

## Phosphine Sulfides as an Anchor Unit for Single Molecule Junctions

Aiko Fukazawa,<sup>\*1</sup> Manabu Kiguchi,<sup>\*2,†</sup> Satoshi Tange,<sup>1</sup> Yasunori Ichihashi,<sup>1</sup> Qiang Zhao,<sup>1</sup> Takuya Takahashi,<sup>2</sup> Tatsuya Konishi,<sup>2</sup> Kei Murakoshi,<sup>2</sup> Yuta Tsuji,<sup>3</sup> Aleksandar Staykov,<sup>3</sup> Kazunari Yoshizawa,<sup>\*3</sup> and Shigehiro Yamaguchi<sup>\*1</sup><sup>1</sup>Department of Chemistry, Graduate School of Science, Nagoya University, Furo, Chikusa-ku, Nagoya, Aichi 464-8602<sup>2</sup>Division of Chemistry, Graduate School of Science, Hokkaido University, N10W8, Kita-ku, Sapporo, Hokkaido 060-0810<sup>3</sup>Institute for Materials Chemistry and Engineering, Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395

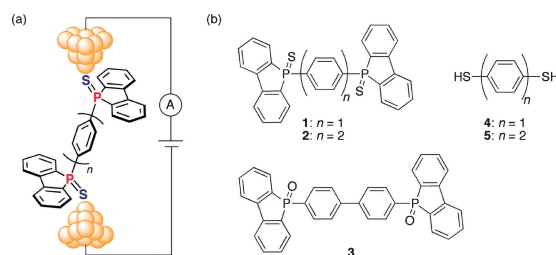
(Received November 22, 2010; CL-100982; E-mail: yamaguchi.shigehiro@b.mbox.nagoya-u.ac.jp)

Phenylene and biphenyl compounds with dibenzophosphole sulfide (DBPS) as an anchoring group for single molecule junctions were synthesized. The conductance measurements revealed that the phosphine sulfide indeed acts as an anchoring group for Au electrodes. Theoretical calculations including metal electrodes demonstrated that the LUMO level of the DBPS-terminated biphenyl is close to the Au Fermi level, leading to the electron conduction of the Au–molecule–Au junction based on the resonance-tunneling mechanism.

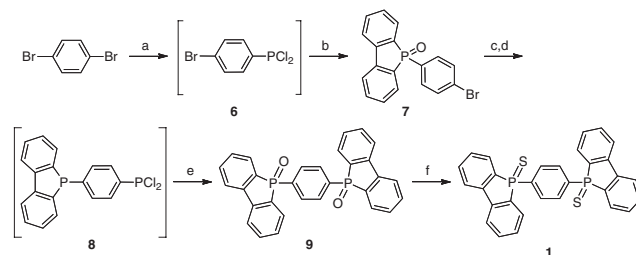
Electron-transport properties through single molecules have attracted growing attention as the basis for fabricating ultrasmall electronic devices.<sup>1,2</sup> Recent extensive studies on a variety of single molecule junctions revealed that the electron conduction through a molecule bonded between two metal electrodes highly depends on the nature of anchoring groups, which affects not only the HOMO–LUMO energy gap of the whole molecular system, but also the alignment of the energy levels of these frontier MOs against the electrode Fermi level.<sup>2,3</sup> The development of a new anchoring group as well as the deep understanding of the conduction mechanism are therefore urgent subjects for the evolution of single molecule electronics. Besides the combination of thiol (–SH) and Au electrodes, a variety of anchoring groups has been investigated, such as pyridine,<sup>4</sup> isocyanide,<sup>5,6</sup> carboxylate,<sup>7</sup> selenide,<sup>8</sup> amine,<sup>9–13</sup> phosphine,<sup>14</sup> C<sub>60</sub>,<sup>15</sup> and carbon<sup>16,17</sup> for various electrodes.

