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Tunneling across SAMs Containing Oligophenyl Groups

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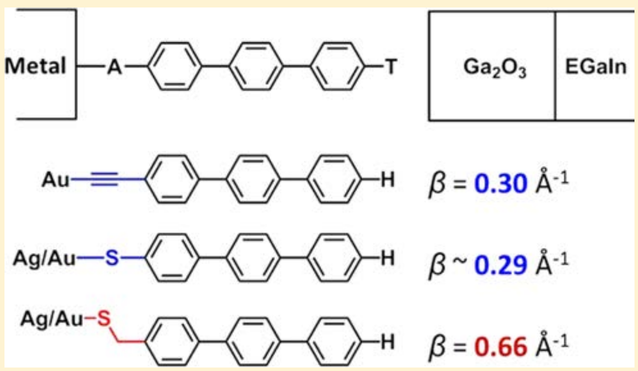
Supporting Information



ABSTRACT: This paper reports rates of charge tunneling across self-assembled monolayers (SAMs) of compounds containing oligophenyl groups, supported on gold and silver, using Ga_2O_3/EGaIn as the top electrode. It compares the attenuation constant, β, and the pre-exponential parameter, J_0, of the simplified Simmons equation across oligophenyl groups (R = Ph_n; n = 1, 2, 3) with three different anchoring groups (thiol, HSR; methanethiol, $HSCH_2R$; and acetylene, HC≡CR) that attach R to the template-stripped gold or silver substrate. The results demonstrate that the structure of the molecular linker between the anchoring group (−S− or −C≡C−) and the oligophenyl moiety significantly influences the rate of charge transport. SAMs of SPh_n and C≡CPh_n on gold show similar values of β and log $|J_0|$ (β = 0.28 ± 0.03 Å^{-1} and log $|J_0|$ = 2.7 ± 0.1 for Au/SPh_n; β = 0.30 ± 0.02 Å^{-1} and log $|J_0|$ = 3.0 ± 0.1 for Au/C≡CPh_n). The introduction of a single intervening methylene (CH_2) group between the anchoring sulfur atom and the aromatic units generates SAMs of SCH_2Ph_n and increases β to ca. 0.66 ± 0.06 Å^{-1} on both gold and silver substrates. (For n-alkanethiolates on gold, the corresponding values are β = 0.76 ± 0.03 Å^{-1} and log $|J_0|$ = 4.2 ± 0.2). Density functional theory calculations indicate that the highest occupied molecular orbitals (HOMOs) of both SPh_n and C≡CPh_n extend beyond the anchoring group and onto the phenyl rings; SAMs composed of these two groups of molecules result in indistinguishable rates of charge transport. The introduction of the CH_2 group, to generate SCH_2Ph_n, disrupts the delocalization of the orbitals, localizes the HOMO on the anchoring sulfur atom, and results in the experimentally observed increase in β to a value closer to that of a SAM of n-alkylthiolate molecules.

INTRODUCTION

The correlation between the structure of self-assembled monolayers (SAMs) containing n-alkyl groups and the rate of charge tunneling in junctions of the form M/A$(CH_2)_n$T//Ga_2O_3/EGaIn (where M is the metal substrate, A is the anchoring group, and T is the terminal group), is surprisingly straightforward: the length of the insulating $-(CH_2)_n-$ group, which presents a high tunneling barrier, largely controls the rate of charge transport. The height and shape of this tunneling barrier make the influence of many structural changes at the interfaces (i.e., changes to the anchoring group, A, and the terminal group, T, and their contacts with the top and bottom electrodes) difficult to detect.[1] Among the exceptions are the observation of a small (and still imperfectly understood) "odd−even effect" in charge transport across n-alkanethiolates on gold,[2−6] the observation of a reduction in current density (by factors of 20−30) when fluorine is present at the SAM//Ga_2O_3 interface,[7] and the observation of rectification of current when T is a redox-active group such as ferrocenyl[6,8,9] or bipyridyl.[10]

