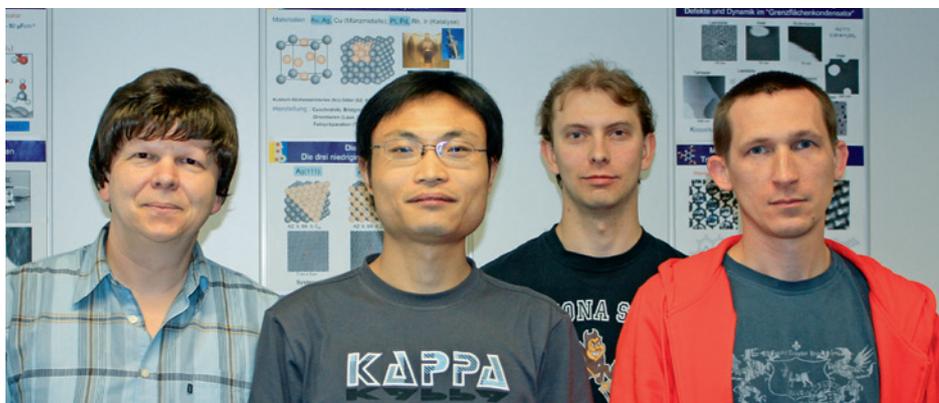


# Charge Transport with Single Molecules – An Electrochemical Approach

Chen Li, Artem Mishchenko, Ilya Pobelov, and Thomas Wandlowski\*

**Abstract:** After an introduction and brief review of charge transport in nanoscale molecular systems we report on experimental studies in gold | (single) molecule | gold junctions at solid | liquid interfaces employing a scanning tunneling microscopy (STM)-based ‘break junction’ technique. We demonstrate attempts in developing basic relationships between molecular structure, conductance properties and nanoscale electrochemical concepts based on four case studies from our own work. In experiments with  $\alpha$ ,  $\omega$ -alkanedithiol and biphenyldithiol molecular junctions we address the role of sulfur-gold couplings and molecular conformation, such as gauche defects in the alkyl chains and the torsion angle between two phenyl rings. Combination with quantum chemistry calculations enabled a detailed molecular-level understanding of the electronic structure and transport characteristics of both systems. Employing the concept of ‘electrolyte gating’ with redox-active molecules, such as thiol-terminated derivatives of viologens (HS-6V6-SH or (HS-6V6)) we demonstrate the construction of symmetric and asymmetric active molecular junctions with transistor- or diode-like behavior upon polarization in an electrochemical environment. The experimental data could be represented quantitatively by the Kutznetsov/Ulstrup model assuming a two-step electron transfer with partial vibration relaxation. Finally, we show that surface-immobilized gold nanoparticles with a diameter of  $(2.4 \pm 0.5)$  nm exhibit features of locally addressable multi-state electronic switching upon electrolyte gating, which appears to be reminiscent of a sequential charging through several ‘oxidation/reduction states’.

**Keywords:** Electrolyte gating · Quantized cluster charging · Single molecule electron transport · STM-based break junction



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## 1. Introduction – Charge Transport in Nanoscale Molecular Systems

The idea of building an electronic device using individual molecules was first proposed by Aviram and Ratner.<sup>[1]</sup> The molecular approach bears several opportunities: i) custom-design of nanoscale molecular units, ii) self-organization and recognition properties of molecular building blocks, iii) implementation of localized functions such as rectification, switching or amplification.<sup>[2–9]</sup> The ability to measure and to control charge transport across nanometer-scale metal | (single) molecule | metal junctions is of considerable fundamental interest and represents a key step towards the development of a molecular-based electronics. Various experimental approaches have been employed to study molecular junctions in two- and three-terminal configurations. These include scanning probe microscopies (STM,<sup>[10–13]</sup> CP-AFM,<sup>[14–16]</sup> STS<sup>[17–20]</sup>), crossed wire<sup>[21]</sup> and nanoparticle junctions,<sup>[22,23]</sup> mechanical<sup>[24–28]</sup> and electromigration break junctions,<sup>[29,30]</sup> nanopores<sup>[31]</sup> and mercury drop electrodes.<sup>[32]</sup> Most experiments refer to *ex situ* conditions, *i.e.* in air or vacuum, and at cryogenic temperatures. Approaches in condensed media, and in particular in an electrochemical environment (liquid electrolytes or solid-state ionic conductors), offer unique opportunities to explore charge transport across single molecules employing the concept of ‘electrolyte gating’.

Molecular wires studied to date can be divided in two classes: i)  $\sigma$ -bonded aliphatic molecules and ii)  $\pi$ -bonded aromatic molecules.<sup>[33,34]</sup>  $\alpha,\omega$ -alkanedithi-

