reliable measurement of the molecular conductance with different twisted angles. However, to further uncover the intramolecular dynamic disorder of many-body rotations, high temporal and singleevent resolution is a prerequisite. In addition, a mechanically stable environment is also essential to characterize the inherent intramolecular rotation. A fixed graphene-based single-molecule junction on a chip is regarded as an ideal candidate owing to the stable anchoring of the molecule by covalent bonds. Furthermore, this setup enables real-time in situ monitoring to characterize the short-lifetime intermediates (21), conversion pathways (22), and correlation among single events (23, 24), which forms the basis for the elucidation of the complex many-body intramolecular rotation.

Here, we report an unconventional detection paradigm capable of long-term accurate monitoring of conformational changes in real time, taking advantage of the high temporal and current resolution of electrical measurements (Fig. 1A). On the basis of systematic temperature-dependent measurements, we found three discrete metastable states of an aromatic molecule featuring two terphenyl moieties [state 1, state 2, and state 3 with different conjugations (Fig. 1, A and B)]. The corresponding rotation trajectories revealed a quantum rotation tunneling effect rather than continuous quasifree motions and clarified the unidirectional and inelastic electron tunneling (IET)-coupled rotations. Notably, the emergent complexity from one to two terphenyl moieties is demonstrated, highlighting the importance of extrapolation from single-molecule to macroscopic properties.

RESULTS

Device fabrication and characterization

To prepare the single-molecule device integrated with a fluorenecentered hexaphenyl aromatic molecule, which consists of two terphenyl moieties linked by σ bonds with both outer phenyl rings (blue) fixed in a fluorene form for simplicity, a graphene sheet was etched by oxygen plasma according to the dashed-line pattern prepared by electron beam lithography. This has been described in detail in a previous report (25), providing the comprehensive characterization of graphene electrodes. The details of the molecular synthesis are provided in the Supplementary Materials (section S1 and fig. S1).

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Fig. 1. Device structure and characterization of the single-molecule junction. (**A**) Schematic of the single-molecule device containing a hexaphenyl aromatic molecule with a fluorene center, showing the IET-coupled quantum rotation. (**B**) Schematic of the three discrete twisting states [corresponding to the three conformations in the top right corner of (A)] from different views, and the corresponding conductance levels. (**C**) Characterization of a single-molecule connection. The super-high-resolution images were obtained by single-molecule electroluminance with $V_d = 4 V$, and the corresponding single molecule was located by the stochastic optical reconstruction microscopy technology. Laser, 405 nm, 5 mW. Five thousand photos were taken through a ×100 oil lens with an exposure time of 50 ms. (**D**) *I-V* curve of a single-molecule junction at 120 K, showing the stochastic switching among the three states. The measured current at relatively high bias voltage is consistent with the extrapolation of state 3, supporting the IET process.

With gradual isotropic etching, the widening of the pattern enables the formation of the nanogap with carboxyl terminals (an open circuit). The amine-terminated molecular bridge can then be integrated via amide bonds, resulting in the recovery of the conductance to some extent, to form a graphene-molecule-graphene single-molecule junction (Fig. 1A). The obtained triangular graphene electrodes and the determined interface coupling enable the long-term monitoring of conformational changes in the molecular bridge. The details of the device fabrication are provided in Materials and Methods. Under the optimized conditions, the integration yield reached ~20%, and ~20 of the 102 devices on the same chip showed recovery of the conductance (fig. S2). Statistical analysis showed that the recovered conductance, with a probability of ~90%, originated from an only-one-molecule connection between the electrodes, which is discussed in the Supplementary Materials (section S3). This was further supported by the single-molecule location using a stochastic optical reconstruction

microscopy technology (Fig. 1C) (26). The only one fluorescent spot between a pair of electrodes provides direct experimental evidence of only one molecular connection in our devices. The covalent anchoring on the chip excludes the coupling between the molecular motion and intramolecular rotation. In addition, this setup limits some of the vibration modes, which contributes to the ability to focus on the intramolecular rotation with high sensitivity.

