Charge Transport Mechanisms

Charge Tunneling along Short Oligoglycine Chains

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Abstract: This work examines charge transport (CT) through self-assembled monolayers (SAMs) of oligoglycines having an N-terminal cysteine group that anchors the molecule to a gold substrate, and demonstrate that CT is rapid (relative to SAMs of n-alkanethiolates). Comparisons of rates of charge transport-using junctions with the structure Au57/SAM/Ga2O3/EGaIn (across these SAMs of oligoglycines, and across SAMs of a number of structurally and electronically related molecules) established that rates of charge tunneling along SAMs of oligoglycines are comparable to that along SAMs of oligophenyl groups (of comparable length). The mechanism of tunneling in oligoglycines is compatible with superexchange, and involves interactions among high-energy occupied orbitals in multiple, consecutive amide bonds, which may be separated by one to three methylene groups. This mechanistic conclusion is supported by density functional theory (DFT).

Understanding mechanisms of charge transport (CT) in proteins is important, both for biology and nanoscience.[1] Self-assembled monolayers (SAMs) of oligopeptides offer the opportunity to investigate charge transport across biologically relevant model structures (and to examine molecular entities present in proteins).[1a,2] CT is fundamental, for example, to photosynthesis,[1a,3] some enzymatic reactions[4] and respiration,[1a] and can be rapid over considerable distances.[5] The mechanisms (such as tunneling, inelastic hopping, or other processes) of CT through peptides are still incompletely defined, and have been variously suggested to depend on the length of the peptide, the presence of secondary structure, and the presence of specific side chains.[1a,6]

Rates of charge tunneling across SAMs composed of n-alkanethiolates have been studied extensively,[7] and most commonly characterized using the parameters of the simplified Simmons equation Eq. (1).[8]

\[ J(V) = J_0(V)e^{-\beta d} = J_0(V)\left(\frac{\pi e^2}{\sqrt{2m^*V}}\right) \]

This equation is a useful (and commonly used) semi-empirical parameterization that suggests that the rate of tunneling should depend exponentially on the width of the barrier (d), assumed to be rectangular, and on \( \beta \) (a parameter related to the height of the barrier).

Values of \( \beta \) for n-alkanethiolates are \( \beta_{70} = 0.9–1.1n_{10}^{-1} \) or \( \beta_{60} = 0.7–0.8 \AA^{-1}. \) The rates of charge transport across SAMs structurally more complex than linear hydrocarbons (that is, SAMs with aryl groups, with heteroatoms embedded in the backbone, and SAMs with the potential for strong interchain interactions) have also been explored (\( \beta_{70} = 0.3–0.6 \AA^{-1} \)).[9]

This work characterized the rates of CT across SAMs containing oligoglycine residues, and compared these rates with those across n-alkanethiolates of approximately matched length. The objectives were to determine i) if oligopeptides provided a better pathway for CT by tunneling than did n-alkanes, and ii) if there were a difference between oligoamides and n-alkanes, to suggest, both experimentally and theoretically, why the two behaved differently.

We investigated CT across SAMs of six compositionally simple derivatives of oligoglycine (Scheme 1) with a terminal cysteine residue (Cys(Gly)\(n\), \( n = 0–5 \)), using a large-area junction having the structure Au57/SAM/Ga2O3/EGaIn, where Au57 is a template-stripped gold surface.[7e,9a,10] SAMs having oligoglycine residues gave values of \( \beta \) that are significantly lower than those measured for SAMs of n-alkanethiolates of similar length. DFT modeling of gold-bound oligoglycines (below) indicates that the high-energy occupied orbitals of peptide groups, which modulate the local tunneling potential, are essential for rapid tunneling. Although the exponential length dependence of tunneling rates in n-alkanethiols can be approximated by a flat, rectangular tunneling barrier [Eq. (1)], the tunneling conductance through chains of oligopeptides is better described.
by a one-dimensional chain of peptide groups coupled electronically. This model was termed superexchange tunneling by McConnell, Ratner, Nitzan, and co-workers, using an analogy with reaction kinetics of processes involving CT\cite{11a,12} and was used not only as a model for CT in peptides\cite{11a,12} but also as a simple qualitative model for molecular conduction.\cite{11a,13} Here, we establish that the superexchange model can be used to interpret experimental tunneling data, by correlating measurements of current density and calculations of electronic structure. We use the superexchange model to derive the relevant model parameters from DFT, and demonstrate that this model is applicable to amide groups separated by methylene groups (\((\text{CH}_2)\), with \(n = 1–3\)). Notably, both the flat-barrier and the superexchange models predict an exponential length-dependence in tunneling rates.\cite{8}

