TOF-MS (matrices: 3-(3-indolyl)acrylic acid, 2,5-dihydroxybenzoic acid, or 2′,4′,6′-trihydroxyacetophenone/ammonium hydrogencitrate), as well as elemental analysis.

[12] The purity of the oligomers was further checked by analytical SEC on two columns (TosoHaas TSKgel G2500 HR (5 μm) and TosoHaas TSKgel G2000 HR (5 μm), 0.78 × 30 cm) connected in series. Vis detection at $\lambda = 400$ nm gave peaks at retention time: $t_R = 13.92$ (**4**), 12.98 (**7**), 12.39 (**8**), 12.03 (**1**), 11.56 (**2**), and 11.30 min (**3**).

[13] a) H. Gregorius, W. Heitz, K. Müllen, *Adv. Mater.* **1993**, *5*, 279–281; b) R. Schenk, H. Gregorius, K. Müllen, *Adv. Mater.* **1991**, *3*, 492–493.

[14] This is in agreement with previous work in which such isomerization was only observed for arylated 1,2-diethynylethenes and tetraethynylethenes and the corresponding oligomeric PTAs, see a) R. E. Martin, J. Bartek, R. R. Tykwinski, V. Gramlich, F. Diederich, E. Meister, A. Hilger, H. P. Lüthi, *J. Chem. Soc. Perkin Trans. 2* **1998**, 233–241; b) J. Wytko, R. R. Tykwinski, R. E. Martin, L. Gobbi, F. Diederich, unpublished results.

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[16] The real longest-wavelength transitions are hidden under an inhomogenously broadened absorption band that arises from molecular vibrations. Therefore, the UV/Vis spectra were deconvoluted by assuming a sum of Gaussian line shapes in energy space, by which all spectra could exactly be reproduced. The software *pro Fit*, Ver. 5.0.0 for Power Macintosh, Quantum Soft Zürich, 1990–96, was utilized for fitting by using a self-written plug-in module.

[17] Raman spectra were measured on a series 2000R NIR FT-Raman spectrometer (Perkin–Elmer). Excitation occurred at 1064 nm (Nd:YAG laser) with a 700–900 mW laser power.

Separation of a Racemic Mixture of Two-Dimensional Molecular Clusters by Scanning Tunneling Microscopy[**]

Matthias Böhringer, Karina Morgenstern, Wolf-Dieter Schneider, and Richard Berndt[*]

The separation of a racemic mixture of chiral molecules into the enantiopure compounds is a fundamental and often challenging problem in chemistry that was first solved by Pasteur in his celebrated experiment in 1848.[1] With a magnifier and tweezers he discriminated and separated small enantiomorphic crystals obtained from a solution of racemic sodium ammonium tartrate. Pasteur took advantage of stereospecific molecular interactions to obtain sufficiently sized crystallites, each composed exclusively of one enantiomer. One hundred and fifty years after Pasteur's pioneering experiment scanning probe microscopies now permit visualization of structures with molecular resolution, and chiral aggregates of achiral,[2–6] racemic,[7, 8] or chiral[8–11] compounds have been discriminated on the molecular scale. However the second part of Pasteur's experiment—separation of the enantiomorphic aggregates—has not been performed, to date, on the nanoscale. We show that enantiomers of supramolecular clusters that exhibit two-dimensional chirality can be discriminated *and* separated from a racemic mixture with a scanning tunneling microscope (STM). The experiment is a molecular scale analogue of Pasteur's experiment.

Figure 1 shows the structural formula of 1-nitronaphthalene (NN) and a STM topograph of the clean reconstructed Au(111) surface. The Au(111) surface is comprised of alternating domains of face centred cubic (fcc) and hexagonal close packed (hcp) stacking of the surface atoms with respect to the underlying crystal.[12] The domain walls where the surface atoms are displaced from the hcp or fcc sites appear in STM images 0.1–0.2 Å higher (brighter) than the domains. On large terraces two domain orientations rotated by 120° alternate and form a herringbone pattern.[13]

