Electrochemical wiring of α,ω-alkanedithiol molecules into an electrical circuit

Slawomir Sek,[ab] Renata Bilewicz[b] and Krzysztof Slowinski[*a]

[a] Department of Chemistry and Biochemistry, California State University, Long Beach, 1250 Bellflower Blvd., Long Beach, CA, United States. E-mail: kslowins@csulb.edu; Fax: +1 562 985 8558; Tel: +1 562 985 4843

[b] Department of Chemistry, University of Warsaw, Warsaw, Poland. E-mail: bilewicz@chem.uw.edu.pl. E-mail: slasek@chem.uw.edu.pl; Fax: +48 22 822 5996; Tel: +48 22 822 0211

The intrinsic electrical conductivity of α,ω-alkanedithiol increases if both ends of the molecule are covalently bonded to metallic contacts.

The effect of a covalent bond between the molecule and a metal electrode on the intrinsic electrical properties of a molecule continues to attract considerable scientific interest.[1,2]
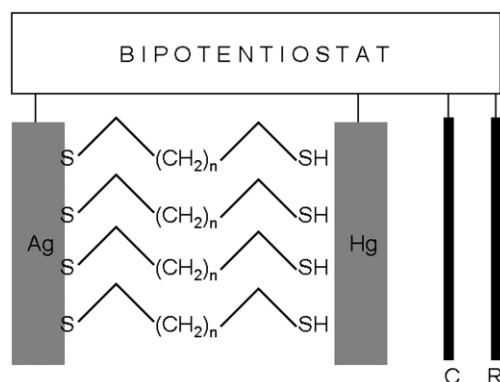
In this communication we report electrical characterization of a novel electrochemically controlled macroscopic Hg–(monolayer of n-alkanethiol or α,ω-alkanedithiol)–Ag tunneling junction. Our experimental approach allows us to induce, *in situ*, the formation of the S–Hg bond within the macroscopic Ag–α,ω-alkanedithiol monolayer/Hg junction while measuring the tunneling current across the monolayer.

Our data show that: (1) the conductivity of a fully bonded Ag–α,ω-alkanedithiol monolayer–Hg junction is at least 8–95 fold larger then the conductivity of an α,ω-alkanedithiol monolayer bonded to the Ag electrode only, and (2) the tunneling decay coefficient, β, is smaller for a fully bonded system indicating a lower energy barrier for long-range electron tunneling.

The Hg/(monolayer or bilayer of organic molecules)/Ele (Ele = Ag, Au, Hg, Si or C) junctions provide a convenient tool to study the effects of the molecular structure and the nature of the electrode/molecule interface on the rates of long-range electron tunneling.[3]

Our experimental approach involves the electrochemically controlled tunneling junction schematically shown in Fig. 1.

The silver electrode is covered with a self-assembled monolayer of α,ω-alkanethiol or n-alkanethiol and is immersed in a deoxygenated water solution containing supporting electrolyte.[4] The Hg and Ag electrodes are polarized independently and simultaneously to the different electrochemical potentials. Subsequently, the Hg drop extruded at the tip of the "L shaped" glass capillary is horizontally brought into contact with the monolayer modified Ag surface using

a micromanipulator. The final surface area of the resulting tunneling junction is equal to *ca.* 0.001 cm^2.[5] The voltage bias, $E = E_{Ag} - E_{Hg}$, causes the flow of tunneling current across the monolayer that can be measured as a function of time as illustrated in Fig. 2.[6]

