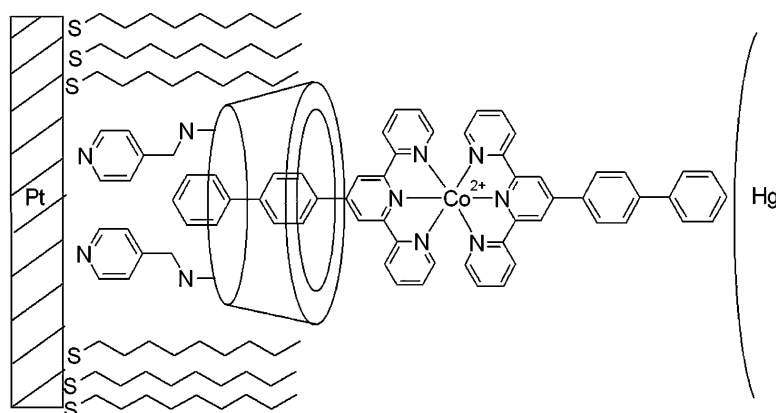


Mercury#Platinum Tunneling Junctions Incorporating Supramolecular Host#Guest Assemblies

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Mercury–Platinum Tunneling Junctions Incorporating Supramolecular Host–Guest Assemblies

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Abstract: Molecular junctions incorporating monolayers of surface-active cyclodextrins have been formed by bringing macroscopic platinum and mercury electrodes together. Monolayers of the host di-6A,6B-deoxy-6-(4-pyridylmethyl)amino- γ -cyclodextrin (CD) have been formed on platinum electrodes and backfilled with 1-nonanethiol. Significantly, the tunneling current for bilayer junctions in which the mercury surface is modified with a C₁₆ alkane thiol depends markedly on the nature of the CD guest. Junctions where nonconjugated guests, such as adamantane, are included in the CD show an order of magnitude lower current than junctions incorporating the conjugated guest C₆₀. Moreover, monolayer junctions of CD backfilled with 1-nonanethiol exhibit potential-dependent currents in the presence of CD guest molecule [Co(biptpy)₂]²⁺ but not for [Co(tpy)₂]²⁺, which is structurally analogous but cannot associate with CD. Significantly, unlike bilayer systems, when only one electrode is modified, mechanical pressure is required to form a stable tunneling junction and these junctions cannot be formed and separated reversibly.

Introduction

Electron tunneling is central to biological processes ranging from respiration to photosynthesis, and understanding the factors that control electron transfer is key to devising and optimizing nano and molecular electronics applications. Tunneling junctions provide powerful insights into electron transfer across either individual molecules or molecular assemblies. A number of elegant tunneling junctions comprising assembled monolayers of either aromatic or aliphatic species have been described.^{1–4} However, in order to probe central issues such as the impact of tuning redox states into resonance, distance dependence, or indeed the extent of delocalization, these approaches require significant synthetic effort. In contrast, exploiting host–guest chemistry in which photo/electro-active metallo-guests self-assemble with immobilized cyclodextrins opens new possibilities. This strategy has a number of advantages over existing approaches. First, it avoids the complex synthesis usually required to covalently link several units together to form a molecular wire. Second, the impact of changing the electronic properties can be easily explored by changing the guest. Third, redox centers with and without “tails” capable of binding to immobilized CDs can be used to probe the impact of host–guest association on the tunneling properties. Fourth, by controlling the properties and sequence of guests, the direction of electron and energy transfer can be controlled. Finally, as noncovalent interactions are pervasive in biology, tunneling junctions involving self-assembled wires based on H-bonding, π stacking, van

der Waals forces, and hydrophobic–hydrophobic interactions may be more relevant model systems for interrogating tunneling in biosystems.