SAMs on template-stripped gold (\(\text{Au}^{75}\)) were prepared according to reported methods.\cite{7e,10a} Detailed surface analyses indicate that SAMs of Cys\((\text{Gly})_n\), are ordered: Infrared absorption-reflection spectroscopy (IRRAS) data indicate that SAMs of oligoglycine form beta-sheet structures, and X-ray photoelectron spectroscopic (XPS) and ellipsometry measurements confirm that the thickness of these SAMs grows linearly with an increase in the number of glycine residues. The Supporting Information contains details on the formation and characterization of the SAMs, of the measurements, and of the DFT calculations.

We derive values of \(\beta\) and \(J_0\) [Eq. (1)] for oligopeptides on gold (Cys\((\text{Gly})_n\), \(n = 0–5\)), and compare these values with those of \(n\)-alkanethiolates, to determine the influence of the differences in their structure on the rates of charge transport by tunneling across them. Linear regression of \(\log |J|\) versus \(n\) (the number of non-hydrogen atoms in the backbone) for SAMs of oligoglycine on \(\text{Au}^{75}\) yielded \(\beta_{\text{Gly}} = 0.5 \pm 0.02\) \(\text{n}_{\text{nom}}^{-1}\) and \(\log J_0_{\text{Gly}} = 2.8 \pm 0.3\) (Figure 1; Supporting Information, Figures S7, S11). Measurements of \(J(V)\) for all peptides resulted in symmetric voltage profiles at forward and reverse biases \(\pm 0.5\) \(\text{V}\); none showed a rectification ratio \(r = |J(+0.5\text{~V})|/|J(-0.5\text{~V})|\) larger than 3 (similar to SAMs of alkanethiolates).\cite{7e} The difference between \(\log J_0\) for SAMs of oligoglycines \(\log J_0_{\text{Gly}} = 2.8 \pm 0.3\) and \(n\)-alkanethiolates, both on gold \(\log J_0_{\text{alk}} = 3.6 \pm 0.3\), was statistically significant, as was the difference between the value of \(\beta\) \(\beta_{\text{Gly}} = 0.50 \pm 0.02\) \(\text{n}_{\text{nom}}^{-1}\), \(\beta_{\text{alk}} = 0.94 \pm 0.02\) \(\text{n}_{\text{atom}}^{-1}\). The \(\log J_0\) for \(n\)-alkanethiolates on gold in units of \(\text{Å}^{-1}\) is approximately 4.\cite{10a,14} The value of \(J_0\) is well-defined experimentally, but requires an extrapolation in the data that makes its interpretation ambiguous; we explain this ambiguity in the Supporting Information.

SAMs of oligoglycines (Scheme 1 and Figure 1) are more conductive by tunneling than SAMs of alkanethiolates. To explain this difference, we tested two hypotheses: i) The presence of an extended network of hydrogen bonds connecting the (Gly)\(_n\) groups inter-molecularly might result in changes in molecular or electronic structure of the junction that would influence the rates of charge transport. ii) The presence of multiple, interacting amide bonds along the chain might increase tunneling by a superexchange tunneling mechanism involving a sequence of high-lying occupied coupled orbitals.\cite{11a,13}

To examine the effect of hydrogen bonds in charge transfer, we compared the current density across Cys\((\text{Gly})_n\),...
and cysteine trisarcosine (Cys(Sar), 19). Substituting a methyl group for a hydrogen atom on the nitrogen atom of the amide groups (a change that converts Cys(Gly)₃ to Cys(Sar)) eliminates the possibility of interchain hydrogen bond formation, and has the potential to influence the conformation of the SAM. Although we have not explicitly addressed the issue of structure in detail, we know from measurements using ellipsometry that both SAMs of Cys-(Gly)₃ and SAMs of Cys(Sar), have comparable thicknesses (Supporting Information, Figure S4b). Measurements of current density for these two compounds yielded indistinguishable values of log |J| for Cys(Gly)₃ (0.0 ± 0.4) and Cys(Sar), (0.0 ± 0.6); this similarity strongly suggests that the tunneling current, in this system, is not influenced by hydrogen bonds or changes in conformation (Figure 2b; Supporting Information, Figure S9).