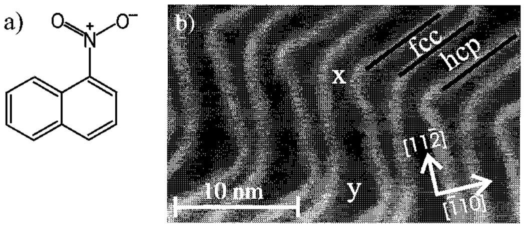

Figure 1. a) Structural formula of 1-nitronaphthalene (NN). b) STM topograph of the reconstructed Au(111) surface. Broad/narrow dark stripes correspond to domains with surface atoms in fcc/hcp positions. Two domain orientations rotated by 120° alternate and form a herringbone pattern. Two inequivalent types of turning points (elbows) of this pattern are observed, which correspond to larger (y elbows) or smaller (x elbows) widths of the fcc domain. Sample voltage $V = -820$ mV, tunneling current $I = 10$ pA.

STM images of the NN covered surface recorded below about 70 K reveal that molecular aggregates of distinct size and geometry have self-assembled (a monolayer corresponds to a thick layered structure with nine surface atoms per NN molecule). If the isolated molecules are disregarded about 85 % of these clusters are composed of ten molecules arranged in a modified pinwheel structure (Figure 2 a). The decamers form within the fcc domains near elbows, which is reminiscent of the preferential nucleation of some metals at these sites.[14] Intriguingly, two related kinds of decamers (*L*, *R*) are observed, which behave in a similar manner to an object and its mirror image and cannot be transformed into one another by rotation and translation within the surface plane. We conclude that the confinement of the NN molecules on the Au(111) surface leads to planar aggregates that exhibit two-dimensional chirality. As a consequence of a planar adsorption geometry already on Au(111) single NN molecules are two-dimensionally chiral on the surface. Equal amounts of enantiomeric NN molecules—denoted here as *l* and *r*—are expected to be present on the surface. In STM images,

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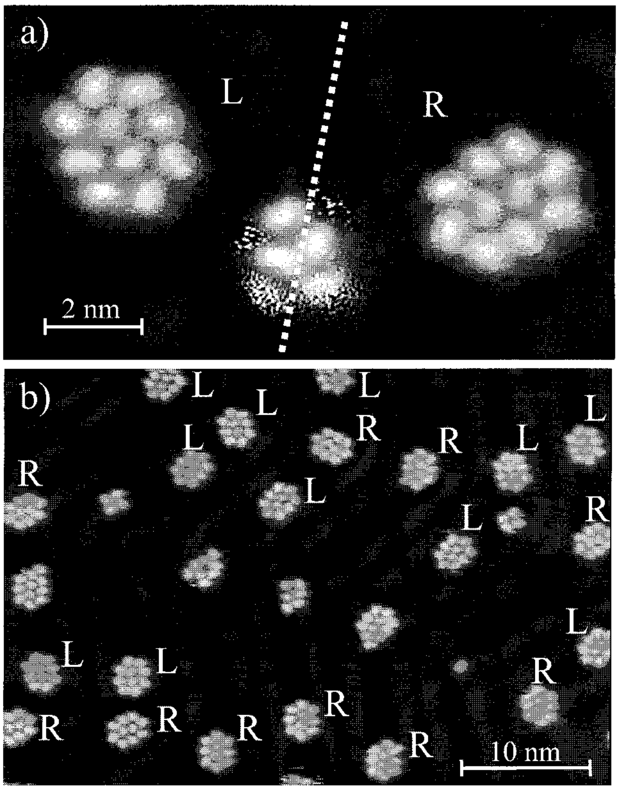

Figure 2. a) Two dimensional chiral decamers (denoted *L* and *R*) formed by NN molecules on the Au(111) surface (imaging conditions: 50 K, −510 mV, 10 pA). b) At 50 K with a coverage of 0.1 monolayers about 85 % of the molecular aggregates are decamers. The remaining clusters are ca. 5 % undecamers, 5 % tetramers, and the rest unordered structures. The decamers nucleate within the fcc domains near y elbows. Equal amounts of (*L*)- and (*R*)-decamers are observed and hence constitute a racemic mixture (50 K, −330 mV, 10 pA).

however, both enantiomers usually appear as ellipsoids and cannot be distinguished.[15] The formation of stable NN decamers may be viewed as the synthesis of two-dimensional chiral supermolecules from an achiral precursor, namely the gas-phase NN. The inversion symmetry of the decamers implies that they are comprised of even numbers of *l* and *r* molecules. Molecular dynamic simulations predict a 8:2 ratio (2:8 for the opposite chirality).[15] This ratio and the equal numbers of adsorbed *r* and *l* molecules imply that the clusters form a racemic mixture. Accordingly, equal numbers of enantiomorphic (*L*)- and (*R*)-decamers are found on the surface (Figure 2b).

