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# Multiple-channel and symmetry-breaking effects on molecular conductance *via* side substituents

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ABSTRACT Chemical substitution represents a pivotal method that enables effective modulation of molecular conductance and production of multiple transport channels, quantum interference effects, and other mechanisms. However, the intricate interplay that occurs between the molecular backbone and the side motifs remains largely unexplored. This study explores the conductance characteristics of molecular junctions that feature different  $\sigma$  and  $\pi$  side groups by using a synergistic approach that combines scanning tunneling microscope break junction experiments with the results of firstprinciples calculations. Our analysis shows that the incorporation of  $\sigma$ -side groups induces symmetry breaking in the frontier orbitals and increases intramolecular scattering, which then leads to reduced conductance. Conversely, the integration of  $\pi$ -side groups augments the molecular conductance through the multiple-channel effect, by which an additional  $\pi$  pathway is introduced for charge transport. The findings reported here provide valuable insights into both molecular functionalization and the future design of potential molecular electronic devices.

**Keywords:** side substituent, multiple-channel effect, symmetrybreaking effect, single-molecule junction

# INTRODUCTION

The extreme miniaturization of electronic components has inspired the development of molecular devices [1–3], which promise to revolutionize the electronics field and enable a wide range of applications to be realized with enhanced performance, functionality, and efficiency [4,5]. Over recent decades, significant strides have been made in the exploration of molecular electronic devices based on functional organic molecules, including rectifiers, switches [6,7], sensors, and other devices. The central concern over the commercial viability of these molecular devices lies in the device stability, integration, and effective modulation of the molecular conductance, and strategies including molecular atom/group substitution, chemical reactions, and conformational modulation have all been investigated. One approach of particular interest involves the strategic design of substituent groups along the molecular pathway [8,9], which is promising as an approach to the use of multiple transport channels, quantum interference effects [10], and other mechanisms that underlie the molecular conductance.

The technologies [4,11] that underpin single-molecule junctions, including mechanically controllable break junctions (MCBJs) [12], scanning tunneling microscope break junctions (STM-BJs), and lithography-defined single-molecule junctions, enable the connection of individual molecules between two electrodes to measure the resulting charge transport. Studies on single-molecule junctions have clarified the intricate correlation between these molecular structures and their conductance properties with remarkable precision [13-15]. By appropriate engineering of the molecular architecture, it becomes possible to perform precise adjustments of the electron distributions and energy levels of the frontier orbitals that are integral to the transport process, thus influencing the quantum effects [16,17] that occur within the molecular system. For example, experimental and theoretical investigations of single-molecule phenomena have demonstrated that both the Breit-Wigner and Fano resonances [18] can be induced through molecular engineering, thus potentially enabling the regulation of the conductance by more than one order of magnitude. Although the quantum effects, electronic effects, and steric effects that arise from conductance channel modulation have drawn extensive attention [19-21], few studies on the interplay that occurs between the molecular backbone and the side motifs have been reported to date.

In this study, we aim to determine the effects of the  $\sigma$  or  $\pi$  side motifs on molecular skeleton charge transport (Fig. 1a). Through a comprehensive investigation that involves the use of both the STM-BJ technique and first-principles calculations, we analyze the conductance properties of a series of 4,4'-methylenedianiline derivatives. Our results reveal that the multiplechannel effect is introduced by the  $\pi$  side groups and that the symmetry breaking of the conductance channel is introduced by the  $\sigma$  groups. By shedding light on the structure-function relationships associated with these side groups, our study will provide valuable insights into the design and fabrication of future molecular nanodevices.

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Figure 1 Design and properties of molecules M0-M3. (a) Schematic of STM-BJ measurements of molecules with side substituents. (b) Chemical structures of M0-M3. (c) Calculated molecular orbital diagrams for M0-M3. The yellow line indicates the Fermi level of the gold electrode (-5.30 eV).

