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Published in:
Advanced Science

Published: 13/06/2022

Document Version:
Final Published version, also known as Publisher’s PDF, Publisher’s Final version or Version of Record

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Publication record in CityU Scholars:
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Published version (DOI):
10.1002/advs.202105667

Publication details:
Zhang, H., Xu, W., Song, K., Lu, T., Zhang, G., Zang, Y., Hong, W., & Zhang, D. (2022). Dual Modulation of Single Molecule Conductance via Tuning Side Chains and Electric Field with Conjugated Molecules Entailing Intramolecular O···S Interactions. Advanced Science, 9(17), Article 2105667. Advance online publication. https://doi.org/10.1002/advs.202105667

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Dual Modulation of Single Molecule Conductance via Tuning Side Chains and Electric Field with Conjugated Molecules Entailing Intramolecular O●●●S Interactions

Hua Zhang, Wei Xu, Kai Song, Taige Lu, Guanxin Zhang, Yaping Zang, Wenjing Hong,* and Deqing Zhang†

Herein, single-molecule conductance studies of TBT1-TBT6 which entails 1,4-dithienylbenzene as the backbone and –SMe groups as the anchoring units, with the scanning tunneling microscope break junction (STM-BJ) technique, are reported. The molecular conductance of TBT1 with intramolecular O●●●S noncovalent interactions is enhanced by about one order of magnitude in comparison to their analogue TBT2 (which contains alkyl instead of alkoxy chains). By replacing the methoxy groups in TBT1 with extending alkoxy chains in TBT3, TBT4, and TBT5, the molecular backbones become twisted and as a consequence the single-molecule conductance decreases gradually, showing that the intramolecular O●●●S noncovalent interaction is influenced by the structural features of alkoxy chains. More importantly, the single-molecule conductance of TBT3, TBT4, and TBT5 can be boosted by increasing the electric field applied to the molecular junctions. Remarkably, the conductance of TBT3, TBT4, and TBT5 can be reversibly modulated due to the conformational changes between twisted and planar ones by varying the electric field. These results demonstrate that molecules with intramolecular O●●●S noncovalent interactions have the potential for in situ control of the electrical properties of molecular-scale devices.

1. Introduction

Single-molecule break junction techniques,[1] such as STM-BJ[2] and mechanically controllable break junction,[3] have been used to explore the relationship between conductance and structures of molecular wires and construct responsive single-molecule devices in the past years.[4] Interestingly, conductance of molecular junctions linked by intermolecular hydrogen bonding, π⋯π stacking, coordination interaction and host-guest interaction was successfully measured and investigated.[5] However, investigations of intramolecular noncovalent interactions through single molecular junction were less conducted.[34]

Recently, intramolecular O●●●S noncovalent interaction have been proposed for designing planar conjugated molecules for high performance organic opto-electric materials.[6,7] Although intramolecular O●●●S noncovalent interaction was proved by analysis including single crystal X-ray diffraction, ultraviolet–visible absorption spectroscopy, nuclear magnetic resonance spectra and density functional theory (DFT) computation,[7,8] there is still a lack of method by means of the single-molecule junction. It is significant to explore the effects of structural parameters and external stimuli such as electric field on intramolecular O●●●S noncovalent interaction. In addition, molecules with noncovalent conformational interactions have the advantage for constructing molecular devices with responsiveness and reversibility.[9,10] More importantly, the strong electric fields within the two nanoelectrodes of the break junction technique offer the unique tool to realize high-performance responsive molecular devices.[11] Thus, it is highly interesting to fabricate molecular level devices by varying the electric fields applied across the junction of molecules with intramolecular noncovalent interactions.

In this paper, we report the single-molecule conductance studies of TBT1–TBT6 (see Figure 1), which entails 1,4-dithienylbenzene as the backbone and –SMe groups as the anchoring units, with the STM-BJ technique. The results show that the molecular conductance of TBT1 with two methoxy groups is about one order of magnitude higher than that of its analogue TBT2 (which contains two ethyl groups instead of alkoxy chains).
This is attributed to the more planar backbone of TBT1 induced by the intramolecular O⋯S noncovalent interaction. Interestingly, by replacing the methoxy groups in TBT1 with extending alkoxy chains as in TBT3, TBT4, and TBT5, the single-molecule conductance decreases gradually under 0.1 V bias voltage. This manifests that the intramolecular O⋯S noncovalent interaction are influenced by the structural features of alkoxy groups in TBT3, TBT4, and TBT5. Remarkably, the single-molecule conductance of TBT3, TBT4, and TBT5 can be boosted by increasing the electric field applied to the molecular junctions. It is worth noting that the conductance of TBT3, TBT4, and TBT5 can be reversibly modulated due to the conformational changes between twisted and planar ones by varying the electric field. We further rationalize these results through characterizations including single crystal X-ray diffraction, ultraviolet–visible absorption spectroscopy, nuclear magnetic resonance spectra and DFT computations. Our work demonstrates for the first time that molecular conformation can be regulated through intramolecular O⋯S noncovalent interactions in single molecular electronics via an external field, and molecules with intramolecular O⋯S noncovalent interaction have the potential to be used for single-molecule electrical switches.