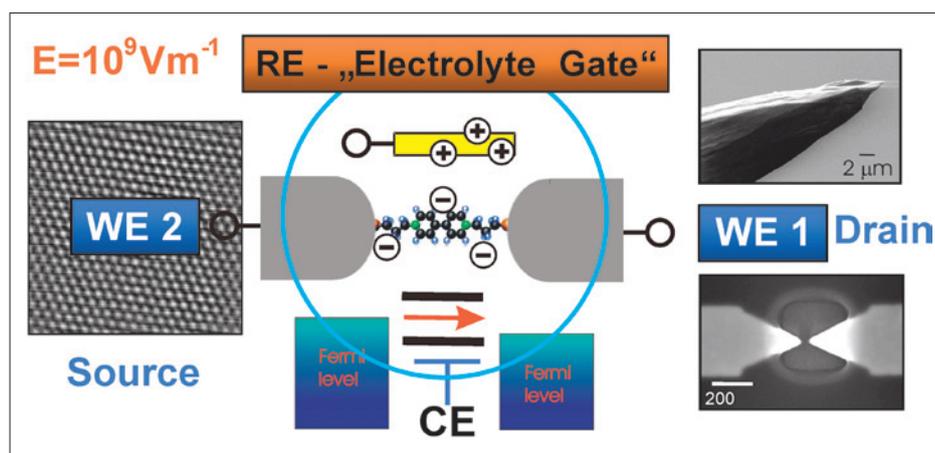


Fig. 1. Principle of ‘electrolyte gating’. Tuning of the Fermi levels of WE 1 and WE 2 relative to the molecular levels enables measuring of current ( $i$ ) – voltage ( $E$ ) characteristics  $i$  vs.  $(E_{WE1} - E_{WE2})$  at fixed  $E_{WE1}$  or  $E_{WE2}$ ;  $i$  vs.  $E_{WE1}$  or  $E_{WE2}$  at fixed bias  $E_{bias} = (E_{WE1} - E_{WE2})$  as well as barrier height profiles  $i$  vs. distance of tailored molecular junctions in a vertical SPM-configuration respective horizontal nanoelectrode assembly.

ols (<sup>[14,15,17,35]</sup> and literature cited therein), oligophenylene vinylene (OPV) and oligophenylene ethynylene (OPE) rods (<sup>[10,16,36]</sup> and literature cited therein) attached to gold electrodes or nanocrystals *via* thiol linkers are prominent examples. Except of a systematic study with aliphatic and aromatic diamines of the Columbia group ref. [32] and literature cited therein, only few reports on other anchoring groups to establish electronic coupling between molecular wires and metal contacts were published. These include carboxylic acid groups,<sup>[38,39]</sup> isocyanide,<sup>[40,41]</sup> nitrile<sup>[40]</sup> and selenol.<sup>[42]</sup> First studies with substituted  $\alpha,\omega$ -alkane derivatives by Huggins<sup>[43]</sup> and Chen *et al.*,<sup>[38]</sup> and aromatic molecular wires by Venkataraman *et al.*,<sup>[37]</sup> Haiss *et al.*<sup>[44]</sup> and us<sup>[45,46]</sup> at solid liquid interfaces illustrated the unique potential of chemical control, *e.g.* the effect of electron-donating respective -withdrawing substituents, molecular conformation or anchoring groups on the conductance signature of single molecular junctions. However, there is still a considerable lack in understanding basic relationships between molecular structure and conductance properties.<sup>[5–9]</sup>

Several groups explored ‘active’ solid state metal | molecule | metal junctions, for instance with redox centers under *ex situ* (ambient) and UHV (cryogenic) conditions. They discovered phenomena such as negative differential resistance (NDR),<sup>[31]</sup> rectification,<sup>[7,47,48]</sup> amplification,<sup>[28,29]</sup> switching and memory effects.<sup>[8,49–51]</sup> Examples of functional molecules used in these studies are 2'-amino-4,4'-di(ethynylphenyl)-5'-nitro-1-benzene thiolate,<sup>[31]</sup> metal organic  $Co^{2+}$ -terpyridine complexes<sup>[29]</sup> or a  $[Co^II L_4]^{8+}$ - $[2 \times 2]$  grid type complex.<sup>[30]</sup> The experimental investigations are currently accompanied by powerful theoretical and computational approaches to interpret

molecular signatures in these transport junctions.<sup>[5]</sup> New challenges and unique opportunities emerge when adapting these studies to nanoscale systems in an *electrochemical environment*.<sup>[52,53]</sup>

## 2. The Electrochemical Approach

The addressing of nanoelectronic assemblies metal | ‘molecule’ (nanocluster) | metal with device-like functions, such as rectifiers, switches, transistors requires a source and a drain and one or more localized electronic levels.<sup>[5]</sup> The roles of source and drain (both as working electrodes WE1 and WE2) may be represented by the tip of a STM combined with an appropriate substrate or, alternatively, a pair of nanoelectrodes (Fig. 1).

Working in an electrochemical environment such as an electrified solid | liquid interface has the advantage that two potential differences can be controlled individually: the bias voltage between the two working electrodes (WE1 and WE2) and the potential drop between each individual working electrode and the reference electrode (RE). The latter acts as an ‘electrochemical gate’ and modulates the tunneling current between source (WE2) and drain (WE1).<sup>[52,53]</sup> The idea of an ‘electrochemical gate’ to control charge transport in molecular electronics was introduced by Wrighton,<sup>[54]</sup> Meulenkaamp,<sup>[55]</sup> Schönenberger,<sup>[56]</sup> and McEuen,<sup>[57]</sup> and further developed by Tao,<sup>[18,58,59]</sup> Ulstrup *et al.*,<sup>[52,53,60]</sup> Lindsay,<sup>[61]</sup> Haiss *et al.*,<sup>[19]</sup> Vanmaekelbergh,<sup>[62]</sup> and us.<sup>[20,63]</sup> The effective gate | molecule distance is determined by the double layer thickness at the electrode | electrolyte interface, which is typically of the size of a few solvated ions. The ‘electrolyte gating’ ensures a strong coupling due to low con-

