Charge Transport Mechanisms

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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 Au^{TS}/SAM//Ga_2O_3/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 by 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,c,2] CT is fundamental, for example, to photosynthesis,[1d,3] some enzymatic reactions[4] and respiration,[1d] 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]

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

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 β (a parameter related to the height of the barrier).

Values of β for *n*-alkanethiolates are $\beta_{SCn} = 0.9\text{–}1.1\ n_{CH_2}{}^{-1}$ or $\beta_{SCn} = 0.7\text{–}0.8\ Å^{-1}$.[7e] 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 ($\beta_{(Ph)n} = 0.3\text{–}0.6\ Å^{-1}$).[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 ($(Cys(Gly)_n$, $n = 0\text{–}5$), using a large-area junction having the structure Au^{TS}/SAM//Ga_2O_3/EGaIn, where Au^{TS} is a template-stripped gold surface.[7e,9a,10] SAMs having oligoglycine residues gave values of β 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

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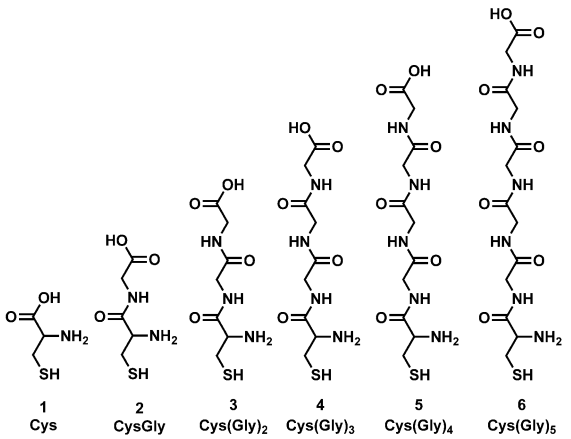

Scheme 1. Cysteine-glycines (Cys(Gly)$_n$) peptides investigated in this work.

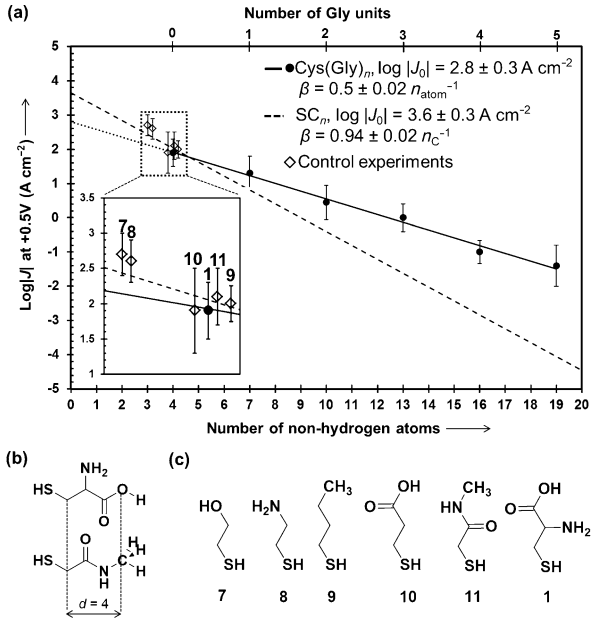

Figure 1. CT along oligoglycine Chains. a) Plot of the Gaussian mean values of log $|J|$ at $+0.5$ V versus molecular length for oligoglycines (solid line) and *n*-alkanethiolate standards (dashed line) using a junction with the structure Au^{TS}/SAM//Ga_2O_3/EGaIn. Error bars represent the standard deviation of Gaussian mean values. Molecules that are shorter than cysteine (**1**), but still possess some structural similarities to it (**7**, **8**), give current densities that fit to the line for *n*-alkanethiolates (dashed line). b) The molecular length is calculated based on the number of non-hydrogen atoms, starting with carbon next to the sulfur atom, and counting to the final non-hydrogen atom (for example, number of atoms for both Cys (**1**) and **11** is 4). c) Structure of "short" molecules that are similar in composition to cysteine. The current densities of these molecules were measured to develop a feeling for the reliability of extrapolation as a method of estimating J_0 for the series. Cys(Gly)$_n$OH.Cysteine-glycines (Cys(Gly)$_n$) peptides investigated in this work.

