# Conductance of Tailored Molecular Segments: A Rudimentary Assessment by Landauer Formulation

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#### Preparation of conductance histograms.

The method of STM by measures I(s) by monitoring the current as a function of the stretching distance of the STM tip after being fused with the substrate. For those exhibiting step-like features at conductance far below 1 G<sub>0</sub> (77.5  $\mu$ S =  $2e^2/h$ , the quantum conductance), the behavior is consistent with those of having molecules bridged across the tip-electrode junction. The conductance values at the steps dominate the occurrence frequency and indicate the probable conductance for the molecule. However, literature reports<sup>\$1,\$2</sup> have addressed the difficulty in locating the conductance peak positions for alkanedithiols when the histogram is generated by using all the acquired I(s) traces. The difficulty is attributed to the thiol-gold binding characteristics as well as the interference from I(s) traces with exponentially decayed or noisy features.<sup>S3</sup> Therefore, these uncharacteristic exponentially and noisy traces are screened to make the conductance peaks apparent. To keep the trace selection from being over-subjective. Venkataraman and co-workers<sup>\$4,\$5</sup> used an automated algorithm. Accordingly, in the present study of alkanedinitriles an algorithm is utilized to select I(s) traces having a sharp drop in current. The criteria and the selection procedures are described in the following. (1) The conductance trace is plotted in a logarithmic scale. The first derivative of the logarithm of conductance trace,  $d(\log G)/ds$ , is computed. (2) Only the traces with  $d(\log G)/ds$  values higher than a cut-off value of 1000 are selected. The cut-off value of 1000 is utilized to retain the traces exhibiting a distinct drop in conductance between neighboring data points. Hence, rupturing a molecular junction is involved in the selected traces. Figure S1 shows that the selection criterion can pick out the sharp-drop trace (the left one) from those exhibiting exponentially decayed or noisy features. For all alkanedinitriles, about 20% of the conductance traces form molecular junctions according to the selected percentage by the algorithm.



**Figure S1.** Conductance traces and the corresponding d(logG)/ds plots for typical (a) tunneling decay, (b) noisy, and (c) sharp drop features. The dashed line (blue) indicates the cut-off value of 1000. Experimental conditions: solution, 1-mM butanedinitrile in toluene; electrode material, gold;  $E_{\text{bias}}$ , 75 mV.



**Figure S2.** Conductance histograms of (a-c) ethanedinitrile, (d-f) hexanedinitrile, and (g-i) octanedinitrile measured by electrodes of (a,d,g) Au, (b,e,h) Pd, and (c,f,i) Pt. The conductance values are reported in Table 1 of the main text. Two sets of conductance are observed for short molecules of ethane-, butane- and hexanedinitrile. For the longest one, octanedinitrile, the LC values are expected to be smaller than the detection limit of the instrument, and hence are unobserved. The experimental conditions are the same as those in Figure 1 of the main text.

## Table S1. Calculated Single-Molecule Conductance of Alkanedinitriles.

	conductance of M–NC–(CH <sub>2</sub> ) <sub>n</sub> –CN–M $(10^{-4} G_0)^a$						
М	Ā	Au	Р	'd	Pt		
n	$\mathrm{HC}^{b}$	$LC^{b}$	НС	LC	НС	LC	
4	4.54	1.32	5.39	1.59	10.76	5.98	
6	1.13	0.357	1.26	0.41	1.80	0.889	
8	0.13	0.046	0.145	0.049	0.372	0.128	

<sup>*a.*</sup> The calculations are carried out by the method of NEGF-DFT (Non-equilibrium Green's Function combined with Density Functional Theory) utilizing a commercial package (Atomistic Toolkit software package, ATK2008). The conductance value is the slope of the *I*–V curve simulated by the integration of the transmission (Figure 5 in the main text) from 0 to 0.2 Volt. The calculated results agree with the experimental measurements with the largest conductance for Pt and the smallest for Au.