Thermodynamics of intramolecular quantum rotations

The measured current showed a smooth response to the voltage at room temperature (fig. S2), indicating a statistical average state owing to the rapid rotation. Such rotation behavior can be classified as a quasi-free rotation, where the internal energy of the molecular bridge is substantially higher than the barriers between different conformations. However, as the temperature decreased to 120 K, slower rotation was measurable, revealing three discrete states rather than the quasi-free rotation, in the range from -120 to 120 mV (Fig. 1D). The noncontinuous transitions among these states indicate a quantized behavior with different degrees of conjugation of the two terphenyl parts (vide infra) (Fig. 1B), which corresponds to a hindered rotation behavior. The computational simulations are provided in the Supplementary Materials (section S4, figs. S3 to S9, and tables S1 to S10), which showed the details of these thermodynamic metastable conformations (figs. S3 and S4 and tables S1 and S2), and provided the assignments to the conductance states (fig. S5). For one individual terphenyl moiety, the dihedral angle between the outer phenyl rings (yellow and blue rings in Fig. 1) showed two switchable states between ~1° (strong conjugation) and ~73° (weak conjugation). For the two terphenyl moieties, they presented three discrete twisting states consisting of two (state 1), one (state 2), and zero (state 3) strongly conjugated parts (Fig. 1, A and B). In addition, only one state was obtained at $|V_d| > \sim 120 \text{ mV}$ in the current-voltage (*I-V*) scan (120 K), indicating an IET process (vide infra), in which the energy lost by the electrons causes the phenyl ring to remain at a high energy level at higher V_d. The conductance switching did not occur at higher bias and also excludes the possibility of charge-trap-induced switching. In detail, a computational simulation of the energy profile showed that the relative Gibbs free energies of the three states are ~0.41 kJ/ mol (state 1, strong conjugation), ~0.00 kJ/mol (state 2, medium conjugation), and ~1.04 kJ/mol (state 3, weak conjugation) (Fig. 1B) (19). This demonstrated that the energy level of state 3 is the highest among the three states, which indicates that the injection of external energy favors the stabilization of state 3. In this scenario, the electron energy at $|V_d| > -120 \text{ mV}$ (i.e., 120 meV) is far beyond the vibration and rotation wave numbers of the phenyl ring, which range from 0 to 200 cm⁻¹ (i.e., 0 to 24.8 meV). Therefore, because of the IET-assisted process, the external energy injection is sufficient to stabilize the phenyl rings to remain in a high energy state.

Kinetics of intramolecular quantum rotations

To demonstrate the detailed process, the intramolecular rotation dynamics were characterized by current-time (I-t) measurements at a constant bias voltage ($V_d = 100 \text{ mV}$) with a time resolution of up to ~17 μ s (Fig. 2A). The rapid switching among different states was measured at 140 K, which is a large step forward in comparison with only conductance measurements. The statistical histogram showed three discrete states (Fig. 2B), which was in line with the I-V scan (Fig. 1D), and it again suggested the quantum rotation behavior rather than a quasi-free rotation process. In addition to the occupancies of the three states, which reflect the thermodynamic preference, we also provide their dwell times, representing the energy barriers hindering the rotation among these states. The dwell times (τ) of three states were extracted and showed two types of distributions (Fig. 2C, left and right), which indicates two conversion pathways with different rates (referred to as $k = 1/\tau$) between each two states. Considering that the transition state (TS) is determined by the direction of the rotation (the results of the computational simulations are provided in figs. S3 and S4 and tables S1 and S2), where the energy barrier is lower at dihedral angles of 0° (between the yellow and green rings, TS1 and TS2) and higher at dihedral angles of 90° (TS1' and TS2') (Fig. 2C, middle), we concluded that the I-t curve contained information about the direction and the rotation angles between each two states. Specifically, the relatively fast (slow) conversion corresponded to the TS with dihedral angle of 0° (90°) and rotation angle of 72°, marked as clockwise (CW) [108°, marked

as counterclockwise (CCW)]. Therefore, in combination with the difference in the dwell time, the *I*-*t* curve provided direct visualization of the intramolecular quantum many-body rotation.