The tunneling current, I, recorded in the experiments shown in Fig. 2 depends exponentially on the distance between the electrodes and it also depends, in a more complex manner, on the voltage applied between the electrodes [eqn. (1)]:[1–3]

$$I(E) = P(E) \exp\left[-\beta(E)\cdot d\right] \tag{1}$$

where E is the voltage applied across the junction, P is the preexponential factor, β is the tunneling coefficient and d is the distance between the electrodes.
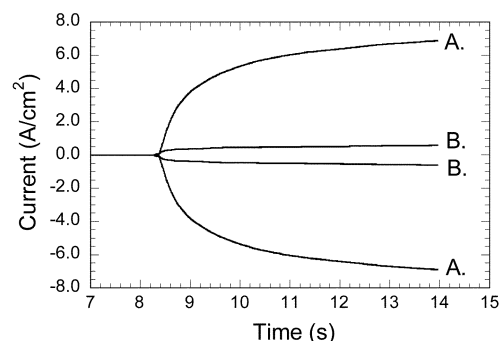
As shown schematically in Fig. 1, the terminal –SH groups react with the Hg surface upon physical contact according to the reaction (2):[8]

$$n\,R–SH + Hg \rightarrow (R–S)_n Hg + nH^+ + ne^-\ \ E' \approx -1\ V\ vs.\ SSCE \tag{2}$$
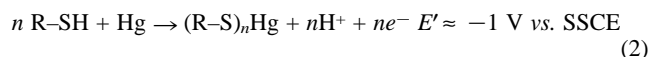
where E' is the potential of the oxidative adsorption of R–SH.[8]

Reaction (2), however, can be thermodynamically allowed or prevented by applying an appropriate electrochemical potential to the mercury drop. In particular, reaction (2) would not occur if the Hg electrode is polarized to a potential substantially more negative than E'. In the assembled junction with $E_{Hg} < E'$ (Fig. 1) the terminal –SH groups would be in physical contact with the Hg surface but the –S–Hg bond would not be formed.

The analysis of the data presented in Fig. 2 clearly indicates that a substantially larger tunneling currents flow if the Hg electrode is polarized to a potential allowing reaction (2) to occur. To study systematically the effect of S–Hg bond formation on the efficiency of electron tunneling through monolayers of various thicknesses, we have investigated three molecular systems based on Ag/Hg tunneling junctions. Fig. 3 shows a plot of the logarithm of tunneling current recorded at 0.4 V voltage bias as a function of the length of a molecule for: (A) α,ω-alkanedithiol for $E_{Hg} < E'$, (B) n-alkanethiol *regardless of the value of E_{Hg} potential*, and (C) α,ω-alkanedithiol for $E_{Hg} > E'$.[9]

Fig. 1 Scheme of an electrochemically controlled Ag/Hg tunnelling junction. The experiment is performed in a thiol-free 1 M KOH or 1 M LiClO$_4$ water solution. The Ag electrode is covered with a self-assembled monolayer of n-alkanethiol, C$_n$H$_{2n+1}$SH (n = 10–18) or α,ω-alkanedithiol, HS-(CH$_2$)$_n$-SH (n = 9–20). The Ag and Hg electrodes are held at constant potentials (E_{Hg}, E_{Ag}). All potentials are measured and reported *vs.* Ag/AgCl, Cl$^-$ (sat.) (SSCE) reference electrode. The C is a counter platinum electrode.

Fig. 2 Current–time curves recorded for a Au–S–(CH$_2$)$_{12}$–SH/Hg tunnelling junction at a constant bias voltage E = 0.4 V.[7] The electrochemical potentials of the electrodes are as follows: (A) E_{Hg} = −0.8 V; E_{Ag} = −0.4 V; (B) E_{Hg} = −1.2 V; E_{Ag} = −0.8 V.
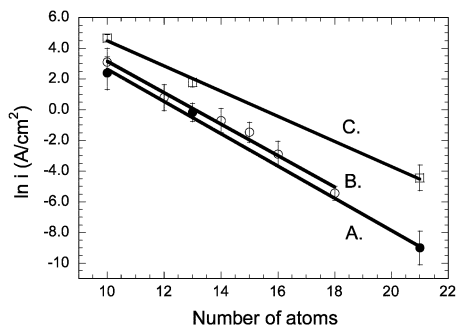
As shown in Fig. 3, all investigated monolayers follow essentially the relationship predicted by eqn. (1) with tunneling coefficient $\beta = 1.05 \pm 0.01/CH_2$ for monolayers A, $\beta = 1.02 \pm 0.06/CH_2$ for monolayers B and $\beta = 0.82 \pm 0.01/CH_2$ for monolayers C. To properly interpret the data presented in Figs. 2 and 3 one must realize that before the formation of a tunneling junction both electrodes are covered with ions and water due to the build-up of the electrical double layer. However, as we have shown previously for Hg–(n-alkanethiol bilayer or monolayer)–Hg junctions, these ions as well as water molecules are expelled from the junction area in the course of its formation.[3a] We point out that the current across n-alkanethiol monolayer does not depend on the potential of the Hg drop. Thus the interlayer structure between the Hg surface and the monolayer does not depend on the potential unless the chemical bond is formed.[10] Fig. 3 indicates that an α,ω-alkanedithiol monolayer for $E_{Hg} < E'$ behaves identically to the well known n-alkanethiol monolayers.[3] On the other hand, the values of tunneling current for α,ω-alkanedithiol for $E_{Hg} > E'$ are not only substantially higher but they also produce different tunneling coefficient, β. This effect might be explained, in part, by the change of distance between the Ag and Hg surfaces due to the chemical reaction between terminal –SH group and Hg surface.