<sup>b.</sup> HC (high conductance) and LC (low conductance) stand for the conductance sets measured under atop-hollow and atop-atop configurations, respectively. The notations are abbreviated for the binding sites of the molecular termini. Based on the experimental scheme of STM bj, three-fold hollow and atop sites of the substrate are proposed to be the dominant contact geometries by Lindsay and Tao<sup>S6</sup> and other experimental<sup>S7</sup> and theoretical<sup>S8</sup> groups.

	condu	ctance of M-S-(	$CH_2)_n$ –S–M (1	$0^{-4} G_0)^a$	conductance of M–SCN–(CH <sub>2</sub> ) $_n$ –NCS–M (10 <sup>-4</sup> G <sub>0</sub> )						
Μ	I	Au		Pt A		Au J		Pd		Pt	
n	HC	LC	НС	LC	НС	LC	НС	LC	HC	LC	
4	_		_		$19 \pm 4$	$2.0 \pm 0.4$	$43 \pm 13$	3.4 ± 1.1	$69 \pm 15$	5.7 ± 1.2	
6	$12 \pm 2$	$2.2 \pm 0.4$	$25 \pm 6$	$3.9\pm0.9$	$2.0\pm0.4$	$0.20\pm0.04$	$5.9 \pm 1.5$	$0.51\pm0.16$	$7.3 \pm 1.7$	$0.64\pm0.16$	
8	$2.6\pm0.4$	$0.59\pm0.06$	$4.8\pm1.4$	$0.85\pm0.19$	$0.34\pm0.07$	$0.043\pm0.009$	$0.66\pm0.21$	$0.060\pm0.016$	$1.0 \pm 0.3$	$0.075\pm0.019$	
10	$0.22 \pm 0.04$	$0.043\pm0.009$	$0.42 \pm 0.11$	$0.078\pm0.021$	_	_	_	_	_	_	

Table S2. Summary of Single-Molecule Conductance Values for Alkanedithiols and Alkanediisothiocyanates.

 $\overline{I}^{a.}$  The conductance values are from Reference S9. The lack of thiol-Pd pairs is due to the difficulty in obtaining step-like I(s) traces. In the previous study,<sup>s9</sup> this difficulty is ascribed to the catalytic cleavage of C–S bond on Pd surface.<sup>s10,s11</sup>

Table S3. Summary of Values of Contact Resistance and Conductance for Alkanedithiols and Alkanediisothiocyanates.<sup>a</sup>

	Au-S-(CH <sub>2</sub> ) <sub>n</sub> -S-Au		Pt-S-(CH <sub>2</sub> ) <sub>n</sub> -S-Pt		Au–SCN–(CH <sub>2</sub> ) <sub>n</sub> –NCS–Au		Pd–SCN–(CH <sub>2</sub> ) <sub>n</sub> –NCS–Pd		Pt–SCN–(CH <sub>2</sub> ) <sub>n</sub> –NCS–Pt	
	НС	LC	НС	LC	HC	LC	НС	LC	НС	LC
$G_{n=0}\left(\mathrm{G}_{0}\right)^{b}$	$0.60\pm0.70$	0.10 ± 0.15	$1.08 \pm 0.81$	$0.33 \pm 0.28$	$0.10 \pm 0.05$	$0.008 \pm 0.004$	$0.29\pm0.23$	$0.020 \pm 0.015$	$0.48\pm0.28$	$0.042 \pm 0.026$
$R_{n=0} (\mathbf{k}\Omega)^b$	$22 \pm 25$	$130 \pm 200$	$12 \pm 9$	$39 \pm 33$	$128 \pm 59$	$1560\pm720$	$45 \pm 36$	$646 \pm 501$	$27 \pm 16$	$307\pm188$

<sup>*a*</sup>. The contact values are from Table 3 of Reference S9. The lack of thiol-Pd pairs is due to the difficulty in obtaining step-like I(s) traces. In the previous study, <sup>S9</sup> this difficulty is ascribed to the catalytic cleavage of C–S bond on Pd surface.<sup>S10,S11</sup>