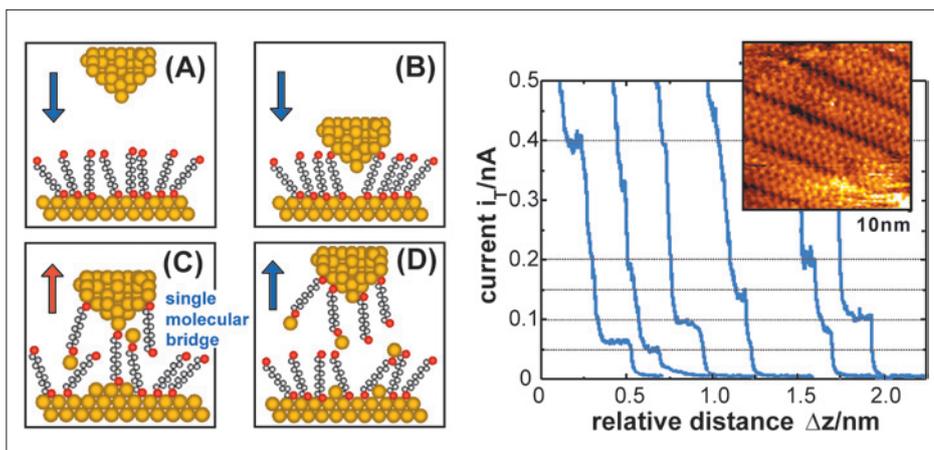


Fig. 2. Left panel: Schematic representation of the STM-type 'contact junction' approach. (A) Approach, (B) Formation of molecular contacts, (C) Pulling and (D) Breaking. Right panel: Typical current-distance retraction curves recorded with a gold STM tip for 0.1 mM 1,9-nonanedithiol in 1,3,5-trimethylbenzene on Au(111)-(1x1), at  $E_{\text{bias}} = 0.10$  V. The setpoint current before disabling the feedback was chosen at  $i_T = 100$  pA. The pulling rate was  $4 \text{ nm s}^{-1}$ . The inset illustrates a high resolution STM image of the striped low-coverage nonanedithiolo phase on Au(111)-(1x1);  $i_T = 0.1$  nA,  $E_{\text{bias}} = 0.1$  V.<sup>[35]</sup>

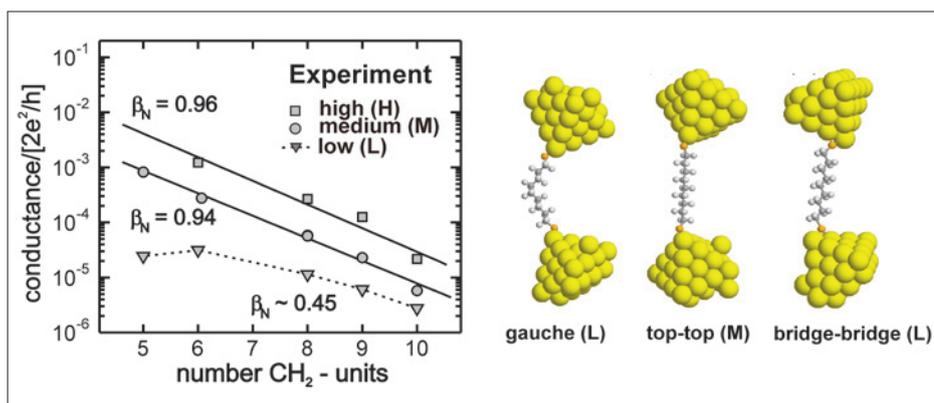


Fig. 3. Left panel: Chain length dependence of the single junction Au | alkanedithiol | Au conductance in a semilogarithmic representation. The three sets of conductance values – high (H), medium (M) and low (L) – are shown as squares, circles and triangles. The straight lines were obtained from a linear regression analysis with decay constants  $\beta_N$  defined per methylene ( $\text{CH}_2$ ) unit. Right panel: Three typical arrangements of a single alkanedithiol molecule bridged between Au electrodes: 1, 9-nonanedithiol (ND) with one gauche defect and both terminal sulfur atoms coordinated in atop position (low, L), ND in all-*trans* conformation and atop-atop coordination (medium, M), (C) all-*trans* ND in a bridge-bridge coordination (high, H).<sup>[35]</sup>

tact resistances, thin adjacent double layers (<1 nm) and high mobility of the charge carriers (ions). The magnitude of the field in the electrochemical double layer (EDL) is close to the gate field required to significantly modulate the current through a molecular-sized nanostructure according to first principle calculations by di Ventra *et al.*<sup>[64,65]</sup>

The electrochemical approach is unique as the measured current represents both the electrical contact to the external circuit and the functional state of the nanostructure (single molecule, nanocluster).

In the following sections we shall discuss selected examples of our own work on

charge transport with tailored molecules and clusters. We present first a STM-based method to investigate charge transport characteristics in single metal | molecule | metal junctions at solid | liquid interfaces. The approach will be illustrated based on two case studies with  $\alpha,\omega$ -alkanedithiols<sup>[35]</sup> and biphenyldithiols.<sup>[45,46]</sup> Then we will discuss single redox-active nanojunctions in an electrochemical environment with viologen-type molecules bound either to one (asymmetric configuration) or to both (symmetrical configuration) adjacent electrodes.<sup>[20,63]</sup> The molecular experiments will be complemented with an example on quantized double layer charging of gold nanoparticles.<sup>[66]</sup>

### 3. Charge Transport in Au | $\alpha,\omega$ -alkanedithiol | Au Junctions at Solid | Liquid Interfaces

Fig. 2 shows a schematic representation of the STM-based contact junctions approach as developed in our group and applied to explore charge transfer characteristics in gold |  $\alpha,\omega$ -alkanedithiol | gold junctions.<sup>[35,67]</sup> The following strategy was applied: A sharp gold STM tip, capable of imaging experiments with atomic resolution, was brought to a preset tunneling position (A). Subsequently, the STM feedback was switched off, and the tip approached the adsorbate-modified substrate surface at constant  $x - y$  position. The approach was stopped typically before reaching point contact with the gold surface ('gentle touch', shown in panel (B)) or upon reaching point contact ('hard touch'). After a dwelling time of 100 ms, sufficient to create molecular junctions between tip and substrate, the tip was retracted and the corresponding current-distance trace recorded. The entire cycle is typically repeated more than 1000 times.

The individual current-distance traces are non-exponential and show characteristic series of plateaus separated by abrupt steps (Fig. 2). The observed currents are 2 to 3 orders of magnitude smaller compared to metal nanocontacts. We ascribe these conductance steps to the breaking of individual respective multi-molecule junctions.

