

# Control of Unipolar/Ambipolar Transport in Single-Molecule Transistors through Interface Engineering

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To realize single-molecule field-effect transistors, a crucial test for evaluating the integrity of single-molecule electronics into conventional circuit architectures, remains elusive. Though interfacial effect is widely accepted to be crucially important in electronic devices, rare reports have studied fine control of the interface in single-molecule transistors. Through molecular engineering, different numbers of methylene groups are incorporated between the diketopyrrolopyrrole (DPP) kernel and anchor groups (AMn-DPP, n = 0-3), and how the molecule-electrode interface affects the performance of single-molecule transistors is investigated. Both experimental and theoretical data demonstrate that p-type charge transport dominates in AM0-DPP and AM1-DPP single-molecule transistors, while AM2-DPP and AM3-DPP systems exhibit ambipolar field-effect behaviors, which is attributed to the HOMO-pinning effect in AM0-DPP and AM1-DPP molecular junctions. Theoretical calculations show that the parity of the methylene number results in two different connection symmetries between the DPP kernel and graphene electrodes, and thus different electronic interactions, leading to different relative molecular energy-level alignments form those of isolated molecules, which has never been reported before. These results provide crucial information for precise control of the interfaces in molecular junctions, new insight into building multifunctional graphene-organic hybrid electronic devices, and the design of functional organic materials.

interest among scientists and witnessed tremendous advances in different directions, reflecting the interdisciplinarity.<sup>[3]</sup> To realize its ultimate goal, the implement of a single-molecule field-effect transistor (FET) is widely considered to be a crucial step.<sup>[3,4]</sup> In single-molecule FETs, the current through a single molecule sandwiched between source and drain electrodes is regulated by applying the voltage on a proximal gate electrode.<sup>[5–6]</sup> This has been achieved in solid back gate configuration, which is used in electromigrated molecular junctions<sup>[7]</sup> and mechanically controllable break junctions (MCBJ),<sup>[8]</sup> as well as the electrochemical gate used tunneling microscope scanning in (STM) break junctions<sup>[9]</sup> and MCBIs.<sup>[10]</sup> In addition to realizing field-induced effects, these molecule-based nanocircuits promise the broad accessibility to the exploration of fundamental quantum transport and intrinsic properties of single molecules.[11-20]

Different from bulky semiconducting FETs, where the current results from the gate-induced carrier density, the current change in single-molecule transistors originates from energy shifts of the molecular transport level

# 1. Introduction

Urged by the physical limitation of current silicon-based electronic devices,<sup>[1,2]</sup> single-molecule electronics has arouse great

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relative to the electrode Fermi level, which are induced by the electrostatic potential of the connected molecule through gate control. To realize efficient gate voltage modulation, several Dr. Y.-P. Zhang, Prof. H.-L. Zhang

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basic factors need to be taken into consideration. 1) For molecules without permanent dipole moments, the high polarizability is critically important to induce the strong Stark effect and thus drastic changes in molecular energy levels.<sup>[21,22]</sup> 2) The molecule-electrode interface coupling strength should be moderate.<sup>[23,24]</sup> If strong, the energy levels in the molecule-which are relatively narrow in the weak coupling case or in isolated molecules in the gas phase-become significantly broadened. As a result, electrons effectively move from source to drain (or in the opposite direction) without interacting with the connected molecule, and the current becomes relatively independent on gate voltages. 3) The molecular length should be comparable to or larger than the thickness of gate dielectric so that the gate field can efficiently modulate the transport capability of carriers in the channel, potentially avoiding the short channel effect.<sup>[25-27]</sup> Until now, most discussions in these considerations are based on theoretical calculations and systematic experimental investigations are in great demand.