As a part of our study of the relation between the structure of the organic groups of SAMs and the rate of charge transfer by tunneling across them, we have examined the relationship between the structure of polyaromatics (molecules that result in a reduction in the height of the tunneling barrier relative to that characterizing aliphatics[11−25]) and the rate of charge transport. We have examined the influence of the chemical structure of the anchoring group and also that of the linker between the anchoring group and the phenyl rings by measuring rates of charge transport across SAMs of oligo(phenyl)thiols (M/SPh_n), oligo(phenyl)methanethiols (M/SCH_2Ph_n), and oligo(phenyl)acetylenes (M/C≡CPh_n), where n = 1−3 and

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M = gold or silver as the metal electrode (Figure 1). Using junctions of the form M/A(Ph)$_n$H//Ga_2O_3/EGaIn, we compared these rates with rates for length-matched n-alkanethiols. Although these SAMs are based on simple oligophenyls and share (we assume) a similar Ph−H//Ga_2O_3 interface, they differ substantially in their physical and electronic interactions with the metal substrates that form the "bottom" interface (M/A). Our results indicate that SAMs of SPh$_n$ and C≡CPh$_n$ on gold (both of which are characterized by the delocalization of high-energy orbitals across the molecule and between the molecule and the electrode[11]) have similar low values of the attenuation factor β and the pre-exponential constant J_0 in the simplified Simmons equation[26] (eq 1),

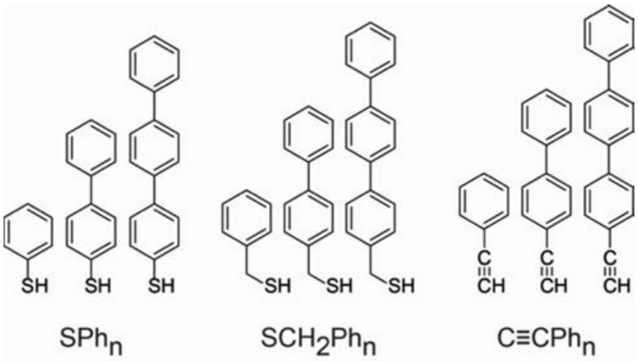

Figure 1. Structures of oligo(phenyl)thiols (SPh$_n$), oligo(phenyl)-methanethiols (SCH$_2$Ph$_n$), and oligo(phenyl)acetylenes (C≡CPh$_n$) used to form SAMs on template-stripped silver and gold substrates (Ag^{TS} and Au^{TS}, respectively). "Ph" indicates a phenylene ring, and n is the number of such rings. For each molecule, we measured the length of the tunneling barrier, d, as the distance from the anchoring atom (sulfur or carbon directly coordinated to the metal substrate) to the distal H atom.

$$J(V) = J_0(V)e^{-\beta d} = J_0(V)10^{-\beta d/2.303} \tag{1}$$

i.e., $\beta = 0.28 \pm 0.03$ Å^{-1} and log $|J_0| = 2.7 \pm 0.1$ for Au/SPh$_n$ and $\beta = 0.30 \pm 0.02$ Å^{-1} and log $|J_0| = 3.0 \pm 0.1$ for Au/C≡CPh$_n$. The introduction of a single intervening CH_2 group into the S−C bond, which converts SPh$_n$ to SCH$_2$Ph$_n$, disrupts the delocalization of the orbitals between the aromatic moiety and the metal electrode[27−29] and increases β to 0.66 ± 0.06 Å^{-1} and log $|J_0|$ to 4.0 ± 0.3; these values are surprisingly close to those derived from SAMs of n-alkanethiols ($\beta_{Au} = 0.76 \pm 0.03$ Å^{-1} and log $|J_0| = 4.2 \pm 0.2$).[2]

SAMs of SPh$_n$ and SCH$_2$Ph$_n$ have been characterized extensively. They form structures that are highly ordered and densely packed on both silver and gold substrates.[30−35] The exception is thiophenol (HSPh), which has been reported to form poorly defined SAMs, possibly because of the weak intermolecular forces between the aromatic rings.[30,31,35] The surface structure of thiolates on metal is the same for SAMs of n-alkanethiolates and SAMs of aromatics (($\sqrt{3} \times \sqrt{3}$)R30° on gold and ($\sqrt{7} \times \sqrt{7}$)R10.9° on silver), but the cant angle (α) for the aromatics is slightly less than that for the alkanethiolates ($\alpha \approx 20°$ for SAMs of terphenylthiol on Au and $\alpha \approx 30°$ for SAMs of n-alkanethiols on Au).[30,36] Oligophenyl groups present in a SAM adopt a near-planar conformation and pack in a herringbone structure.[30,37,38]