The statistical analysis of the plateau currents yields histograms with characteristic peaks. Careful analysis of these conductance peaks allows the identification of three distinctly different sequences of equally spaced maxima, which are attributed to low L, medium M and high H conductance junctions.<sup>[35]</sup> The logarithm of the single molecular junction conductance is linearly dependent on the chain length, with a decay constant  $\beta \sim 1$  for the high and medium type junctions. Distinctly different results were obtained in the low conductance regime. A tentative value of  $\beta \sim 0.45$  is estimated (Fig. 3).

Comparison with quantum chemistry *ab initio* simulations demonstrated that the multiple conductance values of Au | alkanedithiol | Au junctions could be attributed to different Au-sulfur coordination geometries and to different conformations of the alkyl chain. In particular, the 'medium' conductance values M correspond to an all-*trans* conformation of the alkyl chain with one of the sulfur atoms coordinated in atop position to a single Au atom. The 'high' conductance values H represent an all-*trans* alkyl chain in combination with both sulfurs coordinated to two Au atoms in bridge geometry. The sequence of 'low' conductance values

L is attributed to isomers of alkanedithiols with gauche defects (Fig. 3).

#### 4. Chemically Controlled Conductance: Torsion-Angle Dependence in Single-Molecule Biphenyldithiol Junctions

Employing the methodology developed in ref. [35], we investigated the conductance of a family of custom-made biphenyldithiol derivatives with conformationally fixed torsion angles to explore structure-property relationships at the single molecule level.<sup>[45,46]</sup> Biphenyl derivatives consisting of two aromatic rings interconnected by a single C–C bond gained considerable interest as subunits for single molecular rectifying or switching systems as the two  $\pi$ -systems can be either in the same plane or perpendicular to each other representing ‘on’ or ‘off’ states, respectively.<sup>[37,67–70]</sup>

As displayed in Fig. 4, methyl side groups or an alkyl chain of various lengths connected at the 2,2'-positions of the biphenyl system adjust the resulting torsion angle  $\phi$ . In this series of compounds the length of the interfering alkyl chain is the only structural variation, keeping the electronic structure of the biphenyl systems within this family of compounds as uniform as possible. The biphenyl conformation is locked by an intra-molecular bridge with the number of  $-\text{CH}_2$ -units dictating the torsion angle  $\phi$ , lowering the expected motion and conformational variation of each molecule immobilized in the junction considerably. Due to their terminal sulfur anchor groups, the series of compounds forms a stable molecular junction.

The STM-based single molecule experiments revealed that the junction conductance depends on the torsion angle  $\phi$  between the two phenyl rings: twisting the biphenyl system from flat ( $\phi = 0^\circ$ ) to perpendicular ( $\phi = 90^\circ$ ) decreased the conductance by a factor of 30 following a linear  $\cos^2\phi$  dependence. Detailed calculations based on density functional theory (DFT) revealed a HOMO-controlled transport mechanism and support the experimentally obtained  $\cos^2\phi$  correlation between the junction conductance  $G$  and the torsion angle  $\phi$ . A two level model as parameterized by the DFT calculations demonstrated that the transmission factorizes in an ‘off-resonance’ junction, such that ‘ring-to-ring’ and ‘electrode-ring’ transmission components could be separated.<sup>[46]</sup> We found that for all molecules with  $\phi \leq 80^\circ$  one  $\pi$  channel dominates the transport. Contributions from degenerate  $\sigma$ - $\pi$  and  $\pi$ - $\sigma$  channels were only observed for biphenyl derivatives with completely broken conjugation, e.g. for  $\phi = 90^\circ$ . Extending

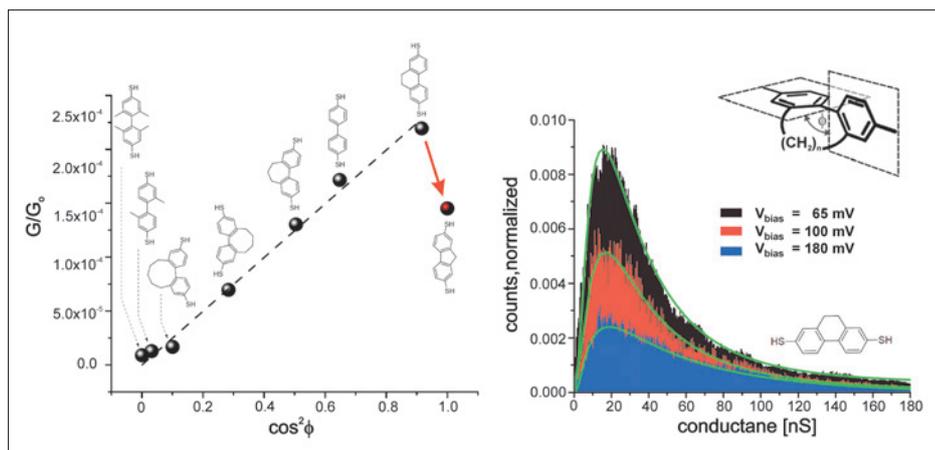


Fig. 4. Left panel: Experimentally determined single junction conductance of thiol-terminated biphenyl molecules vs  $\cos^2\phi$ , where  $\phi$  is the torsion angle of the molecules as given by the X-ray data.<sup>[45]</sup> The dashed line represents the linear fit  $G/G_0 = a_{\text{ex}} \cdot \cos^2\phi$  with  $a_{\text{ex}} = 2.44 \cdot 10^{-4}$  to all molecules studied, except the fluorene derivative. Right panel: Plateau-point histogram for the  $\text{C}_2$ -bridged biphenyldithiol derivative, as recorded from individual current-distance traces in an STM-based break junction experiment (gold tip, Au(111) substrate;  $E_{\text{bias}} = 0.10$  V) at three different bias voltages in mesitylene.<sup>[46]</sup>

the experimental and theoretical studies to biphenyl families with amino-<sup>[37,70]</sup> and cyano-<sup>[71]</sup> anchoring groups revealed that the former exhibit HOMO-controlled transport characteristics while the latter is LUMO-controlled, respectively.