In this study, we explored the possibility of using a phosphine sulfide (P=S) bond as a new anchoring group to form single molecule junctions with Au electrodes. The P=S bond has several characteristics. First, a sulfur atom in the P=S bond has high affinities to various metals, such as Au, Ag, and Cu, leading to strong adsorption.<sup>18</sup> Second, phosphine sulfides have high chemical and thermal stability among the various types of organophosphorus compounds, which guarantees their versatile use for the molecular junction. Moreover, the P=S group acts as a strong electron-withdrawing group. We envisioned that the incorporation of a P=S group as an anchor to a certain  $\pi$ -conjugated skeleton would decrease the LUMO level of the molecular system,<sup>19,20</sup> and thus affect the electron-transport mechanism. To minimize the steric hindrance around the P=S moiety, we decided to employ a dibenzophosphole sulfide (DBPS) skeleton. As a model system, we synthesized the DBPS-terminated phenylene **1** and biphenyl-4,4'-diyl **2** (Figure 1b). We now disclose the electron conductance of these molecular systems and some insights into their conduction mechanism.

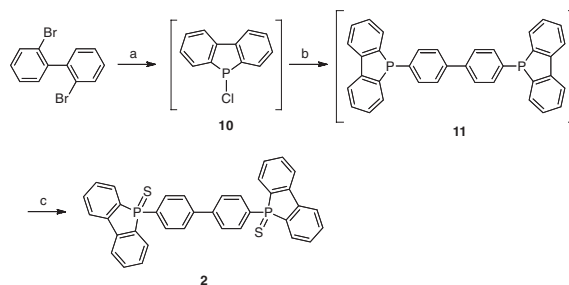
Compounds **1** and **2** were synthesized in different ways, as shown in Schemes 1 and 2, respectively. The biphenyl derivative **2** was readily prepared by the reaction of *P*-chlorodi-



**Figure 1.** (a) Illustration of an assumed contact of the DBPS-terminated oligo(*p*-phenylene)s in a broken gold gap. (b) Structures of the molecules studied in this study.

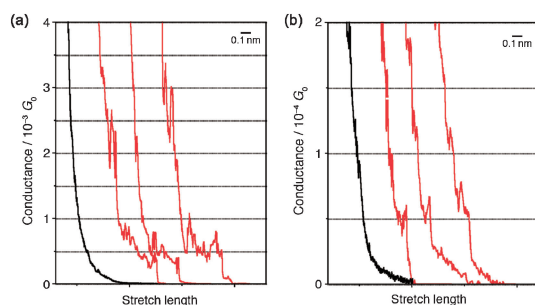


**Scheme 1.** Reagents and conditions for the synthesis of **1**: (a) Mg, Et<sub>2</sub>O, reflux, then PCl<sub>3</sub>, 0 °C to rt; (b) 2,2'-dilithiobiphenyl, Et<sub>2</sub>O, 0 °C, then H<sub>2</sub>O<sub>2</sub> aq., 14% (over 2 steps); (c) HSiCl<sub>3</sub>, toluene, 0 °C; (d) *n*-BuLi, Et<sub>2</sub>O, 0 °C, then PCl<sub>3</sub>, 0 °C to rt; (e) 2,2'-dilithiobiphenyl, Et<sub>2</sub>O, 0 °C, then H<sub>2</sub>O<sub>2</sub> aq., 3% (over 3 steps); (f) Lawesson reagent, toluene, reflux, 36%.



**Scheme 2.** Reagents and conditions: (a) *t*-BuLi, THF, –78 °C, then PCl<sub>3</sub> (excess), –196 °C to rt; (b) 4,4'-dilithiobiphenyl, THF, –78 °C; (c) S<sub>8</sub>, rt, 16% (over 3 steps).

benzophosphole (DBPCL) (**10**) with 4,4'-dilithiobiphenyl, followed by the oxidation with elemental sulfur (Scheme 2). However, a similar route based on the reaction between DBPCL and 1,4-dilithiobenzene did not afford **1** at all. Alternatively, by employing *P*-(4-bromophenyl)-DBP as a precursor, we in situ

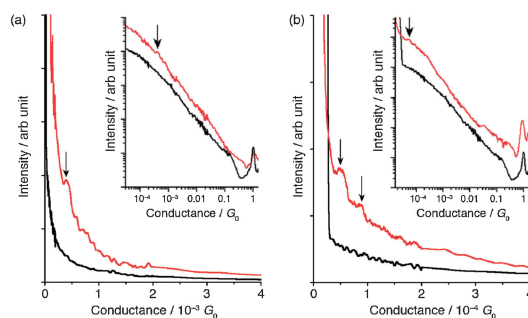


**Figure 2.** Examples of conductance traces of gold nanocontacts measured in the presence (red line) and absence (black line) of (a) **1** and (b) **2** in mesitylene.