2. Results and Discussion

To verify the intramolecular O⋯S noncovalent interactions, we synthesized three molecules TBT1-TBT3 and investigated the single-molecule charge transport properties by conductance measurement using STM-BJ methods. Their molecular structures are shown in Figure 1, and the alkoxy and alkoxy chains were introduced into the benzene of the conjugated backbone flanked by −SMe anchors. The individual stretching traces of were all close to 1.05 nm as shown in the insets of Figure 2d–f. A clear conductance plateau can be observed for each 2D conductance histogram. Further Gaussian analysis of the plateau length distribution in each 2D conductance histogram revealed that the stretching distances of TBT1-TBT3 were all close to 1.05 nm as shown in the insets of Figure 2d–f. After correcting by a 0.5 nm snap-back distance of the gold–gold atomic contact breaking, the calibrated stretching distance for TBT1-TBT3 should be around 1.55 nm. This value is consistent with the distance between the theoretical distance of the two –SMe anchoring groups (1.4 nm) in molecular backbones, suggesting that these junctions are indeed formed across the molecular backbone. We hence hypothesize that the high conductance observed in TBT1 arises from the intramolecular O⋯S noncovalent interactions effect.

To further support the hypothesis that the intramolecular O⋯S noncovalent interactions induced conductance enhancement, the precise configurations of molecules TBT1-TBT3 were obtained by single crystal X-ray diffraction (Figure 3a) and 1H NMR analysis (Figure 3b and Figure S14, Supporting Information). The crystal structure of TBT1 shows that the distances between alkoxy oxygen and thiophene sulfur atoms (2.707(3) Å) are remarkably shorter than the sum of the van der Waals radii of the two atoms (3.25 Å) and such strong intramolecular O⋯S noncovalent interaction induces the π-conjugated block to be a highly planar conformation with a small torsion angle of 1.7°. In contrast, the crystal structure of TBT2 displays a twisted configuration with 52.1° dihedral angle between adjacent thiophene and benzene rings. For molecule TBT3, structural analysis reveals that the distance between oxygen and sulfur is 2.742 (2) Å, which is slightly longer than that in TBT1. However, the existence of alkoxy chains leads to a 20.1° dihedral angle with the
Figure 2. a) Typical individual traces of TBT1 (green), TBT2 (blue), and TBT3 (orange) under 0.1 V bias voltage. b) 1D conductance histograms of TBT1 (green), TBT2 (blue), and TBT3 (orange) under 0.1 V bias voltage. c) Comparison of molecular conductances of TBT1-TBT3 and dihedral angles of TBT1-TBT3. d–f) 2D conductance histograms of TBT1, TBT2, and TBT3 under 0.1 V bias voltage. The distance distributions are shown in the insets.