Our study provides a clear example of the reproducible measurement of a single molecule-specific property, the pronounced  $\cos^2\phi$  variation, its tuning by controlled synthetic chemistry, and the development of a molecular-level understanding by combination with a careful DFT-based analysis of transmission channels.

#### 5. Electrochemically Gate-controlled Electron Transport with Redox-active Molecules

The development of the methodology to measure single molecule electron transport in metal | molecule | metal configurations motivated applications in an electrochemical environment employing the concept of ‘electrolyte gating’.<sup>[52,53,63]</sup> These examples include porphyrines,<sup>[18]</sup> viologens,<sup>[19,20,63,72,73]</sup> aniline and thiophene oligomers,<sup>[74–77]</sup> transition metal complexes,<sup>[78–80]</sup> carotenes,<sup>[81]</sup> nitro-derivatives of oligophenylene ethynylene,<sup>[82,83]</sup> ferrocenes,<sup>[66,84,85]</sup> perylene tetracarboxylic bisimides,<sup>[86–88]</sup> and redox-active proteins.<sup>[89–92]</sup> Despite these qualitative studies with various redox-active molecular hybrid systems, there is still a considerable lack in understanding basic relationships between molecular structures and conductance properties.

In an attempt to contribute to a more advanced understanding of these phenomena, we have carried out recently several

systematic experimental and theoretical studies with redox-active viologens,<sup>[20,63,72]</sup> perylene bisimides<sup>[88]</sup> and ferrocenes.<sup>[86]</sup> As an example, we will describe in the following selected experiments employing gold nanojunctions modified with  $N,N'$ -bis(6-thiohexyl)-4,4'-bipyridinium bromide (HS-6V6-SH) or  $N$ -hexyl- $N'$ -(6-thiohexyl)-4,4'-bipyridinium bromide (HS-6V6), which are composed of the redox-active 4,4'-bipyridinium cation  $\text{V}^{2+}$  (viologen) as a core, two flexible alkyl spacer units attached to each ring nitrogen with either two or one terminal SH anchoring group. The latter ensures the chemical surface immobilization.<sup>[20,63]</sup>

Depending on the applied potential, the redox-active viologen group exists in three different redox states, the oxidized and stable dication  $\text{V}^{2+}$ , or an electron rich radical cation  $\text{V}^{+\bullet}$  respective the neutral species  $\text{V}^0$ . We shall focus on the potential-induced reversible transition between the dication  $\text{V}^{2+}$  and the radical cation  $\text{V}^{+\bullet}$ .

Fig. 5 shows a typical current-potential curve (cyclic voltammogram) for HS-6V6-SH on Au(111) for a low and a densely packed high coverage molecular adlayer. The latter is disordered. At low coverages, however, a highly ordered zig-zag layer of flat lying viologen-type molecules could be identified with submolecular resolution of the sulfur atoms, the alkyl chains and the viologen moiety. The low coverage phase was chosen to explore the single molecular conductance as a function of the redox state.

The STM break junction approach, as introduced before,<sup>[35,67]</sup> was now applied under strict electrochemical potential control.<sup>[20]</sup> The recorded retracting current-distance traces revealed characteristic pla-