Figure 3 displays a series of experiments at 50 K where the manipulation capabilities of the STM are used to line up decamers within one fcc domain. First, Figure 3a is recorded at imaging conditions, that is with negligible interaction between the STM tip and the molecular aggregate (sample bias −600 mV, tunneling current 10 pA). Then the STM tip is positioned above one of the decamers. At this point the tunneling resistance is decreased by three orders of magnitude (−5 mV, 200 pA) in order to move the chosen decamer through an increased interaction with the tip. Using these parameters the tip is moved slowly, within seconds, to an adjacent fcc domain along the path indicated by an arrow. There the decamer is released by changing back to the imaging conditions. This sequence is repeated for the decamers marked in Figure 3a.

The result of the manipulation was inspected at imaging conditions as shown in Figure 3b. One observes that the decamers have indeed been moved without changing their supramolecular arrangement. In particular, the chirality of the decamers remains unaltered. These experiments support the concept that decamers behave as supermolecules whose stability, structure, and chirality are determined by strong intermolecular interactions.[15] We note that an enantiomerization of a (*L*)- to a (*R*)-decamer (or vice versa) requires a change from a 8:2 to a 2:8 ratio of (*l*)- and (*r*)-NN molecules.

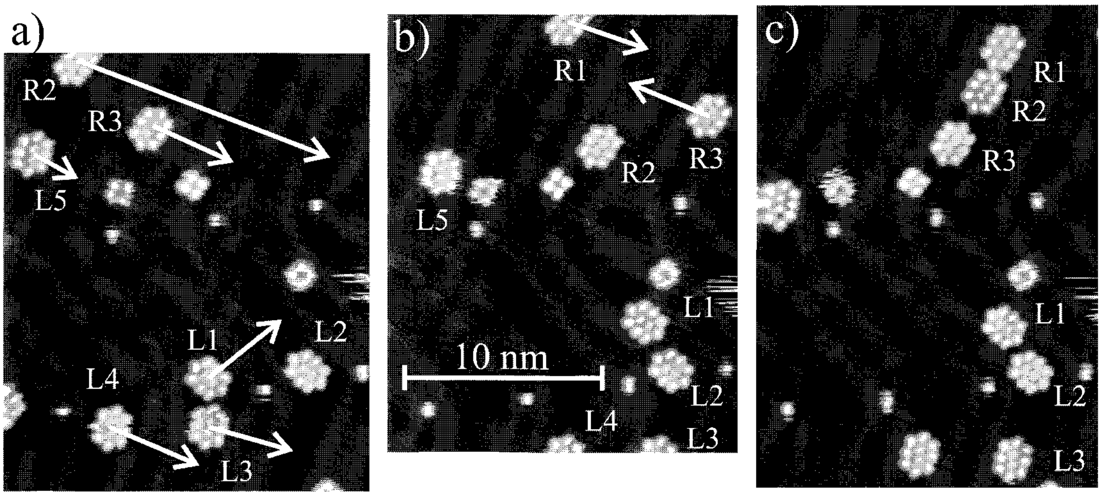

Figure 3. Pasteur experiment in two dimensions on a molecular scale. a) Image (−600 mV, 10 pA) of decamers prior to manipulation. Decamers are subsequently moved by the STM tip along the paths indicated by arrows (tunneling conditions for the manipulation: −5 mV, 200 pA, 50 K). b) Intermediate result of the manipulations. Structure and two-dimensional chirality of the decamers remained unaffected. Decamer *L*5 has been moved into the neigboring hcp domain; this decamer will have only a small interaction with the substrate and will be disturbed by the imaging process and so it is disregarded for the rest of the manipulation experiment. c) Arrangement of the decamers at the end of the manipulation sequence. (*L*)-decamers are located in the lower part and (*R*)-decamers in the upper part of a fcc domain.

