

Thermally Activated Tunneling Transition in a Photoswitchable Single-Molecule Electrical Junction

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S Supporting Information

ABSTRACT: Exploring the charge transport process in molecular junctions is essential to the development of molecular electronics. Here, we investigate the temperature-dependent charge transport mechanism of carbon electrode-diarylethene single-molecule junctions, which possess photocontrollable molecular orbital energy levels due to reversible photoisomerization of individual diarylethenes between open and closed conformations. Both the experimental results and theoretical calculations consistently demonstrate that the vibronic coupling (thermally activated at the proper temperature) drives the transition of charge transport in the junctions from coherent tunneling to incoherent transport. Due to the subtle electron—phonon coupling effect, incoherent transport in the junctions proves to have different activation energies, depending on the photoswitchable molecular energy levels of two different conformations. These results improve fundamental understanding of charge transport mechanisms in molecular junctions and should lead to the rapid development of functional molecular devices toward practical applications.



 ${\bf S}$ ince its very beginning,¹ molecular electronics has aroused considerable interest of researchers with different backgrounds, as it provides the potential of constructing and implementing integrated and multifunctional molecular devices.^{2–7} On the other hand, the exploration of molecular electronics is of great scientific importance, as it serves as a unique platform to reveal the intrinsic properties of molecules at the single-molecule level^{8–12} and thus offers many opportunities to discover novel phenomena which do not exist in bulk materials.^{13–15} Therefore, it is crucially important to investigate the charge transport processes in molecular junctions, which is essential to both fundamental understanding of the working mechanisms and the realization of various functions in molecular devices.

In general, one of the most critical factors influencing charge transport in molecular junctions is the inherent characteristics of molecular orbital energy levels.^{16,17} To tune the molecular energy levels, the most effective strategy is to change the molecular orbital structures with rational chemical designs^{10,18,19} or external stimuli.²⁰ In this regard, photochromic molecules, especially diarylethene molecules, are particularly attractive because when exposed to the light with specific wavelengths, they undergo a reversible conformational

transition, thus leading to the change of molecular orbital energy levels.^{21,22} On the basis of this fact, several experimental approaches have been developed to reveal their different conductance charecteristics.^{23–26} However, up to now, the investigation of temperature-dependent charge transport through these photochromic molecules has not been reported.

In a previous report,²⁷ we experimentally and theoretically demonstrated a fully reversible photoswitching effect between two conductive states, which are stable at room temperature, based on graphene-diarylethene single-molecule junctions (GD-SMJs). Under visible and UV light irradiations, the diarylethene bridges covalently sandwiched between graphene electrodes undergo a transition between two distinct isomers (open/closed forms) (Figure 1a), along with a change of the corresponding molecular orbital energy levels. Therefore, with light-tunable molecular energy levels, a GD-SMJ is an ideal platform for exploring the charge transport process in molecular junctions. In this study, on the basis of such GD-SMJs, we reveal the charge transport mechanism that is

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Figure 1. GD-SJMs with reversible photoswitching characteristics. (a) Schematic of reversible photoswitching of GD-SMJs. (b,c) I-V characteristics and dI/dV spectra of a GD-SMJ in open (b) and closed (c) forms at the temperature of 3.5 K. $V_{\rm G} = 0$ V.

dependent on both temperature and molecular energy levels in molecular junctions.

The procedure to fabricate GD-SMIs was described in a previous report.²⁸ As shown in Figure S2, individual diarylethene molecules were successfully assembled in nanogapped graphene electrodes. When alternately exposed to visible (Vis) and ultraviolet (UV) light, these diarylethene bridges showed reversible conformational changes between open and closed forms, and thus corresponding switching in two distinct (low and high) conductance states (Figure S3). Current-voltage (I-V) characteristics of the junctions in both open and closed forms were further measured at 3.5 K (black lines in Figures 1b,c), where the source electrode was grounded and the sweeping bias voltages were applied to the drain electrode. The differential conductance dI/dV spectra (blue lines in Figures 1b,c) clearly indicate that the diarylethene molecule in open and closed forms have the different energy level alignments. In contrast to the closed form, there is no obvious peak in the dI/dV spectrum of the open form, which is consistent with the calculated transmission spectra (Figure S8). By combining the transmission spectra with the projected molecular orbit analysis (Figures S7 and S8), it is also found that the perturbed highest occupied molecular orbit (p-HOMO) and the perturbed lowest unoccupied molecular orbital (p-LUMO) energies of the closed form are much closer to the Fermi level of graphene electrodes than those of the open form, resulting in greater conductance of the closed one.