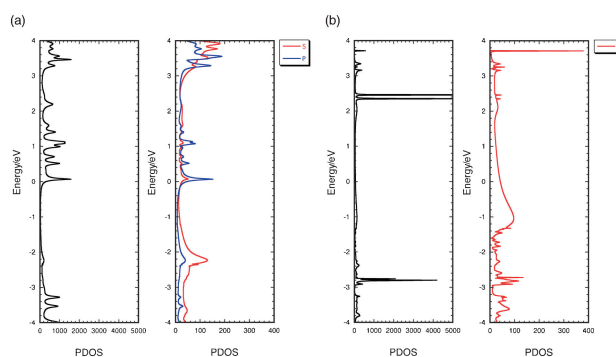
generated a *P*-4-(dichlorophosphanyl)phenyl derivative **8** by the successive treatment with *n*-BuLi and  $\text{PCl}_3$  and then reacted this compound with 2,2'-dilithiobiphenyl. The oxidation of the produced mixture afforded the corresponding phosphine oxide **9**, which was further converted to **1** using Lawesson reagent (Scheme 1). As a reference compound, we also synthesized a dibenzophosphole oxide (DBPO)-terminated biphenyl **3** by a method similar to the synthesis of **2**. The details of these syntheses are described in Supporting Information (SI).<sup>21</sup>

Conductance measurements of the DBPS derivatives **1** and **2** were performed using a modified STM (Figure 1a). Thus, a Au STM tip was repeatedly moved into and out of contact with a Au substrate in a 0.1 or 0.2 mM sample solution in mesitylene. Conductance traces were recorded during breaking under an applied bias of 20 mV between the tip and substrate. The statistical data were obtained from 2000 conductance traces. The individual traces of **1** and **2** exhibited steps at the molecule-dependent conductance values less than the quantum of conductance  $G_0 = 2e^2/h$ . The conductance plateaus correspond to the conduction through a molecule bonded between the two Au point contacts (Figures 2a and 2b). Figures 3a and 3b are conductance histograms of **1** and **2**, respectively, both of which showed obvious peaks. Such peak structures were not observed in either the conductance traces nor histograms obtained in the absence of molecules (Figures 2 and 3). In addition, as shown in the insets in Figures 3a and 3b, both conductance histograms of compounds **1** and **2** on the log–log plot exhibited significant peaks before the contacts were broken under our experimental conditions. Therefore, the last plateau before the contact is broken in the conductance trace and a peak observed in the conductance histogram likely originates from the formation of stable single Au–**1**–Au and Au–**2**–Au junctions. The conductance values of the single molecule junctions were determined to be  $5(2) \times 10^{-4}$  and  $5(2) \times 10^{-5} G_0$  for **1** and **2**, respectively. These results demonstrated that the phosphine sulfide indeed acts as an anchoring group for the Au–molecule junction.

In order to assess these values, we also determined the electron conductance values for DBPO-terminated biphenyl **3** as well as thiol-terminated analogs **4** and **5** under the same measurement conditions.<sup>21</sup> Notably, the conductance histogram of **3** did not show any significant peak, indicative of either its poor electron-conductance or poor adsorption ability on the gold electrode. The use of the P=S group is likely crucial for the formation of the Au–molecule contact. On the other hand, while the conductance of the biphenyl-4,4'-dithiol **5**



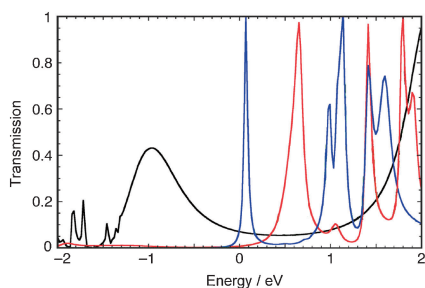
**Figure 3.** Conductance histograms of gold nanocontacts constructed from 2000 traces measured in the presence (red line) and absence (black line) of (a) **1** and (b) **2** in mesitylene. The insets show the conductance histograms on the log–log plot.



