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Long-Range Electron Transfer through Monolayers and Bilayers of Alkanethiols in Electrochemically Controlled Hg–Hg Tunneling Junctions

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Abstract: The rates of electron tunneling through monolayers and bilayers of alkanethiols self-assembled in a potentiostatically controlled Hg–Hg junction are reported. An alkanethiolate monolayer is formed in situ on one or both Hg drops via oxidative adsorption at the controlled potential. Subsequently, the Hg drops are brought into contact using micromanipulators. The junction formation is instantly followed by the flow of a steady-state tunneling current between the two electrodes. A plot of the logarithm of the tunneling current density vs the total number of carbon atoms in each junction yields identical tunneling coefficients, $\beta = 1.06 \pm 0.04/-\text{CH}_2-$ and $\beta = 1.02 \pm 0.07/-\text{CH}_2-$, for monolayers and bilayers of alkanethiols, respectively. Careful examination of the tunneling data indicates that the solvent and ions are ejected from the junction area. The tunneling current recorded for a bilayer of 1-octanethiol or 1-nonanethiol is ca. 2-fold larger than a corresponding tunneling current recorded for monolayers of 1-hexadecanethiol or 1-octadecanethiol, respectively. This result is explained in terms of weak electronic coupling across the noncovalent molecule/electrode interface.

Introduction

The effect of metal–molecule contact on the rate and the mechanism of long-range electron transfer (ET) across a metal–molecule–metal junction is of crucial importance in molecular electronics.^{1,2} In this report we describe ET measurements in a potentiostatically controlled Hg–Hg tunneling junction. Our data shows that electron tunneling across a van der Waals contact between a Hg electrode and a hydrocarbon chain is inefficient compared to ET along the all-trans hydrocarbon chain.

Rates of ET through organic molecules are measured using several experimental methods including: photoinduced ET between a donor and acceptor of electrons synthetically attached to certain points of the molecule,³ electrochemical measurements

of ET between an electrode and a redox probe separated by an organized monolayer film,⁴ and the tunneling junction method.⁵ These measurements show that the rate of ET is sensitive not only to the length but also to the structure and the conformation of a molecular bridge. In particular, ET along a simple hydrocarbon chain (through-bond tunneling) is more efficient than tunneling across van der Waals contacts (through-space tunneling).^{4f} Furthermore, the presence of a lateral hydrogen-bond network enhances the ET across monolayers.^{4a,d} Recent experiments reveal the particularly efficient electronic coupling across strongly π -conjugated monolayer films.^{4b,c,e}

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Among all the methods used to determine the rates of ET, the tunneling junction method is arguably most relevant to molecular electronics applications.⁵ The tunneling junction, consisting of two metal plates separated by molecules of interest, can be assembled using several approaches, among them: scanning tunneling microscopy (with,^{5a} or without,^{5d} the control of the contact force of an STM tip), conductive probe–atomic force microscopy,^{1c,2a,b,e–g,5c} sandwich-type junctions with an evaporated metal layer,^{5e,j} metal-capped nanopores,^{5f} break junctions,^{5g} and crossed wires.^{5b} In all experiments referred to above the nature of the contact between the molecule and a metallic electrode is of crucial importance in determining the true intrinsic electrical properties of the molecule.^{1,2,5} Recent work by Lindsay et al.^{2c–g} has shown that the mechanism of ET and the conductivity of the single saturated hydrocarbon chain depend critically on whether the ends of the molecule are chemically bonded to metallic contacts. In particular, the height of the tunneling barrier is significantly smaller for fully bonded metal–molecule–metal structures in comparison to metal–molecule/metal systems containing a physical gap at the metal/molecule interface.^{2c} Cahen and co-workers have recently observed that the mechanism of electron transport across Hg/alkylsilanes/SiO₂/p-Si junction is substantially different (no distance dependence) from the tunneling across Hg/alkylthiols/SiO₂/p-Si junction.^{2d} They ascribed the difference to the lack of bonding in the alkylsilanes junction.

