Regulating a Benzodifuran Single Molecule Redox Switch via Electrochemical Gating and Optimization of Molecule/Electrode Coupling

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ⓢ *Supporting Information*

ABSTRACT: We report a novel strategy for the regulation of charge transport through single molecule junctions via the combination of external stimuli of electrode potential, internal modulation of molecular structures, and optimization of anchoring groups. We have designed redox-active benzodifuran (BDF) compounds as functional electronic units to fabricate metal–molecule–metal (m–M–m) junction devices by scanning tunneling microscopy (STM) and mechanically controllable break junctions (MCBJ). The conductance of thiol-terminated BDF can be tuned by changing the electrode potentials showing clearly an off/on/off single molecule redox switching effect. To optimize the response, a BDF molecule tailored with carbodithioate ($-CS_2^-$) anchoring groups was synthesized. Our studies show that replacement of thiol by carbodithioate not only enhances the junction conductance but also substantially improves the switching effect by enhancing the on/off ratio from 2.5 to 8.
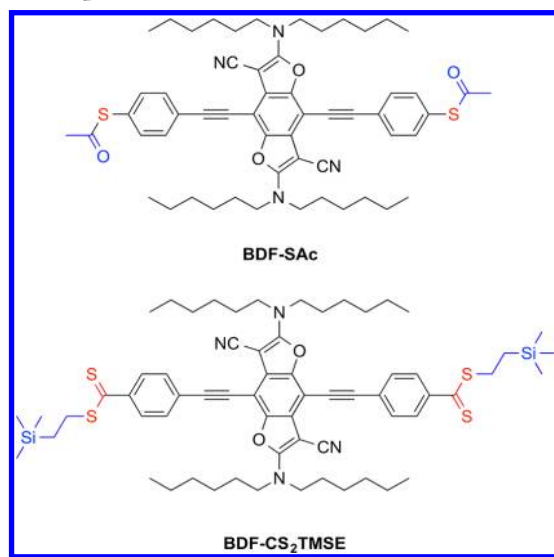
A key step in molecular electronics is to design and construct sophisticated nanoscale devices which can perform functions, such as switching, gating, and regulating, thereby mimicking traditional electronic units.[1−3] In memory and logic, switching represents one of the most basic functions and there is interest to study the switching behavior at the single molecule level.[4] In particular, it is highly desirable to fabricate molecular devices through which the current flows can be regulated by external "stimuli" or parameters. These parameters can be environmental solution pH,[5,6] light irradiation,[7−9] electrode potentials,[10−14] etc. Modulation of current flow through external electrode potential control, so-called electrochemical gating, is one of the most exciting approaches to facilitate conductance switching. In an electrochemical gating experiment, charge transport through molecule-mediated junctions can be regulated by tuning the Fermi level of the junction electrodes with respect to an electrochemical reference electrode.[15] More dramatic changes in the molecular junction conductance can occur when the molecules are switched between different redox states.[16,17]

Single molecule gating experiments can be experimentally achieved using mechanical controllable break junction (MCBJ) or scanning tunneling microscopy break junctions (STM-BJ). In a break junction experiment, individual molecules are wired between two electrodes, the source and drain electrodes, via proper anchoring groups. A reference electrode is used as the gating electrode to adjust the Fermi energy of the source and drain electrodes so that the source−drain (S−D) current through molecular junctions can be regulated/electrochemically gated. Electrochemically induced molecular conductance switching and the resulting gating effect have been detected for redox active molecules such as viologens[15,18,19] and perylenes[16,20] as well as recently for graphene fragments.[21] However, the electrochemical gating effect of benzodifurans (BDFs), an important class of redox-active model molecules,[22−25] has not been explored at the single molecule level. Even the single molecule conductance of BDFs has not been reported yet. Our keen interest in BDFs stems from their unique *p*-type semiconductor characteristics and high hole mobility which render them excellent in organic field effect transistors (OFETs) and organic light emitting diodes (OLEDs).[26,27] Notably, they can undergo a reversible oxidation forming stable cation-radical salts.[22] Furthermore, although it is clear that the molecular/junction conductance can be gated electrochemically, no study has focused on the important question of how the anchoring groups of molecules, or the contact resistance between a molecule and the electrodes, can influence the gating effect.