Temperature-dependent measurements (the long-term I-t curves of three different devices are provided in figs. S10 to S15) further elucidated the activation energy of the rotation. According to the Arrhenius equation, linear fitting to the lnk versus 1000/T curve in the range from 100 to 140 K provided the statistically averaged activation energies: $E_1 \rightarrow 2 = \sim 27.4$ kJ/mol, $E_2 \rightarrow 1 = \sim 26.7$ kJ/mol, $E_{2 \rightarrow 3} = \sim 26.2$ kJ/mol, and $E_{3 \rightarrow 2} = \sim 27.0$ kJ/mol with a fitting error of 0.5 kJ/mol, reflecting the similar environments of the benzene ring in the two terphenyl moieties (Fig. 2D). The higher energy barriers than the computational simulation (~7 kJ/mol for CW and ~11 kJ/mol for CCW; the detailed information is provided in tables S1 and S2) may originate from the steric hindrance of the Si/SiO₂ substrate and the interface coupling between the molecule and electrode. Note that, here, the temperature represents the set of the test chamber. The definition of the temperature of single-molecule junctions is complex. For example, the thermal broadening of the Fermi electronic occupation distribution in the electrode determines the temperature of the tunneling electrons (27). Here, the temperature of the molecule depends on the coupling with the electrode and the nonequilibrium IET process.

Note that the temperature of ~100 K is a critical point that separates the linear and nonlinear regions of the temperature dependence of the rotation rates (Fig. 2D), indicating quantum tunnelingdominated conformational isomerization at lower temperatures (<100 K) owing to the insufficient energy to overcome the energy barrier. In specific, a crucial distinction between the classical and tunneling pathways lies in the temperature dependence of their rates (28, 29). The classical component is a thermally activated process and exhibits a notable reliance on the temperature. In contrast, the tunneling rate is independent of the temperature to some extent. As the temperature decreased below ~100 K, the thermally activated rate became negligibly slow and the tunneling pathway dominated (Fig. 2D). By taking the quantum tunneling into account, a computational simulation (tables S3 to S10 and figs. S6 to S9) showed the same trend in the rate change of the rotation as that in the experiment (Fig. 2D). As an important parameter describing the tunneling effect, the transmission coefficient (κ) notably increased with decreasing temperature and also dominated the contribution to the rotation rate, which indicates an increase in the probability of overcoming the energy barrier by quantum tunneling. It is worth mentioning that for a benzene ring composed of six carbon atoms, as theoretically simulated (tables S4, S6, S8, and S10), its rotation still exhibits weak temperature dependence, showing a six heavy-atom synergistic quantum tunneling effect, which is rare. Theoretically, quantum tunneling is closely related to the width of the energy barrier, which in this case is related to the directions and angles of the rotation. To validate this, the characteristic lifetimes of the states were obtained by I-t measurements with different time resolutions (to obtain sufficient conversion events). The Gaussian fitting of state 3 is shown in Fig. 2E, and those of states 1 and 2 are provided in figs. S16 and S17. In comparison with the relatively fast conversion process (relatively short τ , left panel) with rotation angle of 72°, the relatively slow conversion process (relatively long τ , right panel) with rotation angles of 108° showed stronger temperature dependence. The statistics of the dwell time (Fig. 2E) showed that the CW rotation dominated the conformational rotation with a distribution



Fig. 2. Temperature-dependent measurements of intramolecular quantum rotations. (**A**) *l-t* curve of the intramolecular rotation at 140 K (V_d = 100 mV). (**B**) Corresponding histogram of the *l-t* curve shown in (A), presenting three discrete states. (**C**) Left, corresponding enlarged part marked by gray in (A). Middle, schematic of the conformational change process and the corresponding TSs among the three quantum rotation states, showing two conversion pathways with different rotation modes. The two yellow solid lines in the TS represent the initial and final positions of the yellow phenyl ring, respectively. The yellow dashed line indicates the exact position of the yellow phenyl ring in the TS. The single-headed arrows in the TS indicate the rotation directions. Right, dwell times (τ) of the three states. (**D**) Plots of Ink (*k* is the rate between each two states) versus 1000/T in the temperature range from 40 to 140 K. (**E**) Gaussian fitting to the lifetime of state 3 in the temperature-dependent measurements (60 to 100 K). Left, the relatively fast conversion process (relatively short τ , rotation angles of 72°). Right, the relatively slow conversion process (relatively long τ , rotation angles of 108°).