In the present work, we focused the study on how the molecule–source/drain electrode interface affects the gatecontrolled charge transport behavior based on a series of diketopyrrolopyrrole (DPP)-based single-molecule FETs with ionic liquid gating on the platform of graphene–molecule–graphene single-molecule junctions (GMG-SMJs) (**Figure 1**a). This graphene–molecule–graphene single-molecule transistors with ionic liquid as gate dielectric was previously developed by our group,<sup>[27]</sup> which provides a reliable strategy to modulate charge transport and promises the utilization of exploring gate-dependent quantum transport and novel physical phenomena of single molecules at cryo-genic temperatures. DPP derivatives, as classic organic dyes, have been widely used in constructing semiconductor electronic devices, such as organic FETs,<sup>[28]</sup> solar cells,<sup>[29]</sup> and



**Figure 1.** Device and molecular structures. a) Schematic illustration of GMG-SMJs with ionic liquids as gate dielectric. b) Molecular structures of AMn-DPP (n = 0-3) terminated with amines on both ends as anchoring groups.



organic light-emitting diodes.<sup>[30]</sup> They are structurally based on 2,5-dihydripyrrolo[4,3-c]pyrrolo-1,4-dione with aromatic substituents at the 3 and 6 positions (in the vast majority of situations). As shown in Figure 1b, we chose thiophene to substitute the 3 and 6 positions of the bicyclic dilactam unit due to two specific considerations as follows: 1) Because the  $\pi$ -conjugated bicyclic dilactam moiety is electron-withdrawing and thiophene is electron-donating, electron transfer occurs from thiophene to the bicyclic dilactam moiety; 2) In comparison with the phenyl substitution, where the dihedral angle between the bicyclic dilactam moiety and the phenyl ring is  $\approx 12^{\circ}$ , the smaller thiophene unit with only one  $\alpha$ -hydrogen atom can orient in a nearly coplanar fashion with favorable intramolecular sulphur-oxygen interactions. Both factors contribute to enhancing the polarizability of the DPP molecular kernel, which is prerequisite for achieving efficient gate modulation. Four DPP molecules featuring different numbers of methylene groups between the molecular kernel and amine anchoring group on each side (AMn-DPP, n = 0-3) were designed and synthesized (Figure 1b). This design is important because the insertion of methylene groups proved to be an efficient strategy to gradually weaken molecule-source/ drain electrode electronic coupling by cutting off  $\pi$ -electron delocalization as well as to maintain the strong mechanical contact stability.<sup>[14,31-33]</sup> However, few attempts have been made to regulate interfacial coupling in single-molecule transistors by using this method. To initiate obvious field-induced effects, *N*,*N*-diethyl-N-(2-methoxyethyl)-N-methylammonium bis-(trifluoromethylsulfonyl)-imide (DEME-TFSI) (detailed structures in Figure S1, Supporting Information) was chosen because the similar size of positive and negative ions (≈7.5 Å) can keep the symmetric electric double layer (EDL) under opposite gate voltages. More importantly, the geometrical EDL is  $\approx$ 7.5 Å thick, much less than the molecular length in the range of  $\approx$ 22.5–29.6 Å, thus providing a strong electric field to modulate charge transport through individual molecules.[34,35]

## 2. Results and Discussion

#### 2.1. Design and Fabrication of GMG-SMJs

The synthetic procedure of AMn-DPPs was detailed in the Supporting Information. High-quality single-layer graphene was grown on copper foils through a chemical vapor deposition process, following which graphene films were transferred to the silicon wafer with a 300 nm silicon oxide layer. The source/ drain metal electrode arrays (60 nm Au/8 nm Cr) were patterned by photolithography and thermal evaporation, followed by electron beam evaporation of 30 nm thick SiO<sub>2</sub> to minimize the leakage current between source/drain and gate. The gate electrodes (60 nm Pt/8 nm Cr) were patterned by photolithography and electron beam evaporation. Nanogapped graphene point contacts were fabricated through a dash-line lithographic method described in detail elsewhere.<sup>[36]</sup> Individual AMn-DPPs were connected with graphene electrodes through covalent amide bonds to form stable single-molecule junctions (Figures S2-S6, Supporting Information), by employing a





1-ethy-3(3-dimethylaminopropyl) carbodiimide coupling protocol in pyridine. After 2 d in dark and argon atmosphere, the devices were taken out from the solution and cleaned sequentially by ultrapure water and acetone, then dried by nitrogen gas. After that, a small droplet of DEME-TFSI was placed to cover the array of graphene-based molecular junctions and gate electrodes (Figure S8, Supporting Information).