Characterization of SAMs of C≡CPh$_n$ on gold indicates that the acetylene group binds in an upright configuration on gold.[39−42] Cyganik and co-workers demonstrated that it is possible to form highly ordered SAMs of n-alkylacetylenes on gold in nonoxidizing environments;[43] the presence of O_2 (before or during SAM formation) leads to poorly organized films and to oxidation of the acetylene group. (See the Supporting Information for experimental details on the formation of the SAMs.)

In measurements of charge transport across a metal−SAM−metal junction, charges encounter a tunneling barrier whose shape is determined by the electrical characteristics of at least five components: the SAM, the two electrodes, and the two interfaces between the SAM and the electrodes. The simplified Simmons equation[26,44,45] (eq 1) parametrizes the rate of charge transport assuming a simple rectangular shape for the tunneling barrier. In this approximation, $J(V)$ decays exponentially with increasing width of the tunneling barrier, d, which is often taken to be the distance between the two electrodes. Here we estimated d as the calculated length of the molecule making up the SAM (in Å, from the anchoring atom to the distal hydrogen atom). The Supporting Information summarizes some of the theoretical limitations of this approach.

■ RESULTS AND DISCUSSION

Figure 2 summarizes the rates of charge transport, using a conical Ga_2O_3/EGaIn tip as the top electrode, across SAMs of oligophenyls having thiol (HS−) and methanethiol ($HSCH_2$−) anchoring groups on gold and silver substrates and an acetylene (HC≡C−) anchoring group on gold substrates. (Figures S1 and S2 and Table S2 provide additional details on the measurements). We provide a comparison of β and J_0 for standard n-alkanethiolates on gold and silver substrates. For all of the systems, values of log $|J|$ (the log-Gaussian mean value of the current density) varied linearly with d. Assuming a through-molecule transport mechanism, we approximated d as the length of the molecule from the anchoring atom to the distal hydrogen atom (the diagram in Figure 2 shows this approximation of d.) Linear regression analyses of the values of log $|J|$ versus d yielded the values of the log-injection current (log $|J_0|$, from the intercept at the y axis) and the tunneling parameter (β, from the slope) for each system (Figure 2).

The rates of charge transport across SAMs of n-alkanethiols on gold and silver ($\beta_{Au} = 0.76 \pm 0.03$ Å^{-1} and log $|J_{0,Au}| = 4.2 \pm 0.2$; $\beta_{Ag} = 0.72 \pm 0.05$ Å^{-1} and log $|J_{0,Ag}| = 3.6 \pm 0.3$)[2,46] serve as a reference range against which we correlate the trends in electrical behavior with the changes in molecular and electronic structure. The value of J_0 is indistinguishable for SAMs of SCH$_2$Ph$_n$ and S(CH$_2$)$_n$CH$_3$ on both silver (log $|J_0| = 3.7 \pm 0.3$ for SCH$_2$Ph$_n$ and 3.6 ± 0.3 for S(CH$_2$)$_n$CH$_3$) and gold (log $|J_0|$ = 4.0 ± 0.2 for SCH$_2$Ph$_n$ and 4.2 ± 0.2 for S(CH$_2$)$_n$CH$_3$). Frisbie and co-workers made a similar observation using conducting-probe atomic force microscopy.[47] They reported the same contact resistance (R_0) for SAMs of oligo(phenyl)-methanethiols and SAMs of n-alkanethiols on gold. One possible explanation for the similar values of J_0 is the similarity in the electronic structures of the interfaces between the SAMs and the bottom electrode: both SAMs have a metal/SCH$_2$− interface. SAMs of oligophenyls that lack a methylene spacer, here SPh$_n$ (on gold and silver) and C≡CPh$_n$ (on gold), give values of J_0 (estimated by extrapolation) that are *lower* by about a factor of 10 than J_0 observed for n-alkanethiolates (log $|J_0|$ = 4.2 ± 0.2; Figure 2).