Macroscopic molecular junctions involving alkanethiols were first reported by Slowinski and Majda^{1,3} and by Rampi and Whitesides.^{4,5} Their approaches, which were broadly similar, used liquid mercury as one or both of the contacts in the junction. Electron transfer across the junction occurs by non-resonant tunneling and depends exponentially on distance, according to eq 1:

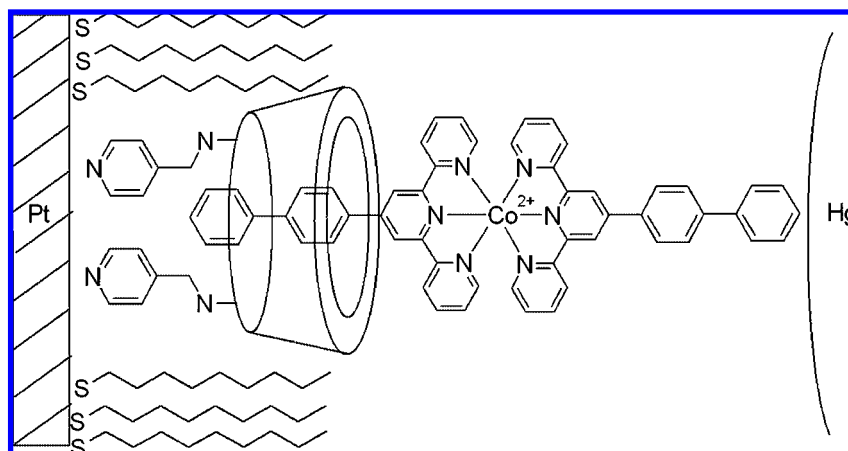
$$i = i_0 \exp(-\beta d) \quad (1)$$

where d is the distance across the junction and β is the tunneling decay constant. Values for β of ~ 1 per CH₂ unit have been reported for these alkanethiol junctions, although the absolute current densities appear to vary significantly.⁶ Rampi and Whitesides also trapped redox centers in alkanethiol bilayer junctions by covalent and electrostatic binding.^{7–9} For these junctions the magnitude of the current depends on the applied potential relative to the formal potential, E° , of the trapped molecules. This result contrasts with simple alkanethiol junctions where the tunneling current typically depends only on the absolute magnitude of the potential bias. However, it appears that neither cycling of the redox molecules between the

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Scheme 1



electrodes, nor electron hopping between molecules, accurately models the current observed.¹⁰

In this contribution, we report on a novel approach to forming tunneling junctions based on immobilized cyclodextrins¹¹ that are capable of forming host–guest complexes with redox-active species ranging from metal complexes to fullerene (Scheme 1). We report on the impact of mechanical pressure on the junction properties by continuing to move the modified platinum electrode into the mercury pool after the molecular junction has been formed. These investigations reveal that mechanical pressure plays a key role in junction formation where only one of the electrodes is modified. Mixed cyclodextrin–alkanethiol layers as part of bilayer junctions behave in a similar way to pure alkanethiol layers and exhibit a response consistent with nonresonant electron tunneling. Importantly, the inclusion of conjugated guests in the CD cavities significantly increases the magnitude of the tunneling current observed. Finally, we show that the potential dependence of the tunneling current for a cyclodextrin–redox active guest, $[\text{Co}(\text{bipty})_2]^{2+}$, junction is dramatically different than that of $[\text{Co}(\text{tpy})_2]^{2+}$, which does not associate with the CD, bipty is bisdiphenylterpyridine and tpy is terpyridine. These findings emphasize the important role that molecular organization, not just energetics, have on the properties of tunneling junctions.

Experimental Section

Materials. 1-Nonanethiol (95%), 1-undecanethiol (98%), 1-hexadecanethiol (95%), sodium sulfate (99%), ethanol (99.5%), tetrabutylammonium tetrafluoroborate (TBABF_4) (99%), *N,N*-dimethylformamide (DMF) (99%), 1-adamantylamine (97%), and acetonitrile (99.9%) were obtained from Sigma and used as received. Cobalt bisdiphenylterpyridine, $[\text{Co}(\text{bipty})_2]^{2+}$, di-6^A,6^B-deoxy-6-(4-pyridylmethyl)amino- γ -cyclodextrin, γ -CD-(py)₂, and cobalt terpyridine $[\text{Co}(\text{tpy})_2]^{2+}$ were synthesized as described previously.^{12,13} C_{60} was purchased from BuckyUSA.

Tunneling Junction Formation. The platinum–mercury (Pt–Hg) junction was formed using a mercury pool and conventional polycrystalline platinum electrodes (radius 1 mm). The mercury pool sits at the bottom of a purpose-built cell. Potential control is achieved by means of a metal contact at the bottom of the cell which is in contact with the mercury but insulated from the solution.