at $\lg [\tau (ms)] = 2.5$ to 3.2 at 60 to 100 K. This corresponds to a timescale of 0.3 to 1.6 s, i.e., the rotation frequency of this process mainly remains in the range of 3 to 0.6 Hz with decreasing temperature. Considering the strongly decayed rotation rates of the other slower CCW process {lg $[\tau (ms)] = 3.9$ to 5.1, i.e., from 0.12 to 0.008 Hz}, the rotation dynamics dominated by the width of the energy barrier further support the contribution of quantum tunneling in the conversion through the CW rotation. In summary, the rotational dynamics of a single benzene moiety have been illustrated, involving the processes of state $1 \rightarrow$ state 2, state $2 \rightarrow$ state 1, state $2 \rightarrow$ state 3, and state 3 \rightarrow state 2. The discrete conductance switching shows quantum rotation of the conformational isomerization rather than continuous quasi-free motions. In addition, the quantum tunneling was also observed through temperature- and width-dependent realtime measurements.

Unidirectional rotation driven by IET

To demonstrate the IET-coupled quantum rotation, bias-voltagedependent measurements were performed at 80 K (the long-term I-t curves of two different devices are shown in figs. S18 to S29). Only the binary switching between state 1 and state 2 was observed at 20 to 32 mV, while the occasional appearance of state 3 was detected at ~38 mV. This indicates that there was only one phenyl rotation at relatively low biases owing to the high energy of state 3 (~1.04 kJ/mol). This was further verified by control experiments using the complex of β -cyclodextrin-molecular bridge 1, which exhibited binary switching at both high and low biases because it allows only one-side rotations (figs. S30 to S41). Note that two types of switching patterns with equal probabilities were obtained at 20 to 32 mV (Fig. 3, A and B) in the same junction, reflecting the flipped dwell times of state 1 and state 2. In detail, relatively long (short) dwell time of state 1 and relatively short (long) dwell time of state 2 are observed in Fig. 3 (A and B), showing an alternating process with TS1 and TS1', i.e., continuous unidirectional rotation of one benzene ring. The unidirectional rotation originates from the axial chiral environment constructed by green benzene and graphene on the chip (Fig. 1A). The mirrored chiral environment at the two sides results in an opposite rotation direction, which corresponds to the two switching modes. Therefore, with an injected electron of 20 to 32 meV and an environmental thermal energy of $k_{\rm B}T = -6.9$ meV, only the continuous unidirectional rotation of one benzene moiety on one side can be randomly triggered. Therefore, the IET drove the molecular junction into a dissipative system, which is far from the thermodynamic equilibrium and operates through the exchange of energy with injected electrons. The energy dissipation overcomes the tendency for random rotation and enables a unidirectional rotation with entropy reduction. The continuous supply of energy allows the sustained dynamic change and complexity emergence of molecular conformations. In detail, the injected energy was mainly used to compensate for the rotational energy ($\sim 80 \text{ cm}^{-1}$, $\sim 9.9 \text{ meV}$) and the entropy reduction $\Delta S = k_{\rm B} T \ln(N_{\rm CW}/N_{\rm CCW}) = \sim 13.2$ meV, where $N_{\rm CW}$ is the number of the dominant rotation direction and $N_{\rm CCW}$ is the number of the opposite direction. Therefore, the unidirectional rotation of the random side driven by IET was observed at the single-molecule junction at relatively low bias voltages.

