

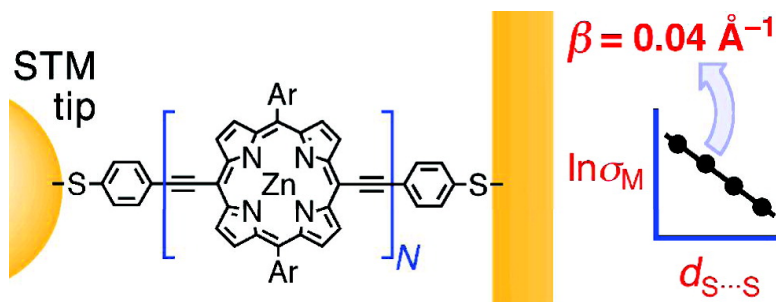
Communication

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Single Molecule Conductance of Porphyrin Wires with Ultralow Attenuation

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Charge transport through organic molecules over long distances is important in many biological systems, in organic photovoltaics, and in molecular electronics. One of the goals of molecular electronics is the design of robust molecular wires which can transport charge efficiently over extended distances, thereby enabling molecules to act as device interconnects. An important parameter in defining charge transport along molecular bridges is the decrease in transmission as a function of distance. For long-range charge transport it is important that this factor is low and that there is strong electronic coupling between the bridge and the terminal contacts. The decrease in transmission as a function of bridge length has commonly been determined through photophysical measurements of charge transfer kinetics between donor and acceptor moieties at the bridge termini,^{1–4} by measurement of rates of electrochemical electron transfer across organic monolayers on electrodes,^{2,5} or by measuring current through organic monolayers between metal electrodes.⁶ Recently it has been possible to directly measure the conductance of single molecules between pairs of gold electrodes,^{7–9} including π -conjugated oligomers.^{10,11} The decrease in transmission as a function of bridge length is commonly observed to follow an exponential distance dependence in single molecule measurements, which is taken to indicate a superexchange (or tunneling) mechanism:

$$\sigma_M \propto e^{-\beta R} \quad (1)$$

where, the conductance (σ_M) exponentially decreases with the bridge length (R), as quantified by the attenuation factor, β . All the major techniques for determining attenuation factors concur that π -conjugated bridges give significantly lower attenuation factors than saturated ones. Ultralow attenuation factors ($<0.1 \text{ \AA}^{-1}$)^{4,12,13} have been reported for highly conjugated, low bandgap systems. In this respect, conjugated porphyrin oligomers are attractive candidates because of their strong electronic coupling.^{14,15} Indeed, photoinduced electron transfer measurements have indicated that porphyrin oligomers can transfer charge efficiently over long distances,^{3,16} and other measurements indicate that these molecules have wire-like behavior.^{15–17} The question that we address here is whether porphyrin oligomers exhibit low attenuation factors when “wired” between metal electrodes at the single molecule level. For this purpose we have synthesized (see Supporting Information) the series of porphyrin oligomers **1–3** (Figure 1a), bearing terminal thioacetates to promote attachment to gold.

The $I(s)$ (current-distance) and $I(t)$ methods previously developed by Haiss et al., using scanning tunneling microscopy (STM), were deployed for the measurement of single-molecule conductance.⁹ In the $I(s)$ technique current is monitored as molecular wires are stretched in the STM gap, while in the $I(t)$ technique the stochastic formation of molecular bridges is followed by monitoring current jumps over time. Single molecular bridges are formed between the gold substrate

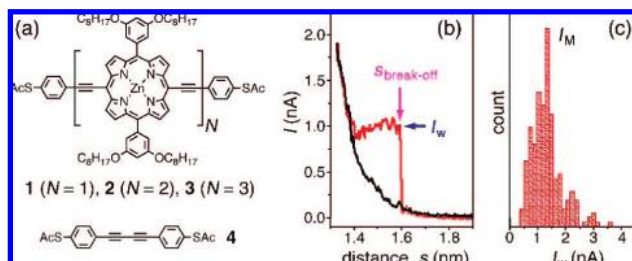


Figure 1. (a) Porphyrin oligomers **1–3** and reference compound **4**; (b) $I(s)$ scans recorded by STM for a low coverage of **1** (adsorption from a $50 \mu\text{M}$ solution in $\text{CHCl}_3 + 1\%$ pyridine) on a Au(111) film under ambient conditions. Curves in the absence (black) and presence (red) of molecular wire formation; $I_0 = 8 \text{ nA}$, $V_{\text{bias}} = 600 \text{ mV}$. The distance s is the distance between the two contacts, calibrated as described in the Supporting Information; (c) Histogram of I_w values for **1** from 145 $I(s)$ scans.

surface and gold STM tip, without the need to first form a metallic junction,⁹ as is the case with the in situ break junction technique.⁸ Current plateau values ($I(s)$ technique) or current-jumps ($I(t)$ technique) are then analyzed statistically to determine the single molecule conductance.⁹

Figure 1b shows an $I(s)$ scan with evidence for the formation of a molecular bridge of porphyrin **1** between the gold STM tip and gold surface (red curve), together with an $I(s)$ trace in which no molecular bridge is formed (black curve). As described in the literature, the plateau seen in the trace is assigned to molecular bridge formation. The current then drops rapidly at the end of this plateau (red curve), at the distance marked as $s_{\text{break-off}}$, due to cleavage of the molecular junction either at the Au–S bond or Au–Au metallic bonds in the contacts. The current plateau values, I_w , measured from $I(s)$ curves such as Figure 1b are then collected in current-histogram plots (Figure 1c), with the major current peak in the histogram (I_M) being used to calculate the conductance at the selected bias voltage.