Recently, the macroscopic tunneling junction method based on a Hg drop coated with a monolayer of alkanethiols has received much attention.⁶ The electrical properties of bilayers of several aliphatic and aromatic thiols sandwiched between electrodes in Hg–Hg,^{6a–c,e,i} Hg–Ag,^{6d–h} and Hg–Au^{6h} junctions were reported. This method was further extended to include carbon–monolayer/Hg⁷ and the silicon/monolayer/Hg structures.^{2c,d}

Electron transport in Hg–alkanethiol bilayer–metal junctions is dominated by electron tunneling with the tunneling current, I , decaying exponentially with the junction thickness according to the eq 1:^{1,2,6}

$$I = I_0 \exp(-\beta N) \quad (1)$$

where β is the decay constant (tunneling coefficient) reflecting the strength of electronic coupling across a particular molecular bridge and N is the number of atoms along the tunneling pathway.

Tunneling coefficients for tunneling through alkanethiols ($\beta = 0.9 \text{ \AA}^{-1}$),^{6a–c,e–g} oligophenylene thiols ($\beta = 0.61 \text{ \AA}^{-1}$)^{6e,g} and benzylic derivatives of oligophenylene thiols ($\beta = 0.67 \text{ \AA}^{-1}$)^{6e,g} trapped in the Hg–Hg and the Hg–Ag junctions were

determined. Furthermore, negative differential resistance caused by changes in molecular dipoles in the Hg–molecule–SiO₂/Si junction was demonstrated.⁸ Molecular rectification was observed in Ag–Hg junction.^{6d} Observations of redox cycling processes within the Hg–Hg junctions were also reported.^{6e} Recently, the subject was thoroughly reviewed by Rampi and Whitesides.^{6c}

In this report we describe a Hg–Hg junction that allows independent control of the electrochemical potential of each Hg electrode. Thus, by controlling the potential of the Hg drops the in situ self-assembly process can be selectively induced allowing, for the first time, reproducible formation of Hg–alkanethiol monolayer/Hg junctions.

Experimental Section

Reagents. Alkanethiols (1-octanethiol, 1-nonanethiol, 1-decanethiol, 1-undecanethiol, 1-dodecanethiol, 1-tetradecanethiol, 1-hexadecanethiol, and 1-octadecanethiol), and lithium perchlorate, 99.99% (ReagentPlus) were purchased from Aldrich and used as received. Mercury (99.9999%, Fluka) or (polarographic grade, Associated Mercury Products, Chatsworth, CA) was used. House-distilled water was passed through a four-cartridge Milli-Q purification system.

Tunneling Junction. The electrochemically controlled tunneling junction consists of two (Kemula–Kublik-type) hanging mercury drop electrodes (HMDEs).⁹ They are mounted coaxially, one above the other in a custom-made stand. In each electrode a 1.50 mm diameter precision stainless steel rod is driven by a micrometric screw (DigimaticMicrometer Head by Mitutoyo, model 350-712-10 with $\pm 1 \mu\text{m}$ resolution) to create a Hg drop of desired size at the tip of a glass capillary. The precision of the surface area of the extruded Hg drop is ca. 0.5%. The tips of the capillaries are aligned using an X-Y-Z micrometer stage (model M-460A, Newport Corp.). The junction is observed and its diameter is measured using a video camera connected to a microscope. The tunneling junction is formed in a two-compartment rectangular cell mounted around and coaxially with the glass capillaries. The cell is filled with a saturated solution of the desired alkanethiol in a 2:8 (v/v) mixture of water and ethanol containing supporting electrolyte. Current–time curves are recorded using a CHI model 730A bipotentiostat (CH Instruments, Inc. Austin, TX) in a four-electrode configuration with a Pt foil as a counter electrode and a silver–silver chloride electrode as a reference electrode. Solutions are deoxygenated for at least 30 min before the experiments. All potentials are reported vs saturated silver–silver chloride electrode.

Results and Discussion

The Hg–alkanethiol bilayer–Hg junctions reported so far relied on a spontaneous self-assembly process.⁶ To ensure reproducibility of tunneling measurements the junctions were usually formed in a solution containing alkanethiol dissolved in an inert solvent.¹⁰ Thus, understandably, only bilayers of alkanethiols were investigated.