The rotation period calculated by $\tau_{\text{state 1}} + \tau_{\text{state 2}}$ was ~944 s (one side) and ~900 s (the other side) at 20 mV (Fig. 3, C and D), corresponding to a frequency of ~1 mHz. With increasing bias, a nearly linear increase in the rotational frequency was observed, up to a

maximum of ~7 mHz (at 32 mV), which was mainly determined by the relatively slow rotation step with an angle of 108° (as shown in the right column of Fig. 2E, only ~30 mHz was observed at 100 mV). On the basis of the observed nearly linear correlation between the rotational frequency and bias voltage (Fig. 3, C and D, blue curves), as well as the nearly linear relationship between the bias voltage and current (Fig. 3, A and B) within this range, it can be concluded that the rotational frequency is proportional to the current (representing the number of electrons involved) (fig. S42), indicating a single electron-assisted process. In addition, increasing the bias voltage also contributes to the additional vibration modes at 0 to 200 cm^{-1} (0 to 24.8 meV), which could assist in quantum tunneling rotation with a high vibrational state and reduce the barrier width. It should be mentioned that owing to the orthogonal direction, the effect of the electric field on the rotation of the benzene ring is within 1° and can be ignored (30).

Emergent complexity of intramolecular quantum rotations

Initially, the crossover of the quantum rotation on the two sides was observed at ~38 mV, which was mediated by state 3 (Fig. 3E). The conversion from state 1 to state 3 involves two modes (fig. S43), that is, the stepwise pathway (state $1 \rightarrow$ state $2 \rightarrow$ state 3) and the concerted pathway (state $1 \rightarrow$ state 3). Considering the time sequence of the direct conversion from state 1 to state 3 during the rotation crossover (inset of Fig. 3E), the interaction between the rotations of the two sides could be realized by IET, where the vibration of the strong conjugated side (at TS1) has weak coupling with the IET and causes the IET on the other side. In addition, under limited energy injection, the vibrational perturbation of the molecular bridge skeleton may also cause the rotations of the phenyl rings on both sides at Peking University to stochastically switch. Therefore, as the number of the σ bond increases, coupling with external energy might lead to the emergence of rotational complexity, which has not been previously adequately considered in the macroscopic system.

The rotation crossover gradually dominated at 54 mV (Fig. 3F), where the phenyl rings on both sides alternately rotated in a single circle with state 1 as an inevitable relay state (Fig. 3G). The strong anticorrelation between the dwell times of τ_N and τ_{N+2} (i.e., two adjacent events) supports the alternating single-cycle rotation (Fig. 3H). The distribution of lg [τ (ms)] at ~5 represented that the frequency of the single-cycle rotations was ~10 mHz, which is determined by quantum tunneling. The thermodynamically unfavorable state 3 was not observed, and the external energy drives the singlemolecule junction to switch between state 1 and state 2, far from the equilibrium. The increased electron energy compensates for the vibration, rotation (0 to 24.8 meV), and entropy reduction of the phenyl rings on two sides ($\Delta S = \sim 26$ meV). The continuous and opposite directional rotation of the two phenyl rings substantially offsets the rotational torque (parallel to the molecular bridge), and it is also consistent with the microscopic Pauli exclusion principle of the two quantum rotation states. Therefore, the external energy plays a key role in the dynamics of conformational changes with emergent complexity.

More complex rotation modes of the two phenyl rings were observed at relatively high bias voltages, including the relatively high energy state 3 (Fig. 4A). The statistics of the conversion time sequence showed two main modes at 68 mV: mode 1, state $1_{\text{short}} \rightarrow 2_{\text{long}} \rightarrow$ $3_{\text{short}} \rightarrow 2_{\text{long}} \rightarrow 1$, and mode 2, state $1_{\text{long}} \rightarrow 2_{\text{short}} \rightarrow 3_{\text{long}} \rightarrow$ $2_{\text{short}} \rightarrow 1$, where the subscripts represent the dwell time and the