Temperature variation is a useful tool to investigate the charge transport properties in molecular electronics as different systems show different conductance characteristics in response to variable temperatures.^{6,29} With liquid nitrogen/helium cooling and a heating stage to accurately control the variable testing temperature, temperature-dependent electrical measurements of the junctions with open and closed forms were carried out in vacuum in the dark. Representative sets of I-V characteristics for a GD-SMJ in both open and closed forms were measured at temperatures varying from 3.5 to 300 K over a \pm 1 V bias range (Figures 2a,b). The conductance of the



Figure 2. Temperature-dependent charge transport characteristics. (a,b) I-V curves of a GD-SMJ in open (a) and closed (b) forms at different temperatures. (c,d) Arrhenius plots of ln (I_D) versus 1/T for open (c) and closed (d) forms at different positive bias voltages.



Figure 3. Mechanistic analysis for the temperature-dependent charge transport transition in a closed junction. (a) Schematic of the charge transport mechanism transition under different bias voltages. (c) Calculated infrared and Raman spectra of the closed diarylethene molecule. The peaks at $41.7-62.6 \text{ cm}^{-1}$ correspond to the twisting vibration of side benzene groups. (d) Activated vibration modes of the molecule at ~90 K. (e) Potential energy diagram for the molecule transforming between three stable conformational states (State 1, State 2, and State 3) with the corresponding transition states (T-State 1 and T-State 2). The simplified configurations for each state are given out with pivotal dihedral angles marked out. (f) dI/dV spectra for the junction at 60 and 120 K. (g) Calculated transmission spectroscopies of the junction with an average contribution of three stable states (S-State) and two transition states (T-State 2).

diarylethene in both forms remained constant at low temperatures (<90 K) and increased when the temperature was higher than 90 K. More importantly, the Arrhenius plots (Figure 2c and Figure S9a for the open form; Figure 2d and Figure S9b for the closed form) clearly shows a transition of transport behaviors at ~90 K. This transition might be from a temperature-independent coherent tunneling at low temperatures to a thermally activated incoherent transport at high temperatures (Figure 3a).³⁰

To figure out such a temperature-dependent charge transport mechanism, we investigated the crossover temperatures of the charge transport transition under different bias voltages for the junctions. By taking a deep analysis of the closed-form case, we found that the subtle crossover temperature is independent of the bias voltage and fluctuates in a range of 80-110 K (Figure 3b). The calculated IR and Raman spectra (Figure 3c) show apparent vibration peaks at 41.7-62.6 cm⁻¹, which include a twisting vibration mode of phenyl rings at each side of the molecule (Figure 3d). The energy of this vibration mode is very close to the thermal energy of the critical temperature (~90 K). Therefore, the twisting vibration can be thermally activated at this temperature. In addition, the diarylethene molecule is

predicted to have three distinct metastable conformations (State 1, State 2, and State 3), as well as two transition states (T-State 1 and T-State 2), with a barrier of \sim 5 kJ/mol (Figure 3e and Figure S11). At low temperatures, the molecule is blocked in one of the metastable conformations. When the temperature is beyond \sim 90 K, the thermal energy is enough to excite the torsional vibration of the phenyl ring at each side of the molecule, which has a particular probability of accumulating enough energy to twist the phenyl ring, and across the transition states, thus providing additional conducting channels for increasing the junction conductance.