The experimental approach described in this report allows the thermodynamic control of the monolayer deposition (Figure 1). By applying an appropriate electrochemical potential to a Hg drop immersed in the alkanethiol solution the self-assembly process can either be allowed or prevented, and thus both

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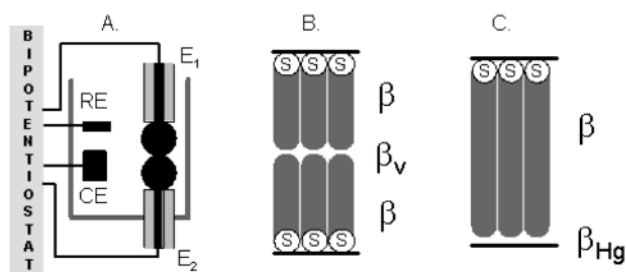


Figure 1. (A) Schematic description of an electrochemically controlled tunneling junction containing a bilayer of 1-nonanethiol (B), or a monolayer of 1-octadecanethiol (C). The Hg drops, polarized to different electrochemical potentials E_1 and E_2 vs reference electrode (RE), are extruded on the tips of glass capillaries in 8:2 (v/v) ethanol/water solution containing 1 M LiClO₄ and saturated with desired *n*-alkanethiol. A Pt wire serves as a counter electrode (CE).

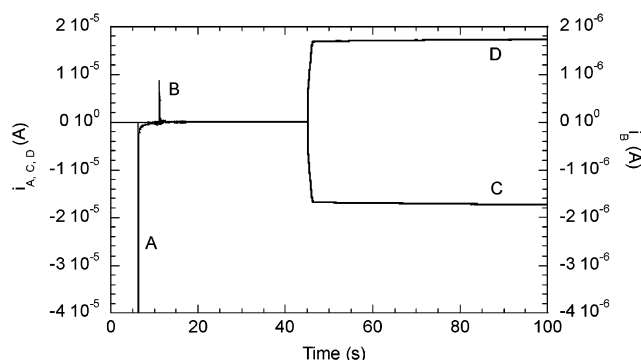
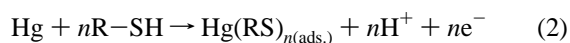


Figure 2. Current–time curves recorded in the course of a junction assembly in the solution saturated with 1-hexadecanethiol. (A) Current–time transient recorded during Hg drop expansion at the potential $E_1 = -0.35$ V. (B) Current–time transient recorded during Hg drop expansion at the potential $E_2 = -0.75$ V. (C, D) The current response recorded after the Hg drops are brought together. The junction area $A = 5.4 \times 10^{-4}$ cm².

monolayer and bilayer Hg–Hg junctions can be formed reproducibly.

An alkanethiolate monolayer is formed in situ on one or both of Hg drops via oxidative adsorption.^{4f,11}



In this approach the mercury electrode is held at the potential at which the formation of a monolayer (eq 2) is allowed, and a fresh Hg drop is rapidly extruded at the tip of a glass capillary. A typical i – t transient recorded during Hg drop expansion at the potential $E_1 = -0.35$ V is shown in Figure 2A.

The rapid current increase and then decay to zero corresponds to a formation of a monolayer of $\text{Hg(RS)}_{n(\text{ads.})}$. Chronocoulometric experiments have shown that the formation of a full monolayer occurs within the time frame of tens of milliseconds.^{4f} Further oxidation of Hg is blocked by a compact alkanethiolate monolayer. The average charge corresponding to the oxidative self-assembly (Figure 2A) is ca. 80 $\mu\text{C}/\text{cm}^2$ independent of the potential in the range of -0.4 to $+0.2$ V in agreement with previous studies.^{4f} The self-assembly process described in eq 2 results in transfer of one electron per hydrocarbon regardless of the stoichiometry of the final product. Thus, the charge due to the self-assembly process corresponds to a mean molecular

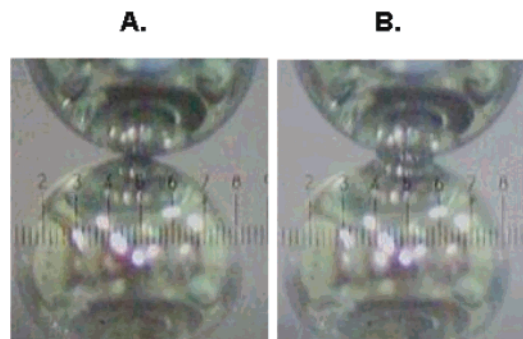


Figure 3. Photographs illustrating the formation of a monolayer junction in the 8:2 (v/v) ethanol/water solution containing 1 M LiClO₄ and saturated with 1-hexadecanethiol. The top Hg drop is polarized to $E_1 = -0.35$ V, the bottom Hg drop is polarized to $E_2 = -0.75$ V vs SSCE. (A) Immediately (<1 s) after the drops are brought into contact. (B) After the “twitch” of the drops. The final junction area $A = 5.4 \times 10^{-4}$ cm².