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,[11] and was used not only as a model for CT in peptides,[1d,2,12] but also as a simple qualitative model for molecular conduction.[11a,b,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 ($(CH_2)_n$ with $n = 1$–3). Notably, both the flat-barrier and the superexchange models predict an exponential length-dependence in tunneling rates.[8]

SAMs on template-stripped gold (Au^{TS}) were prepared according to reported methods.[7e,10a] Detailed surface analyses indicate that SAMs of Cys(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 β and J_0 [Eq. (1)] for oligopeptides on gold (Cys(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 Au^{TS} yielded $\beta_{(Gly)n} = 0.5 \pm 0.02$ n_{atom}^{-1} and log $|J_{0(Gly)n}| = 2.8 \pm 0.3$ (Figure 1; Supporting Information, Figures S7, S11). Measurements of J(V) for all peptides resulted in symmetric voltage profiles at forward and reverse biases (± 0.5 V); none showed a rectification ratio ($r = |J(+0.5\ V)|/|J(-0.5\ V)|$) larger than 3 (similar to SAMs of alkanethiolates).[7e] The difference between log $|J_0|$ for SAMs of oligoglycines (log $|J_{0(Gly)n}| = 2.8 \pm 0.3$), and *n*-alkanethiolates, both on gold (log $|J_{0SCn}| = 3.6 \pm 0.3$), was statistically significant, as was the difference between the value of β ($\beta_{(Gly)n} = 0.50 \pm 0.02$ n_{atom}^{-1}, $\beta_{SCn} = 0.94 \pm 0.02$ n_C^{-1}). The log $|J_0|$ for *n*-alkanethiolates on gold in units of Å^{-1} is approximately 4.[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.[11a,b,15]

To examine the effect of hydrogen bonds in charge transfer, we compared the current density across Cys(Gly)$_3$

and cysteine trisarcosine ($Cys(Sar)_3$, **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 $Cys(Sar)_3$) 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 $Cys(Sar)_3$ 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 $Cys(Sar)_3$ (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.[10a] 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 CH_2 groups between the amide bonds, compound **25** has three CH_2 groups between the amide bonds, and compound **26** has four CH_2 groups. The data in Figure 2b show that four -CH_2- units between the amide groups are

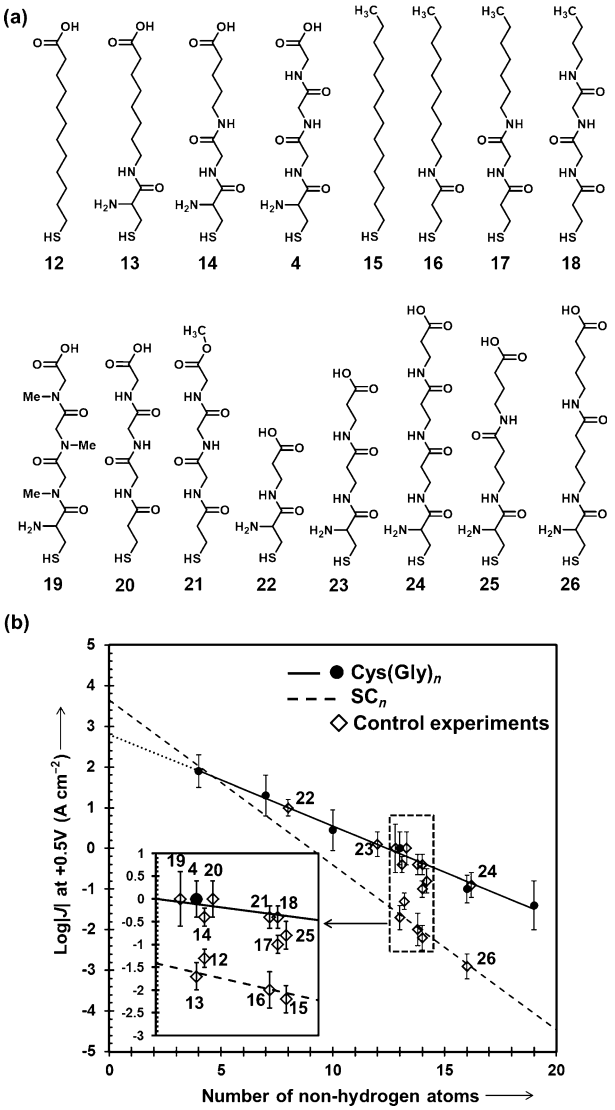

Figure 2. Control experiments for understanding the influence of an amide bond in CT across oligoglycines. a) Structure of the compounds used for control experiments. b) Influence of an amide bond on current density. The solid line represents the fit for Gaussian mean values of $\log|J|$ at +0.5 V for oligoglycines, and the dashed line represents the line for *n*-alkanethiolate on Au^{TS}. The numbers corresponds to compounds in Figure 2a. The molecular length is calculated based on the number of non-hydrogen atoms from the sulfur atom to the final atom. Error bars represent the standard deviation of Gaussian mean values.