The platinum electrode was lowered from above through the solution by a Burleigh IW-700 piezo-electric stage at a rate of $25 \mu\text{m s}^{-1}$. Current–distance (i – d) curves for the platinum electrode were collected using a CH instruments scanning electrochemical microscope SECM electrochemical workstation (Model 900A) and these plots formed the basis of the data reported. The bias between platinum and mercury electrodes was maintained at 0.4 V unless otherwise stated during acquisition of the i – d curves and a standard four-electrode system was employed. Potentials are quoted versus the Ag/AgCl (sat. KCl) reference electrode. The potential of the mercury electrode was typically held between -0.3 and -0.1 V to avoid desorption of the alkanethiols. Platinum electrodes were cleaned by manual polishing and electrochemical cycling in acid as previously described.¹² Monolayers of alkanethiols were prepared on platinum by immersing the cleaned electrode in a millimolar solution of the desired alkanethiol in ethanol for 24 h. Monolayers of alkanethiol on mercury were prepared by including the desired alkanethiol in the cell solution, typically at millimolar concentrations in a mix of ethanol/water (typically 25:75 v/v). The monolayers were formed on the mercury electrode at open circuit potential. Sodium sulfate was used as the electrolyte, typically at concentrations of 0.15 M. Mixed CD/alkanethiol monolayers were prepared as described previously on platinum.¹² The junctions incorporating $[\text{Co}(\text{bipty})_2]^{2+}$ as a CD binding guest were preformed in solutions of 9:1 water/acetonitrile with 0.18 M sodium sulfate as the electrolyte.

Results and Discussion

Pt–Hg Junctions Using Alkanethiol Bilayers. In seeking to probe the electron-tunneling properties of molecular assemblies, a key issue is contact resistance which can cause the tunneling current or rate to be underestimated. A distinctive feature of the approach used here is that the platinum electrode is mechanically moved even after the tunneling junction is formed. This continuous movement provides an insight into the mechanical stability of the junction and how mechanical pressure affects the tunneling current. Figure 1 shows the dependence of the junction current as a platinum electrode, modified with a C_{11} alkanethiol monolayer, is advanced toward a mercury surface that is also modified with C_{11} alkanethiol. The lower x axis shows the separation between the two electrodes, while the upper x axis shows the time, which can be useful for understanding the temporal characteristics of the junction. The potential of the mercury and platinum electrodes was held at -0.3 and 0.1 V, respectively.

This figure demonstrates that when the monolayer-modified platinum electrode is far from the mercury surface the current is very low, at 560 ± 29 nA, and is independent of vertical

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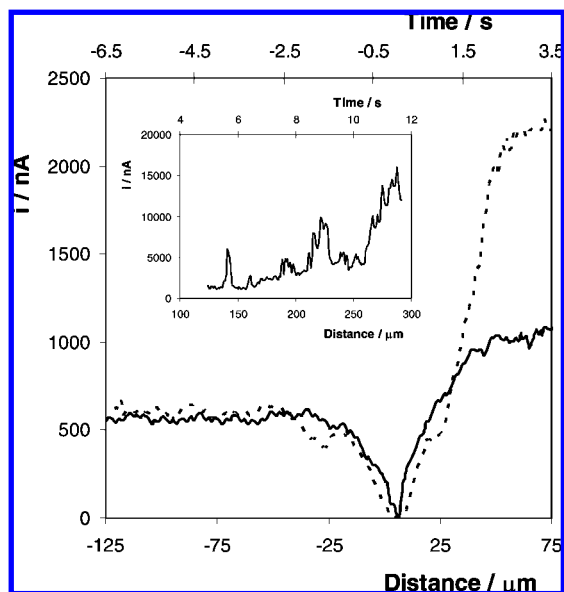


Figure 1. Current–distance curve showing formation and characteristics of a C_{11} – C_{11} bilayer Pt–Hg tunneling junction at 0.4 V potential bias. The solid and dashed curves represent the extremes of behavior observed over seven different junctions. The solution was composed of 9 mM $C_{11}SH$ in 1:1 ethanol/water with 0.1 M Na_2SO_4 as the supporting electrolyte. The inset illustrates current “spiking” observed once the junction has been formed.