Herein, we report the design of redox-active benzodifurans terminated by thiols (acetyl protected) and carbodithioate (TMSE protected) anchoring groups, as shown in Chart 1, for the formation of molecular junctions. The synthesis of BDF derivatives involves a palladium-catalyzed Sonogashira cross-coupling of 2,6-bis(dihexylamino)-4,8-diiodo-benzo[1,2-*b*:4,5-*b'*]difuran-3,7-dicarbonitrile with 4-ethynyl-1-thioacetylbenzene and 4-ethynyldithiobenzoic acid 2-(trimethylsilyl)ethyl ester, respectively. The details of the preparation procedure and characterization can be found in the Supporting Information. While previous studies only investigated how different core

Chart 1. Chemical Structures of the Functionalized BDF Derivatives with Thiolacetyl and Carbodithioic Acid TMSE Ester Groups

Figure 1. (A) Schematic of a break junction measurement with a molecule wiring between two electrodes. (B, C) Current histogram constructed from current−distance traces measured at 0.1 V in an STM break junction for **BDF-S⁻** (B) and **BDF-CS₂⁻** (C). Inset in B and C: sample current−distance traces.

structures affected the gating behavior, our experiments show that the anchoring groups (contact resistance) also play an essential role in the single molecule electrochemical conductance gating.

STM-BJ and MCBJ techniques employed to investigate the charge transport through molecular junctions in the present study have been described in our previous reports[5,28−30] and Supporting Information. Basically, in both techniques, metal junctions are formed and subsequently broken in the presence of target molecules to form metal−molecule−metal (m−M−m) junctions (Figure 1A) while current versus distance traces are recorded. Then these current−distance traces are used to construct current/conductance histograms to obtain the statistical single molecule conductance values.[30−34]

Single molecule conductance experiments were first performed on **BDF-S⁻** molecule, with mesitylene as the solvent, using STM break junction techniques. Junctions were formed and broken repeatedly allowing thousands of current− distance traces to be recorded for statistical analysis. The detailed data analysis and trace selection criteria can be found in the Supporting Information. The current histogram in Figure 1B was constructed using 450 stepped traces from 2000 total traces, showing a current maximum at about 2.3 nA at a bias voltage of 0.1 V, corresponding to a single molecule conductance of 23 nS (2.9×10^{-4} G_o, where G_o is the quantum of conductance and equals 77 500 nS). This is consistent with the conductance value, revealed by current steps, from individual traces (Figure 1B, inset).

