



Correlation of electrochemical properties of expanded pyridinium compounds with their single molecule conductance

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ABSTRACT

A series of four expanded pyridinium molecules were used to investigate the correlation between a single molecule conductance (electron transport) and redox (electron transfer) properties at the electrode|electrolyte interface. Quantum chemical calculations of the transmission functions using DFT and non-equilibrium Green's function approach confirmed LUMO-mediated electron transport in the break junction experiment. Single molecule conductance data can be rationalized within the framework of the non-resonant tunneling mechanism. More interestingly, a linear correlation was found between the conductance values and the apparent electron transfer rate constants for three molecules of this series.

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1. Introduction

Expanded pyridinium compounds (possessing multiple aromatic substituents) show versatile electrophoric activity. Depending on their chemical structure (branched or fused) two electrons per pyridinium electrophore can be transferred either stepwise or in a single step allowing for a potential compression or even inversion [1,2]. Potential inversion in the reduction of pyridinium electrophore means that the standard redox potential of the second electron transfer has less negative value compared to the standard redox potential of the first electron transfer, i.e. it is energetically more favorable. In this work we present the electrochemical characterization of a series of expanded pyridinium molecules (formal redox potentials and heterogeneous electron transfer rate constants) and correlate these electrochemical properties with their single molecule conductance values obtained by a scanning tunneling microscopy break junction (STMBJ) technique. This

approach will contribute to understanding of the relationship between the electron transfer (ET) and electron transport properties of molecules aiming at their possible use in molecular electronics.

Experimental work leading to better comprehension of such a relationship is rare [3–10] in spite of the fact that theoretical studies suggest such correlation [11–20]. Common to all of the theoretical works dealing with redox systems is to consider charge transport in the metal|redox-active molecule|metal junction as a sequence of individual charge transfer steps (hopping mechanism) with their corresponding charge transfer rate constants being treated within the framework of Marcus ET theory [11–13,17,20]. A sequential two-step electron transport formulated by Kuznetsov and Ulstrup falls into this category [17]. Alternatively, description of charge transport through a resonant coherent one-step tunneling has been proposed [21–23]. Since most of the STMBJ experiments are done under the non-resonant conditions the conductance in the junctions of redox-active molecules is also being treated within the framework of a non-resonant direct tunneling (superexchange) model [3,10].

Experiments to examine the relationship between single molecule conductance and ET rate constant from the electrode to

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molecule are difficult to design since they both require rather different experimental conditions. Theoretical work first explained the magnitude of tunneling current in electrochemical STM arrangement as a function of the substrate potential at constant bias voltage, where the tip was not covalently coupled to the molecule (thus tunneling current). In such a case the measured tunneling current exhibited a maximum at the potential corresponding to the standard redox potential of the redox-active molecule [17]. This principle was later utilized for tuning the single molecule conductance values in the metal|redox-active molecule|metal junction by electrochemical gating [6,23–32]. To the best of our knowledge only one paper correlated directly the energetics of the ET process with single molecule conductance values, namely, redox potentials obtained by cyclic voltammetry (CV) for oxidation of a series of aromatic molecular wires with their single molecule conductance values [3]. Authors found reasonable correlation between the logarithm of conductance and redox (oxidation) potential for a series of aromatic amines and concluded that charge transport in these molecules is analogous to a hole transport in the molecular films sandwiched between two metallic electrodes. They assumed non-resonant tunneling through the HOMO level (with effective barrier height $|\Delta e| = \epsilon^{\text{HOMO}} - \epsilon_{\text{F}} \neq 0$), where ϵ^{HOMO} is the energy of HOMO level and ϵ_{F} is the Fermi level of gold. They obtained good correlation between the logarithm of the conductance and $\sqrt{|\Delta e|}L$, where L is the molecular length.

The relationship between the ET rate constants and single molecule conductance values was addressed later. Zhou et al. [10] performed STMBJ and CV experiments employing self-assembled monolayers (SAMs) of redox active molecules and determined ET rate constants of the order of 10^6 s^{-1} for chemisorbed SAMs as well as conductance values of individual molecules in the break junction arrangement. Authors concluded that fast systems indeed give higher conductance, whereas conductance variation with electrode potential suggests the superexchange mechanism. The correlation between molecular conductance and charge transfer rate constants was studied also for a series of alkane and nucleic acid oligomers as a function of their length, structure and charge transport properties [4]. A power law correlation was observed, which was contrary to the theoretical predictions of simple proportionality between the molecular conductance and charge transfer rate constant [11–13,16]. This non-linear relationship was explained by different charge transfer energy barrier heights and different environmental decoherence rates for the two different experimental settings [5].