displacement/time. This current most likely arises from a combination of capacitance and Faradaic processes associated with low concentrations of impurities in the solution. Because of the significant velocity of the electrode, $25 \mu m s^{-1}$, transport of electrolyte ions and any impurities to the electrode tip occurs under forced convection conditions similar to those found at a wall jet electrode. These conditions make the double-layer capacitance sensitive to ions in solution. For example, Weaver and co-workers¹⁴ demonstrated sensitive ion detection in HPLC using a wall-jet electrode configuration. Also, rapid mass transfer by convection will enhance the faradaic current observed for any redox active impurity in solution. As the electrode approaches the surface, the current decreases due to blocking of any solution phase reactions as the solution is squeezed out. In addition, the double-layer capacitance is likely to decrease due to the differences in dielectric constants of mercury and water. Once the junction is formed, the current increases due to tunneling across the bilayer before reaching a steady-state value when the platinum electrode is displaced $\sim 75 \mu m$ from the point where the electrodes first make contact. One of the challenges in seeking to create tunneling junctions is reproducibility. Figure 1 shows the two extremes of the response observed for this system over at least seven independent measurements. Significantly, the current observed prior to junction formation and the approach to the mercury surface are very reproducible. However, the tunneling current observed varies between 1060 ± 30 and 2150 ± 50 nA, i.e., the average tunneling current for these alkane thiol monolayer junctions is 1505 ± 500 nA ($n = 7$). It is perhaps important to note that because the mercury pool is mobile it distorts as the platinum electrode makes contact and the distance scale in Figure 1 may not accurately represent the extent to which this electrode penetrates the pool. The current plateau is consistent with the formation of a stable tunneling junction with the magnitude of the current being controlled by

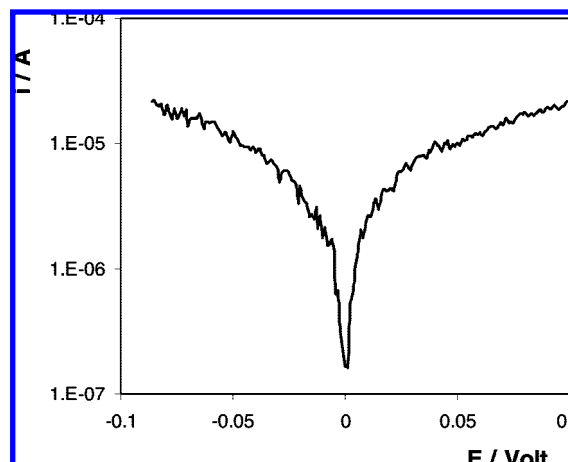


Figure 2. Current–voltage curve for a C_{11} – C_{11} bilayer Pt–Hg tunneling junction. The solution was composed of 9 mM $C_{11}SH$ in DMF with 0.1 M TBABF₄ as the supporting electrolyte. The potential of the mercury pool electrode was held constant at -0.2 V, and the potential of the platinum was scanned between -0.1 and 0.1 V with respect to the potential of the mercury.

the electrical properties of the monolayer. The time required to reach a stable tunneling current is only 3 s. Significantly, the inset of Figure 1 shows that relatively large current spikes are observed. The magnitude and frequency of the current spikes are approximately independent of the platinum displacement rate, v , for $10 \leq v \leq 50 \mu m s^{-1}$, suggesting that mechanical translation does not induce the spikes. Similar spikes are also observed for junctions formed under vibration isolation conditions and for junctions where the platinum electrode displacement is stopped once the junction is formed. We attribute these spikes to temporary shorting of the junction. The defects responsible for shorting self-repair because of the mobility of the alkanethiol molecules on mercury. Typically, the junctions are stable for periods up to several minutes and just prior to permanent shorting due to metal–metal contact the frequency of the spikes increases.