area of 20 Å² per hydrocarbon. The electrochemical experiments described above, confirmed by Grazing-incidence X-ray diffraction studies,¹² indicate that the alkanethiols form closely packed monolayers on Hg with hydrocarbons oriented perpendicularly to the electrode surface. The extrusion of a second Hg drop, (Figure 2b), performed at a more negative potential, $E_2 = -0.75$ V, results in a small cathodic i – t transient consistent with the electrical double-layer charging in the absence of adsorbed monolayer of alkanethiols.¹³ Subsequently, the Hg drops are brought into contact using micromanipulators. Immediately after achieving a point contact between the Hg drops a sudden “twitch” leading to a substantial increase of a junction area is observed. The “twitch” event, shown in Figure 3, is identical for monolayer and bilayer junctions.¹⁴

The junction formation is followed by the flow of a steady-state tunneling current between the two electrodes as shown in Figure 2, C and D. Electron tunneling from the bottom Hg drop (E_2 , curve D) to the top electrode (E_1 , curve C) across the hexadecanethiolate monolayer is caused by the bias voltage between them, $V = |E_1 - E_2|$.¹⁵ An analogous approach can be used to measure the tunneling current through in situ formed alkanethiol bilayer. In the latter case both the E_1 and E_2 potentials are sufficiently positive to allow the monolayer formation on each of the Hg drops.

The steady-state tunneling current (Figure 2, C and D) is observed for at least 5–400 s for each tunneling junction indicating constant thickness of a monolayer/bilayer within this time frame.¹⁶ Thus, possible squeezing of the hydrocarbons out of the junction area under electrostatic pressure does not influence our tunneling measurements.¹⁷

The fundamental problem in interpreting the tunneling data in Hg–Hg junctions arises from the unknown structure of the

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(14) The diameter of a Hg drop varied between 0.84 and 1 mm. The final diameter of a spontaneously formed tunneling junction was always ca. 26% of a drop diameter for both monolayer and bilayer junctions. The current density was independent of the junction radius.
(15) The bias voltage can be varied by changing the potential of one drop while keeping the potential of the second drop constant. The symmetric current–voltage dependences, for both monolayer and bilayer junctions, are analogous to that reported earlier for two-electrode Hg–Hg junctions (see refs 6a–c). Within the voltage bias range of ± 0.4 V we did not observe any rectification behavior.

nonbonded $-\text{CH}_3/\text{CH}_3-$ and $-\text{CH}_3/\text{Hg}$ interfaces. Therefore we have probed the possible intercalation of solvent and ions within the tunneling junction and possible electrostatic repulsion between the Hg drops.

First, we consider interactions of the electrical double layers formed on both mercury drops. The interactions between the electrical double-layers formed on the bare, electrochemically polarized Hg drops in aqueous solutions were previously investigated by Usui and co-workers.¹⁸ These authors determined the critical potentials of Hg coalescence as a function of supporting electrolyte concentration and the electrochemical potential. Clearly the quantity and the distribution of charge stored in the electrical double layer depend on both the salt concentration and on the electrode potential.^{13a} We have found no influence of supporting electrolyte (lithium perchlorate) concentration on the tunneling currents, indicating no substantial influence of diffuse parts of double layers built on both drops on the junction formation.¹⁹ Another way to probe the double-layer effects in Hg–Hg junction is to measure the tunneling current across both monolayer or bilayer junctions at different Hg potentials (E_1 , E_2) while keeping a constant bias voltage ($E_2 - E_1 = \text{const.}$).²⁰ No influence of potential on the magnitude of tunneling current was observed. The described experiments indicate that the solvent and ions are ejected from the junction area in the course of its formation. This conclusion is not surprising in view of: (i) strong adhesion between a hydrophobic monolayer and a hydrophobic Hg surface (or a second monolayer),²¹ (ii) strong attractive dispersion forces between relatively large Hg drops separated by a very short distance,^{5i,22} (iii) electrostatic attraction of two drops due to the bias voltage.^{6b} To further prove this conclusion we have investigated the possible intercalation of 1-hexanol present in the solution (with concentrations ranging from 1 mM up to the saturation level) within the tunneling junction. 1-Hexanol adsorbs on both alkanethiol monolayer surfaces and Hg surfaces. For example, Creager and co-workers have found that the kinetics of hexoxymethylferrocene oxidation on a Au electrode coated with a dodecanethiol monolayer is suppressed in the presence of 1-octanol.^{23a} The same authors determined that alcohols ranging from 1-butanol to 1-decanol aggregate from the aqueous solution onto the surface of a hydrophobic monolayer of alkanethiols self-assembled on the Au electrode.^{23b} On the other hand, aliphatic alcohols are known to adsorb on