#### **EXPERIMENTAL SECTION**

#### Materials and characterizations

The gold wire (99.99%; diameter: 0.25 mm) that was used to produce the scanning tunneling microscopy (STM) tip was purchased from ZhongNuo Advanced Material (Beijing) Technology Co., Ltd. Electrochemical corrosion was used to form the gold tip. The substrates were prepared by evaporating 10-nm-thick chromium and 100-nm-thick gold layers onto silicon wafers with suitable dimensions (usually 1 cm  $\times$  1 cm). All molecules were purchased from Bide Pharmatech Ltd. with 99% purity. The molecular solution used contained 0.1 mM of the target molecule.

#### STM-BJ measurements

In the STM-BJ experiments, a bias voltage was applied, with the real-time current serving as the feedback signal to control the tip's movements. Conductance-displacement traces were recorded during iterative tip retraction and approaching cycles, with a focus on the acquisition of the traces from the approaching cycles for the subsequent analysis. Single-molecule conductance assessments were performed using the Xtech STM-BJ apparatus developed by Prof. Wenjing Hong's group at Xiamen University, with the data analysis being conducted using the XMe open-source code [22].

#### I-V characterization

Current *versus* voltage (I-V) characterizations were performed using methodologies that were established in previous studies. An automated control program was used to identify plateaus in the results by applying preset conductance ranges. Movement of the piezoelectric stack was halted upon the detection of sampling points within this range, thus indicating the emergence of a conductance plateau. Subsequently, the measurement mode was shifted to I-V measurements, which were completed within 150 ms. Following the I-V measurement process, the control program transitioned to the current-time curve measurement mode. I-V curves that fell within a preset conductance range were retained for the statistical analysis, while those that occurred outside the range were discarded.

#### Theoretical calculations

First-principles calculations for the isolated molecules were conducted using density functional theory (DFT) within the Gaussian software package. The B3LYP/6-31G\* functional and the GD3BJ dispersion correlation were used for the electron exchange-correlation effects. Atom relaxation continued until the forces fell below 0.02 eV  $Å^{-1}$ , with a total energy criterion of  $1 \times 10^{-5}$  eV. For the DFT-non-equilibrium Green's function (NEGF) calculations, an electrode-central region-electrode junction setup was used, with the electrodes extending in a semiinfinite manner on either side. A Au (100) surface (AB-stacking)  $8 \times 4 \times 1$  supercell served as the electrode (128 atoms) and the central region comprised the molecule and the adjacent Au atoms. Variations in the electrode size (i.e., the number of atomic layers) from four to eight layers had a negligible impact on the junction transmission. Optimized junction structures were attained using the Gaussian package while maintaining the use of parameters that were consistent with previous relaxation procedures. Transmission coefficients (T(E)) were obtained via an ab initio NEGF approach within the QuantumATK package [23] using a single- $\zeta$  plus polarization (SZP) basis set and a cutoff energy of 100 Ry for energy convergence.

## **RESULTS AND DISCUSSION**

#### Design of 4,4'-methylenedianiline derivatives M0-M3

A series of 4,4'-methylenedianiline derivatives named M0 to M3 (Fig. 1b) were designed to investigate the interplay between the molecular backbone and the side motifs, with an sp<sup>3</sup> carbon at the center of the molecular bridge connecting with the  $\sigma$  (M0, M1) and  $\pi$  (M2, M3) side substituents. The hydrogen (M0), cvclohexane (M1), phenyl (M2), and fluorene (M3) substituents all have minimal effects on the anchor-to-anchor distance. These substituents act as intramolecular regulatory regions during unequivocal anchor-to-anchor transport along the molecular bridge. To gain further insights into the electronic characteristics of these molecules, the highest occupied molecular orbital (HOMO; Fig. 1c lower) and the lowest unoccupied molecular orbital (LUMO; Fig. 1c upper) were calculated using DFT. A gradual red shift in the LUMO from M0 to M3 and a gradual blue shift in the HOMO from M0 to M3 result in a narrowed HOMO-LUMO gap. It should be noted that the HOMO of M1 shows strong symmetry-breaking characteristics (Figs S1 and S2).