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corresponding conversion rate to the next state according to $k = 1/\tau$ (Fig. 4B). According to the unidirectional and opposite rotation of the phenyl rings on both sides, it can be determined that these two modes are also alternating rotation but with a half-cycle delay, which leads to the appearance of state 3 (Fig. 4, F and G). The difference between modes 1 and 2 is the side of the initial rotation. The alternating fast- and slow-rotation rates show the pathway with quantum tunneling separated by classical Arrhenius processes (Fig. 4A, right inset). High-vibrational quantum states that pass through the classical TS without complete vibrational relaxation may contribute to subsequent quantum tunneling with a smaller width. As the bias increased to 74 mV, modes 3 and 4 with continuous quantum tunneling were observed (Fig. 4E)

showed a gradual increase in the total frequency with increasing bias, indicating stronger coupling between the intramolecular quantum rotation and external energy. The maximum total frequency, which is determined by quantum tunneling, was observed at ~7 mHz. The occupancies of modes 1 and 2 gradually decreased after the total frequency reached the maximum (Fig. 4E), indicating the increasing disorder of the rotation modes. The conversion time sequence was diamond-shaped below 74 mV, which has statistical significance, while the total disorder was obtained at $V_d > 74$ mV (figs. S29 and S44), which can be attributed to the energy left from the energy window of the phenyl rotation. In addition, high-energy injection can also increase the vibration and rotation of the middle green phenyl ring, disrupting the chiral environment around the yellow ring and thus resulting



Fig. 4. Emergent complexity of the intramolecular quantum rotations in bias-voltage-dependent measurements (60 to 74 mV) at 80 K. (A) Recorded *l-t* curve of the quantum rotations ($V_d = 68$ mV). Insets, enlarged representative *l-t* curves of the two main rotation modes and the corresponding energy profiles (mode 1, state 1_{short} $\rightarrow 2_{long} \rightarrow 3_{short} \rightarrow 2_{long} \rightarrow 1$; mode 2: state $1_{long} \rightarrow 2_{short} \rightarrow 3_{long} \rightarrow 2_{short} \rightarrow 1$). (B) Statistics of the total conversion time sequence from the data in (A). (C) Recorded *l-t* curves of the quantum rotations ($V_d = 74$ mV). Insets, enlarged representative *l-t* curves of the four rotation modes (mode 1, state $1_{short} \rightarrow 2_{long} \rightarrow 3_{short} \rightarrow 2_{long} \rightarrow 1$; mode 2, state $1_{long} \rightarrow 2_{short} \rightarrow 3_{long} \rightarrow 2_{short} \rightarrow 2_{long} \rightarrow 1$; mode 2, state $1_{long} \rightarrow 2_{short} \rightarrow 3_{long} \rightarrow 2_{short} \rightarrow 3_{long} \rightarrow 2_{short} \rightarrow 2_{long} \rightarrow 1$; mode 2, state $1_{long} \rightarrow 2_{short} \rightarrow 3_{long} \rightarrow 2_{short} \rightarrow 3_{long} \rightarrow 2_{short} \rightarrow 2_{long} \rightarrow 1$; mode 2, state $1_{long} \rightarrow 2_{short} \rightarrow 3_{long} \rightarrow 2_{short} \rightarrow 3_{long} \rightarrow 2_{short} \rightarrow 3_{long} \rightarrow 2_{short} \rightarrow 3_{long} \rightarrow 2_{short} \rightarrow 1$. (D) Statistics of the total conversion time sequence from the data in (C). (E) Rotation frequencies of the four modes versus the bias voltage. (F to I) Schematics of the four rotation modes. The thick arrows between two states represent the relatively fast conversion rates, and the thin arrows represent the relatively slow conversion rates.

in rotation of the benzene ring in a completely random equilibrium state.

DISCUSSION

Covalently fixed stable electrodes enable real-time and precise monitoring of intramolecular rotation, preventing the interference between the motion and partial vibration. Therefore, using static graphene-based single-molecule junctions can be considered to be a universal strategy for detecting intramolecular conformational changes. In combination with single-event resolution, the emergent complexity with increasing number of conformation-change units can be demonstrated from bottom to up.