For comparison, we performed single molecule conductance experiments in 0.25 mM solution of **BDF-SAc** in tetrahydrofuran/mesitylene (1:4 v/v) using the MCBJ technique. The **BDF-SAc** molecules were deprotected *in situ* by adding tetra-*n*-butylammonium hydroxide (TBAOH) to the solution (~0.1 mM). The two-dimensional conductance versus relative distance histogram shown in Figure 2A was constructed from 514 successive traces recorded at a bias voltage of 0.2 V without data filtering. To generate the histogram, all conductance traces were aligned to the sharp conductance drop below 1 G_0. This representation provides a useful overview of the breaking process for all breaking cycles performed. A well-defined
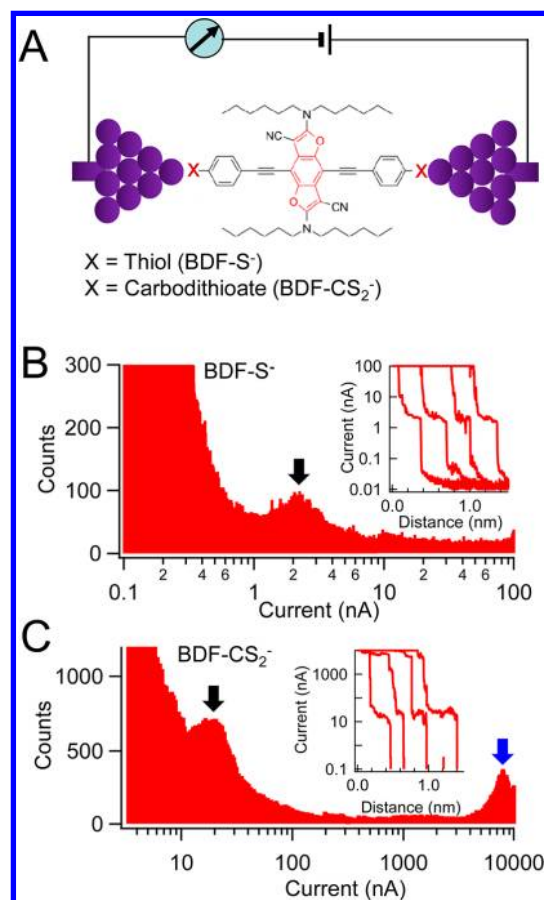
accumulation of counts can be observed in the conductance range from 1×10^{-4} G_o to 2.5×10^{-3} G_o. Note that we observe only one clear accumulation region, supporting the idea that the junction formation and breaking is statistically dominated by a well-defined geometry of the molecular junction. Most conductance traces break at a push-rod extension lower than 25 μm, which corresponds to a breaking distance of ~6.9 Å using our typical average attenuation factor of 2.75×10^{-5}. This corresponds well to the observed breaking distances in the STM break junction traces shown in Figure 1B and 1C. The accumulation of data points at conductances close to and lower than 10^{-6} G_o arises due to the presence of the deprotection agent in the liquid cell. The one-dimensional histogram in Figure 2B clearly shows the corresponding conductance peak with a maximum at 28 nS (3.7×10^{-4} G_o), consistent with the conductance obtained in STM break junction experiments (Figure 1B).

Replacement of thiol anchoring groups by carbodithioate groups results in an enhanced single molecule conductance of 210 nS (Figure 1C). The increase of conductance by the introduction of carbodithioate groups has been reported for biphenyl,[35] and OPE,[36] systems and supported by theoretical calculations, which indicates that the carbodithioate group can increase the molecule−electrode coupling and thus reduce the electrode−molecule contact resistance.
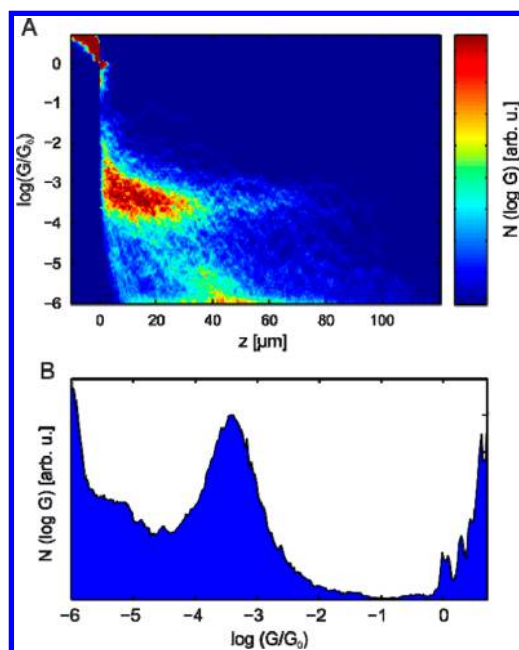
Figure 2. (A) Two-dimensional conductance versus push-rod displacement histogram constructed from 514 traces recorded at a bias voltage of 0.2 V for **BDF-S⁻**. (B) One-dimensional conductance histogram for **BDF-S⁻** showing a conductance peak at 28 nS (3.7×10^{-4} G_o).

Figure 3. (A) Cyclic voltammograms of **BDF-S⁻** (red) and **BDF-CS₂⁻** (blue) on Au(111) electrodes in 0.1 M HClO₄. Scan rate: 0.5 V/s. (B) Single molecule conductance of **BDF-S⁻** (red circles) and **BDF-CS₂⁻** (blue squares) as a function of gating (substrate electrode) potential determined from STM-BJ experiments.