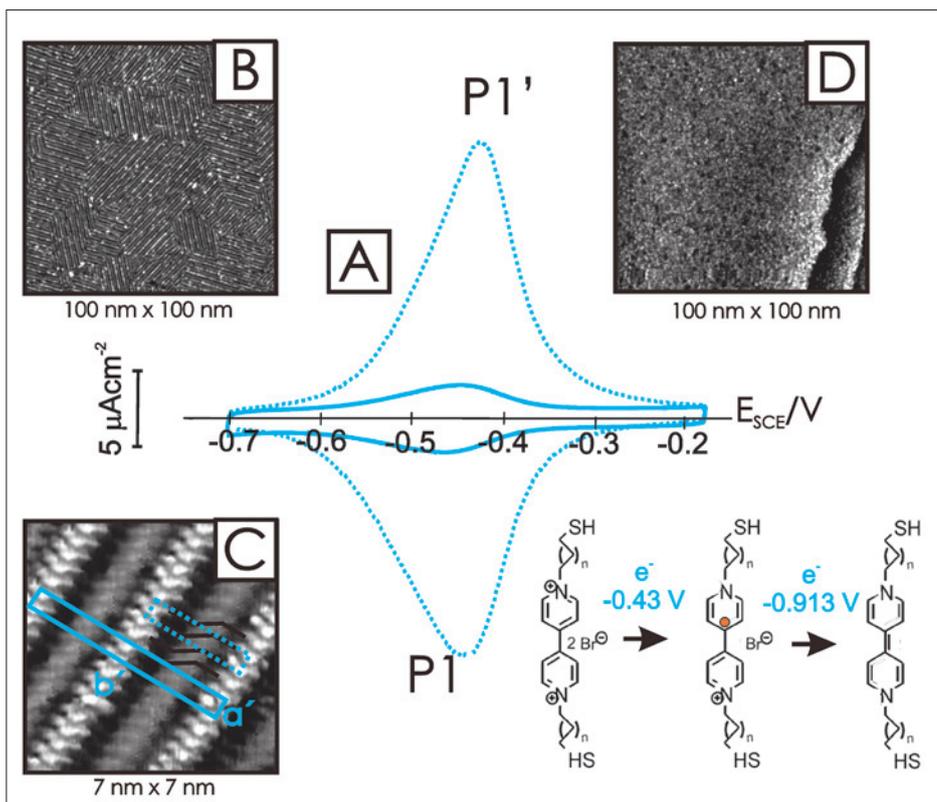


Fig. 5. (A) Cyclic voltammogram of an Au(111)-(1x1) electrode in 0.05 M KClO<sub>4</sub>, pH ~ 7, modified with a low coverage (solid line) and a high coverage (dotted line) adlayer of HS-6V6-SH for the reversible one-electron oxidation/reduction between the viologen dication V<sup>2+</sup> and the radical cation V<sup>+</sup> form. (B) Large scale *in situ* STM image of the low coverage striped phase of HS-6V6-SH, E<sub>S</sub> = -0.25 V, E<sub>bias</sub> = -0.10 V, i<sub>T</sub> = 60 pA; (C) high resolution image of the striped phase, E<sub>S</sub> = -0.35 V, E<sub>bias</sub> = 0.08 V, i<sub>T</sub> = 40 pA; (D) high coverage adlayer of HS-6V6-SH, E<sub>S</sub> = -0.25 V, E<sub>bias</sub> = -0.09 V, i<sub>T</sub> = 60 pA.<sup>[20]</sup>

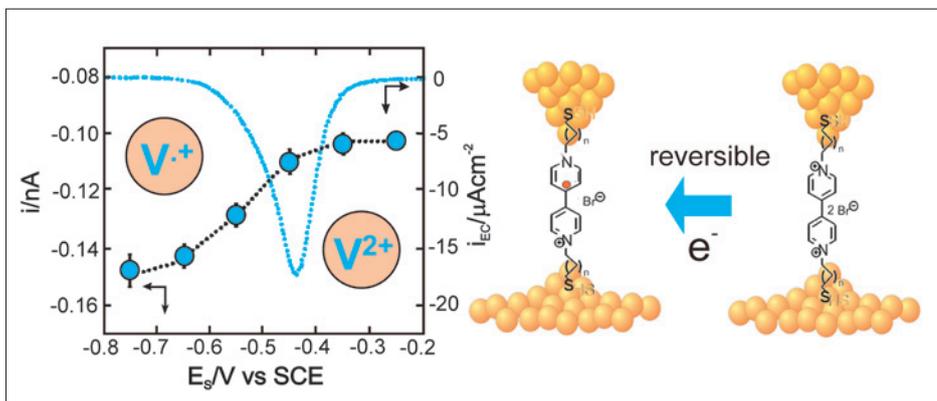


Fig. 6. Plot of the single molecule conductance currents *i* of Au(T) | HS-6V6-SH | Au(S) junctions vs. the substrate potential E<sub>S</sub> at fixed bias (E<sub>S</sub> - E<sub>T</sub>) = -0.100 V. Each data point was obtained from conductance histograms as constructed from several hundreds of individual current-distance pulling curves. The dotted line corresponds to the macroscopic current-voltage curve for the reduction of V<sup>2+</sup> → V<sup>+</sup> (c.f. cyclic voltammograms in Fig. 5).<sup>[20]</sup>

teaus of 0.2 to 0.3 nm separated by abrupt steps. The statistical analysis of these stretching curves leads to single molecular conductance data of the oxidized and reduced form of the viologen bridge by appropriate substrate and tip polarization (Fig. 6). The single molecular conductance of the HS-6V6-SH junctions is rather constant in the stability range of the oxidized viologen dication V<sup>2+</sup>, and increases at

more negative potentials by *ca.* 50% until a plateau is reached at E ≤ -0.700 V, *e.g.* past the formal potential of the one-electron redox switching is attributed to the higher electron density and the higher degree of conjugation of the radical cation as compared to the dication.<sup>[20]</sup> Quantum chemical calculations of Bagrets *et al.* suggested additional contributions from interactions

of the tunneling electrons with molecular vibrations.<sup>[91]</sup>

We note that a particular large effect upon electrolyte gating was observed for molecular junctions formed with thiol- and pyridyl-group terminated perylene bisimide derivatives attached to two gold electrodes.<sup>[88]</sup> Here we found an increase in the single molecule conductance of up to 100, *i.e.* from 1 nS to ~ 100 nS, upon reduction of the redox-active perylene unit in aqueous LiClO<sub>4</sub> as electrolyte.

Besides the above transport experiment in a symmetric Au | HS-6V6-SH | Au junction, we also developed a single molecule tunneling experiment.<sup>[20,63,72]</sup> Here, a redox-molecule modified tunneling junction is created with an asymmetric viologen HS-6V6 bound either to the Au tip or to the Au(111) substrate surface (Fig. 7). After establishing stable tunneling junctions, the STM feedback was switched off, and subsequently we recorded at constant xyz position the tunneling current as a function of the applied voltage while keeping the voltage difference between tip and substrate (bias voltage) constant. In other words, the Fermi levels of tip and substrate were shifted relative to the discrete molecular levels. In both cases, *i.e.* a viologen-modified tip or substrate, an enhanced tunneling current with a well-defined maximum close to the equilibrium potential E<sup>o</sup> of the redox couple was observed, which is attributed to the 'opening' or 'gating' of an additional molecular tunneling channel and resembles a transistor-like behavior. The experimental observations could be quantitatively explained by a sequential two-step electron transfer process accompanied with partial vibration relaxation.<sup>[63]</sup> This model was recently developed by Kuznetsov and Ulstrup.<sup>[52,53]</sup> Our analysis leads to characteristic parameters, such as reorganization energy, potential drop, and overpotential across the tunneling gap, and demonstrates that the magnitude of the tunneling enhancement depends on the initial redox state of HS6V6 (V<sup>2+</sup> or V<sup>+</sup>).