Tunneling Spectroscopy. Figure 2 shows the i – V response of a $C_{11}SH$ bilayer at low bias potentials. The current depends approximately linearly on the applied potential, E_{app} , for $|E_{app}| \leq 10$ mV and yields a resistance of 4.6 k Ω (junction area 0.09 cm²). Similar junction resistances for C_{11} bilayer junctions were reported previously by York and Slowinski.^{15,16} Preliminary data indicate that the junctions are less stable when polarized but junction breakdown is observed within several minutes irrespective of the applied potential. The breakdown voltage for these junctions has not been measured because mercury oxidizes at potentials where junction breakdown would be expected.⁴ However, plots of the tunneling current vs potential are linear (data not shown), for potentials up to 0.4 V. This shows that the tunneling decay constant, β , is potential independent up to this voltage, which is consistent with previous reports.¹⁶ This behavior is consistent with the large HOMO–LUMO gap present in alkanethiol molecules⁶ and shows that the electron transfer mechanism at these low bias voltages is likely to be nonresonant tunneling.

Alkanethiols are attractive dielectrics for molecular junctions, as the thickness of the junction can be changed by varying the

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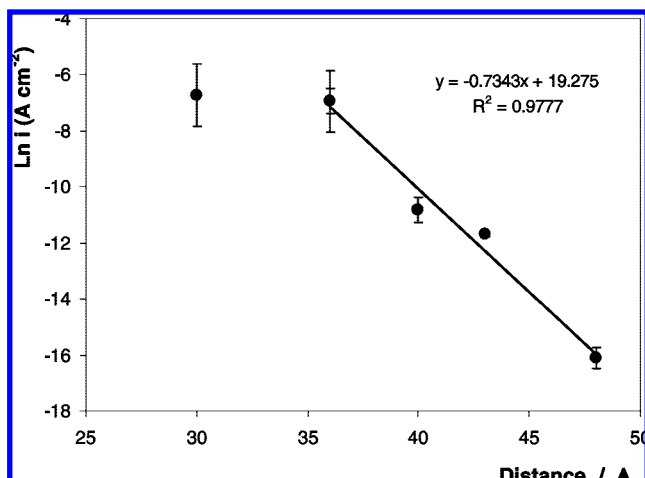


Figure 3. Variation of the natural logarithm of the current density at 0.4 V potential bias with the number of carbon atoms present in the Pt–Hg junction. The error bars represent the standard deviations of at least five independent junction measurements.

chain length of the molecules. If nonresonant tunneling is the dominant mechanism, then the current is expected to decrease exponentially with increasing distance, according to eq 1. Figure 3 shows the dependence of $\ln(i/A \text{ cm}^{-2})$ at 0.4 V vs the number of carbon atoms in the bilayer junction for at least five independent measurements. The solid line is the linear fit of the data excluding the first point and its linearity indicates that eq 1 is an appropriate model for the current variation with distance, at least at thick junction values. This plot yields β as 0.88 ± 0.01 per CH_2 , which agrees closely with previously reported values.^{3,5} As shown in Figure 3, the C_9 bilayer deviates from this model where the current is lower than expected. The overall result is in good agreement with previous work carried out on similar systems and demonstrates that the Pt–Hg junction can be used to determine tunneling currents and to probe tunneling mechanisms.

Mixed CD–Alkanethiol Bilayer Pt–Hg Junctions. We have previously shown that mixed alkanethiol–CD monolayers can be formed on platinum using C_9SH and di-6A,6B-deoxy-6-(4-pyridylmethyl)amino- γ -cyclodextrin, γ -CD-(py)₂.¹² The CD host molecules in the layer can accommodate solution-phase guests, such as 1-adamantylamine. Moreover, electrochemical blocking studies reveal that the mixed CD/ C_9 layer in the presence of 1-adamantylamine effectively blocks the electrode surface from redox active solution phase species such as $[\text{Fe}(\text{CN})_6]^{2+}$.¹² This result suggests the mixed layer is tightly packed and that when the CD cavities are filled the defect density is low. Significantly, unlike other approaches where the energetics, e.g., the LUMO–HOMO separation, can only be controlled through synthesis, here the guest can be chosen so that it has particular redox/electrical properties. Therefore, asymmetric bilayers, i.e., an alkanethiol layer on the mercury and a CD monolayer on platinum into which guests can dock, have been used to create tunneling junctions. For example, saturated hydrocarbon guests such as adamantane can be introduced and their properties compared with tunneling across alkane thiols.