To explore the device functions of these molecule-mediated junctions, we examined the potential-induced single molecule conductance switching effect of BDF derivatives in electrochemical electrolyte. Au(111) electrodes covered with immobilized thiol or carbodithioate terminated BDF derivatives show apparent redox peaks around 0.50 V (vs SCE). Cyclic voltammograms (CV) were measured in 0.1 M HClO₄ solution in an STM electrochemical cell with a sweep rate of 0.50 V/s (Figure 3A). Multiple CVs at different scan rates (0.05 to 1 V/s) are illustrated in the Supporting Information (Figure S4). Cyclic voltammetry experiments carried out in ionic liquid did not show such well-defined peaks. Therefore, we performed single molecule break junction measurements in HClO₄ instead of in ionic liquid.

The single molecule conductance of **BDF-S⁻** and **BDF-CS₂⁻** were measured by the STM break junction in 0.1 M HClO₄ electrolyte solution at different substrate potentials across the range of the electrochemical redox peaks. The general trend in both cases is that the molecule conductance increases gradually when the substrate potential steps positively from −0.05 V toward the formal electrochemical potentials (Figure 3A). The single molecule conductance reaches a maximum around 0.50 V, consistent with the electrochemical redox formal potentials (about 0.48 V) observed in the cyclic voltammograms (Figure 3A).

Single molecule gating experiments show that the conductance of BDF molecules changes as a function of the gating (substrate electrode) potential, exhibiting an off/on/off switching behavior (Figure 3B). However, an enhancement of the on/off ratio was observed when thiols were replaced by carbodithioate anchoring groups. For example, for **BDF-S⁻** the initial conductance is about 20 nS, and the maximum gated conductance is 48 nS (Figure 3B, red and Supporting Information) resulting in an on/off ratio of ∼2.5. In contrast, the on/off ratio is enhanced to be 8 as the conductance changes
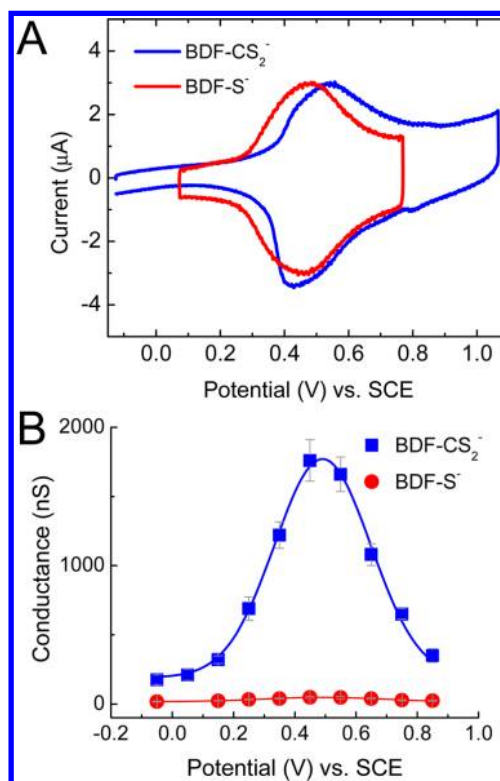
from the initial 220 nS to 1760 nS at the maximum for **BDF-CS₂⁻**. The increased on/off ratio is a consequence of the use of the CS₂ anchoring group as rationalized by a simple model and calculation presented in the Supporting Information. Conductance of **BDF-S⁻** (20 nS) at a sample potential of −0.05 V, away from the redox formal potential, has a similar conductance with the one measured in the mesitylene (23 nS), indicating that the solvent effect on single molecule conductance is negligible for the studied system.

In summary, we have demonstrated the first study of single molecule charge transport through a benzodifuran core—a novel category of redox-active molecules for functional molecular devices—using both STM-BJ and MCBJ techniques. Single molecule conductance values were determined by STM break junction to be 23 nS (consistent with 28 nS by MCBJ measurement). Replacing the thiol by carbodithioate anchoring groups led to an increase of conductance to 220 nS, further supporting our hypothesis that CS₂⁻ anchoring groups have a small contact resistance and can enhance the junction conductance. Furthermore, electrochemical gating experiments in electrolyte show that both BDF derivatives terminated with thiol or carbodithioate anchoring groups exhibit an off/on/off gating effect, with an on/off ratio of 2.5 for the former and 8 for the latter. This result indicates that reducing the contact resistance between molecules and electrodes can improve the gating effect. These experiments represent the first attempt to correlate the molecule/electrode contact resistance to the electrochemical gating, an important type of molecular switching. Therefore, the present study may have a fundamental impact on molecular devices and nanoelectronics, for example,