Complementary tunneling spectroscopic experiments were also carried out in variable bias mode with a fixed substrate potential and the tip potential varied in a wide range. The resulting current response is asymmetric and resembles the characteristics of a diode.<sup>[63]</sup> At high tip potentials a small current due to direct tunneling at fixed gap geometry is observed, while an enhanced exponential-like tunneling response is found at negative tip potentials due to the opening of a redox-mediated tunneling channel. As an example, the 'on/off ratio' between the negative and the corresponding positive branches of the tunneling current-voltage curve at a bias voltage of ± 0.4 V is *ca.* 20.

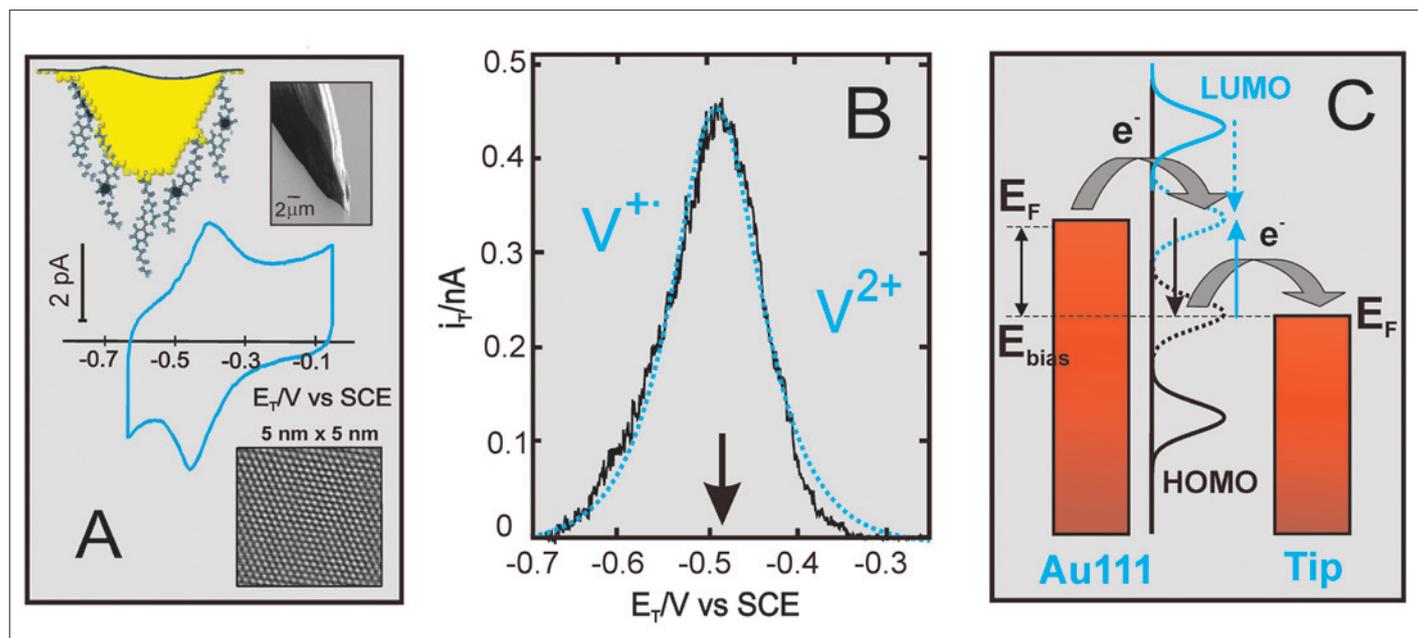


Fig. 7. (A) Set-up of the redox-mediated tunneling experiment with a viologen-modified Au tip; (B) Average  $i_T$  vs.  $E_s$  curves recorded in constant bias spectroscopy mode,  $i_T = 0.1$  nA,  $E_{\text{bias}} = 0.050$  V, after base line correction. The sweep started in the stability region of  $V^{+}$ . The dotted blue line represents the fit using the Kuznetsov/Ulstrup model of sequential two-step electron transfer with partial vibration relaxation.<sup>[20,52,53,63]</sup> (C) Schematic energy level diagram of a two-step electron transfer process mediated by a redox-active molecule. The electron is transferred from the Fermi level of the substrate (left)  $E_s$  to the LUMO of the molecule and after partial vibrational relaxation to the Fermi level of the tip  $E_T$  (right).

We would like to point out that the asymmetric Au | HS-6V6 | Au configuration is distinctly different from the symmetric Au | molecule | Au configuration.<sup>[63]</sup> The latter exhibits modifications of the junction conductance due to structure changes of the redox-active unit ('inner sphere reorganization energy'), while the former exhibits a maximum of the tunneling current due to the coexistence of the oxidized and the reduced forms with dominant contributions of the dynamics of the solvent molecules in the gap ('outer sphere reorganization energy'). We also like to note that the observed enhancement of the tunneling current in an electrochemical environment is not restricted to viologen-based junctions.

## 6. From Redox Gating to Quantized Charging of Nanometer-sized Gold Clusters

Metal nanoparticles (NP) represent another typical nanoscale object with unique electronic, optical, catalytic and magnetic properties, which are distinctly different from both molecular and bulk regimes.<sup>[93]</sup> Their electronic and electrochemical properties can be tuned through metal core and ligand shell. For instance, Au-NPs with a core diameter  $\leq 1$  nm behave like a similar sized molecule with a discrete electronic spectrum at a wide HOMO-LUMO gap. Bulk properties are observed for larger NP  $\geq 3$  nm.<sup>[94–97]</sup> Intermediate-sized Au-NP, 1–3 nm, display electrochemically detect-

able quantum confinement effects such as quantized double layer charging.<sup>[96–105]</sup> This observation implies that, within the stability range of the clusters, multiple accessible and addressable electronic levels exist.