The dI/dV spectra for the charge transport mechanism transition of a junction before (60 K) and after (120 K) (Figure 3f) show that the main conducting peak at 0.2–0.5 V shifts to the low bias voltage, and an extra conducting peak at around 0.3 V appears at high temperature. In addition, from transition voltage spectroscopies (TVSs) of the junction before and after the transport mechanism transition (Figure S12), the smaller inflection values for 120 K are observed. As the inflection point in TVSs means the trail of the conducting channel that enters the bias window,³¹ the main conducting orbitals at high temperatures are closer to the Fermi level than those at low



Figure 4. Energy level-dependent charge transport mechanism transition. (a) Different charge transport situations for open and closed junctions. (b) Bias-dependent activation energies for thermally activated transport through open and closed junctions. (c,d) Bias-dependent transmission spectra for open (c) and closed (d) junctions.

temperatures. This movement of the conducting channel can be explained by the broadening of its tail state due to the electron-vibration coupling. Another possible reason is related to the conversion among three distinct metastable conformations (States 1-3 and Figure 3d). The energy barriers for conversion among metastable structures are 5-6 kJ/mol, which corresponds to a jumping of the conversion rate at \sim 90 K. The calculated transmission spectroscopy for a junction in the closed form with an average contribution of three stable states (S-State) and two transition states (T-State), demonstrates that p-HOMO of the diarylethene molecule with the flatter structure shifts closer to the Fermi level of the system (Figure 3g). However, no apparent conductance switching that proves the conformational change among metastable states has been found. Therefore, the transition from coherent tunneling at low temperatures to incoherent transport at high temperatures should be attributed to electron-vibration coupling, which offers thermally activated additional conducting channels and facilitates charge transport through the junction. In addition, as similar thermally activated vibrations at ~ 90 K (Figure S13) and varied conducting energy levels at different temperatures (Figure S14) were observed for the open junction; this explanation also works well for the open form.

More fundamentally, the charge transport mechanism of molecular junctions is mainly determined by the time that a charge spends in the junction, referred to as the traversal time τ .^{30,32} For both open and closed junctions, p-HOMO is the dominated molecular orbital contributing to the conduction. In the open form, p-HOMO of the molecule is located at more than one electronvolt below the Fermi level of the electrode (Figure S8a). In the sweeping bias range, p-HOMO is always outside the bias window, thus nonresonant tunneling takes place in the junction (left of Figure 4a). During such nonresonant tunneling, the traversal time τ is mainly

determined by the injection gap ΔE , which is the energy difference between the electrode's Fermi level and the energy levels of the conducting molecular orbital (p-HOMO or p-LUMO). The traversal time obtained in the deep tunneling limit for a square barrier of energy height ΔE and width D is $\tau = D\sqrt{m/2\Delta E}$, where *m* is the electron mass.³² In the closed form, p-HOMO is close to the Fermi level, which comes into the bias window and leads to resonant tunneling (right of Figure 4a). During resonant tunneling, a measure of this time scale τ is $\tau = \hbar/\Gamma$, where Γ is the width of the molecular orbital resonance due to the electrode coupling. The scale \hbar/Γ can also be viewed as the lifetime of an electron escaping into the electrodes. To cover both nonresonant and resonant tunneling situations, a unified expression $\tau = \hbar/(\sqrt{\Delta E^2 + \Gamma^2})$ can be used as an estimate of the traversal time. When proceeding through a molecule, the electron can exchange energy by exciting the vibrational modes of the molecule. Such electronphonon interaction is usually quantified with M, the vibronic coupling. At low temperatures, the weak electron-phonon coupling, $|M/\sqrt{\Delta E^2} + (\Gamma/2)^2| \ll 1$, leads to coherent tunneling in the junction. At high temperatures, M, which is also related to the vector of nuclear coordinates and the molecular primary normal mode,³⁰ becomes strong as the molecule can access more configurations with increasing the temperature. In addition, because of thermal broadening of the electronic energies of both the electrodes and the molecule,³³ ΔE becomes small at high temperatures. Therefore, strong electron-vibration coupling takes place at high temperatures and makes the electronic motion completely incoherent, which can be described by a successive classical rate process.