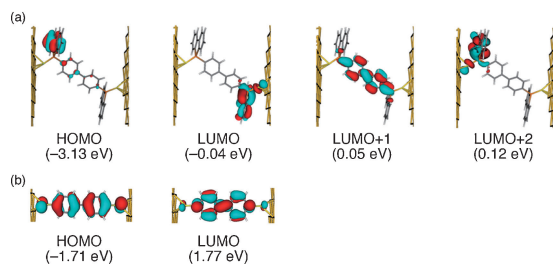
**Figure 4.** (a) The PDOS of **2** (black) and the projection onto the terminal sulfur atoms (red) and phosphorus atoms (blue). (b) The PDOS of **5** (black) and the projection onto the terminal sulfur atoms (red).

( $3(1) \times 10^{-5} G_0$ ) was two-orders-of-magnitude lower than that of the benzene-1,4-dithiol **4** ( $3(1) \times 10^{-3} G_0$ ),<sup>22</sup> the difference in conductance between the DBPS-terminated phenylene **1** and biphenyl-4,4'-diyl **2** was only one-order-of-magnitude. These results imply that the conduction mechanism in the DBPS-anchored systems is different from that in the thiol-anchored systems.

To elucidate the difference in the conduction properties between the DBPS- and thiol-anchored systems, we performed theoretical calculations using the nonequilibrium Green's function combined with density functional theory (NEGF-DFT).<sup>23–25</sup> PDOS (phonon density of states) and zero-bias transmission spectra of the Au–molecule–Au junctions of the DBPS- and thiol-terminated biphenyls **2** and **5** are shown in Figures 4 and 5, respectively. Whereas in the thiol **5** the Fermi level (where  $E = 0$ ) is located in the middle of the HOMO–LUMO gap, the DBPS-biphenyl **2** has a rather low-lying LUMO, which is closer to the Fermi level. According to differential pulse voltammetry (DPV) measurements in THF, compounds **1** and **2** indeed exhibited the first reduction waves with low peak potentials at  $-1.90$  and  $-1.91$  V vs. ferrocene/ferrocenium couple, respectively. These results are due to the electron-withdrawing nature of the P=S moiety. Notably, this low-lying LUMO plays an important role in the electron-transport properties. In the transmission spectra (Figure 5), while **5** has a broad peak below the Fermi level, **2** shows a sharp transmission peak close to the Fermi level. This suggests that while the electron transport of



**Figure 5.** The zero-bias transmission spectra of the Au-molecule-Au junctions of compounds **1** (red), **2** (blue), and **5** (black).



**Figure 6.** MPSH states of (a) **2** and (b) **5** for applied bias of 0 V.

**5** occurs based on tunneling, the electron transport of **2** is attributable to the resonance tunneling through the LUMO and close-lying unoccupied MOs.<sup>26</sup> This mechanism should be responsible for the comparable low bias conductance value of **2** to that of **5**. According to the molecular projected self-consistent Hamiltonian states (MPSH) analysis of **2** including the Au electrodes, the spatial distributions of its unoccupied MOs are rather localized and the amplitudes of the terminal sulfur atoms are small (Figure 6). Whereas this suggests that the electron transport between **2** and the electrodes occurs via a through-space process, this may not have any serious detrimental effect on the conductance in the low-bias regime when the resonance condition for **2** is fulfilled. However, in the high-bias regime, when the resonance condition is also fulfilled for **5**, the observed conductance for **5** will significantly exceed that for **2**.

In summary, we demonstrated the utility of phosphine sulfide as an anchoring group at the Au-molecule junction. The high stability as well as strong electron-withdrawing effect makes this functional group a distinctive anchor unit. In particular, the DBPS-anchored biphenyl provides a good example that allows electron conduction through the resonance-tunneling mechanism.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 17069011; M.K. and S.Y.) and Research and Education Funding for Inter-University Research Project (Kyoto Univ./Nagoya Univ./Kyushu Univ.; K.Y. and S.Y.) from the MEXT, Japan, and PRESTO, Japan Science and Technology Agency (M.K.).