Chen *et al.* reported on quantized double layer charging based on macroscopic voltammetric experiments with a monolayer of alkanethiol-protected Au-NP immobilized on a Au(poly) substrate.<sup>[106]</sup> Single electron Coulomb charging was observed for different types and sizes of individual metal nanoparticles in vacuum or in air employing specifically STM and STS.<sup>[11,99,107–109]</sup> Albrecht *et al.* showed in a proof-of-principle experiment the possibility of intrinsic multi-state switching of Au nanoclusters through electrochemical gating.<sup>[110]</sup>

Motivated by this pioneering report we created a thiol-based self-assembled template monolayer on Au(111) electrodes with immobilized and uniformly distributed gold cluster of  $2.4 \pm 0.5$  nm diameter and a rather narrow size distribution (Fig. 8).<sup>[66]</sup> Constant bias mode electrochemical scanning tunneling spectroscopy (STS) experiments with the gold tip positioned above a single gold cluster (asymmetric tunneling junction) revealed up to seven clearly resolved, rather narrow current peaks with an equal peak-to-peak spacing of  $0.11 \pm 0.02$  V. Based on the distribution of peak spacings and peak heights we attribute our observations to a modulation of the tunneling current by sequential capacitive charging of single gold nanoclusters. Following

this hypothesis we estimate<sup>[96,97,100,101]</sup> the average particle capacitance  $C = e/\Delta E = 1.5 \pm 0.2$  aF. The observed feature of sequential capacitive charging is reminiscent of a successive electronic charging of redox molecules through several oxidation/reduction states. However, the latter are usually much wider than the former.

## 7. Summary and Outlook

We have presented and discussed in this paper selected examples of our own work on charge transport in gold | (single) molecule | gold junctions at solid | liquid interfaces employing a scanning tunneling microscopy (STM)-based 'break junction' technique. After an introduction of the experimental technique we discussed four case studies with 'inactive'  $\alpha,\omega$ -alkanedithiols and biphenyldithiols, 'redox-active' thio-alkylated viologens and surface immobilized gold nanoclusters in the quantum confinement range. The combination of these reproducible and statistical relevant single-molecule measurements with quantum chemistry and transport calculation revealed important new aspects in the understanding of basic relationships between molecular structure and conductance properties. In particular, the observations on the intrinsic electronic properties of locally addressable single 'redox-molecules' and gold nanoclusters employing the concept of 'electrolyte gating' open new experimental and theoretical perspectives toward multi-state electronic switch-

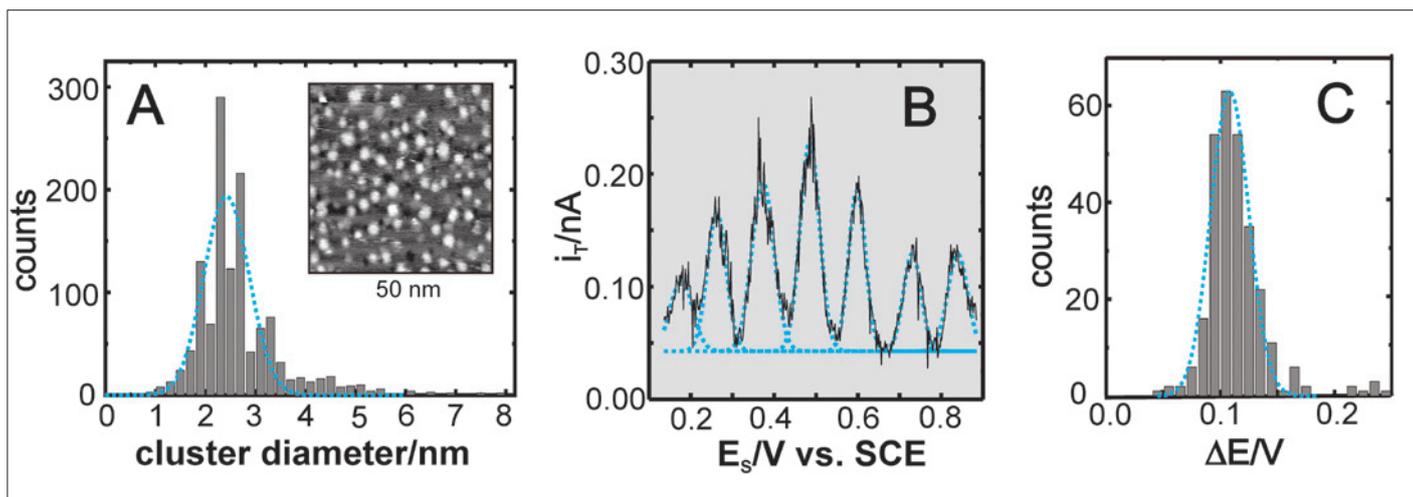


Fig. 8. (A) STM image ( $i_T = 0.05$  nA,  $E_S = 0.7$  V,  $E_T = 0.1$  V; vertical scale 0.4 nm) and size distribution histogram of gold nano-clusters formed within a self-assembled template monolayer on Au(111) in 1.0 M  $\text{HClO}_4$ . The dotted line represents the Gaussian fit. The corresponding parameters are the average cluster diameter 2.42 nm and the standard deviation  $\sigma = 0.45$  nm. (B) Example of a constant bias current-voltage response of a single gold cluster as triggered by 'electrolyte gating',  $E_{\text{bias}} = 0.1$  V,  $i_T = 0.05$  nA. The dotted traces represent its fit by a series of Gaussians. (C) Peak spacing histogram and Gaussian fit for a data set 361 individual traces, such as shown in (B). The corresponding parameters are the average spacing  $\Delta E = 0.11$  V and  $\sigma = 0.017$  V.

ing, current amplification, rectification or other nanoscale electronic functions in condensed media at room temperature. These studies may also open up unique opportunities in the newly developing field of nanoscale molecular electrochemistry.

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