Figure 3. a) Top views of the single crystal structures of TBT1, TBT2, and TBT3. b) $^1$H NMR spectra for TBT1 and TBT3 in CDCl$_3$. 
Figure 2c shows that the dihedral angle between adjacent thiophene and benzene rings follows the trend of 
\( TBT_1 < TBT_3 < TBT_2 \) and the trend of the molecular conductance variation is opposite. It also suggested that the contribution of conductance enhancement is mainly dominated by the \( O \cdots S \) noncovalent interaction induced coplanarity rather than the charge transport through the \( O \cdots S \) interaction itself. Intramolecular \( O \cdots S \) noncovalent interactions in \( TBT_1 \) and \( TBT_3 \) were also identified in the \(^1\)H NMR measured under the same condition. As shown in Figure 3b, hydrogens on thiophenes close to benzene ring were defined as \( \alpha-H \) marked in red, the other hydrogens on thiophenes were defined as \( \beta-H \) marked in green. \( TBT_1 \) shows two signals for hydrogens on thiophenes, a broad singlet at \( \delta 7.3636 \) for \( \alpha-H \), and a doublet at \( \delta 7.0632 \) for \( \beta-H \) consistent with the structure.\(^{[12]}\) \( TBT_3 \) (\( \delta 7.3583 \) and 7.0515) show two doublets of hydrogens on thiophenes. In contrast, \( TBT_2 \) shows two high-field signals in the \(^1\)H NMR spectrum at \( \delta 7.0612 \) and 6.9039 (see Figure S14, Supporting Information). As a result, \(^1\)H NMR signals for both \( \alpha-H \) and \( \beta-H \) on thiophenes of \( TBT_1 \) and \( TBT_3 \) with intramolecular \( O \cdots S \) noncovalent interaction were downfield shifted slightly, being consistent with more planar molecular backbone. The above results are consistent with the conductance trend in Figure 2a and support the proposed hypothesis. Additionally, the solution ultraviolet–visible absorption spectroscopy shows that the absorption maxima of \( TBT_1 \) (389 nm) are redshifted compared with \( TBT_2 \) (319 nm), as shown in Figure S13 (Supporting Information), being consistent with intramolecular noncovalent interactions and planarization in solution. Consequently, the single-molecule conductance increased with the enhancement of intramolecular \( O \cdots S \) interactions, providing a promising strategy to achieve extended \( \pi \)-electron systems with high charge transport capability.

To clarify intramolecular \( O \cdots S \) noncovalent interactions at high bias, we carried out the conductance measurements at 0.5 V. As shown in Figure 4a, unlike the conductance of \( TBT_1 \) with methoxyl groups, the conductance of \( TBT_3 \) increased remarkably from \( \approx 10^{-3.10} G_0 \) to \( \approx 10^{-3.17} G_0 \) when changing the applied bias voltage from 0.1 to 0.5 V. By contrast, there is no apparent change in the conductance of the molecule with ethyl chains at different bias voltages. Furthermore, 2D conductance histograms were constructed to acquire more information from the stretching process (see Figure 4c and Figure S18, Supporting Information). We note from the 2D histograms that the molecular length of \( TBT_1-TBT_3 \) all remained unchanged under different applied bias voltages (0.1 V and 0.5 V). As shown in the insets.

molecular backbones. Although the dihedral angle is smaller than \( TBT_2 \), it is not surprising to predict that the flexible alkoxy chain will result in an increasing torsion angle in the solution.
of Figure 4c and Figure S18 (Supporting Information), the measured molecular lengths are in accordance with the calculated ones (≈1.4 nm). These results demonstrate that the variation of molecular conductance observed in different bias voltages is due to the changes of molecular electronic structures instead of altering the electrode-molecule contact locations. These results show that molecules with intramolecular O⋯S noncovalent interactions enable conductance modulations by varying bias between two electrodes. Notably, these conductance modulations are more prominent for molecules with large alkoxy groups.

To further explore the impact of an electric field on the conductance of molecules with intramolecular O⋯S noncovalent interactions, we synthesized the other three molecules TBT4-TBT6 (see Figure 1) and performed conductance measurements at both 0.1 V and 0.5 V. As shown in Figure 4d,e, the conductance of TBT4 and TBT5 increases at 0.5 V. Specifically, the conductance of TBT4 with n-pentyl group increases from ≈10⁻³.⁷⁷ G₀ to ≈10⁻³.⁰ G₀ by varying the bias from 0.1 to 0.5 V, while TBT5 with bulky alkoxy groups shows a more obvious conductance increase from ≈10⁻⁴.⁴⁴ G₀ to ≈10⁻⁴.² G₀. By contrast, there is no noticeable conductance change for TBT6 containing alkyl substitution under 0.1 V (≈10⁻⁴.³ G₀) and 0.5 V (≈10⁻⁴.⁴ G₀). The conductance modulation trend for these molecules further implies that the electric field affects the intramolecular O⋯S noncovalent interactions and thus the molecular conductance. We therefore hypothesize that the twisted molecules containing large alkoxy groups become more planar under a high electric field, thus yielding a high conductance comparable with that of TBT1 with more planar conformation.

To better explore the conductance modulation of TBT3 under different bias voltages, we examined the conductance by applying 0.1 V and 0.5 V alternatively using the STM-BJ technique (see Figure 5 and Figure S19, Supporting Information). It can be seen that the conductance of TBT3 switches reversibly between the high and low conductance states, and the two states show approximately one order of magnitude difference in conductance. These results demonstrated that molecules with intramolecular O⋯S noncovalent interactions have the potential for in situ control of electrical switches.