bare Hg electrodes.^{13,24} Both capacitance measurements and kinetic measurements of redox processes indicate that alcohols form monolayers on Hg.²⁴

1-Hexanol, present in the solution in the course of the Hg–Hg junction formation, does not influence the magnitude of the tunneling currents through both monolayers and bilayers of alkanethiols.²⁵ Interestingly, the “twitch” observed in every case of junction assembly (see Figure 3) occurs after substantially longer time (2–20 s) in the presence of 1-hexanol, indicating relatively slow kinetics of its removal from the junction. It is worth noting that no measurable tunneling current flows before the “junction twitch” occurs (Figure 3A). This behavior is consistent with the model proposed by Creager and co-workers in which the alcohols form a relatively thick (10–15 Å) disordered layer on the top of self-assembled monolayer.²³ The apparent removal of the hexanol molecules from the junction area in the course of its assembly strongly suggests that both monolayer and bilayer Hg–Hg junctions do not contain an entrapped layer of water.

Finally, the comparison can be made between the electrochemically formed tunneling junction (Figures 1 and 2) and the “classical” tunneling junction assembled in a hexadecane solution and without supporting electrolyte. In the latter configuration the tunneling current is measured as a function of a voltage bias applied to both drops.⁶ For example the tunneling current recorded for Hg–S–C₉/C₉–S–Hg junction under conditions of $E_1 = 0$ and $E_2 = -0.4$ V is ca. 0.02 A/cm² or 4×10^{-17} A per pair of hydrocarbons. The identical current is measured in a “classical” tunneling junction assembled in hexadecane solution if bias voltage of 0.4 V is applied.^{6a} This result reaffirms the conclusion that ions or solvent do not intercalate at the $-\text{CH}_3/\text{CH}_3-$ interface.

The plot of the logarithm of the tunneling current density vs the total number of carbon atoms in each junction yields tunneling coefficients for monolayers ($\beta = 1.06 \pm 0.04/-\text{CH}_2-$) and bilayers ($\beta = 1.02 \pm 0.07/-\text{CH}_2-$) of alkanethiols in agreement with previously reported data for analogous systems.⁶ The identical values of β for monolayer and bilayer systems indicate that the structure of both junctions is homologous except for an additional $-\text{S}-\text{Hg}$ in a bilayer junction. Furthermore the linearity of $\ln i$ vs n plots indicate that there is no substantial difference in the structure of junctions of different thicknesses.²⁶

As can be seen in Figure 4 the tunneling current recorded for a bilayer of 1-octanethiol or 1-nonanethiol is ca. 2-fold larger than a corresponding current recorded for the monolayers of 1-hexadecanethiol or 1-octadecanethiol, respectively. This is a surprising effect since the geometric thickness of a bilayer of alkanethiols is larger than the thickness of a monolayer containing the same number of carbon atoms.