From the ultraviolet-visible (UV-Vis) absorption spectroscopies and calculated energy diagrams (Figure 2a,b), we found



**Figure 2.** Frontier orbital characteristics of isolated AMn-DPPs. a) Normalized UV–vis absorption spectra for all four molecules. b) Calculated molecular orbital energy levels of isolated molecules and the graphene Fermi level deduced from experimental results. c) Density of scattering state distribution for HOMO (left panel) and LUMO (right panel) of AMn-DPPs.

that changing the number of methylene groups between the functional DPP center and terminal amine groups had a negligible effect on the energy gap of AMn-DPPs. However, the energy levels of frontier molecular orbitals (FMOs) shifted downwards from AM0-DPP to AM2-DPP, and were almost the same for AM2-DPP and AM3-DPP. As shown in the calculated molecular orbital diagrams (Figure 2c, for isolated molecules), the orbital density of states (DOS) at the N sites of the terminal  $NH_2$  group drastically decreased with the number of methylene groups changing from 0 to 2, and revealed no obvious change in the situation of AM2-DPP and AM3-DPP.

#### 2.2. Zero-Bias Transmission Spectroscopies

We analyzed the theoretically calculated zero-bias transmission function for four single-molecule junctions (Figure 3), where the information in two aspects was provided. In one aspect, we extracted the full width at half maximum of the HOMO resonance ( $\Gamma_{\rm H}$ ) and LUMO resonance ( $\Gamma_{\rm I}$ ), which is in positive correlation with the strength of molecule-electrode coupling. As shown in Table S1 (Supporting Information), the interface coupling becomes weaker from AM0-DPP to AM3-DPP and two methylene groups between the functional DPP center and the terminal amine group are enough to minimize the interface coupling between AMn-DPPs and graphene electrodes, which are in accordance with the corresponding calculated frontier molecular orbitals. Note that the electronic properties of both the functional units and the electrodes, as well as the anchor groups, should be taken into consideration when choosing the number of methylene groups to control the interface coupling, thus resulting in variation of the methylene number among different systems.<sup>[37-39]</sup> In the second aspect, we found that the relative HOMO and LUMO resonance alignment among four single-molecule junctions displayed an odd-even effect. This finding is similar to previous reports, where the structural odd-even behaviors led to electronic odd-even effects in either ferrocene-electrode coupling[38] or molecular rectification<sup>[40]</sup> of ferrocenyl-alkanethiolate self-assembled monolayers. While odd-even conductance variation was previously observed in carbon atomic wires<sup>[41]</sup> and n-alkanes<sup>[42]</sup> when the length of the transport junction was increased, here the odd-even effect is regarding to the FMO alignment going from AM0-DPP to



**Figure 3.** Calculated zero-bias transmission spectroscopies for AMn-DPPs molecular junctions without gate.



AM3-DPP. When attached to graphene electrodes, the FMO energy levels of AM1-DPP and AM3-DPP moved higher while those of AM0-DPP and AM2-DPP are lower. These FMO relative alignments are different from those of isolated molecules in the gas phase (Figure 2b). As shown in Figure S9 (Supporting Information), the parity of methylene number in AMn-DPPs gives rise to two symmetries for AMn-DPP-based single-molecule junction where methylene and amide play a role as the linker between the functional DPP center and graphene electrodes: C2 symmetry (even methylene number) and C<sub>i</sub> symmetry (odd methylene number). In addition, Table S2 (Supporting Information) summarizes the calculated energy levels of the HOMO for AMn-DPP where hydrogen atom at both ends run away in order to be attached to graphene electrodes as well as their charge changes after the connection process. Distinctly, the frontier molecular orbitals of AMn-DPP are renormalized after removing the hydrogen atoms at the end. The renormalized HOMO energy levels of AM1-DPP and AM3-DPP moved higher relative to those of AM0-DPP and AM2-DPP, which dominates the level alignment between AMn-DPP and electrodes (Figures S10-S13, Supporting Information). Therefore, the different symmetries and orbital renormalizations induced by the parity of methylene number caused the odd-even effect found in HOMO and LUMO resonance alignment of AMn-DPPs with graphene electrodes.