To further explore the impact of intramolecular O⋯S noncovalent interactions on the charge transport in single molecular junctions, we performed density functional theory (DFT) calculations on the junctions formed through Au-S contacts. As shown in Figure 6a, we first obtained the optimized geometries without application of external field for TBT1-TBT3. In agreement with the above experimental results, the planar conformational molecule TBT1 shows more planar structure (dihedral angles: −3.⁹° and 3.⁷°) than TBT2 (dihedral angles: −2.⁶° and 2.⁷°). For TBT3, the dihedral angles (−6.⁶° and 4.⁵°) are also smaller than TBT2 but larger than TBT1 due to the steric effect caused by the bulky alkoxy groups. Additionally, we calculated the transmission functions using the nonequilibrium Green’s function (NEGF) formalism to further understand the charge transport. Figure 6b shows that the transmission probability at Fermi follows the trend of TBT1 > TBT3 > TBT2, which is consistent with the experimental results.

To further explore the effect of the electric field, we performed similar calculations under an applied electric field of 1 Vnm⁻¹ (Figure S16, Supporting Information and Figure 6b). Notably, under the electric field, TBT3 becomes more planar (dihedral angles: 3.¹° and −1.²°), while the conformations of TBT1 and TBT2 do not show obvious changes. This conformational planarization under a high bias is attributed to the existence of a relatively larger dipole in TBT3, and is responsible for the observed conductance increases under a high applied bias voltage (as reflected by the increase of transmissions). The calculation qualitatively explains the conductance enhancement for TBT3 with intramolecular O⋯S noncovalent interaction induced under high electric field.

3. Conclusion

In conclusion, we show the enhancement of single-molecule conductance for molecules with intramolecular O⋯S noncovalent interactions. Furthermore, the results reveal that the intramolecular O⋯S interactions are influenced by the structural features of alkoxy groups in TBT3, TBT4, and TBT5 and the electric field applied to the molecular junctions. Interestingly, it was found...
that molecules with intramolecular O•••S noncovalent interactions enable conductance modulation by varying the applied electric field between two electrodes, especially those with large alkoxy groups. In particular, the single-molecule conductance of TBT3 can be modulated reversibly by one order of magnitude. It is noted that the regulation of molecular conformation through intramolecular O•••S noncovalent interactions in single molecular electronics via external field was never reported before. Consequently, molecules with intramolecular O•••S noncovalent interactions offer an efficient and in situ approach for establishing single-molecule electrical switches.

4. Experimental Section

Materials: The reagents and starting materials were commercially available and used directly without further purification unless otherwise specified. Gold wires (99.99%, 0.25 nm diameter) were purchased from Beijing Jiaming Platinum Nonferrous Metal Co. Ltd. Crystallographic data (excluding structure factors) reported in this paper were deposited in the Cambridge Crystallographic Data Centre (CCDC No. 2070566 for compound TBT1, CCDC No. 2070565 for compound TBT2, CCDC No. 2103035 for compound TBT3).

General Synthetic Procedures for TBT1, TBT3-TBT5: To a Schlenk tube equipped with a magnetic stir bar was charged with 1, 4-dibromo-2,5-dialkoxybenzene (1.0 eq.), S-(methylthio)thiophene-2-boronic acid pinacol ester (3.0 eq.), [Pd2(dba)3] (0.1 eq.), K3PO4 (3.0 eq.), SPhos (0.2 eq.) and toluene. The mixture was stirred at 110 °C for 10 h under N2 atmosphere. Then the reaction mixture was concentrated under vacuum and the residue was purified by silica gel column chromatography with hexane and CH2Cl2 as eluent.

Synthesis of TBT1: TBT1 (221 mg) was obtained as a yellow solid in 33% yield. For compound TBT1, m.p. 112.2–112.8 °C. 1H NMR (300 MHz, CDCl3): δ (ppm) 7.37 (s, 2H), 7.18 (s, 2H), 7.07 (s, 2H), 3.95 (s, 6H), 2.54 (s, 6H), 2.54 (s, 6H). 13C NMR (75 MHz, CDCl3): δ (ppm) 149.85, 140.97, 137.36, 130.73, 125.45, 122.75, 111.41, 56.28, 22.05. HR-MS (MALDI-TOF): calc'd for C18H18O2S4 (M+): 506.1436; found: 506.1433.