The absolute distance between the STM tip and gold surface was obtained through calibration (see Supporting Information). This enables the correlation between computed S...S distance for **1–4** and the experimentally observed break-off points ($s_{\text{break-off}}$ in Figure 1b) to be analyzed (Figure 2a). The spread in individual break-off points for **1–3** illustrates the stochastic nature of the junction breaking process. However it is noteworthy that for each compound the maximum measured break-off point is close to the computed S...S separation. These break-off distances reassure us that we are indeed measuring porphyrin oligomer molecules bridging the junction between the two gold contacts.

The single molecule conductance value for the monomer **1** determined by the $I(s)$ technique is $2.13 \pm 0.28 \text{ nS}$ and that for the $I(t)$ technique is $2.17 \pm 0.45 \text{ nS}$, demonstrating that there is very good agreement between the two techniques. Similar measurements have been made for **2–4** and the data are summarized in Figure 2b (see also Supporting Information). Single molecule conductances for molecules **1–4** are plotted logarithmically against the calculated S...S

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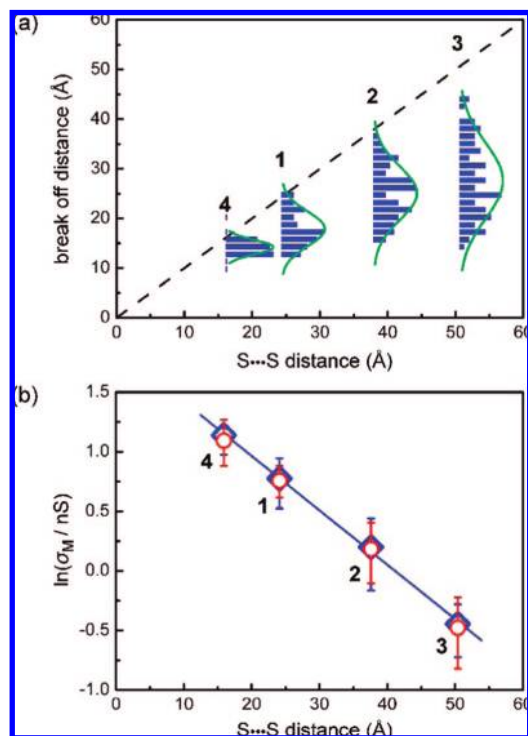


Figure 2. (a) The break-off distance, $s_{\text{break-off}}$, versus the computed sulfur...sulfur distance for 1–4; histograms show the full distributions of recorded $s_{\text{break-off}}$ values (histogram bars represents the frequency of events with a given $s_{\text{break-off}}$); the dashed black line is the expected limit, at $s_{\text{break-off}} = \text{S}\cdots\text{S}$ distance; (b) Dependence of the single molecule conductance (at $V_{\text{bias}} = 0.6$ V) as determined by the $I(t)$ (blue \diamond) and $I(s)$ (red \circ) methods on the molecular length for wires 1–4.

distance in Figure 2b, giving a very low attenuation factor, $\beta = (0.04 \pm 0.006) \text{ \AA}^{-1}$. This is considerably lower than generally observed for π -conjugated organic bridges, which typically give β values in the range $0.1\text{--}0.6 \text{ \AA}^{-1}$.¹³ There are a few reports of low attenuation factors ($\beta \leq 0.1 \text{ \AA}^{-1}$) from photoinduced electron transfer measurements across other types of conjugated bridges,^{4,12} and very recently single molecule conductance measurements on a series of oligothiophenes were reported with $\beta = 0.1 \text{ \AA}^{-1}$,¹¹ but to the best of our knowledge this is the first time that attenuation factors as low as $\beta < 0.1 \text{ \AA}^{-1}$ have been demonstrated from single molecule conductance measurements.

Although the linear dependence of $\ln \sigma_M$ versus distance (equation 1) is consistent with superexchange,¹⁸ low attenuation is often taken as an indication of hopping mechanisms. Hopping mechanisms show rates of charge transfer which are characterized by a shallow distance dependence ($k_{\text{ET}} = N^{-\eta}$) with respect to the number of hopping steps N , where the value of η lies between 1 and 2. Indeed, a linear fit to the distance data is obtained with $\eta = 1$ (see Supporting Information). The contact and bridge energetics are expected to have a marked influence on the transport mechanism. An estimation of the energetics suggests that the bridge is off resonance (by >0.5 eV) for the bias voltage window examined, which is consistent with experimental I – V data (see Supporting Information). However, even in a significantly off-resonance condition both hopping and superexchange mechanisms are a priori conceivable, particularly at the single-molecule level, where bridge energy levels may be subjected to strong environmental fluctuations of more than 0.5 eV.¹⁹ Superexchange and hopping mechanisms are not mutually exclusive; indeed, it has been shown that both may be present within one system.²⁰

Low attenuation factors for oligo-porphyrin wires have also been revealed by photophysical experiments, but in that case the exponential

dependence of Figure 2b was not observed.³ This points to a pronounced difference between the direct electrical charge transport and intramolecular charge transfer, arising from differences in electronic coupling between the donor/acceptor and the bridge states in the donor–bridge–acceptor systems and the electrode Fermi levels and the bridge states in metal–molecule–metal junctions, and illustrates that β cannot be treated as simply a bridge-specific parameter.¹³ Given the ultralow attenuation factors for porphyrin oligomers demonstrated here, this issue of electronic coupling between the contacts or terminal groups and the bridge is crucial for the overall junction transmission. The field of single molecule electronics will benefit from further studies in which direct electrical and photophysical measurements are compared for the same homologous group of molecules.²¹

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Supporting Information Available: Complete ref 21b; synthesis and characterization of compounds 1–4, further details of $I(s)$ and $I(t)$ methods and results, histograms of conductance values, analysis of gap separation behavior, analysis of hopping mechanisms, and full author list for ref 21b. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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