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fabricating complex molecular switching and electrical regulators.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental section, details about synthesis of compounds **BDF-SAc** and **BDF-CS$_2$TMSE**, intuitive model and calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Nitzan, A.; Ratner, M. A. *Science* **2003**, *300*, 1384.
(2) Donhauser, Z. J.; Mantooth, B. A.; Kelly, K. F.; Bumm, L. A.; Monnell, J. D.; Stapleton, J. J.; Price, D. W.; Rawlett, A. M.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **2001**, *292*, 2303.
(3) Yan, H. J.; Bergren, A. J.; McCreery, R.; Della Rocca, M. L.; Martin, P.; Lafarge, P.; Lacroix, J. C. *Proc. Natl. Acad. Sci. U.S.A.* **2013**, *110*, 5326.
(4) van der Molen, S. J.; Liljeroth, P. *J. Phys. Condens. Matter* **2010**, *22*, 133001.
(5) Li, Z.; Smeu, M.; Afsari, S.; Xing, Y.; Ratner, M. A.; Borguet, E. *Angew. Chem., Int. Ed.* **2014**, *53*, 1098.
(6) Xiao, X. Y.; Xu, B. Q.; Tao, N. J. *J. Am. Chem. Soc.* **2004**, *126*, 5370.
(7) Roldan, D.; Kaliginedi, V.; Cobo, S.; Kolivoska, V.; Bucher, C.; Hong, W.; Royal, G.; Wandlowski, T. *J. Am. Chem. Soc.* **2013**, *135*, 5974.
(8) Martin, S.; Haiss, W.; Higgins, S. J.; Nichols, R. J. *Nano Lett.* **2010**, *10*, 2019.
(9) Tam, E. S.; Parks, J. J.; Shum, W. W.; Zhong, Y. W.; Santiago-Berrios, M. B.; Zheng, X.; Yang, W. T.; Chan, G. K. L.; Abruna, H. D.; Ralph, D. C. *ACS Nano* **2011**, *5*, 5115.
(10) Li, Z. H.; Liu, Y. Q.; Mertens, S. F. L.; Pobelov, I. V.; Wandlowski, T. *J. Am. Chem. Soc.* **2010**, *132*, 8187.
(11) Kay, N. J.; Higgins, S. J.; Jeppesen, J. O.; Leary, E.; Lycoops, J.; Ulstrup, J.; Nichols, R. J. *J. Am. Chem. Soc.* **2012**, *134*, 16817.
(12) Leary, E.; Higgins, S. J.; van Zalinge, H.; Haiss, W.; Nichols, R. J.; Nygaard, S.; Jeppesen, J. O.; Ulstrup, J. *J. Am. Chem. Soc.* **2008**, *130*, 12204.
(13) Guo, S. Y.; Artes, J. M.; Diez-Perez, I. *Electrochim. Acta* **2013**, *110*, 741.
(14) Capozzi, B.; Chen, Q.; Darancet, P.; Kotiuga, M.; Buzzeo, M.; Neaton, J. B.; Nuckolls, C.; Venkataraman, L. *J. Am. Chem. Soc.* **2014**, *14*, 1400.
(15) Haiss, W.; van Zalinge, H.; Higgins, S. J.; Bethell, D.; Hobenreich, H.; Schiffrin, D. J.; Nichols, R. J. *J. Am. Chem. Soc.* **2003**, *125*, 15294.
(16) Xu, B. Q.; Xiao, X. Y.; Yang, X. M.; Zang, L.; Tao, N. J. *J. Am. Chem. Soc.* **2005**, *127*, 2386.