Synthesis of TBT3: TBT3 (97 mg) was obtained as an yellow solid in 27% yield. For compound TBT3, m.p. 35.1–35.7 °C. 1H NMR (300 MHz, CDCl3): δ (ppm) 7.37 (d, J = 3.0 Hz, 2H), 7.18 (s, 2H), 7.06 (d, J = 3.0 Hz, 2H), 3.97 (d, J = 3.0 Hz, 4H), 2.53 (s, 6H), 1.89–1.81 (m, 2H), 1.65–1.43 (m, 8H), 1.37–1.31 (m, 8H), 0.98–0.89 (m, 12H). 13C NMR (100MHz, CDCl3): δ (ppm) 149.25, 141.24, 137.12, 130.57, 125.60, 122.65, 122.75, 111.98, 72.60, 69.24, 28.39, 22.46, 22.05, 14.04. HR-MS (MALDI-TOF): calc'd for C36H32O2S4 (M+): 926.6133; found: 926.6132.

Synthesis of TBT4: TBT4 (198 mg) was obtained as an yellow solid in 32% yield. For compound TBT4, m.p. 80.0–80.5 °C. 1H NMR (400 MHz, CDCl3): δ (ppm) 7.27 (s, J = 4.0 Hz, 2H), 7.17 (s, 2H), 7.06 (d, J = 4.0 Hz, 2H), 4.07 (t, J = 8.0 Hz, 4H), 2.53 (s, 6H), 1.95–1.88 (m, 4H), 1.54–1.48 (m, 4H), 1.46–1.37 (m, 4H), 0.95 (t, J = 8.0 Hz, 6H). 13C NMR (75MHz, CDCl3): δ (ppm) 149.14, 141.24, 137.06, 130.57, 125.21, 122.75, 111.98, 72.60, 28.39, 22.46, 22.03, 14.04. HR-MS (MALDI-TOF): calc'd for C26H34O2S4 (M+): 590.2375; found: 590.2369.

Synthesis of TBT5: TBT5 (396 mg) was obtained as an yellow liquid in 35% yield. 1H NMR (400 MHz, CDCl3): δ (ppm) 7.26 (d, J = 4.0 Hz, 2H), 7.17 (s, 2H), 7.04 (d, J = 4.0 Hz, 2H), 3.95 (d, J = 4.0 Hz, 4H), 2.51 (s, 6H), 1.92–1.86 (m, 2H), 1.59–1.51 (m, 4H), 1.47–1.25 (m, 6H), 0.89 (t, J = 8.0 Hz, 6H). 13C NMR (100MHz, CDCl3): δ (ppm) 149.20, 141.28, 137.04, 130.42, 125.21, 122.60, 111.76, 72.24, 38.14, 31.90, 31.50, 30.04, 29.68, 29.64, 26.91, 29.34, 29.63, 22.67, 21.93, 14.09. HR-MS (MALDI-TOF): calc'd for C26H34O2S4 (M+): 590.2369; found: 590.2368.

General Synthetic Procedures for TBT2 and TBT6: To a Schlenk tube equipped with a magnetic stir bar was charged with 1, 4-dibromo-2,5-dialkoxybenzene (1.0 eq.), S-(methylthio)thiophene-2-boronic acid pinacol ester (3.0 eq.), [Pd2(dba)3] (0.1 eq.), K3PO4 (3.0 eq.), SPhos (0.2 eq.) and toluene. The mixture was stirred at 110 °C for 10 h under N2 atmosphere. Then the reaction mixture was concentrated under vacuum and the residue was purified by silica gel column chromatography with hexane and CH2Cl2 as eluent.
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available in the supplementary material of this article.

Keywords
electric fields, intramolecular conformational tuning, molecular switch, single-molecule conductance

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

Acknowledgements
H.Z., W.X., and K.S contributed equally to this work. Financial support from the National Natural Science Foundation of China (21933012, 31871877, and 22021002), the Ministry of Science and Technology of China (2017YFA0404902 and 2018YFA0703200), Chinese Academy of Sciences (KDBB13 and GJTDS-2020-02), the Fundamental Research Funds for the Central Universities (2072020068 and 2072019002), and the Beijing National Laboratory for Molecular Sciences (No. BNLMMS200205) are gratefully acknowledged. This work was also supported by the CAS-Croucher Funding Scheme for Joint Laboratories.

Conflict of Interest
The authors declare no conflict of interest.

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