<sup>b.</sup>  $R_{n=0}$  and  $G_{n=0}$  are, respectively, the contact resistance and contact conductance obtained from the intercepts of Figure 4 of Reference S9.  $G_0 = 2e^2/h \approx (12.9 \text{ k}\Omega)^{-1}$ .

	contac	t values	1 / 6		
headgroup	$R_{n=0}$ (k $\Omega$ )	$G_{n=0}$ (G <sub>0</sub> )	remarks/reference		
HS-x-SH	187	0.069	values extracted from the conductance of benzenedithiol <sup>S12</sup> and tetraphenyldithiol <sup>S13</sup>		
$H_2N$ -x- $NH_2$	331	0.039	values extracted from Table 1 of the paper <sup>S14</sup>		
Me <sub>3</sub> SnCH <sub>2</sub> -x-CH <sub>2</sub> SnMe <sub>3</sub>	2.13	6.1	values extracted from Figure 2 of the paper <sup>S15</sup>		
MeS-x-COOH	600	0.022	values reported by the authors <sup>S16</sup>		
MeS-x-SMe	270	0.048	values reported by the authors <sup>S17</sup>		
HS-x-NH <sub>2</sub>	83	0.16	values estimated from Table 1 of the paper <sup>S18</sup>		
py-x-py <sup>a</sup>	HC: 22000 LC: 76000	HC: 0.00058 LC: 0.00017	values extracted from Figure 4 of the paper <sup>S19</sup>		

**Table S4.** Summary of Contact Resistance on Gold from Literature Reports.

<sup>*a*</sup>. Multiple contact geometries have been reported for pyridyl headgroup. Reference S19 carried out DFT-based conductance simulations and suggests that the LC set has the Au–N bond parallel to the aromatic ring while the HC set has the pyridyl ring tilted on gold surface. Hence, HC set exhibits stronger  $\pi$  characteristics than LC set.

#### Derivation of molecular backbone conductance via a tight-binding model

In a coherent elastic tunneling (super-exchange) regime, the current *I* through a molecular junction can be expressed as  $I = \frac{2e}{h} \int_{-\infty}^{\infty} T(E)(f_L(E) - f_R(E))dE$ , where T(E) is the transmission function for a tunneling electron at energy *E* and  $f_{L(R)}(E)$  is the Fermi function of the left (right) electrode. In order to facilitate the theoretical analysis, we use the Landauer formula,  $G = \frac{2e}{h}T(E_F)$ , to analyze molecular conductance, where  $E_F$  denotes the Fermi level.

In a single-particle Green's Function approach, the transmission function is expressed as  $T(E_F) = Tr(\Gamma_L \mathbb{G}_{mol}^R \Gamma_R \mathbb{G}_{mol}^A)$ , <sup>S20–S22</sup> where  $\mathbb{G}_{mol}^{R(A)} = (E_F - H_{mol} - \Sigma_L^{R(A)} - \Sigma_R^{R(A)})^{-1}$  is the retarded (advanced) molecular Green's function and  $\Gamma_{L(R)} = i(\Sigma_{L(R)}^R - \Sigma_{L(R)}^A)$  is the left(right)-electrode coupling function, where *i* is the imaginary unit  $(\sqrt{-1})$  and  $\Sigma_{L(R)}^{R(A)}$  is the retarded (advanced) self-energy contributed from the left (right) electrode.