#### Exploring electronic characteristics of M0-M3

To study the differences between the electronic characteristics of the substituents, the charge transport processes of substituents M0–M3 were measured using the STM-BJ technique. Specifically, the molecules were dissolved in a 1,2,4-trichlorobenzene (TCB) solution that contained 0.1 mM of the target molecules. Then, the single-molecule junctions were repeatedly broken and formed; conductance traces featuring integer multiples of  $G_0$  ( $G_0$ =  $2e^2/h$ ) that indicated Au atomic breakage and the transport features below  $G_0$  at specific molecular values were then observed. Thousands of these conductance traces were then combined to produce two-dimensional (2D) conductance-displacement histograms. The numbers of conductance traces that comprise these histograms are marked in their respective captions. Then, the conductance plateaus were counted to form one-dimensional (1D) conductance histograms. The 2D conductance-displacement histograms acquired from substituents M0 to M3 are presented in Fig. 2a-d, respectively, while the 1D conductance histograms derived from substituents M0 to M3 are presented in Fig. 2e-h, respectively. M0 shows a conductance peak at ~ 1 × 10<sup>-4</sup>  $G_0$  ( $\approx$ 7.8 nS), as shown in the Gaussian fitted peak in Fig. 2b, which can be regarded as the standard conductance for comparison with the other molecules. M1 demonstrates a conductance peak at ~6.5 × 10<sup>-5</sup> G<sub>0</sub> ( $\approx$ 5.1 nS), which is reduced by nearly half when compared with M0. This difference can be attributed to the asymmetry of the HOMO in M1. M2 and M3 both exhibit enhanced conductance when compared with that of M0. The conductance peaks of M2 and M3 appear at ~5.0  $\times$  10<sup>-4</sup> G<sub>0</sub> ( $\approx$ 38.8 nS) and ~ 1.6  $\times$  10<sup>-4</sup> G<sub>0</sub> ( $\approx$ 12.3 nS), respectively. Typical single traces are also shown in Fig. 2j for each molecular junction and single traces that indicate tunneling decay after the rupture of a Au atomic contact measured in the pure TCB solvent are shown as black lines for comparison.

Introduction of different  $\sigma$  or  $\pi$  side groups allows the molecular conductance to be tuned by nearly 10 times (based on the comparison of M2 to M1), which is comparable to the conductance modulation achieved *via* intramolecular quantum interference. This enhanced conductance from M1 to M2 indicates that  $\pi$  motifs can aid molecular charge transport even when



Figure 2 Single-molecule electrical measurements of molecules M0-M3. (a-d) The 2D conductance-displacement histograms for M0 (a), M1 (b), M2 (c), and M3 (d) constructed by ~15,000 traces. The color bar indicates the number of counts. (e-h) The 1D conductance histograms for M0 (e), M1 (f), M2 (g), and M3 (h). Insets: the molecular structures. (i) Electron localization functions of M1 and M2, respectively. (j) Typical single-molecule conductance traces of the respective molecular junctions.

the side group's  $\pi$  electron is oriented vertically with respect to the molecular bridge pathway. Additionally, the introduction of the  $\sigma$  motif results in the breaking of the orbital symmetry and reduction of the conductance. To provide a further demonstration of the dominant role of the  $\pi$  motifs in charge transport, a method to evaluate the degree of electron localization, i.e., the electron localization function (ELF), was used. The  $\pi$ -electron localization degrees of M1 and M2 are shown in Fig. 2i. The figure shows that the  $\pi$ -electron is delocalized on the phenyl ring in M2, whereas the cyclohexane is undistributed. This provides an intuitive image to aid in explaining different conductance characteristics obtained from the cyclohexane and phenyl substitutions, showing that the  $\pi$ -electron movement and eases the charge transport process.