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** ($\log|J| = 1.9 \pm 0.6$) and Cys (**1**) ($\log|J| = 1.9 \pm 0.4$), and **4** ($Cys(Gly)_3$, -0.1 ± 0.4) and compound **20** (0 ± 0.3) confirm

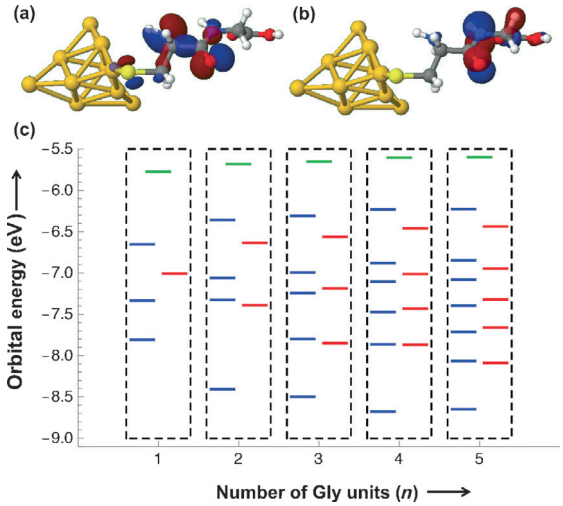

Figure 3. Relevant high-lying occupied orbitals of Cys(Gly)$_n$ peptides from DFT calculations. a) In-plane occupied orbital of the peptide bond. b) Out-of-plane occupied orbital of the peptide bond. c) Orbital energies of the sulfur lone pair orbitals (green), in-plane (blue), and out-of-plane (red) occupied orbitals of the amide bonds in oligoglycine complexes (Au_{10}-Cys(Gly)$_n$) peptides as function of number of Gly units(n).

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** ($\log|J| = 0 \pm 0.3$) to -COOMe in **21** ($\log|J| = -0.4 \pm 0.3$) or -CH_2CH_3 in **18** ($\log|J| = -0.4 \pm 0.3$) does not influence CT beyond the small difference ($\Delta\log|J| = 0.4$) 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.[16] ii) SAMs of oligoglycines are more conductive by tunneling than SAMs of alkanethiolates of the same length. Tunneling current densities across increasing lengths of oligoglycines in SAMs on gold showed a lower value of β ($\beta_{(Gly)n} = 0.50 \pm 0.02$ n_{atom}^{-1}) than that measured for SAMs of *n*-alkanethiolates ($\beta_{SCn} = 0.94 \pm 0.02$ n_C^{-1}) (Figure 1a). This differences can be large for long chains (for instance J(Cys-(Gly)$_4$)/J(S(CH$_2$)$_{16}$H $\approx 10^2$). Charge tunneling through SAMs of oligoglycines is thus faster than that through SAMs of alkanethiolates of the same length, and that difference becomes larger as the chains become longer. iii) The presence of multiple high-lying, occupied, interacting amide orbitals is responsible for the high conductivity of oligoglycines. iv) Superexchange by this mechanism plays a dominant role in CT, and non-nearest-neighbor coupling between in-plane orbitals is possible. Surprisingly (but supported by calculations) -(CONH)(CH$_2$)$_n$(CONH)- (with $n = 1$–3) all enhance the rates of tunneling relative to the length-matched (CH$_2$)$_n$ groups. v) The rate of CT by tunneling through oligoglycines is comparable with linear polyaromatics. The attenuation of the rate of CT by tunneling through SAMs of (Gly)$_n$ is comparable with values of β ($\beta_{(Gly)n} = 0.45 \pm 0.02$ Å^{-1}) reported for linear polyaromatics ($\beta_{(Ph)n} = 0.3$–0.6 Å^{-1}).[9d,e]

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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