Figure 4 shows the tunneling characteristics of a mixed C_9/CD bilayer junction in which the CD cavities have been filled by the adamantane guest molecule. The solid and dashed lines represent the extreme responses observed for five independent junctions demonstrating that the CD-based junctions form reproducibly. This figure shows that the current–distance

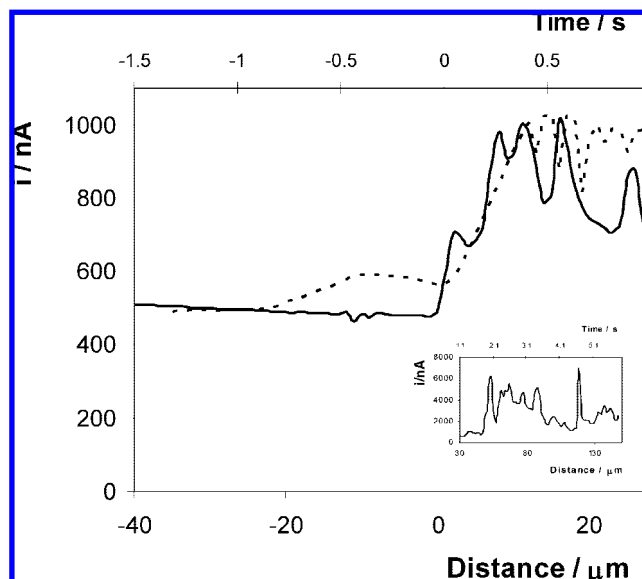


Figure 4. Current–distance curve showing formation and characteristics of a mixed CD/ C_9 – C_{16} bilayer Pt–Hg tunneling junction at 0.4 V potential bias. The solid and dashed curves represent the extremes of behavior observed over five different junctions. The solution was composed of 1 mM C_{16}SH in 1:4 ethanol/water with 0.15 M Na_2SO_4 as the supporting electrolyte.

behavior is broadly similar to that observed for pure alkanethiol bilayers. The current decreases slowly prior to junction formation which is attributed to isolation of the platinum electrode from the background solution. This decrease in current is less pronounced than that found for junctions in which both electrodes are modified with alkanethiol monolayers. This behavior arises because the capacitance of the mixed CD layers is higher than that of pure alkanethiol layers causing the current dip prior to junction formation to be less pronounced. Following junction formation the current increases and current spikes, or temporary shorts, are also evident. As shown in the inset of Figure 4, spikes occur with greater frequency and intensity in the mixed CD layer than in pure alkanethiol SAMs. However, the current spikes appear to overlay a steady baseline as in the case of the alkanethiol junctions. The average current ($n = 6$), ignoring the current spikes associated with transient shorts, is $24 \pm 14 \mu\text{A cm}^{-2}$ for this mixed CD/ C_9 monolayer in conjunction with a C_{16} layer assembled on the mercury electrode. Despite the large standard deviation, the similarity of this value to that obtained for a pure C_9 – C_{16} ($20 \mu\text{A cm}^{-2}$) junction (see Figure 3) suggests that the conductivity of the two bilayers are similar.

A key objective is to elucidate how conjugated guests within the CD cavity influence the magnitude of the current observed. Fullerene, C_{60} , has been shown to form a stable inclusion complex with γ -CD monolayers, provided it is double capped, i.e., another non-surface-active CD is bound to the other side of the fullerene.¹⁷ Therefore, the CD monolayer backfilled with C_9 alkanethiol was exposed to a solution of C_{60} capped with a single CD overnight to form a backfilled CD- $\text{C}_{60}/\text{C}_{16}$ junction. Multiple measurements ($n = 7$) yielded an average current of $240 \pm 150 \mu\text{A cm}^{-2}$ for this junction. The thickness of this junction is expected to be greater than that where the guest is adamantane since the C_{60} does not fully include within the CD cavity and a second CD sits on the other side of the fullerene.

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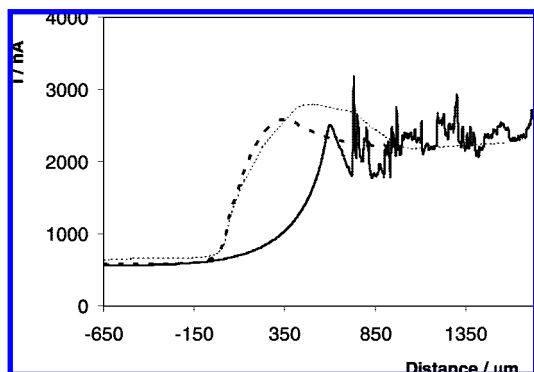


Figure 5. Current–distance curves for mixed CD/C₉ monolayer junction in a 9:1 ratio of H₂O/acetonitrile with 0.18 M Na₂SO₄ as the supporting electrolyte and in an identical solvent system with 70 μM [Co(tpy)₂]²⁺ present (dashed curves, the two dashed lines represent the extreme responses observed for seven independent junctions). Potentials of the electrodes are Pt/Hg, 0.3/–0.1 V.