To facilitate the analysis, we use a tight-binding model to describe the bridged molecule as follows,

$$\begin{aligned} H_{mol} &= |\ell > \varepsilon_{\ell} < \ell | + t_{\ell,1} (|\ell > 1| + |1 > < \ell |) \\ &+ \sum_{n=1}^{N} |n > \varepsilon_{n} < n | + \sum_{n=1}^{N-1} t_{n,n+1} (|n > n+1| + |n+1 > < n |) \\ &+ t_{N,r} (|N > < r| + |r > < N |) + |r > \varepsilon_{r} < r |, \end{aligned}$$
(S1)

where  $\varepsilon_{\ell(r)}$  is the on-site energy of the left (right) anchoring group,  $\varepsilon_n$  is the on-site energy of site *n* of the molecular backbone, and  $t_{m,m'}$  is the resonance integral (also known as hopping integral) between sites *m* and *m'* (Note that m(m') = n,  $\ell$ , and *r*). The subscripts L(R) and  $\ell(r)$  stand for the left (right) electrode and the left (right) anchoring groups, respectively. Because the molecular backbone is not directly coupled to the two electrodes, we assume that the self-energy contributed from the two electrodes only affects the anchoring groups (see Equation S2).

$$\Sigma_{L(R)}^{R(A)} = \Sigma_{L}^{R(A)} + \Sigma_{R}^{R(A)} = |\ell \rangle (\Sigma_{L}^{R(A)})_{\ell,\ell} < \ell |+|r \rangle (\Sigma_{R}^{R(A)})_{r,r} < r |.$$

$$(S2)$$

$$(\Sigma_{L(R)}^{R(A)})_{\ell,\ell(r,r)} = (\Delta_{L(R)})_{\ell,\ell(r,r)} \mp \frac{i}{2} (\Gamma_{L(R)})_{\ell,\ell(r,r)},$$

where the real ( $\Delta$ ) and imaginary ( $\Gamma$ ) parts describe, respectively, the energy level shift and broadening arising from the interactions with the electrodes. The negative (positive) sign corresponds to the imaginary term of the retarded (advanced) self-energy. By using Equations S1 and S2, the retarded molecular Green's function can be expressed in a matrix form.

$$\mathbf{G}_{mol}^{R} = (E_{F} - H_{mol} - \Sigma^{R})^{-1} \\ = \begin{pmatrix} E_{F} - \varepsilon_{\ell} - (\Sigma_{L}^{R})_{\ell,\ell} & t_{\ell,1} & 0 & 0 & 0 & 0 \\ t_{\ell,1} & E_{F} - \varepsilon_{1} & t_{1,2} & 0 & 0 & 0 & 0 \\ 0 & t_{1,2} & E_{F} - \varepsilon_{2} & \ddots & 0 & 0 & 0 \\ 0 & 0 & \ddots & \ddots & \ddots & 0 & 0 \\ 0 & 0 & 0 & \ddots & E_{F} - \varepsilon_{N-1} & t_{N-1,N} & 0 \\ 0 & 0 & 0 & 0 & t_{N-1,N} & E_{F} - \varepsilon_{N} & t_{N,r} \\ 0 & 0 & 0 & 0 & 0 & t_{N,r} & E_{F} - \varepsilon_{r} - (\Sigma_{R}^{R})_{r,r} \end{pmatrix}^{-1}$$
(S3)

As  $\min |E_F - \varepsilon_m - (\Sigma_{L(R)}^R)_{m,m}| >> \max |t_{m,m'}|$ ,  $(\mathbb{G}_{mol}^R)_{\ell,r}$  can be approximated as<sup>S23</sup>

$$(\mathbf{G}_{mol}^{R})_{\ell,r} = \frac{t_{\ell,1}}{E_F - \varepsilon_\ell - (\Sigma_L^{R})_{\ell,\ell}} \cdot \frac{t_{N,r}}{E_F - \varepsilon_r - (\Sigma_R^{R})_{r,r}} \cdot \frac{1}{E_F - \varepsilon_N} \cdot \frac{1}{\prod_{n=1}^{N-1} \frac{t_{n,n+1}}{E_F - \varepsilon_n}}$$
(S4)

