# Supplementary Information Probing Charge Transport through Peptide Bonds

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## 1. Additional Experimental Data



Figure S1: One-dimensional conductance-displacement histograms for C7 and F1 showing multiple Gaussian fits to the data.



Figure S2: Two-dimensional conductance-displacement histograms for A, AA, G/C1, GG, GGG, C3, C5 and C7. Conductance values are binned logarithmically with 100 bins/decade and displacement values are binned linearly. All traces are aligned at 0.5  $G_0$  prior to creating the histogram.

### 2. Additional Computational Details

#### a. Binding motif

For our theoretical calculations, we specifically explore binding geometries and energetics of a R-COO<sup>-</sup> terminal group and a trimer motif on an Au lead, following from the fact that experimental evidence indicates that C-terminal group of the peptides in the junction is deprotonated.<sup>1</sup> There are multiple ways in which O-Au covalent bonds can occur between such a terminal group and undercoordinated gold.<sup>2</sup> To find stable binding configurations most relevant to a molecular junction, we calculate the binding energies of Alanine (**A**) with a COO<sup>-</sup> terminal group (where the proton that has been removed is placed on a neighboring Au atom) on a gold lead. In our lead calculations, we use an Au trimer motif placed on a Au(111) surface with 16 Au atoms per layer and 4 layers (Figure S3). The unit cell is charge neutral.



Figure S3: Examined binding geometries for the COO-Au binding, and the corresponding relative binding energy (black dots) for each configuration. The "trimer" motif (see text for details) is found to be energetically preferable and was used for the transmission calculations.

We examine four different binding motifs and examine their relative binding energies with density functional theory using the VASP package.<sup>3</sup> All the coordinates of the Au atoms are fixed and all

the coordinates of the molecule and hydrogen atom are allowed to relax, until the Hellmann-Feynman forces are less than 0.04 eV/Å. These constraints accelerate the relaxations without loss of accuracy: for select geometries, we perform relaxations of the Au trimer and the top two layers of Au atoms, in addition to the molecule and the hydrogen atom, and we obtain qualitatively the same trend. For all relaxations, we use the Perdew-Burke-Ernzerhof (PBE) functional<sup>4</sup>; we also use the projector augmented wave (PAW) method<sup>5</sup> with a plane wave basis and an energy cutoff of 400 eV. A 4×4×1 k-mesh is used. We find the most stable configuration to be one in which the two oxygen atoms in COO<sup>-</sup> endgroup bind individually to two Au atoms of the trimer motif, which we denote as "trimer" in Figure S3. The calculated junction structure is demonstrated for AAA in Figure S4.



Figure S4: Example molecular junction structure of the AAA junction, with the "super-molecule" subsystem framed, including the isolated peptide and the Au trimer.

# <u>b. DFT+ $\Sigma$ generalization for covalent O-Au binding</u>

As described previously<sup>6</sup>, DFT+ $\Sigma$  is an approximate GW-like self-energy correction that consists of two main parts to ameliorate erroneous DFT energy level alignment in the junction. Here, in these two parts are generated as follows: (1) molecular gas-phase energy levels are corrected using an optimally-tuned range-separated hybrid (OT-RSH) functional<sup>7</sup>; and (2) an electrostatic imagecharge correction is computed and used to account for screening of the molecular addition and removal levels by the leads <sup>8</sup>. The DFT+ $\Sigma$  approach requires that the electronic resonances important for transport in the junction can be clearly identified with a molecular orbital of the gasphase molecule. Thus, the standard DFT+ $\Sigma$  approximation is expected to be effective when the molecule is "weakly coupled" to the leads, junctions for which hybridization between lead and molecule states is relatively weak, and for which the electronic coupling results in well-defined Lorentzian-like lineshapes, such as junctions formed with donor-acceptor bonds<sup>9</sup>. In this weakcoupling limit, corrections to the DFT molecular orbital energies can be obtained from calculations on a gas-phase "reference" molecule, additively augmented with image charge corrections (as described above). This standard DFT+ $\Sigma$  approach is challenged if the molecular states are covalently bonded to those of the lead: in such a case, it is no longer clear that the relevant reference system for constructing this approximate self-energy correction is the gas-phase molecule. In fact, in the case of this manuscript, since strong molecule-lead binding is involved, significant hybridization results in features in the transmission that cannot be easily associated with either the lead or molecule alone. These features can be connected to mixed lead-molecule states that emerge upon junction formation. Predicting corrections to DFT for such states requires a modification of the "standard" DFT+ $\Sigma$  correction<sup>10</sup>, where the gas-phase correction is determined from the molecular bridge in the gas-phase.



