15% denaturing polyacrylamide gel. The ApA hydrolysis by the 2:1 Zn^{II}–TPBA complex was followed by reverse-phase HPLC. The 2′,3′-cyclic monophosphate of adenosine as the intermediate was rapidly hydrolyzed to the 2′- and 3′-monophosphates; thus, not much intermediate accumulated.

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[8] The weak bands in the 3′ side of the main scission site in lane 10 are tentatively ascribed to catalysis by zinc(II) hydroxide clusters formed at a high Zn^{II} concentration ($[Zn^{II}]_0 = 0.5$ mM).

[9] When $[Zn^{II}]_0 = [TPBA]_0 = 2.5$ mM in D_2O, TPBA gave one set of ^1H NMR signals which differed from those of the free ligand. Upon increasing the $[Zn^{II}]_0/[TPBA]_0$ ratio, another set of signals (corresponding to the 2:1 complex) gradually appeared. At a ratio of 2, only signals for the 2:1 complex were observed.

An STM Study of Chemically Deposited Silver Nanoclusters on Mixed Self-Assembled Monolayers**

Ulrich-Walter Grummt,* Matthias Geissler, Till Drechsler, Harald Fuchs, and Ralf Staub

Single electron tunneling (SET) processes in quantum-confined low-dimensional systems have gained increasing interest over recent years.[1, 2] Understanding of the mechanism of charge transport through single molecules is a prerequisite for the rational design of electronic devices based on single molecules.[3] A challenging problem is to establish metallic contacts in a stable and reproducible way to individual molecules. Mixed self-assembled monolayers (SAMs) containing a small number of the molecules to be studied as guests in a matrix of inert host molecules offer the possibility to address single molecules by the STM tip (STM = scanning tunneling microscopy). The basic idea of the present study is to generate silver clusters as small as Ag_4 in the immediate vicinity of a four-electron reducing agent which is incorporated in a monolayer of long-chain alkanethiols (Figure 1).[4] In connection with an STM tip the silver nanoclusters provide a vertical double tunnel junction, which should allow the observation of SET processes, even at room temperature if the cluster capacitance is sufficiently small ($e^2/2C \gg kT$). Chemical deposition of silver clusters on SAMs is a simple and more gentle alternative to deposition from a cluster beam[5] and evaporation techniques.[6]

A series of aromatic methyl sulfides were synthesized bearing two adjacent terminal hydroquinone units. For this study the compound BHQ1 (Figure 1) was selected to form mixed SAMs with an excess of *n*-decanethiol (nDT). On Au(111) nDT forms layers with a hexagonal $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure.[7] Molecular resolution was achieved with pure nDT SAMs. All variants of superlattices described by Delamarche et al. could be observed.[8] The MM3 simulations of SAMs where one of 18 nDT molecules was replaced with BHQ1 predict that BHQ1 should protrude beyond the nDT surface. However, not unexpectedly, single molecules of BHQ1 could not be resolved. On the other hand, phase segregation of nDT and BHQ1 to form separate domains could be ruled out.

The treatment of the mixed SAMs with an aqueous ammonia-containing solution of silver nitrate (5 M $AgNO_3$ in water/ethanol 2/1, pH 10) results in the formation of silver

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[*] Prof. Dr. U.-W. Grummt, Dipl.-Chem. M. Geissler
Institut für Physikalische Chemie der Universität
Lessingstrasse 10, D-07743 Jena (Germany)
Fax: (+49) 3641-948302
E-mail: cug@pc04.chemie.uni-jena.de

Dipl.-Phys. T. Drechsler, Prof. Dr. H. Fuchs
Physikalisches Institut der Universität Münster (Germany)