It is evident that  $N \ge 2$  in Equation S4. For a homologous series, it is reasonable to assume that  $t_{n,n+1} = t$  and  $\varepsilon_n = \varepsilon$ , and we can derive the transmission function

$$T(E_{F}) = Tr(\Gamma_{L}\mathbf{G}_{mol}^{R}\Gamma_{R}\mathbf{G}_{mol}^{A}) = (\Gamma_{L})_{\ell,\ell}(\Gamma_{R})_{r,r} |(\mathbf{G}_{mol}^{R})_{\ell,r}|^{2}$$
$$= \frac{(\Gamma_{L})_{\ell,\ell} |t_{\ell,1}|^{2}}{|E_{F} - \varepsilon_{\ell} - (\Sigma_{L}^{R})_{\ell,\ell}|^{2}} \cdot \frac{(\Gamma_{R})_{r,r} |t_{N,r}|^{2}}{|E_{F} - \varepsilon_{r} - (\Sigma_{R}^{R})_{r,r}|^{2}} \cdot \frac{1}{|t|^{2}} \cdot \left|\frac{t}{|E_{F} - \varepsilon}\right|^{2N}$$
(S5)

From Equation S5, the transmission function can be expressed in terms of the following

$$T_{L} = \frac{(\Gamma_{L})_{\ell,\ell} t_{\ell,1}}{|E_{F} - \varepsilon_{\ell} - (\sum_{L}^{R})_{\ell,\ell}|^{2}}$$
(S6)

$$T_R = \frac{(\Gamma_R)_{r,r} t_{N,r}}{|E_F - \varepsilon_r - (\Sigma_R^R)_{r,r}|^2}$$
(S7)

$$T_{backbone} = \frac{t_{\ell,1} t_{N,r}}{|t|^2} \cdot \left| \frac{t}{E_F - \varepsilon} \right|^{2N}$$
(S8)

where  $T_{L(R)}$  is the transmission of the tunneling electron from the left (right) electrode to the left (right) anchoring group, and  $T_{backbone}$  is the transmission of the tunneling electron from the left (right) anchoring group passing through the backbone of the molecule and then to the right (left) anchoring group.

Furthermore, we can define the transmission of the molecular backbone unit  $T_{unit}$  and the contact transmission  $T_{contact}$  (=  $T_{n=0}$ ) as follows,

$$T_{unit} = \left| \frac{t}{E_F - \varepsilon} \right|^2 \tag{S9}$$

$$T_{contact} = T_L T_R \frac{t_{\ell,1} t_{N,r}}{|t|^2}$$
(S10)

Substituting Equation S5 into the Landauer formula, we can derive

$$G = \frac{2e^2}{h} T_{contact} (T_{unit})^N = G_Q T_{contact} \exp[-N \ln \frac{1}{T_{unit}}]$$
(S11)

where  $G_Q = G_0 = \frac{2e^2}{h}$  is the quantum conductance and note that  $N \ge 2$ . In addition, from experimental

observations, the conductance of a molecular junction in the coherent elastic tunneling (super-exchange) regime has the form,

$$G = G_{contact} \exp[-\beta_n N] = G_{contact} \exp[-\beta L]$$
(S12)

where  $G_{contact}$  (=  $G_{n=0}$ ) is the contact conductance. So far we have derived the expression of  $G_{contact}$  and  $\beta$  by comparing Equations S11 and S12.

$$G_{contact} = G_Q \cdot T_{contact} \tag{S13}$$

$$\beta_n (per unit) = 2\ln \left| \frac{E_F - \varepsilon}{t} \right|$$
(S14)

$$\beta(per \stackrel{o}{A}) = \frac{2N}{L} \ln \left| \frac{E_F - \varepsilon}{t} \right|$$
(S15)

We found that the approximation gives  $T_{backbone}$  and  $\beta$  values independent from molecule–electrode interactions and determined by the intrinsic property of molecular backbone.