We note that Hg–monolayer/monolayer–Hg and Hg–monolayer/Hg junctions both contain a mechanical break in their

- (16) The stability of a junction depends on the chain length of the alkanethiol and not on the total number of carbon atoms across the junction. For example the octadecanethiol monolayer junction is more stable (the steady-state current is observed for a longer time) than the decanethiol monolayer junction. On the other hand, an octadecanethiol monolayer junction is more stable than a nonanethiol bilayer junction.
- (17) For longer times, beyond the steady-state conditions, the current decreases or increases in an irreproducible manner. Clearly, the electrostatic squeezing changes tunneling efficiency (gauche defects formation), and it also changes the junction thickness (see ref 6b). Only steady-state current values are used in our data analysis.
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- (26) In view of the tunneling law (eq 1) the linearity of the $\ln i$ vs n plot indicates that addition of each $-\text{CH}_2-$ group results in the constant change in the Hg–Hg distance. The argument can be made that shorter thiols form more “liquidlike” and less ordered monolayers. This scenario would result in a more shallow $\ln i$ vs n dependence for shorter thiols.

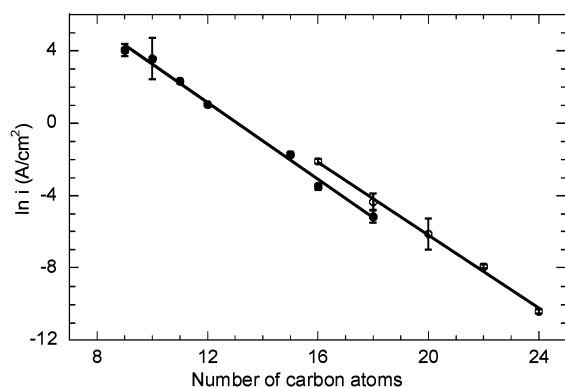


Figure 4. Plot of the natural logarithm of current density measured at the 400 mV bias voltage as a function of the number of carbon atoms in monolayers ($n = 9$ – 18) and bilayers ($n = 16$ – 24) of alkanethiols in a Hg–Hg tunneling junction. The experimental points represent the averages and standard deviations from 5 to 10 measurements for each junction.

structure. In view of the previous studies, the physical (non-bonded) contact (van der Waals gap) between molecules is associated with substantially weaker electronic coupling (larger β) in comparison with tunneling along the fully bonded hydrocarbon chain (through-bond, superexchange tunneling).^{2c–g,4f,6f} Hence, the “least efficient element” in the tunneling pathway through a bilayer of alkanethiols is a van der Waals contact (see Figure 1) at the monolayer/monolayer interface (abbreviated as v). Analogously, the van der Waals contact between a monolayer and an uncoated electrode (abbreviated as Hg) exhibits different electronic coupling than a σ -bonded hydrocarbon. According to a model recently developed for analysis of tunneling measurements using STM, the overall current recorded in both cases can be approximated as a product of the probability of tunneling across the hydrocarbon chain and the tunneling probability across either a monolayer/monolayer (abbreviated as “v”) or monolayer/Hg (abbreviated as “Hg”) gap.^{5d} In view of this model, the tunneling current in a Hg–monolayer/monolayer–Hg junction can be described as:

$$I_B = I_0 \exp(-\beta N) \exp(-\beta_v d_v) \quad (3)$$

where β is the tunneling coefficient for the “through bond” tunneling, N is the number of atoms within the “through bond” tunneling pathway, β_v is the tunneling coefficient for the tunneling across the monolayer/monolayer gap, and d_v is the length of the monolayer/monolayer gap.

Analogously, the tunneling current in a Hg–monolayer/Hg junction can be described as:

$$I_M = I_0 \exp(-\beta N) \exp(-\beta_{Hg} d_{Hg}) \quad (4)$$

where β_{Hg} is the tunneling coefficient for the tunneling across the $-\text{CH}_3/\text{Hg}$ interface.

Therefore, the ratio of tunneling currents through a bilayer (I_B) and a monolayer (I_M) of alkanethiols containing the same number of carbon atoms can be expressed as (see Figure 1):

$$I_B/I_M = [\exp(-\beta(N_C + 1)) \exp(-\beta_v d_v)] / \exp(-\beta N_C) \exp(-\beta_{Hg} d_{Hg}) \quad (5)$$

where N_C is the total number of carbon atoms across a monolayer or bilayer of alkanethiols.