Figure S5: Theoretical transmission of (a) alkane series, (b) glycine and (c) alanine peptides examined in this work, calculated using the generalized  $DFT+\Sigma$  scheme presented in the main text.

Here, we use the molecule and three additional Au atoms covalently bound to the COO<sup>-</sup> terminal group as a "super-molecule" (which is neutral), as shown for AAA in Figure S4, and compute the

corresponding DFT+ $\Sigma$  gas-phase and image charge corrections. This approximation is acceptable because frontier molecular orbitals (specifically HOMO-2 and LUMO+2) associated with the "super-molecule" can be directly associated with the near-Fermi level peaks in the transmission function of the junction, and therefore the "super-molecule" serves as a good reference for applying self-energy corrections. We construct the  $\Sigma$  correction for this "super-molecule" following prior work, with orbital-dependent gas-phase energy level corrections and image-charge correction calculated for the HOMO-2 for all orbitals. OT-RSH gas-phase energies are calculated using 20% exact exchange in the short range. The optimally-tuned range-separation parameter  $\gamma$ , as well as the resulting HOMO and LUMO levels, the image charge components, and the resulting conductance are reported in Table S1. As shown in the main text and in Table S1 and Figure S5, applying DFT+ $\Sigma$  in this manner leads to quantitative agreement with measurements, whereas DFT without corrections leads to large overestimation of experimental results. Further elaboration of the theoretical method developed in this work will be presented in a future publication. Table S1: Junction (N-C) lengths (Å) and Au-O bond lengths (Å); OT-RSH optimized rangeseparation parameter  $\gamma$  (Bohr<sup>-1</sup>) and the corrected HOMO (ionization potential) and LUMO (electron affinity) energy levels (eV); Image charge corrections (ICC) of occupied and unoccupied states for the 'super-molecule'; and conductance, calculated using DFT and the generalized DFT+ $\Sigma$  scheme within a Non-Equilibrium Green's Function approach<sup>11</sup>, compared to experimental conductance.

	Length Au-O		Г	НОМО	LUMO	ICC	ICC	Conductance (G <sub>0</sub> )		
	(Å)	bonds (Å)	(Bohr <sup>-1</sup> )	(eV)	(eV)	(occ.)	(unocc.)	DFT	DFT+S	Exp.
Alkanes										
C1	2.52	2.28 2.27	0.20	-7.5	-1.2	1.5	1.3	3.42E-02	1.01E-02	7.94E-03
С3	5.05	2.24 2.26	0.19	-7.6	-1.8	1.5	1.3	4.48E-03	1.12E-03	1.05E-03
C5	7.54	2.23 2.25	0.20	-7.6	-1.9	1.5	1.3	1.16E-03	3.08E-04	1.86E-04
C7	10.11	2.22 2.24	0.20	-7.5	-1.86	1.6	1.2	1.93E-04	5.78E-05	2.00E-05
Alanine										
Α	2.52	2.29 2.30	0.20	-7.6	-2.1	1.4	1.3	2.85E-02	7.85E-03	7.43E-03
AA	6.06	2.29 2.30	0.20	-8.0	-2.2	0.85	1.3	1.39E-03	2.24E-04	3.49E-04
AAA	9.79	2.29 2.31	0.18	-8.1	-2.4	0.7	1.2	7.78E-05	7.20E-06	8.07E-06
Glycine										
GG	6.02	2.29 2.29	0.19	-8.0	-2.3	1.3	1.3	1.47E-03	3.46E-04	2.04E-04
GGG	9.77	2.29 2.29	0.20	-8.2	-2.3	0.7	1.2	7.41E-05	8.91E-06	1.48E-05

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