In this work, a fluorene-centered hexaphenyl aromatic molecule was covalently integrated into nanogapped graphene electrode pairs to quantitatively investigate the general benzene rotation dynamics as well as the emergent complexity of the two phenyl rotations on both sides. The weak temperature dependence of the rotation dynamics at low temperature showed the quantum tunnelingdominated process, which was also affected by the rotation angle (barrier width). The tunneling rates determined the maximum rotation frequency, for example, 7 mHz at 80 K. The coupled rotation with IET led to emergent complexity. By constructing the dissipative system in a single-molecule junction, the unidirectional one-side rotation, crossover of the two sides, and alternating rotation with multi-, single-, and half-circle delays were observed with increased bias voltage to compensate for the entropy reduction. The observation and regulation of the multimode rotations provides profound insights into the reexamination and design of target molecular materials with desirable functions.

Real-time monitoring of the many-body quantum rotation showed the dynamic disorder of the conformational changes coupled with external energy in a general molecule. This would greatly affect the performance of materials, which is always masked by the ensemble average. Therefore, extrapolating the understanding of single-unit conformational changes to Avogadro's number still remains a huge challenge, which invites intensive research to precisely manipulate the conformation at the single-molecule scale and regulate the emergent complexity from the single molecule to the ensemble in the future.

MATERIALS AND METHODS

Molecular synthesis and characterization

The details of the synthetic route and characterization of the products are given in the Supplementary Materials.

Fabrication of the graphene field-effect transistor array

A copper sheet with a thickness of 25 μ m was pretreated with acetic acid to etch the surface oxide layer, rinsed with deionized water and ethanol in sequence, and finally dried by N₂. Single-layer graphene was grown on the pretreated copper sheet by a chemical vapor deposition process. The copper-substrate graphene was then spin-coated with a layer of polymethyl methacrylate (PMMA) 950 to form PMMA-graphene-copper layers. The copper substrate was then removed with FeCl₃ solution, leading to transfer of the graphene layer from the copper substrate to PMMA. Through successive rinsing with HCl solution and deionized water, the PMMA-supported graphene was transferred to a pretreated silicon wafer (1.5 cm by 1.5 cm) with a 300-nm-thick SiO₂ layer. After removing the PMMA layer with acetone, photolithography and thermal evaporation were used to deposit gold marks on the above graphene-silicon wafer. A graphene ribbon with a width of 40 μ m was then prepared by photolithography and oxygen plasma etching. Next, 8-nm-thick Cr and 60-nm-thick Au were successively evaporated on the Si wafer as electrodes. A 40-nm-thick SiO₂ layer was then deposited by electron beam evaporation to prevent current leakage in the liquid phase. On the basis of the dashed-line lithographic method, the graphene fieldeffect transistor arrays were then spin-coated by a layer of PMMA, and they were then exposed via electron beam lithography to open windows on the PMMA layer. Through oxygen plasma etching, nanogaps with carboxyl terminals between the graphene point contact electrodes were obtained.

Fabrication of the single-molecule device

The above newly cut graphene device was added to a roundbottomed flask containing 0.1 mM molecular bridge 1, 1 mM 1-(3dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride, and 10 ml of pyridine solution. After 48 hours, the device was removed, carefully rinsed with deionized water, and dried by N₂. Last, the device was characterized by an *I-V* scan. The recovery of the *I-V* response showed that the molecular bridge was successfully integrated into the graphene electrodes.

Electrical characterization

The single-molecule device was placed in Physical Property Measurement System during the experiments. The *I-V* curves were measured with an Agilent 4155C semiconductor parameter system. The output terminal of the UHFLI lock-in amplifier provided a constant bias for the *I-t* measurement. The current signal of the molecular loop was amplified by a DL1211 amplifier and then recorded by a high-speed acquisition card (NIDAQ).

Theoretical calculations

The details of theoretical calculations are given in the Supplementary Materials.

Supplementary Materials

This PDF file includes: Supplementary Text Figs. S1 to S44 Tables S1 to S10 References

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