During the calculation of the zero-bias transmission spectroscopies for single-molecule junctions based on AM0-DPP and AM1-DPP, we noticed that there existed HOMO-level pinning effect. Figure 2b plots the energy level alignment of isolated AMn-DPPs and p-doped graphene electrodes. Clearly, the HOMOs of AM0-DPP and AM1-DPP align higher than the graphene Fermi level. When AM0-DPP and AM1-DPP were attached with p-doped graphene, graphene electrodes served as a reservoir for electrons and therefore pinned the HOMO level. Therefore, the FMO resonance of AM0-DPP and AM1-DPPbased single-molecule junctions aligned much closer to the graphene Fermi level than that of AM2-DPP and AM3-DPP-based single-molecule junctions. These can be clearly verified by charge distribution of AMn-DPP-based single-molecule junctions in the real space (Figure S14, Supporting Information) and the FMO resonance results of AMn-DPPs with intrinsic graphene (Figure S15, Supporting Information). All the above information lays a solid foundation for the investigation of how the charge transport behavior changes in these four single-molecule junctions upon a gate field effect.

#### 2.3. Gate-Controlled Charge Transport Behaviors

We measured the current–voltage  $(I_D-V_D)$  characteristics of these four AMn-DPP-based single-molecule junctions with gate voltages changing from –1.5 to 1.5 V. As shown in **Figure 4**, the gate electric field can effectively modulate the  $I_D-V_D$  characteristics. The gate voltage-dependent charge transport behavior can be generally classified into two types. For AM0-DPP- and AM1-DPP-based single-molecule junctions, the conductance decreased monotonically as the gate voltage changed from –1.5 to 1.5 V, which indicates p-type unipolar field-effect behavior. For AM2-DPP- and AM3-DPP-based single-molecule junctions,



interestingly there existed ambipolar characteristics: the conductance was the lowest at zero gate voltage, and then enhanced monotonically when the applied gate voltage increased in the absolute value of both positive and negative ranges, respectively. In this case, we speculate that the transporting charge changed from hole to electron around zero gate voltage when the applied gate swept from negative to positive.

As the conductance characteristics of these four single-molecule junctions behaved in the similar tendency when the gate voltage was negative, this provided a chance to analyze how the interface coupling strength affected the effectiveness of gate control. We calculated the current ratios between its maximum and minimum values (when gate voltage is -1.5 and 0 V, respectively) at  $\pm 0.5$  V bias, for each AMn-DPP-based single-molecule junctions. As summarized in Table S3 (Supporting Information), the current ratios increased from AM1-DPP to AM3-DPP, which is consistent with previous reports that the weaker the interface coupling, the more effective of gate modulation. Note that the current ratios for AM0-DPP and AM1-DPP were close, which might originate from the HOMO-pinning effect.

To rule out potential artifacts, we also measured the gate voltage-dependent conductance characteristics of graphene ribbons with the similar device structure (Figure S16, Supporting Information), which were totally different from those of singlemolecule devices. The transfer curve revealed that the graphene was p-doped due to the wet transfer process during the device fabrication procedure. What is more, the conductance of the graphene ribbon (even at Dirac point) was much larger than that of single-molecule junctions. Therefore, the gate-controlled conductance characteristics of AMn-DPP single-molecule junctions should entirely result from the molecules.

#### 2.4 Mechanism Analyses of Gate Modulation

To understand the gate-controlled conductance characteristics, we need to consider how the relative alignment of the FMO energy levels and Fermi level of graphene electrodes changes upon the gate electric field. Generally, a positive/negative gate voltage induces downshift/upshift of the FMO energy levels and upwards/downwards movement of the graphene Fermi level. In the case of GMG-SMJ systems, the FMO energy levels shift downwards and upwards relative to the Fermi level of graphene electrodes upon positive and negative gate fields, respectively. As shown in Figure 5, we simulated the effect of the gate electric field on charge transport of all these four AMn-DPP-based single-molecule junctions. Detailed description of theoretical methods and device models are shown in Figures S17-S20 (Supporting Information). The left panels show how the 0.2 V bias transmission spectroscopies of these four molecular junctions changed upon the positive and negative gate fields, respectively. The right panels show the calculated gate-dependent conductance characteristics for these four molecular junctions, which are consistent with experiment phenomena, especially for the positive bias side. For AM0-DPP- and AM1-DPP-based single-molecule junctions, the situation seems a little complex. When the gate voltage was negative, the perturbed-FMO (p-FMO) energy level changed little relative to the Fermi level of graphene electrode, due to