Thus, the main difference in tunneling efficiency across homologous monolayer and bilayer junctions is in relative efficiency of the tunneling across $-\text{CH}_3/\text{CH}_3-$ and $-\text{CH}_3/\text{Hg}$ gaps. This efficiency, in a form of βd product, can be expressed as:

$$\beta_{Hg} d_{Hg} = \beta_v d_v + \ln(I_M/I_B) + \beta \quad (6)$$

In view of the ratio of currents for homologous monolayers and bilayers, $I_B/I_M = 2.2$, and $\beta = 1$ (see Figure 4), the $\beta_{Hg} d_{Hg} = \beta_v d_v + 1.8$. Therefore, the tunneling across the $-\text{CH}_3/\text{Hg}$ gap is slightly less efficient than tunneling across $-\text{CH}_3/\text{CH}_3-$ contact. It was postulated that the efficiency of the tunneling across the van der Waals gap between two hydrocarbon chains is similar, in terms of rate decay, to the tunneling across 5 σ bonds.^{4f,6f,27} Thus according to the eq 6, the tunneling across a $-\text{CH}_3/\text{Hg}$ contact would be an equivalent of tunneling across 6.8 σ bonds. This estimation assumes that geometries of $-\text{CH}_3/\text{CH}_3-$ and $-\text{CH}_3/\text{Hg}$ contacts are the same. In reality, the $-\text{CH}_3/\text{Hg}$ gap is likely to be smaller than $-\text{CH}_3/\text{CH}_3-$ gap thus generating even larger tunneling coefficient, β_{Hg} . The above analysis neglects the role of Hg–S and C–S bonds in the tunneling efficiency. From this standpoint the described results indicate that the electron transfer across the CH_3/Hg contact is less efficient than electron transfer across $\text{CH}_3/\text{CH}_3 + \text{C–S} + \text{S–Hg}$.

While the theoretical explanation of the observed effect clearly requires further studies we note that there is a substantial difference in a dipole moment at the $-\text{CH}_3/\text{Hg}$ and $-\text{CH}_2-\text{S–Hg}$ interfaces. This in turn may change the potential drop profile at both ends of a molecule. We further emphasize that the obtained tunneling efficiency ($-\text{CH}_3/\text{Hg}$ interface = ca. 7 σ bonds) is based on the assumption that the tunneling efficiency across the $-\text{CH}_3/\text{CH}_3-$ gap is well-known. Literature reports indicate that the current loss during tunneling between two adjacent hydrocarbon chains is similar to the current loss during tunneling along hydrocarbon chain containing between 5 and 10 σ bonds.^{4f,6f,27,28} While in our judgment the value of 5 σ bonds is more reliable, the true efficiency of ET across the $-\text{CH}_3/\text{Hg}$ interface could be even lower than reported here. Nevertheless, there is no explicit experimental evidence (as of yet) on the efficiency of electron tunneling along the $-\text{CH}_3/\text{CH}_3-$ gap between the pair of aligned hydrocarbons such as the one in our bilayer junctions. Therefore the estimation of the efficiency of ET across CH_3/Hg contact should be treated with caution.

Our work supports recent CP-AFM results obtained by Lindsay and co-workers.^{2e–g} These authors have shown that the conductivity of 1,8-octanethiol depends critically on whether ends of the molecule are chemically bonded to metallic Au contacts. To this end our results disagree with the recent measurements of contact resistance by CP-AFM.^{2a} These measurements indicate that the electrical properties of the tip- CH_3 and substrate-S contacts are comparable. We note however that contact resistance is measured at the low voltage regime while the Hg–Hg junction measurements were obtained at 400 mV voltage bias.

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Finally, we would like to emphasize that the presented analysis does not account for any possible defects within the alkanethiol monolayers on Hg. However, electrochemical experiments point out that alkanethiols form remarkably well-ordered and ion-impermeable monolayers on Hg.²⁹ Furthermore, the electron tunneling across alkanethiols is a dominating mechanism for ET between the Hg and a redox couples in the solution for monolayers ranging from nonanethiol to octadecanethiol.^{29a,c,e} Unlike in the case of monolayers on Au or Ag, pinholes are never detected within Hg/alkanthiol assemblies,

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and the tunneling measurements using both electrochemical approach and the tunneling junction approach are not burdened by a large standard deviation.

Tunneling measurements involving electrochemically controlled Hg–Hg junctions provide experimental evidence for weak electronic coupling across the noncovalent molecule/electrode interface and thus emphasize the critical importance of the nature of metal–molecule contact on the efficiency of electron transport in nanostructures.

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