The lengths of Hg–S and H–S bonds are equal to 1.1 Å and 1.3 Å respectively. The distance between the terminal –H atom and the surface of mercury is expected to be smaller than 2 Å.[11] Consequently the difference in length between the "–CH$_2$–S–Hg" and the "–CH$_2$–S–H/Hg" structures should be in the order of 2.2 Å. In view of eqn. (1), this difference in distance should produce $ca.$ 9 fold difference in tunneling current.[12] This is clearly less than the observed $ca.$ 90 fold difference for tunneling junctions containing α,ω-docosanedithiol.

A similar effect was recently observed by Lindsay and coworkers for conductivities of α,ω-alkanedithiol measured using conductive probe–atomic force microscopy.[2c,d] These authors postulate that the energy difference between the Fermi level and the molecular orbital that mediates tunneling is different in a molecule connected at both ends to the metallic contacts compared to a molecule chemically connected to the electrode at one end only. For the fully bonded systems, the overall increase in conductivity is combined with smaller values of the tunneling coefficient and in turn with smaller height of the tunneling barrier.

Finally, we would like to emphasize that the presented analysis does not account for any possible changes in the conformation of hydrocarbons upon the reaction of terminal –SH group with Hg. We point out however that such a change would likely result in a disorder of hydrocarbons within the monolayer thus causing overall decrease (and not an increase) of electronic coupling.[3c]

In conclusion, our experimental results strongly support the hypothesis that the relative energy of the molecular orbitals mediating electron tunneling strongly depend on whether the molecule is fully bonded into the electrical circuit thus emphasizing the importance of contact in molecular electronics.

Notes and references

1 (a) A. Nitzan and M. A. Ratner, $Science$, 2003, **300**, 1384; (b) W. Wang, T. Lee and M. A. Reed, $Phys.\ Rev.\ B$, 2003, **68**, 35416; (c) J. G. Kushmerick, D. B. Holt, J. C. Yang, J. Naciri, M. H. Moore and R. Shashidhar, $Phys.\ Rev.\ Lett.$, 2002, **89**, 86802.

2 (a) B. Xu and N. J. Tao, $Science$, 2003, **301**, 1221; (b) Y. Selzer, A. Salomon and D. Cahen, $J.\ Phys.\ Chem.\ B$, 2002, **106**, 10432; (c) X. D. Cui, A. Primak, X. Zarate, J. Tomfohr, O. F. Sankey, A. L. Moore, T. A. Moore, D. Gust, L. A. Nagahara and S. M. Lindsay, $J.\ Phys.\ Chem.\ B$, 2002, **106**, 8609; (d) X. D. Cui, A. Primak, X. Zarate, J. Tomfohr, O. F. Sankey, A. L. Moore, D. Gust, G. Harris and S. M. Lindsay, $Science$, 2001, **294**, 571.