The measurement and interpretation of the parameter J_0 in the simplified Simmons equation[26,44,45] (eq 1) are both

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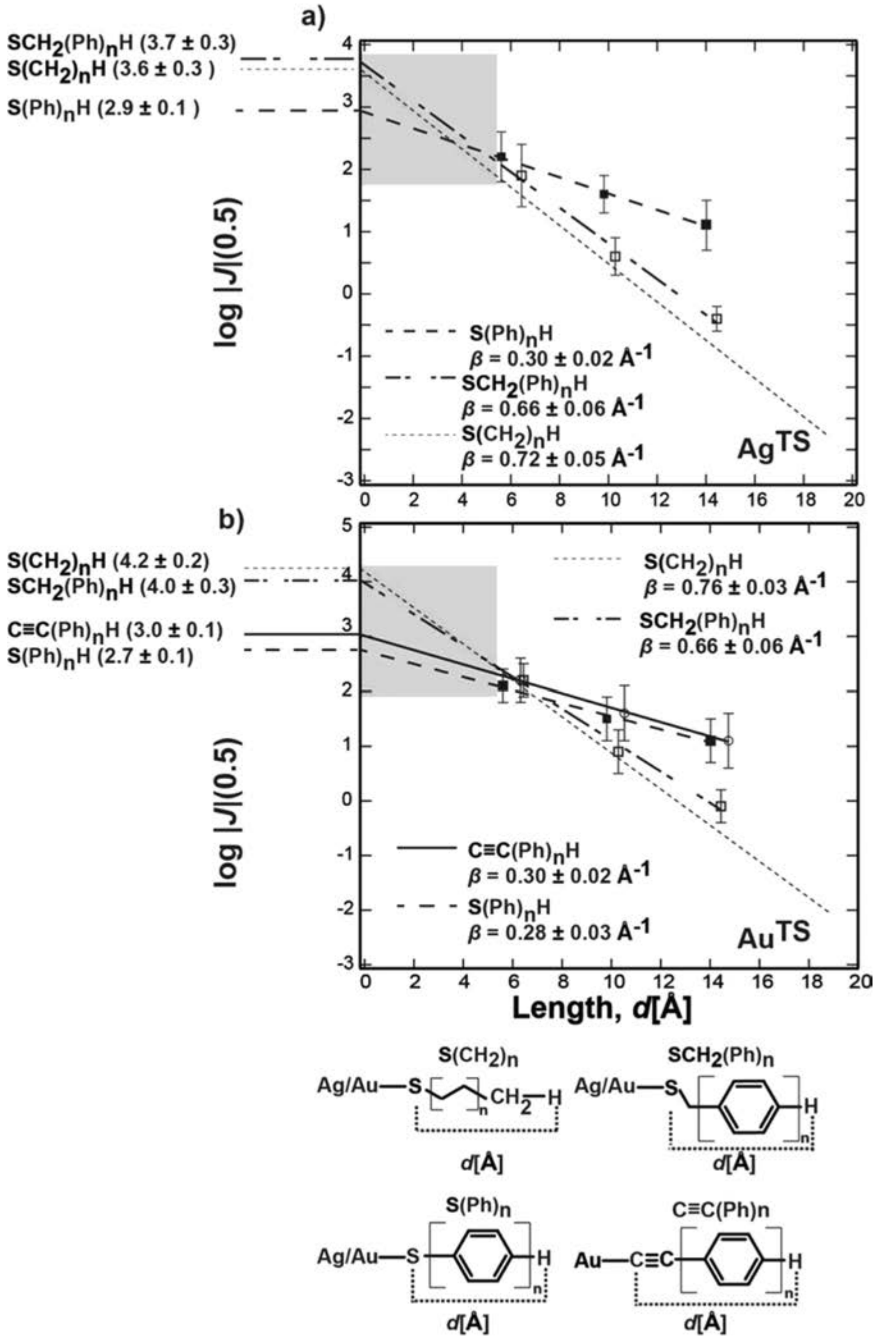