R. Staub
Institut für Angewandte Photophysik der Technischen Universität Dresden (Germany)

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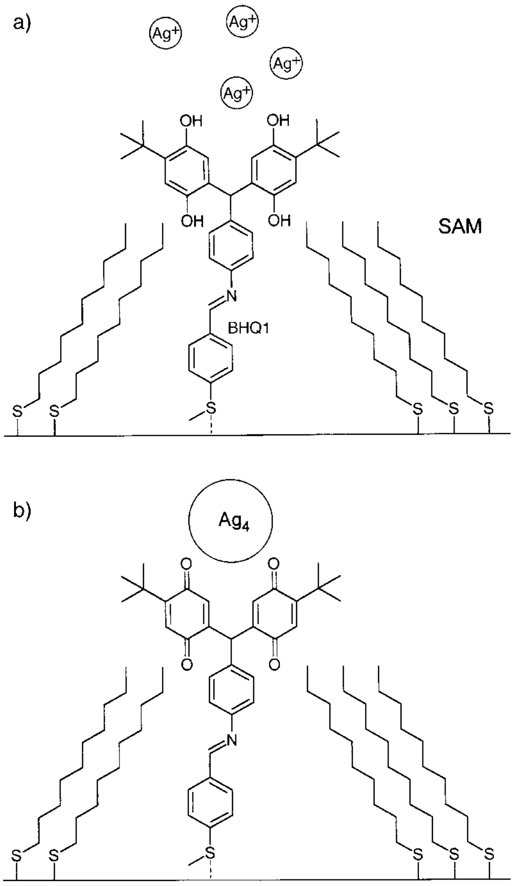

Figure 1. Contacting single molecules (BHQ1 with nDT on Au(111)). A solution of Ag^+ (pH 10) is added (a), and clusters such as Ag_4 form upon oxidation of the hydroquinone units of BHQ1 (b). See the text for further details.

nanoclusters. The presence of the clusters consisting of silver was proven by secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS). The SIMS spectrum of a mixed SAM with silver clusters (Figure 2) shows the peaks of the isotopes ^{107}Ag and ^{109}Ag with the natural ratio of 51:49. The signals at m/z 129–136 are the Xe isotopes peaks. The following XPS signals were found: $Ag_{3d5/2}$: $E = 367.6$ eV ($\Delta E = -0.4$ eV), $Ag_{3d3/2}$: $E = 373.4$ eV ($\Delta E = -0.6$ eV), $Ag_{3p3/2}$: $E = 572.6$ eV ($\Delta E = -0.4$ eV). The shifts ΔE are given relative to bulk silver; $Au_{4f7/2}$ was used as reference. The line positions agree reasonably well with literature data.[9] Most of the clusters are disklike with a height of 0.62 nm, corresponding to two atomic layers. Clusters containing 400–2000 atoms were observed by STM. A typical diameter is 5 nm, corresponding to about 510 atoms. An example is given in Figure 3.

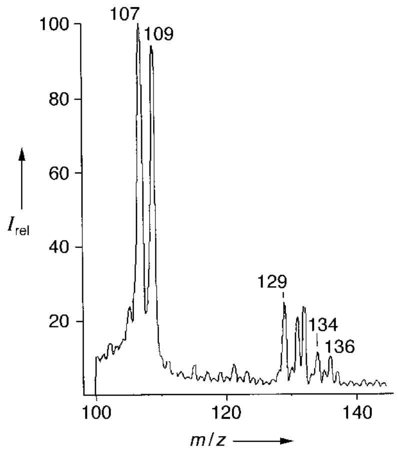

Figure 2. SIM spectrum of silver on a mixed SAM. I_{rel} = relative intensity.