The electron-vibration coupling strength in the junction can be evaluated by the activation energy E_a for thermally activated charge transport.³⁰ Through calculation with the equation $E_a =$

-(1/k) [d ln(1)/d ln(1/T)],²⁹ the activation energy for the open form is found to gradually increase from \sim 3 meV to \sim 7 meV when the bias moves positively forward (blue line in Figure 4b). By contrast, for the closed form, the activation energy fluctuates around a certain value about ~7.5 meV (brown in Figure 4b). Such changing tendencies of the activation energies are consistent with the corresponding crossover temperatures of the charge transport mechanism transition, as the crossover temperature gradually increases from 60 to 100 K for the open form (Figure S10) and fluctuates around ~100 K for the closed form (Figure 3b). This illustrates that the thermal energy needed for activating incoherent transport is associated with the activation energy, which further confirms the thermally activated transport mechanism of the junction. From the bias-dependent transmission spectra for the open form with nonresonant tunneling (Figure 4c), it can be observed that, during bias sweeping, the bias-induced energy level shift of p-HOMO is too small in contrast to the change of the bias window. For the positive bias range, as the bias becomes large, p-HOMO is closer to the bias window, and ΔE becomes smaller. The electron traversal time τ , which is inversely proportional to ΔE , becomes larger, thus inducing the increase of the activation energy. For the closed form, p-HOMO comes into the bias window during the bias sweeping (Figure 4d), which is a resonant situation. As previously mentioned, the electron traversal time τ is determined by the molecule-electrode interface coupling Γ , which is equal to the full width at half-maximum (FWHM) of the transmission peak. Although the transmission peak of p-HOMO shifts under different biases, the FWHM changes little. Therefore, the electron traversal time τ remains almost constant, resulting in the fluctuation of the activation energy at around 7.5 meV.

In summary, we fully revealed the temperature-dependent charge transport mechanism in graphene-diarylethene singlemolecule junctions, which have the capability of photomodulating their molecular orbital energy levels due to the reversible isomerization between open and closed conformations of individual diarylethenes that are immobilized into nanogapped graphene electrodes. The junctions in both forms exhibit the transition from coherent tunneling at low temperatures to incoherent transport at high temperatures, which is ascribed to the thermally activated torsion of the phenyl ring at each side of the molecule, thus leading to the increase of the vibronic coupling and providing additional conductance channels. Because of the subtle electron-phonon coupling effect, which is related to the energy difference between the electrode Fermi level and the dominant transport molecular orbital energy level, the activation energies of incoherent transport for the junction in open and closed forms show different bias-dependent changing tendencies. Such fundamental understanding of the structure-function relationship at the molecular level offers new design insights into developing novel types of molecule-based devices with desired functions.

ASSOCIATED CONTENT

Supporting Information

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Experimental details, theoretical calculations, and supporting figures and analysis (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Aviram, A.; Ratner, M. A. Molecular Rectifiers. *Chem. Phys. Lett.* **1974**, 29, 277–283.

(2) Lörtscher, E. Wiring Molecules into Circuits. Nat. Nanotechnol. 2013, 8, 381–384.

(3) Xiang, D.; Wang, X.; Jia, C.; Lee, T.; Guo, X. Molecular-Scale Electronics: from Concept to Function. *Chem. Rev.* **2016**, *116*, 4318–4440.

(4) Perrin, M. L.; Frisenda, R.; Koole, M.; Seldenthuis, J. S.; Celis Gil, J. A.; Valkenier, H.; Hummelen, J. C.; Renaud, N.; Grozema, F. C.; Thijssen, J. M.; Dulić, D.; van der Zant, H. S. J. Large Negative Differential Conductance in Single-Molecule Break Junctions. *Nat. Nanotechnol.* **2014**, *9*, 830–834.

(5) Capozzi, B.; Xia, J.; Adak, O.; Dell, E. J.; Liu, Z.; Taylor, J. C.; Neaton, J. B.; Campos, L. M.; Venkataraman, L. Single-Molecule Diodes with High Rectification Ratios through Environmental Control. *Nat. Nanotechnol.* **2015**, *10*, 522–527.