Figure 2. Plots of the Gaussian mean values of log |*J*| at +0.5 V vs molecular length d (in Å) for SAMs on (a) Ag^{TS} and (b) Au^{TS}. The value of d (shown by the dotted lines at the bottom) was calculated as the distance from the anchoring atom, which is bound covalently to the bottom electrode, to the distal hydrogen atom, which is in van der Waals contact with the Ga_2O_3/EGaIn electrode, under the assumption of an all-trans extended conformation. The gray box in each panel indicates the region over which the data must be extrapolated to estimate $J_0(V)$ at $d = 0$. Since the structural elements in this region differ from those in the region where there are data (the region of Ph_n), extrapolation may be inappropriate for $S(Ph)_n$ and $C{\equiv}C(Ph)_n$, although the correctness of this extrapolation is well-validated for *n*-alkanethiolates on gold and silver.[2,49]

complicated. The value of J_0 (determined by extrapolation of the best-fit line to $d = 0$) across aromatics has been less discussed than that for β, in substantial part because of differences in the reported values of J_0 across techniques. The Supporting Information lists some of the issues that make this empirical parameter difficult to interpret. Given the difficulties in interpreting J_0, we focus our analysis on β.

Measurements of charge tunneling across SAMs of SPh_n with n increasing from 1 to 3 yielded $\beta_{Ag} = 0.30 \pm 0.02$ Å^{-1} and $\beta_{Au} = 0.28 \pm 0.03$ Å^{-1} (Figure 2); these values agree with previous experimental reports using single-molecule and large-area junctions.[15,16,34,48−53] The results presented here also agree with theoretical calculations by Ratner and co-workers;[11] using density functional theory (DFT), those authors predicted a β value of ca. 0.3 Å^{-1} for SAMs of poly(phenyl)dithiolates by assuming continuous conjugation of the molecules with the metal electrodes.

We compared the electrical properties of SAMs of SPh_n to SAMs of $C{\equiv}CPh_n$ on Au^{TS} (Figure 2b). Both molecular systems are conjugated (i.e., the π electrons are delocalized

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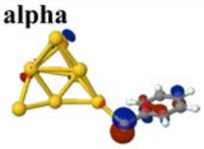
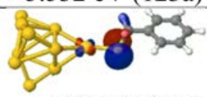
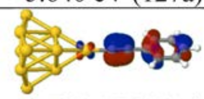
across the molecular backbone), but they differ by the chemical structure of the anchoring group (−S− vs −C≡C−). The values of β for these two series of SAMs are indistinguishable (β = 0.28 ± 0.03 $Å^{-1}$ for Au/SPh$_n$ and β = 0.30 ± 0.02 $Å^{-1}$ for Au/C≡CPh$_n$).

To help correlate the experimental measurements of the rate of charge transport with changes in the molecular structure of the SAM at the interface, we performed DFT calculations of the electronic structures of the series of molecules studied here (Tables 1 and S3−S5). The computational details are given in the Supporting Information. We optimized the structures of the SPh$_n$, SCH$_2$Ph$_n$, and C≡CPh$_n$ compounds (n = 1−3) attached to silver and gold cluster models.

Table 1. α (Spin-Up) Orbital Energies (in eV) and Shapes of the High-Lying Occupied Molecular Orbitals of the Anchoring Groups Oriented Parallel to the Ring Plane in Au$_{10}$/SPh ($n_\parallel$), Au$_{10}$/SCH$_2$Ph ($n_\parallel$), and Au$_{10}$/C≡CPh ($\pi_\parallel$)[a]

Cluster	MO, alpha
Au$_{10}$/SPh	 −5.532 eV (123a)
Au$_{10}$/SCH$_2$Ph	 −5.640 eV (127a)
Au$_{10}$/C≡CPh	 −5.723 eV (121a)

[a]The α (spin-up) and β (spin-down) orbitals differ in energy by less than 0.1 eV. The results for the whole series of compounds (Au/SPh$_n$, Au/SCH$_2$Ph$_n$, and Au$_{10}$/C≡CPh$_n$; n = 1−3) are shown in the Table S3.