#### Exploring bias-dependent characteristics of M0-M3

To delve deeper into these charge transport properties, the I-Vand conductance versus voltage (I/V-V) characteristics were also investigated. Specifically, the I-V characterizations were implemented by allowing the gold tip to hover when the corresponding conductance plateau was formed during the break junction measurements. When the tip was held for 150 ms, the bias voltage was scanned from -1.0 V to 1.0 V in steps of 0.5 mV. The collected I-V traces were then used to construct 2D I-V histograms. Fig. 3a-d show the I-V characteristics of M0-M3, respectively, and the calculated conductance characteristics derived from the *I*-*V* results are shown in Fig. 3e-h for M0-M3, respectively. The conductance characteristics of M0 and M1 remain nearly intact up to the bias voltage, showing flat features, whereas the conductance characteristics of M2 and M3 show a dramatic rise when the bias voltage is increased. These phenomena can be attributed to the more mobile nature of the  $\pi$ electron for the  $\pi$  motifs (M2 and M3), which is more responsive to the electric field and thus enables improved charge conductance when compared with the  $\sigma$  motifs (M0 and M1). Moreover, when a potential field is applied along the molecules to simulate the electric field effect during the STM-BJ experiments, M2 and M3 are predicted to show dramatic deformations, while M0 and M1 show little change (Table S1). This simulation also supports higher conductance changes for M2 and M3 when compared with those of M0 and M1 because of the field-induced deformation effect.

#### Theoretical analysis of M0-M3

To gain a deeper understanding of the impact of the  $\sigma$  and  $\pi$  side substituents on the molecular charge transport behavior, firstprinciples conductance simulations of the single-molecule M0-M3 junctions were performed (Fig. S3). The dihedral angles between the phenyl planes on both sides of M0-M2 are nearly orthogonal, ranging from 86° to 89°. Despite M3 exhibiting a smaller phenyl-plane dihedral angle of 67°, owing to the steric hindrance effect of the substituent, it is essential to highlight that this difference in plane orientation does not dictate the molecular transport (Fig. S4). The molecules were placed between two Au (111) electrodes with symmetrical interfaces. One side of the electrode simulates the Au STM tip and the other simulates the nonplanar surface used in the STM-BJ measurements. Using a combination of DFT and NEGFs, the zero-bias transmission functions for M0-M3 were calculated with optimized geometries using the Gaussian software (Fig. 4a and Fig. S5). The computed transmission spectra indicate that a nonresonant tunneling process occurs at low bias voltages, where the transmission function varies smoothly around the Fermi level. In these cases, the zero-bias conductance can be evaluated by determining the transmission at the Fermi level using the Landauer approach, where  $G/G_0 = T(E_F)$ . The transmission near the Fermi level indicates the electron transmission probability within the lowbias region, where the result that M2 > M3 > M0 > M1 is consistent with the conductance measurements.

These transmission characteristics can be attributed to the varied ease of access to dominant transport channels provided by the perturbed HOMOs (p-HOMOs) of different molecules. The molecular projected self-consistent Hamiltonians (MPSHs) of the p-HOMOs of these molecular junctions were then calculated (Fig. 4c, and Figs S6, S7), and were very similar to the isolated molecular orbitals. Furthermore, the p-HOMO is distributed almost evenly over the entire molecule in M2 and M3,



Figure 3 Bias-dependent measurements of molecules M0-M3. (a-d) The 2D I-V histograms for M0 (a), M1 (b), M2 (c), and M3 (d). (e-h) The 2D conductance versus voltage (I/V-V) histograms for M0 (e), M1 (f), M2 (g), and M3 (h).



**Figure 4** Theoretical analysis of molecules M0-M3. (a) Calculated transmission spectra of M0-M3. (b) Transmission pathways of M1 and M2. The overall transmission from the left electrode to the right electrode is colored blue while the reflected transmission from right to left is colored green. (c) Molecular projected self-consistent Hamiltonian (MPSH) of M0-M3 junctions. (d) PLDOS of M0-M3 junctions.