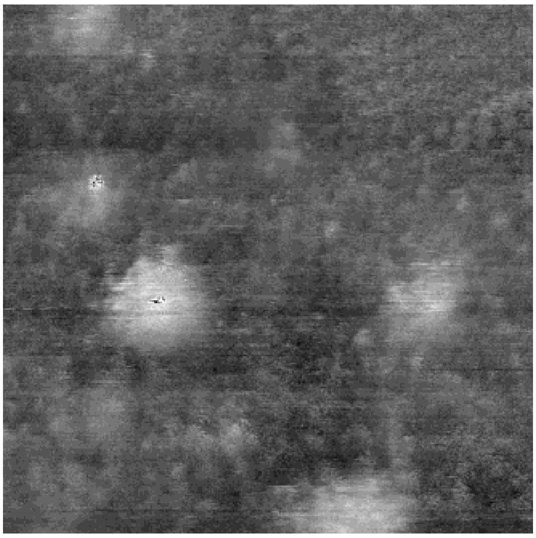

Figure 3. STM image of silver clusters generated on a mixed SAM of nDT/BHQ1 (3/1). The area is 20×20 nm^2. Constant-current mode, 0.19 nA, 1.19 V.

The resulting surface density of Ag atoms after the reduction process was obtained from statistical evaluations of the STM images (Figure 4). The straight line shows the surface density calculated with the assumption of a 1:1 replacement of nDT with BHQ1 under purely kinetic control of the SAM formation. The experimental deviations at low BHQ1 admixtures might indicate that the assumption of kinetic control is not fully justified. The curvature of the experimental relationship has to be expected because the assumption of an 1:1 replacement must become invalid at

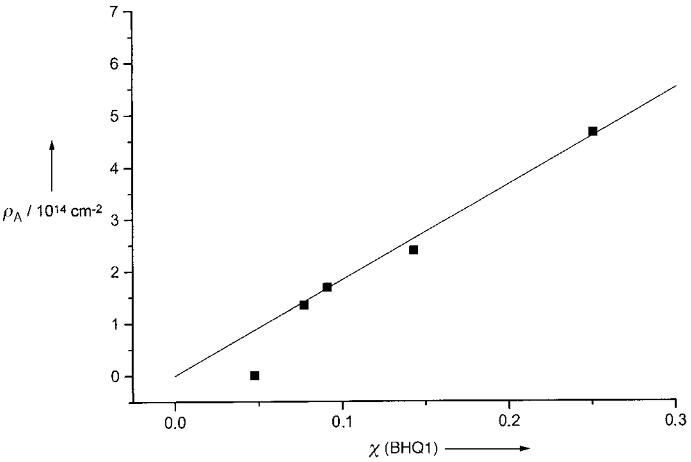

Figure 4. Surface density ρ_A of silver as a function of the mole fraction of BHQ1 in solution.

least with increasing admixtures of BHQ1. Since preformed BHQ1 aggregation is absent in the mixed SAM, we conclude that there is significant lateral surface diffusion of silver atoms or of very small clusters during the reduction process. The interaction of silver with terminal methyl groups of alkanethiol surfaces is very weak.[10] To reduce the surface mobility of silver, we also used 1-ω-sulfanyl alcohols as host matrices. However, the mean cluster size was insignificantly reduced.

Three types of current/voltage curves were observed, as shown in Figure 5. With the tip positioned above a cluster-free region of the SAM, sigmoid curves were obtained which never showed a staircase shape. Most of the clusters give approximately linear curves with a more or less sigmoid distortion, indicating Ohmic behavior. As shown by Czanderna et al., silver deposited from a vacuum may rapidly penetrate through octadecanethiol SAMs.[11] It is also readily conceivable that upon heating the SAMs up to 150 °C the clusters come into direct Ohmic contact to the substrate due to desorption of organic molecules and diffusion of clusters to defect sites. Unequivocal observation of the typical XPS signals (S(2p$_{3/2}$): $E = 162.1$ eV, S(2p$_{1/2}$): $E = 163.7$ eV for thiolate SAMs and S(2p$_{3/2}$): $E = 169.5$ eV for RSCH$_3$ SAMs[12]) proves that desorption of the organic material is at worst only partial. In particular, if clusters are sufficiently enlarged by physical development,[4] then Ohmic behavior becomes dominant. Apparently the probability of direct electric contact at some defect sites of the SAM increases with the cluster size.