The DFT results show that the highest occupied molecular orbital (HOMO) for both Au/SPh$_n$ and Au/C≡CPh$_n$ is partially delocalized; that is, although it is located predominately on the anchoring group, it also includes contributions from the orbitals on the adjacent phenyl rings (Table 1). The values of the HOMO energies of the two molecules are comparable (−5.5 eV for SPh$_1$ and −5.7 eV for C≡CPh$_1$). The electronic structures of the conjugated systems differ from those of saturated n-alkylthiols, where the HOMO is localized on the anchoring atom (ca. −5.6 eV for Au/S(CH$_2$)$_n$CH$_3$) with little to no participation by orbitals on the adjacent atoms of the CH$_2$ groups in the alkyl chain.[1]

Calculations on the Au$_{10}$/C≡CPh cluster illustrate the relevant interactions between the high-lying occupied orbitals of the conjugated molecular systems (Figure 3a), which include the π orbitals of the C≡C triple bond oriented both parallel ($\pi_\parallel$(C≡C)) and perpendicular to the ring plane ($\pi_\perp$(C≡C)) and the π orbitals of the benzene ring (π_{1a}(Ph) and π_{1b}(Ph)). The $\pi_\parallel$(C≡C) and π_{1a}(Ph) orbitals have the same symmetry and show a strong interaction between the anchoring group and the phenyl π system; at the same time, because of their symmetries, the $\pi_\perp$(C≡C) and π_{1b}(Ph) orbitals remain localized on their respective moieties. The same trend is observed for the Au$_{10}$/SPh cluster but not for the Au$_{10}$/SCH$_2$Ph cluster (Figure S4). The presence of the methylene spacer prevents the interaction between the anchoring group and phenyl π system even for the orbitals that have the same symmetry (Figure S4b). The π_{1a}(Ph) orbitals of the phenyl rings interact strongly with each other in the Au/C≡CPh$_n$, Au/SCH$_2$Ph$_n$, and Au/SPh$_n$ series of compounds (n = 1−3), as evidenced by their large energy splittings (Figure 3b−d).

The presence of a single methylene spacer in the Au/SCH$_2$Ph$_n$ compounds (n = 1−3), however, is sufficient to prevent the interaction between the $n_\parallel$(S) lone-pair orbital of the anchoring group and the π_{1a}(Ph) orbital of the phenyl π system, in contrast to the Au/SPh$_n$ compounds (n = 1−3) (Table 1). Disruption of the delocalization of orbitals from the anchoring groups onto the phenyl rings and the metal substrate (Table 1) is correlated with experimentally observed changes in the rate of charge transport (Figure 2). Specifically, the introduction of an insulating methylene spacer between the sulfur anchoring atom and the adjacent phenyl ring—a modification that generates SCH$_2$Ph$_n$—increases the attenuation factor across the molecule to β_{Ag} = 0.66 $Å^{-1}$ and β_{Au} = 0.66 $Å^{-1}$, which are close to those for n-alkylthiolates on Ag and Au (β_{Ag} = 0.72 $Å^{-1}$ and β_{Au} = 0.76 $Å^{-1}$).[2] These values for SCH$_2$Ph$_n$ are similar to that reported previously by us using a mercury junction (β_{Ag} = 0.66 $Å^{-1}$)[48] but somewhat higher than those reported by Frisbie and co-workers (β_{Au} = 0.41 $Å^{-1}$)[47] and Chiechi and co-workers (β_{Au} = 0.46 $Å^{-1}$)[54] for SAMs of SCH$_2$Ph$_n$ on Au.

We investigated the influence of increasing the number of insulating CH$_2$ groups from n = 1 to n = 2 and 3 on the current density (Figure S3). The values of $J(V)$ measured for S(CH$_2$)$_2$Ph, S(CH$_2$)$_2$Ph$_2$, and S(CH$_2$)$_3$Ph fit to the linear regression lines of the oligo(phenyl)methanethiols and n-alkylthiolates. These measurements indicate that the introduction of one insulating CH$_2$ group between the anchoring atom and the adjacent phenyl ring has an influence on the electrical measurements similar to the influence of two and three CH$_2$ groups (a conclusion reached previously for sulfur by Chiechi and co-workers).[54]