Despite the likely increase in thickness, the current is an order of magnitude greater than that observed when adamantane is the guest. This behavior is attributed to the greater conductivity of the fullerene due to its extended π system. This result demonstrates that the host–guest chemistry of the CD can be successfully exploited to vary the tunneling properties of the Pt–Hg junctions, in this instance comparing conductivity of an aromatic and nonaromatic guest.

Backfilled CD Monolayer/Bare Hg Junctions. We have also explored the properties of junctions in which the platinum electrode is modified with a CD monolayer backfilled with alkanethiol but where the mercury surface is unmodified. The solid curve of Figure 5 shows the current–distance/time curves where the solution contains only the electrolyte, 0.18 M Na₂SO₄, in a 9:1 ratio of water and acetonitrile, i.e., the CD cavities are empty and the solution does not contain any redox-active species. The dashed curve shows the response observed when the same junction is formed in the presence of 70 μM [Co(tpy)₂]²⁺ which does not associate with the CD cavity, tpy is terpyridine. The potential of the electrodes during formation of the junction is 0.3 and –0.1 V for platinum and mercury electrodes, respectively, versus Ag/AgCl. The formal potential of the Co^{2+/3+} couple is 0.15 V, i.e., it lies between these values allowing the complex to be oxidized at one electrode and reduced at the other which one might expect to enhance the junction current. However, both curves show a similar current response in which the current increases as the junction is formed and the change in current density caused by junction formation, $\sim 25 \mu\text{A cm}^{-2}$, is similar in both cases. This tunneling current is similar to that observed for the backfilled CD/C₉–C₁₆ bilayer junctions. Significantly, this tunneling current is lower than expected because the junction thickness is smaller since the mercury is unmodified. This lower than expected conductivity suggests that electronic coupling between the CD and the mercury surface (physical contact only) is weaker than between separate CD and C₁₆ monolayers. This behavior may arise because of interpenetration of the two monolayers in the bilayer junction.

A striking and very consistent difference between the two experiments is that current spikes are observed in the absence but not the presence of [Co(tpy)₂]²⁺. Significantly, if the tunneling junction is formed and then the two electrodes separated before shorting, the capacitance of the platinum electrode as measured in blank electrolyte solution increases

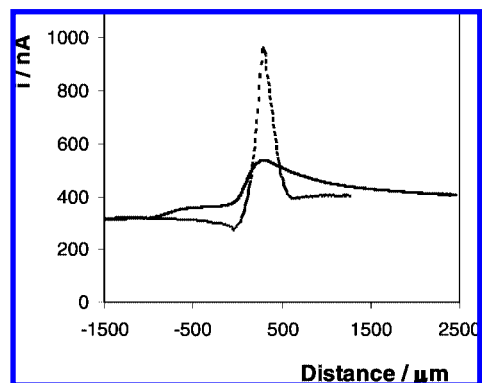


Figure 6. Current–distance curves for mixed CD/C₉ monolayer junction formed in a solution containing 70 μM [Co(bipty)₂]²⁺ in a 9:1 ratio of H₂O/acetonitrile with 0.18 M Na₂SO₄ as the supporting electrolyte. The solid curve corresponds to junction electrode potentials of Pt/Hg, 0.3/–0.1 V, while the dashed curve corresponds to potentials of Pt/Hg, 0.1/–0.3 V.

significantly and is indistinguishable from that found for a clean, unmodified electrode. This observation suggests that junction formation and separation causes the CD monolayer to desorb, i.e., a tunneling junction cannot be formed and disassembled reversibly. Moreover, unlike the bilayer junctions discussed above, the rise in current illustrated in Figure 5 depends strongly on the movement of the platinum electrode, i.e., stopping the electrode movement at any point during the current rise causes the current to immediately level or even decline. Therefore, mechanical pressure is required to establish a tunneling junction and mechanical stress or strong physisorption of the CDs onto the mercury surface under this mechanical pressure is the most probable cause of the destruction of the mixed CD/C₉ layer.