Several experimental papers were focused on the charge transport through redox-active pyridinium-based compounds at a single molecule level. These included charge transport through 4,4'-bipyridinium (one viologen unit)-based molecular wires as model systems [24,29,33–36]. Compounds with multiple expanded pyridinium moieties, so-called extended viologen molecules have been used as efficient charge transport wires [37]. It was argued that their single molecule conductance properties indicate the hopping charge transport mechanism, which could be inferred also from their redox mechanism of the multiple non-interacting redox centers [38]. Recently, substituted pyridiniums have been used to design a new family of highly conductive molecular wires with electrocatalytic activities provided by a metallophthalocyanine unit [39]. None of these works dealt with the correlation of the charge transport with charge transfer properties of these systems.

A series of expanded pyridinium-based compounds **1** to **4** (see Chart 1) was selected in this work for probing the relationship between standard ET rate constants and single molecule conductance values. Pyridine termini were selected for their recognized efficiency as anchoring groups for gold (electrodes), thereby ensuring the proper stability of junctions, that is, gold–molecule–gold assemblies, via their *N*-heterocyclic lone pairs. Such anchoring

groups promote further a LUMO-dominated charge transport, which is also expected in the presence of pyridinium-based redox centers. Electrochemical ET rate constants were obtained in the absence of adsorption in dimethylsulfoxide-based electrolyte at gold microelectrodes, whereas single molecule conductance values were obtained in the molecular junction arrangement in the ethanol/mesitylene mixture to increase the solubility of charged pyridinium-based compounds.

2. Experimental

2.1. Chemicals

Argon gas (Messer, 99.998% purity), absolute ethanol (99.8%, molecular biology grade, AppliChem GmbH, Darmstadt, Germany and p.a. Penta, Czech Republic), 1,3,5-trimethylbenzene (mesitylene, 98% Sigma Aldrich), ferrocene (98% Sigma Aldrich) and nitric acid (65% p.a. Lach-Ner, Czech Republic) were used as received. Tetrabutylammonium hexafluorophosphate TBAPF₆ (p.a. for electrochemical analysis, $\geq 99\%$ Sigma Aldrich) was dried at 80 °C before use. Dimethyl sulfoxide (DMSO, puriss p.a, dried, $\leq 0.02\%$ water, $\geq 99.9\%$ Sigma Aldrich) was further dried with activated molecular sieves (0.3 nm, Lachema, Czech Republic). Ultrapure deionized water with a minimum resistivity of 18.2 M Ω ·cm and maximum TOC of 3 ppb was obtained by means of a Milli-Q Integral 5 water purification system (Merck Millipore, France). Expanded pyridinium compounds **1** to **4** (for chemical structures see Chart 1) were synthesized according to the general reaction scheme shown in Section 1 of the Supporting Information (SI), which contains also further experimental details and complete product characterization.

2.2. Experimental methods

All glassware, Kalrez O-rings, PTFE and Kel-F liquid cell parts for single molecule conductance experiments, were cleaned in boiling 30% nitric acid, which was followed by repeated boiling in ultrapure water and drying at 105 °C. Glass cell and cell parts for electrochemical experiments were cleaned by chromosulfuric acid followed by copious washing with ultrapure water and drying at 105 °C.

An original STM tubular scanner from Agilent 5500 Scanning Probe Microscope (Agilent Technologies, USA) was used for scanning tunneling microscopy break junction (STMBJ) measurements. STMBJ measurements were done at disabled *z*-piezo voltage feedback control. An in-house built double-output current-to-voltage converter circuit capable of recording current in a wide dynamic range from 5 pA to 200 μ A with approximately 1 kHz bandwidth was integrated within the scanner head. This setup enables generating ramp voltage for controlling the *z*-axis piezo position, including one triggering event for detecting the metallic contact formation during the probe approach, and another triggering event for detecting the complete breaking of the junction during probe withdrawal process with ability to vary independently the approaching and retracting rates as well as waiting times at both vertex positions. The STMBJ measurements were performed at constant bias voltage of 130 mV between the gold probe and gold substrate. The gold probe was prepared by cutting the 0.25 mm gold wire (99,999% GoodFellow). Gold substrate (99,95% GoodFellow, 1 cm \times 1 cm \times 0.1 cm) was annealed and cooled down in the nitrogen atmosphere. Molecules **1** to **4** for STMBJ measurements were first dissolved in absolute ethanol and this stock solution was used for preparation of 2×10^{-4} M solution of **1** to **4** in 15% (v/v) ethanol in mesitylene. Experiments were obtained at different probe retraction rates ranging from 7.2 to 36 nm s⁻¹. Typically 2000

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