The data presented here for oligo(phenyl)methanethiols (SCH$_2$Ph$_n$), phenylethylthiols (S(CH$_2$)$_2$Ph$_n$, n = 1, 2), and phenylpropylthiols (S(CH$_2$)$_3$Ph) as well as those from our previous measurements on oligo(phenyl)carboxylates (O$_2$CPh$_n$) on silver (β_{Ag} = 0.60 $Å^{-1}$)[55] indicate that disruption of the delocalization of orbitals from the bottom electrode and the anchoring group to the Ph$_n$ group is correlated with values of β higher than those observed for SAMs of oligo(phenyl)-thiolates (SPh$_n$). In the case of oligo(phenyl)carboxylates, it is the presence of an orbital node on the carbon atom of the carboxylate group that disrupts the delocalization of orbitals from the CO_2^- group to the Ph$_n$ moiety and produces an electronic effect similar to the presence of an intervening methylene group in SCH$_2$Ph$_n$. Additional studies on oligo-(phenyl)carboxylates showed that decoupling the HOMO from strong interactions with the adjacent oligophenyl groups in the SAM allows the permutation of the order of electronically distinct functional groups in the junction. That is, the position of functional groups with different electronic properties (e.g., R$_1$ = (CH$_2$)$_n$ and R$_2$ = (C$_6$H$_4$)$_m$) does not influence the overall rate of charge transport when the HOMO is localized on the anchoring group.[56]

■ CONCLUSIONS

This study reports values of β and J_0 (obtained using conical EGaIn top electrodes) for three series of aromatic SAMs

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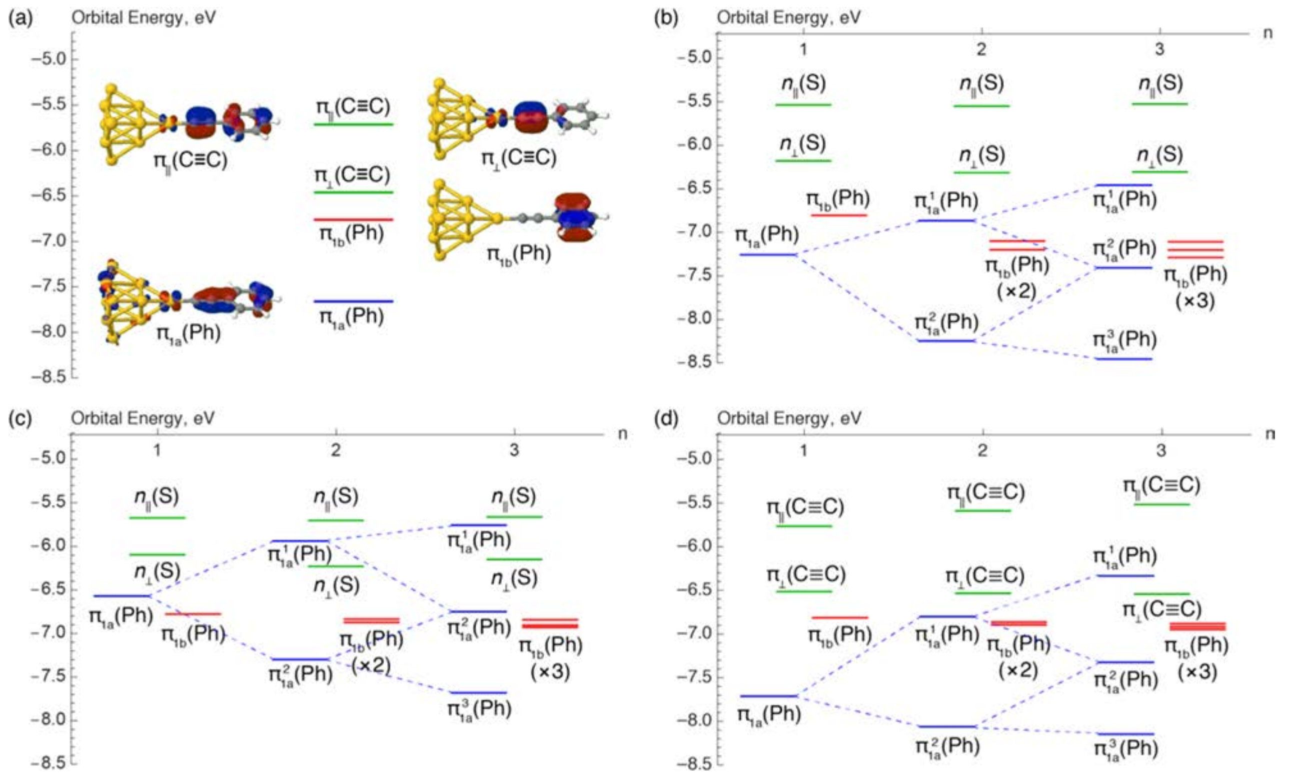