The manipulation sequence was continued and the decamers were lined up along one fcc domain to separate the racemic mixture into the pure compounds with the (*R*)-decamers in the top right part of the domain and the (*L*)-decamers below (Figure 3c). We note that in terms of the two-dimensional chiral NN molecules this is equivalent to an enantiomeric excess of 60%.

The present experiment adds the important capability of enantiomer separation to the previous studies on atomic-scale manipulation,[16] selective dissociation,[17–19] conformational analysis,[20] and chiral recognition.[2–11] Hence scanning probe based techniques are emerging as an important arsenal for nanochemistry. Both chiral recognition and enantioselective manipulation are key capabilities for future stereoselective chemical reactions on a single molecule basis.

Experimental Section

The NN clusters were obtained by dosing sub-monolayer amounts of NN (purified by vacuum sublimation at 300 K prior to use) onto the clean Au(111) substrate at room temperature in ultra-high vacuum and with subsequent cooling to 50 K within 24 h.

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The Carbonyl Chlorine(I) Cation $[ClCO]^+$**

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The cation $[ClCO]^+$ belongs to a family of linear, three-atom molecules with 30 electrons (such as OCS, ONP, ONS^+, and $ArCN^+$) which are of interest to theoreticians and which exhibit interesting spectroscopic properties. The carbonyl halogen(I) cations $[XCO]^+$ (X = F, Cl, Br) are also of practical importance as reactive intermediates in Friedel–Crafts reactions and in plasma etching processes. Whereas the $[XCO]^+$ ions (X = F,[1, 2] Cl,[3] Br[4]) have been extensively studied in the gas phase (mass spectra, dissociation energies, electron affinities,[2] rotational[5] and photoelectron[6] spectra for $[FCO]^+$), and both $[FCO]^+$[5] and $[ClCO]^+$[7, 8] have also been the subjects of theoretical calculations, there is only a single report in which the cations $[XCO]^+$ (X = Cl, Br, I) have been detected in the condensed phase as transients.[9] In this study[9] of the reaction of CO with Cl_2, Br_2, or I_2 in SO_2ClF/SbF_5 by ^{13}C NMR spectroscopy at $-78\,^{\circ}C$, three new singlets at $\delta = 133.7$, 127.0, and 100.4 are observed and attributed to the $[XCO]^+$ ions (X = Cl, Br, I) by comparison to the spectra of the corresponding X_2CO molecules. Thus short-lived carbon species are produced in superacidic solutions; however, ^{13}C NMR resonances alone are not sufficient evidence to conclusively and unambiguously establish the existence of the carbonyl halogen cations in the condensed phase.

While this manuscript was in preparation, we became aware, from two presentations at conferences,[10, 11] and of a comprehensive, so far unpublished, study of the $[ClCO]^+$ ion,[12] in which vibrational and ^{13}C NMR spectra as well as thermodynamic and ab initio calculations are discussed. The results appear to confirm and complement our observations, which are reported here.

We generated the $[ClCO]^+$ ion accidentally during attempts to synthesize the homoleptic carbonyl cation $[Fe(CO)_6]^{3+}$. In the reaction of $Fe(CO)_5$ with CO and Cl_2 as oxidizing agent in SbF_5, the salt $[Fe(CO)_6][Sb_2F_{11}]_2$ was obtained in high yield and found to be thermally stable to 100 °C.[13–15] The IR spectrum of this salt contains a new band at $2256\ cm^{-1}$, which was tentatively attributed to the unknown $[Fe(CO)_6]^{3+}$ ion,[13, 14] because the IR-active fundamental $\tilde{\nu}_{CO}$ (F_{1u}) of $[Ir(CO)_6]^{3+}$[16] is observed at $2254\ cm^{-1}$. We have found in the meantime that the band at $2256\ cm^{-1}$ is also observed when CO and Cl_2 are combined in SbF_5 in the absence of $Fe(CO)_5$. Hence the band is re-assigned as the $\tilde{\nu}_{CO}$ band of the $[ClCO]^+$

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