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**Figure 4.** Gate-controllable current characteristics in AMn-DPP-based single-molecule transistors. a)  $I_D$ – $V_D$  characteristics of AM0-DPP-based single-molecule junctions. b)  $I_D$ – $V_D$  characteristics of AM1-DPP-based single-molecule junctions. c,d)  $I_D$ – $V_D$  characteristics of AM2-DPP-based single-molecule junctions. e,f)  $I_D$ – $V_D$  characteristics of AM3-DPP-based single-molecule junctions. The gate voltage varied from –1.5 to 1.5 V.

HOMO-level pinning as previously discussed. When the gate voltage was positive, HOMO-level pinning disappeared and the p-FMO energy levels shifted downwards relative to the Fermi level of graphene electrodes. Even under the gate field of 1 V, the perturbed HOMO (p-HOMO) aligned closer to the graphene Fermi level than the perturbed LUMO (p-LUMO), and acted as the dominant role in charge transport. This is the reason why the conductance decreased monotonically

observed in the experiments. For AM2-DPP- and AM3-DPPbased single-molecule junctions, the graphene Fermi level aligned in the middle of p-HOMO and p-LUMO resonance at the equilibrium of zero gate voltage. Under positive/negative gate voltages, p-LUMO/p-HOMO moved toward the graphene Fermi level and thus the conductance increased. This led to the ambipolar conductance behavior with the turning point of around zero gate voltage.







**Figure 5.** Working mechanism of AMn-DPP-based single-molecule transistors. a,c,e,g) Effects of the gate electric field on the 0.2 V bias transmission spectroscopies for AMn-DPP-based single-molecule junctions. b,d,f,h) Simulated gate-dependent conductance behaviors for AMn-DPP-based single-molecule junctions.

In addition to the HOMO-pinning effect, it is obvious that the gate electric field can effectively tune the molecular energy levels, which proves the design rationality of the thiophene-substituted DPP functional center. The reason why the current on/off ratio is moderate should originate from the narrow HOMO–LUMO energy gap, which contributes to the relatively large off-state current. The different gate-controlled conductance characteristics between AM0-DPP/AM1-DPP-based and AM2-DPP/AM3-DPP-based single-molecule junctions mainly arise from the differences in energy level alignments between FMOs and graphene Fermi level at the equilibrium of zero gate voltage. This inspires us a novel structure of single-molecule transistors in which graphene electrodes and molecular energy levels can be controlled separately by different gate voltages. In this way, the alignment between the FMO and graphene Fermi level can be changed easily to minimize the off current, thus realizing various gate-controlled conductance characteristics in one kind of single-molecule junctions. In general, this idea provides new insight into building multifunctional graphene–organic hybrid electronic devices.

# 3. Conclusions

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This work demonstrated the capability of controlling the field-effect performance at the single-molecule level through holistic consideration of the choice of device architecture, the design of molecular materials and the control of interface coupling. Inserting methylene groups between the functional center and source/drain electrodes proves to be a universal method to weaken the interface electronic coupling in molecular junctions, thus improving the device performance. Molecular engineering proves to be a useful method to achieve highly effective gate control of molecular energy levels, where weak interface coupling and highly polarizable functional center are the key factors. The energy level alignment between the FMOs and electrode Fermi level and the interfacial contact structure (both geometric and electronic) are the two main influences that affect the performance of single-molecule transistors. For the AMn-DPP molecular systems (with small energy gap  $\approx 2.1$  eV), the gate control of HOMO-pinning/-unpinning effect is key to the unipolar field effect behavior. These systematic investigations promote deep mechanism understanding of single-molecule charge transport, thus offering crucial insights into designing and building future practical single-molecule devices and graphene-organic hybrid electronic devices. In addition, to choose the number of methylene group between conjugated functional groups should be an efficient way to tune the electronic interactions as well as relative energy alignment, which helps the design of functional organic materials.

# **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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# **Conflict of Interest**

The authors declare no conflict of interest.

## **Keywords**

ambipolar transport, diketopyrrolopyrrole, graphene, interface engineering, single-molecule transistors, unipolar transport

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