## References and Notes

† Present address: Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8551

- C. Joachim, M. A. Ratner, *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 8801.
- A. Salomon, D. Cahen, S. Lindsay, J. Tomfohr, V. B. Engelkes, C. D. Frisbie, *Adv. Mater.* **2003**, *15*, 1881.
- T. Tada, K. Yoshizawa, *ChemPhysChem* **2002**, *3*, 1035.
- B. Xu, N. J. Tao, *Science* **2003**, *301*, 1221.
- J. M. Beebe, V. B. Engelkes, L. L. Miller, C. D. Frisbie, *J. Am. Chem. Soc.* **2002**, *124*, 11268.
- M. Kiguchi, S. Miura, K. Hara, M. Sawamura, K. Murakoshi, *Appl. Phys. Lett.* **2006**, *89*, 213104.
- F. Chen, X. Li, J. Hihath, Z. Huang, N. Tao, *J. Am. Chem. Soc.* **2006**, *128*, 15874.
- L. Patrone, S. Palacin, J. P. Bourgoin, *Appl. Surf. Sci.* **2003**, *212–213*, 446.
- L. Venkataraman, J. E. Klare, I. W. Tam, C. Nuckolls, M. S. Hybertsen, M. L. Steigerwald, *Nano Lett.* **2006**, *6*, 458.
- L. Venkataraman, J. E. Klare, C. Nuckolls, M. S. Hybertsen, M. L. Steigerwald, *Nature* **2006**, *442*, 904.
- L. Venkataraman, Y. S. Park, A. C. Whalley, C. Nuckolls, M. S. Hybertsen, M. L. Steigerwald, *Nano Lett.* **2007**, *7*, 502.
- S. Y. Quek, L. Venkataraman, H. J. Choi, S. G. Louie, M. S. Hybertsen, J. B. Neaton, *Nano Lett.* **2007**, *7*, 3477.
- M. Kiguchi, S. Miura, K. Hara, M. Sawamura, K. Murakoshi, *Appl. Phys. Lett.* **2007**, *91*, 053110.
- Y. S. Park, A. C. Whalley, M. Kamenetska, M. L. Steigerwald, M. S. Hybertsen, C. Nuckolls, L. Venkataraman, *J. Am. Chem. Soc.* **2007**, *129*, 15768.
- C. A. Martin, D. Ding, J. K. Sørensen, T. Bjørnholm, J. M. van Ruitenbeek, H. S. J. van der Zant, *J. Am. Chem. Soc.* **2008**, *130*, 13198.
- S. Ranganathan, I. Steidel, F. Anariba, R. L. McCreery, *Nano Lett.* **2001**, *1*, 491.
- A. M. Ricci, E. J. Calvo, S. Martin, R. J. Nichols, *J. Am. Chem. Soc.* **2010**, *132*, 2494.
- T. S. Lobana, in *The Chemistry of Organophosphorus Compounds: Phosphine Oxides, Sulphides, Selenides and Tellurides*, ed. by F. R. Hartley, Wiley, Chichester, **1992**, Vol. 2, Chap. 8, p. 409.
- A. Fukazawa, Y. Ichihashi, Y. Kosaka, S. Yamaguchi, *Chem. Asian J.* **2009**, *4*, 1729.
- H. Tsuji, K. Sato, Y. Sato, E. Nakamura, *J. Mater. Chem.* **2009**, *19*, 3364.
- For the conductance histograms of compounds **3**, **4**, and **5**, see SI. Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.
- Recently, several reports regarding the observation of different conductance peaks ascribed to different contact geometries have appeared for the thiol-anchored single molecule junctions for instance, see: a) C. Li, I. Pobelov, T. Wandlowski, A. Bagrets, A. Arnold, F. Evers, *J. Am. Chem. Soc.* **2008**, *130*, 318. b) W. Haiss, C. Wang, R. Jitchati, I. Grace, S. Martin, A. S. Batsanov, S. J. Higgins, M. R. Bryce, C. J. Lambert, P. S. Jensen, R. J. Nichols, *J. Phys.: Condens. Matter* **2008**, *20*, 374119. Although compounds **4** and **5** may also adopt several different contact geometries, we observed only broad signals corresponding to the molecular conductance under our experiment condition. See SI for details.
- M. Brandbyge, J.-L. Mozos, P. Ordejón, J. Taylor, K. Stokbro, *Phys. Rev. B* **2002**, *65*, 165401.
- K. Stokbro, J. Taylor, M. Brandbyge, J.-L. Mozos, P. Ordejón, *Comput. Mater. Sci.* **2003**, *27*, 151.
- ATK Version 2008.07, quantumwise; <http://www.quantumwise.com>.
- For the transmission spectra upon applying an external bias, see SI.