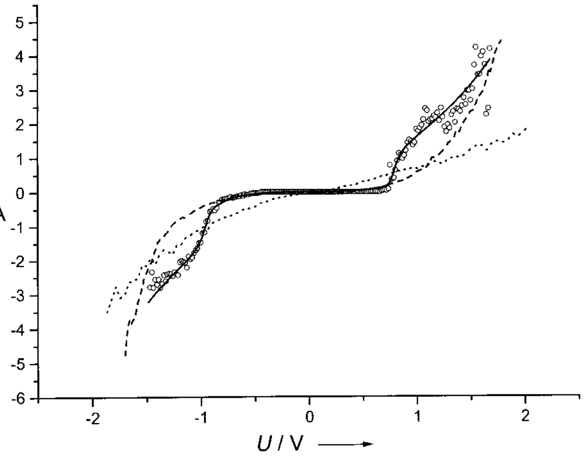

Figure 5. Current/voltage curves obtained from a cluster-free region of a SAM (–––, × 10) and of a silver cluster penetrating the SAM (- - - -, × 10; both under ulta-high vacuum (UHV) and at room temperature) as well as of a silver cluster with the STM tip positioned above an isolated cluster (○, UHV, 100 K, $I = 40$ pA, $U = -1.0$ V).

On the other hand, we can unequivocally state that clusters do exist which are well isolated from the Au substrate. The observed staircase curve in Figure 5 is to be interpreted in terms of SET Coulomb blockades. The curve can be fitted using a semiclassical model of a two-junction system with the parameters C_i and R_i, the capacitance and resistance, respectively, of the ith junction, and a fractional charge Q_0 (Figure 6).[13] The parameter Q_0 originates from differences of the work functions of tip and sample. The least-squares fit of the data yields $R_1 = 13.0\,\text{M}\Omega$, $C_1 = 1.01 \times 10^{-19}$ F, $R_2 = 643.5\,\text{M}\Omega$, $C_2 = 0.93 \times 10^{-19}$ F, and $Q_0/e = 0.051$. With the expression $C = 4\pi\varepsilon_r\varepsilon_0 r$ ($C \approx 1 \times 10^{-19}$ F, $\varepsilon_r = 3$) a cluster height of 0.6 nm could be estimated in a first approximation which agrees very well with the STM data.

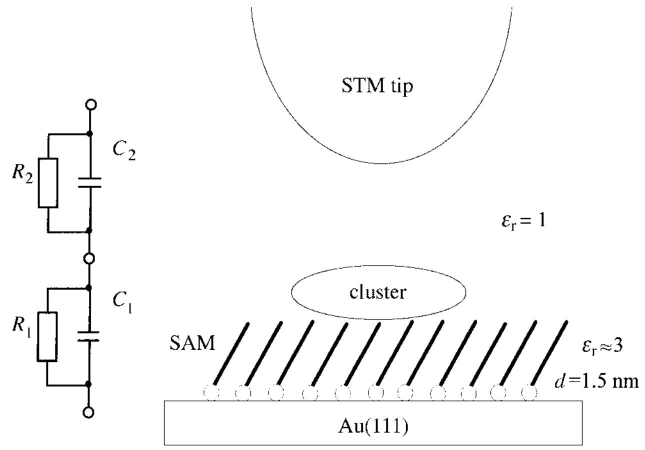

Figure 6. Geometrical model arrangement for estimating the electrical properties of the double junction.