3 (a) R. L. York, P. T. Nguyen and K. Slowinski, $J.\ Am.\ Chem.\ Soc.$, 2003, **125**, 5948–5953; (b) K. Slowinski, H. K. Y. Fong and M. Majda, $J.\ Am.\ Chem.\ Soc$, 1999, **121**, 7257; (c) K. Slowinski and M. Majda, $J.\ Electroanal.\ Chem$, 2000, **491**, 139; (d) M. L. Chabinyc, X. X. Chen, R. E. Holmlin, H. Jacobs, H. Skulason, C. D. Frisbie, V. Mujica, M. A. Ratner, M. A. Rampi and G. M. Whitesides, $J.\ Am.\ Chem.\ Soc$, 2002, **124**, 11730; (e) M. A. Rampi and G. M. Whitesides, $Chem.\ Phys.$, 2002, **281**, 373; (f) R. E. Holmlin, R. F. Ismagilov, R. Haag, V. Mujica, M. A. Ratner, M. A. Rampi and G. M. Whitesides, $Angew.\ Chem.,\ Int.\ Ed.$, 2001, **40**, 2316; ($g$) F. Anariba and R. L. McCreery, $J.\ Phys.\ Chem.\ B$, 2002, **106**, 10355.

4 100 nm of silver was evaporated in 5×10^{-7} Torr vacuum on the glass slide covered with a 5 nm "adhesive" Cr layer. In order to form self-assembled monolayer, the 24 h self-assembly was performed from a diluted ethanolic solution of an appropriate n-alkanethiol or α,ω-alkanedithiol.

5 The junction is observed and its diameter is measured using a video camera connected to a microscope. We estimate that the junction diameter can be typically measured with $ca.$ 5% precision.

6 We are actually recording two tunneling currents: the electrons leaving Hg electrode are recorded as "cathodic current", and the electrons entering Ag electrode are recorded as "anodic current". These two currents are equal to each other at any given time after junction formation. We did not detect any Faradaic processes in the solution within the range of electrochemical potentials used in our experiments. Therefore ion mobility does not contribute to the measured tunneling currents.

7 We have never observed truly steady-state currents because of junction collapse. We notice, however, that the current rise observed between the 10th and 14th second of the experiment on Fig. 2 translates into less than 0.2 Å difference in thickness (assuming tunneling coefficient $\beta \approx 1/\text{Å}$, see eqn. (1)). The junction is stable for 4–300 s after its formation.

8 (a) K. J. Stevenson, M. Mitchell and H. S. White, $J.\ Phys.\ Chem.\ B$, 1998, **102**, 1235; (b) K. Slowinski, R. V. Chamberlain, C. J. Miller and M. Majda, $J.\ Am.\ Chem.\ Soc.$, 1997, **119**, 11910; (c) N. Muskal, J. Turyan and D. Mandler, $J.\ Electroanal.\ Chem.$, 1996, **409**, 131.

9 The number of atoms is calculated as follows: for n-alkanethiols, only carbon atoms are counted, for α,ω-alkanedithiols one sulfur atom is added to the overall length of the molecule.

10 We have demonstarted previously that the hexanol molecules physically adsorbed on the Hg surface are expelled from the junction formed between the Hg drop and an alkanethiol monolayer (see ref. 3a). This experiment indicates that the "squeezing" forces remove solvent and ions form the Hg/monolayer gap.

11 The electronic structure calculations indicate that the terminal –H atom is about 1.68 A below the ideal Au surface in the Au--alkanethiol/Au structure. See ref. 2c.

12 Assuming tunneling coefficient $\beta = 1/\text{Å}$.

Fig. 3 Logarithm of the current density $vs.$ number of atoms in tunnelling junctions: (A) α,ω-alkanedithiols, $E_{Hg} = -1.2$ V; $E_{Ag} = -0.8$ V; (B) n-alkanethiols, $E_{Hg} = -0.8$ V to -1.2 V; $E_{Ag} = -0.4$ V to -0.8 V, bias voltage $E = 0.4$ V; (C) α,ω-alkanedithiols, $E_{Hg} = -0.8$ V; $E_{Ag} = -0.4$ V.