(6) Reddy, P.; Jang, S. Y.; Segalman, R. A.; Majumdar, A. Thermoelectricity in Molecular Junctions. *Science* **2007**, *315*, 1568–1571.

(7) Bogani, L.; Wernsdorfer, W. Molecular Spintronics Using Single-Molecule Magnets. *Nat. Mater.* **2008**, *7*, 179–186.

(8) Vazquez, H.; Skouta, R.; Schneebeli, S.; Kamenetska, M.; Breslow, R.; Venkataraman, L.; Hybertsen, M. S. Probing the Conductance Superposition Law in Single-Molecule Circuits with Parallel Paths. *Nat. Nanotechnol.* **2012**, *7*, 663–667.

(9) Park, J.; Pasupathy, A. N.; Goldsmith, J. I.; Chang, C.; Yaish, Y.; Petta, J. R.; Rinkoski, M.; Sethna, J. P.; Abruña, H. D.; McEuen, P. L.; Ralph, D. C. Coulomb Blockade and the Kondo Effect in Single-Atom Transistors. *Nature* **2002**, *417*, 722–725.

(10) Dell, E. J.; Capozzi, B.; Xia, J. L.; Venkataraman, L.; Campos, L. M. Molecular Length Dictates the Nature of Charge Carriers in Single-Molecule Junctions of Oxidized Oligothiophenes. *Nat. Chem.* **2015**, *7*, 209–214.

(11) Warner, B.; El Hallak, F.; Pruser, H.; Sharp, J.; Persson, M.; Fisher, A. J.; Hirjibehedin, C. F. Tunable Magnetoresistance in an Asymmetrically Coupled Single-Molecule Junction. *Nat. Nanotechnol.* **2015**, *10*, 259–263.

(12) Jia, C.; Ma, B.; Xin, N.; Guo, X. Carbon Electrode-molecule Junctions: a Reliable Platform for Molecular Electronics. *Acc. Chem. Res.* **2015**, *48*, 2565–2575.

(13) Thiele, S.; Balestro, F.; Ballou, R.; Klyatskaya, S.; Ruben, M.; Wernsdorfer, W. Electrically Driven Nuclear Spin Resonance in Single-Molecule Magnets. *Science* **2014**, *344*, 1135–1138.

(14) Perrin, M. L.; Verzijl, C. J. O.; Martin, C. A.; Shaikh, A. J.; Eelkema, R.; van Esch, J. H.; van Ruitenbeek, J. M.; Thijssen, J. M.; van der Zant, H. S. J.; Dulic, D. Large Tunable Image-Charge Effects in Single-Molecule Junctions. *Nat. Nanotechnol.* **2013**, *8*, 282–287.

(15) Su, T. A.; Li, H. X.; Steigerwald, M. L.; Venkataraman, L.; Nuckolls, C. Stereoelectronic Switching in Single-Molecule Junctions. *Nat. Chem.* **2015**, *7*, 215–220.

(16) Jia, C.; Guo, X. Molecule-Electrode Interfaces in Molecular Electronic Devices. *Chem. Soc. Rev.* **2013**, *42*, 5642–5660.

(17) Moth-Poulsen, K.; Bjornholm, T. Molecular Electronics with Single Molecules in Solid-State Devices. *Nat. Nanotechnol.* 2009, 4, 551–556.

(18) Choi, S. H.; Kim, B.; Frisbie, C. D. Electrical Resistance of Long Conjugated Molecular Wires. *Science* **2008**, 320, 1482–1486.

(19) Lo, W. Y.; Bi, W.; Li, L.; Jung, I. H.; Yu, L. Edge-on Gating Effect in Molecular Wires. *Nano Lett.* **2015**, *15*, 958–962.

(20) Kim, W. Y.; Kim, K. S. Tuning Molecular Orbitals in Molecular Electronics and Spintronics. *Acc. Chem. Res.* **2010**, *43*, 111–120.

(21) Li, J.; Speyer, G.; Sankey, O. F. Conduction Switching of Photochromic Molecules. *Phys. Rev. Lett.* **2004**, *93*, 248302.