Experimental Section

Characterization of BHQ1. Elemental analysis calcd for C$_{35}$H$_{39}$NO$_4$S ($M_r = 569.76$): C 73.78, H 6.90, N 2.46, S 5.63; found: C 73.50, H 6.98, N 2.48, S 5.55; MS (DCI with H$_2$O): m/z (%): 93 (100), 404 (94.5), 343 (93.7), 570 (70.2), 153 (67.2), 228 (57.1), 253 (23.5), 325 (19.3), 285 (16.8), 514 (12.6); ^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 1.29$ (s, 18 H), 2.48 (s, 3 H), 5.83 (s, 1 H), 6.25 (s, 2 H), 6.61 (s, 2 H), 7.00 (d, $J = 8.38$ Hz, 2 H), 7.17 (d, $J = 8.38$ Hz, 2 H), 7.35 (d, $J = 8.47$ Hz, 2 H), 7.84 (d, $J = 8.46$ Hz, 2 H), 8.30 (s, 2 H), 8.40 (s, 2 H), 8.55 (s, 1 H); ^{13}C NMR (63 MHz, [D$_6$]DMSO): $\delta = 14.16$, 29.43, 33.91, 41.66, 113.37, 117.60, 120.54, 125.38, 127.83, 128.89, 129.73, 132.67, 133.07, 142.49, 142.60, 146.61, 147.54, 148.75, 158.79.

Sample preparation: For the majority of the experiments, Au(111) surfaces were prepared by high vacuum deposition of about 250 nm gold (99.99 %, Edelmetalle Freiberg, Germany) onto freshly cleaved mica at 300 °C.[14] Furthermore, Au(111) surfaces obtained by flame annealing of 200 nm Au/8 nm Cr on Tempax glass slides (SQ1 and BQ3, Sico Jena GmbH, Germany) were used as substrates.[15] The STM investigations show the expected hexagonal facet structure of atomically flat plateau areas with a step height of 0.24 nm. In most cases they also display the characteristic long-range $23 \times \sqrt{3}$ reconstruction. The SAMs were obtained by adsorption from 1 mM solutions of mixtures of nDT (Aldrich) with BHQ1 in ethanol for at least 10 h at room temperature. The samples were rinsed with ethanol and dried with nitrogen.

Apparatus: The STM images were recorded with a Nanoscope 2 (Digital Instruments) under ambient conditions using Pt/Ir tips. For low-temperature STS investigations a home-built beetle-type low-temperature STM under ultra-high vacuum (UHV; for detailed information see ref. [16]) was used. Current/voltage curves were taken with an Omicron combined AFM/STM after heating the sample for one hour at 150 °C in under UHV. Mass spectra were recorded on a SSQ-710 (Finnigen MAT). Elemental analyses were performed with a Leco CHNS-932 analyzer. The ^{1}H and ^{13}C NMR spectra were recorded with an AC-250 (Bruker). The XPS experiments were performed on a Specs EA 200 equipped with a multichannel hemispherical analyzer.

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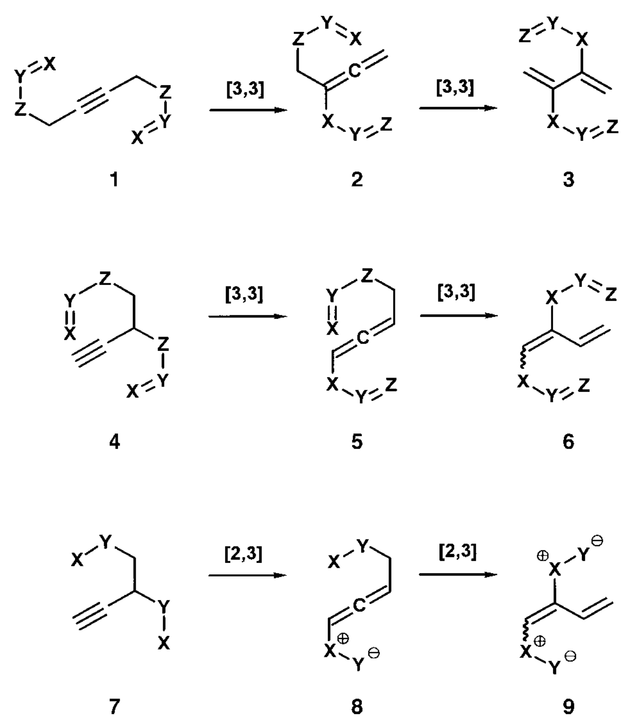
Synthesis of 1,2-Difunctionalized 1,3-Butadienes through a Sequence of Sigmatropic Rearrangements**