while apparent asymmetric orbital distributions were found for M1 and M3. The projected local density of states (PLDOS) was also calculated to determine the transmission pathways associated with different energy behaviors (Fig. 4d). The PLDOS shows the distribution along the device direction and the local density of states is then plotted according to the energy level. M0 exhibits a single conducting channel, while the introduction of the  $\sigma$  motif in M1 leads to a symmetry breaking of the conductance pathway. Specifically, the primary conductive channels corresponding to p-HOMO and p-HOMO-1 show symmetrybreaking characteristics and are cut off from the left to right side of the device, thus reducing the charge transport capability. In contrast, the introduction of the  $\pi$ -side groups results in an additional  $\pi$  conducting channel. For M2, the PLDOS shows two relatively independent and continuously conductive channels that correspond to the p-HOMO and the p-HOMO-1. We attribute this feature to the multiple-channel effect. In the case of M3, both symmetry-breaking and multiple-channel effects exist and compete with each other, leading to slight splitting and relatively conductive p-HOMO and p-HOMO-1 channels. Furthermore, we analyzed the transport characteristics of the dominant transport orbitals, i.e., the p-HOMO transmission pathways of M0-M3 (Figs S8 and S9). As Fig. 4b shows, the transmission pathway of M1 exhibits stronger transmission reflection (green) and strong scattering across the cyclohexane ring, which both weaken the charge transport ability. The transmission pathway of M2 mainly follows the  $\pi$ -electron distribution, which is minimally scattered, and little reflection is thus observed. These results indicate that the introduction of the  $\sigma$ -side groups reduces molecular conductance because of the stronger scattering that occurs as a result of the symmetrybreaking effect. Specifically, with the appearance of the orbital symmetry-breaking phenomenon, the main conductive channel cannot support the electrons to effectively pass through the  $\sigma$ region; most of the electrons are scattered within the system, which leads to a reduction in the conductance. We adjust the

size of  $\sigma$  orbital and predict the symmetry-breaking effect and the reduction of transmission in other systems (Fig. S10). In contrast, the  $\pi$ -side groups bring additional  $\pi$  channels and provide more efficient charge transport, thus enhancing the molecular conductance.

### CONCLUSIONS

In summary, a series of molecular wires featuring diverse  $\sigma$  and  $\pi$  side groups were designed in this study and their transport characteristics were investigated using a combined approach involving STM-BJ experiments and DFT+NEGF simulations. The  $\sigma$  side substitution leads to reduced molecular conductance, whereas the  $\pi$  side substitution enhances the conductance. Theoretical analysis shows that the incorporation of the  $\sigma$ -side groups leads to symmetry-breaking in the frontier orbitals and strong scattering around the  $\sigma$ -motif, which culminates in reduced conductance. Conversely, the integration of the  $\pi$  side groups enhances the molecular conductance by forming additional  $\pi$  channels and minimally scattered transport pathways. These findings clarify the interactions between the side groups and the molecular backbone, which is crucial for molecular functionalization and the fabrication of molecular electronic devices.

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**Author contributions** Guo X, Jia C, and Wang J conceived the idea of the paper. Hao J carried out the experimental measurements. Hao J and Wang B performed the theoretical calculations. Guo X, Jia C, Wang J, Hao J, Wang B, Zhao C, and Huo Y analyzed the data and wrote the paper. All authors contributed to the general discussion.

**Conflict of interest** The authors declare that they have no conflict of interest.

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# 基于侧基多通道和对称性破缺效应的分子电导调控

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**摘要** 化学取代是有效调节分子电导,产生多通道输运、量子干涉效应和 其他机制的关键方法. 但分子骨架和侧基之间存在复杂的相互作用,目前 仍未被研究清楚. 在本工作中,我们结合扫描隧道显微镜裂结实验技术和 第一性原理计算方法,深入研究了具有不同σ和π侧基的分子电导. 实验结 果及理论分析表明, σ侧基的加入引起了分子前线轨道的对称性破缺并加 剧了分子内散射,从而导致电导的降低. 相反, π侧基引入了额外的电荷传 输通道,实现了电荷传输的多通道效应,增加了分子的电导. 这些发现为未 来分子功能化和分子电子器件的设计提供了坚实的基础.