Figure 3. Orbital energy diagrams of high-lying occupied molecular orbitals in the Au/C≡CPh$_n$, Au/SPh$_n$, and Au/SCH$_2$Ph$_n$ series (n = 1−3). (a) Orbital energies and shapes of the high-lying occupied molecular orbitals in Au/C≡CPh. The energy levels of the π orbitals of the C≡C bond parallel ($\pi_{\parallel}$(C≡C)) and perpendicular ($\pi_{\perp}$(C≡C)) to the plane of the benzene ring are shown in green; the energy levels of the π orbitals of the phenyl ring (π_{1a}(Ph) and π_{1b}(Ph)) are shown in blue and red, respectively; only the shapes of the α (spin-up) orbitals are shown. (b−d) Orbital energy diagrams of the (b) Au/SPh$_n$, (c) Au/SCH$_2$Ph$_n$, and (d) Au/C≡CPh$_n$ series of compounds (n = 1−3).

(SPh$_n$, SCH$_2$Ph$_n$, and C≡CCH$_2$Ph$_n$) on gold and silver substrates. These results demonstrate significant sensitivity of the tunneling current through these junctions to the molecular and electronic structures of the interface between the metal (Au or Ag) bottom electrode and the SAM; others (Frisbie, Chiechi, Tokumoto, Bjørnholm, and co-workers)[47,54,57,58] also concluded that tunneling currents are sensitive to the characteristics of the interfaces. At least in the systems described here, this sensitivity seems to be based largely on the extent of delocalization of the HOMO—here, an orbital centered on −SR or −C≡CR—onto the proximate parts of the SAM. The magnitude of this sensitivity is clear from a comparison of two observations.

(i) The value of the attenuation of the tunneling current with distance (β) is indistinguishable for SAMs of SPh$_n$ and C≡CPh$_n$ on gold. These two series of SAMs have substantially different anchoring groups (−S− vs −C≡C−) but both are characterized by the delocalization of high-lying orbitals between the anchoring group and the adjacent phenyl rings.

(ii) The introduction of a single CH$_2$ group between the aromatic group and the sulfur anchoring atom—generating SCH$_2$Ph$_n$—increases β to a value very similar to that of a length-matched saturated aliphatic SAM. We attribute this increase in β to a disruption in the delocalization of orbitals from the anchoring group to the phenyl rings.

In addition to characterizing the rates of charge transport across a series of oligophenyls that have structurally distinct interfaces with the bottom electrode, this study highlights some important features of the tunneling barrier that went undetected in earlier studies using insulating alkanethiolates with a localized HOMO on the anchoring sulfur atom. Our previous investigations of the influence of the metal/SAM interface on the rate of charge transport considered alkyl-based SAMs having anchoring groups (e.g., SR, C≡CR, and O$_2$CR)[49] in which the HOMO (centered on the anchoring group) was not delocalized into the R = (CH$_2$)$_n$H group. On the basis of the indistinguishable values of β and J_0, that study suggested that the interface between the metal and the SAM is not important in determining the rate of charge transport in junctions of the structure M/A(CH$_2$)$_n$H//Ga$_2$O$_3$/EGaIn, where A is the "anchoring group" (e.g., S, C≡C, O$_2$C).[59] The current study analyzed conjugated molecular systems where the HOMO extends beyond the anchoring group and onto the adjacent phenyl rings and established that interfaces characterized by high-lying occupied molecular orbitals that are localized and delocalized *are* quite different. Furthermore, changes in the molecular structure of the interface that disrupt the delocalization of the HOMO increase the value of β.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b01253.

Detailed experimental and computational procedures, histograms of current densities, and summary of junction measurements (PDF)

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Notes

The authors declare no competing financial interest.

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