Klaus Banert,* Wolfgang Fendel, and Jana Schlott

Dedicated to Professor Günter Marx
on the occasion of his 60th birthday

Sequential [3,3] sigmatropic rearrangements such as the well-known reaction **1**→**2**→**3**, for example where XYZ = NCO,[1] NCS,[2] NCSe,[3] N_3,[4] $SCONMe_2$,[5] SCN,[6] $C{-}CO_2R$[7] (orthoester Claisen rearrangement), C–C=C[8] (Cope rearrangement), can be used to transform the 2-butyne-1,4-diyl precursors **1** into the 2,3-difunctionalized 1,3-butadienes **3** (Scheme 1). The synthesis of similar products proceeds analogously through two consecutive [2,3] sigmatropic isomerizations, for instance in the reaction of phosphinites to phosphane oxides,[9] phosphites to phosphonates,[10] sulfinates to sulfones,[11] or sulfenates to sulfoxides.[11, 12] To the best of our knowledge, however, sigmatropic rearrangements have not been employed to prepare 1,2-difunctionalized 1,3-butadienes. We describe here a sequence of sigmatropic isomerizations that provide a convenient approach to these target compounds. In this connection [3,3] migrations such as **4**→**5**→**6** as well as [2,3] shifts **7**→**8**→**9** are used to direct both functional groups into vinylic positions.



Scheme 1. Synthesis of doubly functionalized 1,3-butadienes by two consecutive sigmatropic rearrangements.

The hydroxyl groups of the readily available diols **10**[13] can be easily transformed into isomerizable functional groups (Scheme 2). The subsequent gas-phase thermolysis (flash vacuum pyrolysis)[14] of the imidate **11a** and the heating of the thiono carboxylates/carbamates/carbonates **13a,d** or sulfinates **17a,c** in solution lead to the 1,2-difunctionalized 1,3-butadienes **12a**, **14a,d**, and **18a,c**, respectively. The reactions of **10** to give **15a** or **16a–d** require no warming and succeed in one-pot procedures. The products **12a** and **14a**, which result from [3,3] sigmatropic rearrangements, are formed as mixtures of separable *E*/*Z* isomers. However, the [2,3] isomerizations afford the dienes **15a**, **16a–d**, and **18a,c** with exclusive *E* configuration. The sulfoxides **16a–d** are obtained as mixtures of *like*/*unlike* diastereomers as a consequence of the stereocenters at the sulfur atoms.[15] A subsequent isomerization of the C-C double bond is not observed on thermolysis in solution. For example, a constant ratio of 1:1 is detected for the distribution of products with *E* and *Z* configuration when the transformation **13aγ**→**14aγ** is investigated both immediately after low conversion and after very long reaction times (about 50 half-life periods of **13aγ**). In the case of **13dβ** the sequences of [3,3] sigmatropic migrations prove to be stereospecific. Thus, *meso*-**13dβ** furnishes nearly exclusively (*E*)-**14dβ**, while *rac*-**13dβ** leads almost solely to (*Z*)-**14dβ**.

The bis(sulfenate) derived from *meso*-**10d** can give rise not only to **16dα** but also to a hexa-1,2,4,5-tetraene compound by

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[*] Prof. Dr. K. Banert, Dr. W. Fendel, Dipl.-Chem. J. Schlott
Lehrstuhl für Organische Chemie der Technischen Universität
Strasse der Nationen 62, D-09111 Chemnitz (Germany)
Fax: (+49)371-531-1839
E-mail: klaus.banert@chemie.tu-chemnitz.de

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