(22) Jia, C.; Wang, J.; Yao, C.; Cao, Y.; Zhong, Y.; Liu, Z.; Liu, Z.; Guo, X. Conductance Switching and Mechanisms in Single-Molecule Junctions. *Angew. Chem., Int. Ed.* **2013**, *52*, 8666–8670.

(23) van der Molen, S. J.; Liao, J.; Kudernac, T.; Agustsson, J. S.; Bernard, L.; Calame, M.; van Wees, B. J.; Feringa, B. L.; Schönenberger, C. Light-Controlled Conductance Switching of Ordered Metal-Molecule-Metal Devices. *Nano Lett.* **2009**, *9*, 76–80.

(24) Tam, E. S.; Parks, J. J.; Shum, W. W.; Zhong, Y.; Santiago-Berríos, M. B.; Zheng, X.; Yang, W.; Chan, G. K.-L.; Abruña, H. D.; Ralph, D. C. Single-Molecule Conductance of Pyridine-Terminated Dithienylethene Switch Molecules. *ACS Nano* **2011**, *5*, 5115–5123.

(25) Kim, Y.; Hellmuth, T. J.; Sysoiev, D.; Pauly, F.; Pietsch, T.; Wolf, J.; Erbe, A.; Huhn, T.; Groth, U.; Steiner, U. E.; Scheer, E. Charge Transport Characteristics of Diarylethene Photoswitching Single-Molecule Junctions. *Nano Lett.* **2012**, *12*, 3736–3742.

(26) He, J.; Chen, F.; Liddell, P. A.; Andréasson, J.; Straight, S. D.; Gust, D.; Moore, T. A.; Moore, A. L.; Li, J.; Sankey, O. F.; Lindsay, S. M. Switching of a Photochromic Molecule on Gold Electrodes: Single-Molecule Measurements. *Nanotechnology* **2005**, *16*, 695–702.

(27) Jia, C.; Migliore, A.; Xin, N.; Huang, S.; Wang, J.; Yang, Q.; Wang, S.; Chen, H.; Wang, D.; Feng, B.; Liu, Z.; Zhang, G.; Qu, D. H.; Tian, H.; Ratner, M. A.; Xu, H. Q.; Nitzan, A.; Guo, X. Covalently Bonded Single-Molecule Junctions with Stable and Reversible Photoswitched Conductivity. *Science* **2016**, *352*, 1443–1445.

(28) Cao, Y.; Dong, S.; Liu, S.; He, L.; Gan, L.; Yu, X.; Steigerwald, M. L.; Wu, X.; Liu, Z.; Guo, X. Building High-Throughput Molecular Junctions Using Indented Graphene Point Contacts. *Angew. Chem., Int. Ed.* **2012**, *51*, 12228–12232.

(29) Selzer, Y.; Cabassi, M. A.; Mayer, T. S.; Allara, D. L. Thermally Activated Conduction in Molecular Junctions. *J. Am. Chem. Soc.* **2004**, *126*, 4052–4053.

(30) Galperin, M.; Ratner, M. A.; Nitzan, A. Molecular Transport Junctions: Vibrational Effects. J. Phys.: Condens. Matter 2007, 19, 103201.

(31) Araidai, M.; Tsukada, M. Theoretical Calculations of Electron Transport in Molecular Junctions: Inflection Behavior in Fowler-Nordheim Plot and Its Origin. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2010**, *81*, 235114.

(32) Galperin, M.; Ratner, M. A.; Nitzan, A.; Troisi, A. Nuclear Coupling and Polarization in Molecular Transport Junctions: Beyond Tunneling to Function. *Science* **2008**, *319*, 1056–1060.

(33) Poot, M.; Osorio, E.; O'Neill, K.; Thijssen, J. M.; Vanmaekelbergh, D.; van Walree, C. A.; Jenneskens, L. W.; van der Zant, H. S. J. Temperature Dependence of Three-Terminal Molecular Junctions with Sulfur End-Functionalized Tercyclohexylidenes. *Nano Lett.* **2006**, *6*, 1031–1035.