Let's go back to discuss the case of N = 1 (*viz.*, molecules without repeated units) and show how we derive the conductance of the molecular backbone unit from the experiment. For N = 1 case, we can get its Green's function and transmission function  $T_1(E_F)$ 

$$(\mathfrak{G}_{mol}^{R})_{\ell,r} = \frac{t_{\ell,1}}{E_F - \varepsilon_{\ell} - (\Sigma_L^{R})_{\ell,\ell}} \cdot \frac{t_{1,r}}{E_F - \varepsilon_r - (\Sigma_R^{R})_{r,r}} \cdot \frac{1}{E_F - \varepsilon_1}$$
(S16)

$$T_{1}(E_{F}) = T_{L} \cdot T_{R} \cdot t_{\ell,1} \cdot t_{1,r} \left| \frac{1}{E_{F} - \varepsilon_{1}} \right|^{2}$$
(S17)

The conductance of the molecular backbone unit is defined as (in this article)

$$G_{unit} \equiv G_Q \frac{T_1}{T_{contact}} = G_Q \left| \frac{t}{E_F - \varepsilon} \right|^2$$
(S18)

Equation S18 indicates that (i)  $G_{unit}$  is independent from the self-energy contributed from the electrodes. That is,  $G_{unit}$  is not sensitive to molecule-electrode contacts such as anchoring groups and the surface configurations of electrodes, consistent with our experiment observations. (ii) According to  $T_{unit} = \left|\frac{t}{E_{R-R}}\right|^2$  (Equation S9) for molecules without repeated units, Equation S18 indicates

$$G_{unit} = G_Q \left| \frac{t}{E_F - \varepsilon} \right|^2 = G_Q T_{unit}$$
(S19)

which corresponds to the transmission of the molecular backbone unit derived from the case  $N \ge 2$ . Therefore, even for N = 1 case, we still can derive the conductance and the transmission of the molecular backbone unit.

To sum up, we have the following conclusions in our analysis: (i) As  $\min |E_F - \varepsilon_m - (\Sigma_{L(R)}^R)_{m,m}| \gg \max |t_{m,m'}|$  (the weak couplings between two sites),  $T_{unit}$  is independent from the self-energy contributed from the electrodes. That is,  $T_{unit}$  is not sensitive to molecule-electrode contacts such as anchoring groups and the surface configurations of electrodes. As a result, in the case that the types of two electrodes are the same (with the same Fermi level), we can define the conductance of the molecular backbone unit. (ii) In the case of the weak couplings between two sites as well as two electrodes with similar Fermi levels, the conductance of the molecular backbone unit should be similar. (iii) As  $\min |E_F - \varepsilon_m - (\Sigma_{L(R)}^R)_{m,m}| \sim \max |t_{m,m'}|$ , Equation S4 is not valid, indicating that the transmission

cannot be separated into the form,  $T = T_L T_R T_{backbone} = T_{contact} (T_{unit})^N$ . In such cases, the conductance of the molecular backbone unit cannot be defined. (iv) Note that our conclusions are only valid in the case that the energies of HOMO or LUMO are far away from the Fermi levels, the couplings between two molecular backbone units are weak, the molecular backbones have no direct coupling to electrodes, and the anchoring groups have weak couplings to electrodes.

## Glossary

- T(E): the transmission function for a tunneling electron at energy E
- $T_{L(R)}$ : the transmission of the tunneling electron from the left (right) electrode to the left (right) anchoring group
- $T_{backbone}$ : the transmission of the tunneling electron from the left (right) anchoring group passing through the molecular backbone and then to the right (left) anchoring groups