Effect of Incorporating a Redox Active Guest. Biphenyl-terpyridine is capable of including into the CD cavity through the biphenyl moiety without significantly perturbing the energetics of the electron tunneling compared to the nonassociating [Co(tpy)₂]²⁺ complex. The formation constant is $1.45 \times 10^5 \text{ M}^{-1}$ and the formal potential of the Co^{2+/3+} complex is 0.25 V when associated with the mixed CD/C₉ layer.¹² Figure 6 shows the current–distance characteristics of the monolayer junction where 70 μM [Co(bipty)₂]²⁺ is present in a solution composed of 9:1 water/acetonitrile with 0.18 M Na₂SO₄ as the supporting electrolyte. The solid curve shows the behavior observed when the potentials of the electrodes are Pt/Hg, 0.3/–0.1 V while the dashed curve shows behavior at potentials of Pt/Hg, 0.1/–0.3 V vs Ag/AgCl. The current–distance curve for the Pt/Hg, 0.1/–0.3 V junction (dashed curve in Figure 6) is similar to those seen in Figure 5 for junctions without CD cavity guests. The formation of the junction is followed by a sharp rise in the junction current.

However, when the Pt and Hg electrodes are polarized to 0.3 and –0.1 V, respectively, (solid curve in Figure 6), the current rises above those found far from the mercury surface before the current rises corresponding to junction formation. This initial rise in current corresponds to positive feedback in which the oxidized complex produced at the platinum electrode surface is re-reduced at the mercury surface resulting in an enhanced current. The average increase in this initial current rise is $1.2 \pm 0.6 \mu\text{A cm}^{-2}$ ($n = 7$). Significantly, this behavior was not observed with [Co(tpy)₂]²⁺, which does not form a CD cavity guest. This result is consistent with previous investigations which reveal that the CD monolayers can effectively block

interfacial transfer and that only when a redox active guest is present can solution phase species be electrolyzed. The average charge associated with this initial peak is $3.3 \pm 1.8 \mu\text{C cm}^{-2}$ ($n = 5$), which is ~ 20 times that needed to oxidize one monolayer of $[\text{Co}(\text{bipy})_2]^{2+}$ bound at the CD-modified interface. This suggests that the $[\text{Co}(\text{bipy})_2]^{2+}$ molecules mediate more than one electron in this time scale.

The second current rise is attributed to a process similar to that observed for Pt/Hg, 0.1/–0.3 V junctions or for junctions without CD guests. Like that process, it is destructive and dependent on the physical displacement of the platinum electrode again suggesting that, unlike the situation where both electrodes are modified with monolayers, mechanical pressure is required to form a tunneling junction when only the platinum electrode is modified.

Conclusion

A novel macroscopic Pt–Hg junction has been characterized using alkanethiol bilayers for the purpose of incorporating CD host–guest chemistry into molecular junction experiments. The mixed CD/C₉ layers are used as a part of a bilayer junction and as monolayer junctions. The bilayer junctions revealed that the conductance of the mixed CD/C₉ layer is approximately the same as for pure alkanethiol layers when nonconjugated guests,

such as adamantane, are included in the CD cavity. However, when C₆₀ is included in the cavity, the current is an order of magnitude greater. Uncertainty over the thickness of the junction means that β values cannot be obtained, but the electron transfer is clearly influenced by the nature of the CD guest. The redox-active CD guest $[\text{Co}(\text{bipy})_2]^{2+}$ has been investigated in the mixed CD/C₉ monolayer junction. The current–distance curves show a potential-dependent current, which is absent in the presence of $[\text{Co}(\text{tpy})_2]^{2+}$, which lacks the biphenyl CD docking ligand. This confirms this behavior is mediated by host–guest assembly of the redox center into the layer. The origin of the current is most likely due to redox cycling. Significantly, we find that where a CD monolayer modified electrode approaches an unmodified mercury surface, a tunneling junction is only formed in the presence of mechanical pressure and breaking apart a formed junction destroys the monolayer integrity.

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