(17) Liao, J. H.; Agustsson, J. S.; Wu, S. M.; Schonenberger, C.; Calame, M.; Leroux, Y.; Mayor, M.; Jeannin, O.; Ran, Y. F.; Liu, S. X.; Decurtins, S. *Nano Lett.* **2010**, *10*, 759.
(18) Haiss, W.; van Zalinge, H.; Hobenreich, H.; Bethell, D.; Schiffrin, D. J.; Higgins, S. J.; Nichols, R. J. *Langmuir* **2004**, *20*, 7694.
(19) Li, Z.; Han, B.; Meszaros, G.; Pobelov, I.; Wandlowski, T.; Blaszczyk, A.; Mayor, M. *Faraday Discuss.* **2006**, *131*, 121.
(20) Diez-Perez, I.; Li, Z. H.; Guo, S. Y.; Madden, C.; Huang, H. L.; Che, Y. K.; Yang, X. M.; Zang, L.; Tao, N. J. *ACS Nano* **2012**, *6*, 7044.
(21) Diez-Perez, I.; Li, Z. H.; Hihath, J.; Li, J. H.; Zhang, C. Y.; Yang, X. M.; Zang, L.; Dai, Y. J.; Feng, X. L.; Muellen, K.; Tao, N. J. *Nat. Commun.* **2010**, *1*, 31.
(22) Shukla, R.; Wadumethrige, S. H.; Lindeman, S. V.; Rathore, R. *Org. Lett.* **2008**, *10*, 3587.
(23) Yi, C. Y.; Blum, C.; Lehmann, M.; Keller, S.; Liu, S. X.; Frei, G.; Neels, A.; Hauser, J.; Schürch, S.; Decurtins, S. *J. Org. Chem.* **2010**, *75*, 3350.
(24) Keller, S.; Yi, C. Y.; Li, C.; Liu, S. X.; Blum, C.; Frei, G.; Sereda, O.; Neels, A.; Wandlowski, T.; Decurtins, S. *Org. Biomol. Chem.* **2011**, *9*, 6410.
(25) Li, H.; Ding, J.; Chen, S. J.; Beyer, C.; Liu, S. X.; Wagenknecht, H. A.; Hauser, A.; Decurtins, S. *Chem.—Eur. J.* **2013**, *19*, 6459.
(26) Tsuji, H.; Mitsui, C.; Sato, Y.; Nakamura, E. *Adv. Mater.* **2009**, *21*, 3776.
(27) Tsuji, H.; Mitsui, C.; Ilies, L.; Sato, Y.; Nakamura, B. *J. Am. Chem. Soc.* **2007**, *129*, 11902.
(28) Li, Z.; Borguet, E. *J. Am. Chem. Soc.* **2012**, *134*, 63.
(29) Gruter, L.; Gonzalez, M. T.; Huber, R.; Calame, M.; Schonenberger, C. *Small* **2005**, *1*, 1067.
(30) Gonzalez, M. T.; Wu, S. M.; Huber, R.; van der Molen, S. J.; Schonenberger, C.; Calame, M. *Nano Lett.* **2006**, *6*, 2238.
(31) Xu, B. Q.; Tao, N. J. *Science* **2003**, *301*, 1221.
(32) Li, C.; Pobelov, I.; Wandlowski, T.; Bagrets, A.; Arnold, A.; Evers, F. *J. Am. Chem. Soc.* **2008**, *130*, 318.
(33) Choi, S. H.; Kim, B.; Frisbie, C. D. *Science* **2008**, *320*, 1482.
(34) Huber, R.; Gonzalez, M. T.; Wu, S.; Langer, M.; Grunder, S.; Horhoiu, V.; Mayor, M.; Bryce, M. R.; Wang, C. S.; Jitchati, R.; Schonenberger, C.; Calame, M. *J. Am. Chem. Soc.* **2008**, *130*, 1080.
(35) Tivanski, A. V.; He, Y. F.; Borguet, E.; Liu, H. Y.; Walker, G. C.; Waldeck, D. H. *J. Phys. Chem. B* **2005**, *109*, 5398.
(36) Xing, Y. J.; Park, T. H.; Venkatramani, R.; Keinan, S.; Beratan, D. N.; Therien, M. J.; Borguet, E. *J. Am. Chem. Soc.* **2010**, *132*, 7946.