 $T_{unit}$ : the transmission of a single unit of the molecular backbone

- $T_{contact}$ : the contact transmission
- $f_{L(R)}(E)$ : Fermi function of the left (right) electrode
  - $E_F$ : Fermi level of the electrodes
  - $\mathbf{G}_{mol}^{R(A)}$ : the retarded (advanced) molecular Green's function
- $(\mathbf{G}_{mol}^{R(A)})_{\ell,r}$ : the matrix element at row  $\ell$  and column r of  $\mathbf{G}_{mol}^{R(A)}$ ; this term means that a tunneling electron propagates from the left (right) anchoring group to the right (left) anchoring group.
  - $\Sigma_{L(R)}^{R(A)}$ : the retarded (advanced) self-energy contributed from the left (right) electrode
  - $\Gamma_{L(R)}$ : the imaginary part of the self-energy; this term corresponds to the left(right)-electrode coupling function and  $\Gamma_{L(R)}/\hbar$  corresponds to the electron transfer rate.
  - $\Delta_{L(R)}$ : the real part of the self-energy; this term corresponds to the energy-level shift of the molecule influenced by the left (right) electrode
  - $\varepsilon_{\ell(r)}$ : the on-site energy of the left (right) anchoring group
    - $\varepsilon_n$ : the on-site energy of the *n*<sup>th</sup> unit of the molecular backbone
  - *t<sub>m,m</sub>*: the resonance integral between the site *m* and *m'*. Note that *m* and *m'* include *n*,  $\ell$ , and *r* which are, respectively, *n*<sup>th</sup> unit and anchoring groups at the  $\ell$  and *r* termini.

### References

- [S1] Ulrich, J.; Esrail, D.; Pontius, W.; Venkataraman, L.; Millar, D.; Doerrer, L. H., Variability of Conductance in Molecular Junctions. J. Phys. Chem. B 2006, 110, 2462-2466.
- [S2] Frei, M.; Aradhya, S. V.; Hybertsen, M. S.; Venkataraman, L., Linker Dependent Bond Rupture Force Measurements in Single-Molecule Junctions J. Am. Chem. Soc. 2012, 134, 4003-4006.
- [S3] Taniguchi, M.; Tsutsui, M.; Mogi, R.; Sugawara, T.; Tsuji, Y.; Yoshizawa, K.; Kawai, T., Dependence of Single-Molecule Conductance on Molecule Junction Symmetry. J. Am. Chem. Soc. 2011, 133, 11426-11429.
- [S4] Park, Y. S.; Whalley, A. C.; Kamenetska, M.; Steigerwald, M. L.; Hybertsen, M. S.; Nuckolls, C.; Venkataraman, L., Contact Chemistry and Single-Molecule Conductance: A Comparison of Phosphines, Methyl Sulfides, and Amines. J. Am. Chem. Soc. 2007, 129, 15768-15769.
- [S5] Quek, S. Y.; Venkataraman, L.; Choi, H. J.; Louie, S. G.; Hybertsen, M. S.; Neaton, J. B., Amine–Gold Linked Single-Molecule Circuits: Experiment and Theory. *Nano Lett.* 2007, 7, 3477-3482.
- [S6] Li, X.; He, J.; Hihath, J.; Xu, B.; Lindsay, S. M.; Tao, N., Conductance of Single Alkanedithiols: Conduction Mechanism and Effect of Molecule–Electrode Contacts. J. Am. Chem. Soc. 2006, 128, 2135-2141.
- [S7] Zhou, X. S.; Chen, Z. B.; Liu, S. H.; Jin, S.; Liu, L.; Zhang, H. M.; Xie, Z. X.; Jiang, Y. B.; Mao, B. W., Single Molecule Conductance of Dipyridines with Conjugated Ethene and Nonconjugated Ethane Bridging Group J. Phys. Chem. C 2008, 112, 3935-3940.
- [S8] Kaun, C. C.; Seideman, T., Conductance, Contacts, and Interface States in Single Alkanedithiol Molecular Junctions. *Phys. Rev. B* **2008**, *77*, 033414.
- [S9] Ko, C.-H.; Huang, M.-J.; Fu, M.-D.; Chen, C.-h., Superior Contact for Single-Molecule Conductance: Electronic Coupling of Thiolate and Isothiocyanate on Pt, Pd, and Au. J. Am. Chem. Soc. 2010, 132, 756-764.
- [S10] Yang, Z.; Klabunde, K. J.; Sorensen, C. M., From Monodisperse Sulfurized Palladium Nanoparticles to Tiara Pd(II) Thiolate Clusters: Influence of Thiol Ligand on Thermal Treatment of a Palladium(II)–Amine System. J. Phys. Chem. C 2007, 111, 18143-18147.
- [S11] Ramallo-Lóez, J. M.; Giovanetti, L.; Craievich, A. F.; Vicentin, F. C.; Marín-Almazo, M.; José-Yacaman, M.; Requejo, F. G., XAFS, SAXS and HREM Characterization of Pd Nanoparticles Capped with *n*-Alkyl Thiol Molecules. *Phys. B* 2007, 389, 150-154.
- [S12] Xiao, X.; Xu, B.; Tao, N. J., Measurement of Single Molecule Conductance: Benzenedithiol and Benzenedimethanethiol. *Nano Lett.* 2004, 4, 267-271.
- [S13] Diez-Perez, I.; Hihath, J.; Lee, Y.; Yu, L. P.; Adamska, L.; Kozhushner, M. A.; Oleynik, I. I.; Tao, N., Rectification and Stability of a Single Molecular Diode with Controlled Orientation. *Nat. Chem.* 2009, 1, 635-641.
- [S14] Venkataraman, L.; Klare, J. E.; Nuckolls, C.; Hybertsen, M. S.; Steigerwald, M. L., Dependence of Single-Molecule Junction Conductance on Molecular Conformation. *Nature* 2006, 442, 904-907.