To test the hypothesis that orbital interactions between the amide bonds are important, we compared the tunneling current between two sets of molecules (4 and 12–14, and 15–18; Figure 2). In each set, the number of amide bonds increased sequentially; the difference between the two series is the presence of an amine functional group on cysteine. This analysis shows that increasing the number of amide bonds within molecules of the same length increases their conductivity (Figure 2).

DFT calculations on the oligoglycines (see the Supporting Information for details), and their analogues, indicate that each amide group contributes two high-lying occupied orbitals; these orbitals arise from the lone pairs on oxygen and nitrogen. In the all-trans conformation, these orbitals are distinguishable by their symmetry: that is, they are either in plane or perpendicular to the plane of the amide group (Figure 3a,b). For an isolated amide bond of CysGly, the orbital energies of the lone pairs on oxygen and nitrogen are found at approximately −6.6 and −7.0 eV. As a result of symmetry, only interactions within groups of “in-plane” or “out-of-plane” occupied orbitals are possible. These sets generate two independent manifolds of high-lying occupied orbitals with energies between −6 and −8 eV. We observe that the orbital energies within each manifold follow a pattern consistent with the predictions of the superexchange tunneling model, which assumes a linear chain of localized orbitals with nearest-neighbor interactions (Figure 3c).[11a,b,15] In turn, the superexchange model predicts that large nearest-neighbor couplings lead to rapid tunneling rates, as observed experimentally in measurements of current density across SAMs of oligoglycine. The strength of the interaction is sensitive to the relative orientation of the amide groups and is influenced by the (yet unknown) details of the molecular conformation. By comparison, the occupied orbitals on the C–H bond of alkanethiols are at approximately −8.1 eV.[16] The Supporting Information describes these DFT calculations.

To determine how the distance between the amide bonds influences CT, we measured current density across increasing lengths of cysteine-β-alanine (compounds 22–24). These structures have two CH₂ groups between the amide bonds, compound 25 has three CH₂ groups between the amide bonds, and compound 26 has four CH₂ groups. The data in Figure 2b show that four -CH₂- units between the amide groups are necessary to reduce the tunneling current density to a value close to a length-matched n-alkanethiolate. This finding is consistent with the computed nearest-neighbor interactions between amide groups obtained from DFT calculations. Fitting of the occupied orbital energies (calculated by DFT; Figure 3b) to the superexchange model shows that the strength of nearest-neighbor interactions between the in-plane occupied orbitals in the compounds 22–25 is similar to that in oligoglycines.

A comparison of log |J| values between compound 10 (log |J| = 1.9 ± 0.6) and Cys (1) (log |J| = 1.9 ± 0.4), and 4 (Cys(Gly)), −0.1 ± 0.4) and compound 20 (0 ± 0.3) confirm...
that the amine group does not influence the tunneling current (Figures 2, 3). Measurements of current density through compounds 20, 21, and 18 showed that changing the terminal -COOH group in 20 (log $|J| = 0.0 ± 0.3$) to -COOME in 21 (log $|J| = -0.4 ± 0.3$) or -CH$_2$CH$_2$ in 18 (log $|J| = -0.4 ± 0.3$) does not influence CT beyond the small difference (Δlog $|J| = 0.4$) expected for an additional carbon.

This study of charge transport across short sequences of oligoglycines results in five key conclusions. i) Tunneling is the dominant mechanism for CT through short sequences of oligoglycines. The results indicate that charge transport by tunneling occurs across SAMs of oligoglycines having the structure of CysGly$_n$, (with $n = 0–5$); there was no apparent change in the mechanism of CT (for example, from tunneling to hopping) within this series of compounds. We do not exclude the possibility that other oligopeptides (such as oligoprolines) will have different mechanisms of charge transport: clarifying the mechanism of CT across peptides structurally more complex than glycine is one focus of future work. ii) SAMs of oligoglycines are more conductive by attenuation compared with SAMs of alkanethiolates of the same length. iii) SAMs of oligoglycines are more conductive by attenuation with values of $\beta$ ($\beta$ = 0.45 ± 0.02 Å$^{-1}$) reported for linear polyaromatics ($\beta$ = 0.3–0.6 Å$^{-1}$).[3-4]

The superexchange tunneling model predicts that two structural factors are responsible for rapid hole tunneling through oligoglycine chains relative to n-alkanethiolates: i) the high-lying occupied orbitals on the amide bonds, and ii) the substantial nearest-neighbor couplings between them. This insight provides us with a useful design strategy for new tunneling conductors based on maximizing the nearest-neighbor couplings between high-lying occupied orbitals in organic molecules.

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