- [S15] Chen, W. B.; Widawsky, J. R.; Vazquez, H.; Schneebeli, S. T.; Hybertsen, M. S.; Breslow, R.; Venkataraman, L., Highly Conducting π-Conjugated Molecular Junctions Covalently Bonded to Gold Electrodes. J. Am. Chem. Soc. 2011, 133, 17160-17163.
- [S16] Ahn, S.; Aradhya, S. V.; Klausen, R. S.; Capozzi, B.; Roy, X.; Steigerwald, M. L.; Nuckolls, C.; Venkataraman, L., Electronic Transport and Mechanical Stability of Carboxyl Linked Single-Molecule Junctions. *Phys. Chem. Chem. Phys.* 2012, 14, 13841-13845.
- [S17] Park, Y. S.; Whalley, A. C.; Kamenetska, M.; Steigerwald, M. L.; Hybertsen, M. S.; Nuckolls, C.; Venkataraman, L., Contact Chemistry and Single-Molecule Conductance: A Comparison of Phosphines, Methyl Sulfides, and Amines. J. Am. Chem. Soc. 2007, 129, 15768-15769.
- [S18] Chen, F.; Li, X.; Hihath, J.; Huang, Z.; Tao, N., Effect of Anchoring Groups on Single-Molecule Conductance: Comparative Study of Thiol-, Amine-, and Carboxylic-Acid-Terminated Molecules. J. Am. Chem. Soc. 2006, 128, 15874-15881.
- [S19] Kamenetska, M.; Quek, S. Y.; Whalley, A. C.; Steigerwald, M. L.; Choi, H. J.; Louie, S. G.; Nuckolls, C.; Hybertsen, M. S.; Neaton, J. B.; Venkataraman, L., Conductance and Geometry of Pyridine-Linked Single-Molecule Junctions. J. Am. Chem. Soc. 2010, 132, 6817-6821.
- [S20] Hsu, L.-Y.; Li, E. Y.; Rabitz, H., Single-Molecule Electric Revolving Door. Nano Lett. 2013, 13, 5020-5025.
- [S21] Hsu, L.-Y.; Jin, B.-Y., An Investigation of Quantum Transport by the Free-Electron Network Model: Resonance and Interference Effects. *Chem. Phys.* **2009**, *355*, 177-182.
- [S22] Hsu, L.-Y.; Huang, Q.-R.; Jin, B.-Y., Charge Transport through a Single Molecular Wire Based on Linear Multimetal Complexes: a Non-Equalibrium Green's Function Approach. J. Phys. Chem. C 2008, 112, 10538-10541.
- [S23] Nitzan, A., A Relationship between Electron-Transfer Rates and Molecular Conduction. J. Phys. Chem. A 2001, 105, 2677-2679.