The measured difference in red shifts of $\Delta - \Delta^* = 13\ \mathrm{cm}^{-1}$ for **Rr** and **Rs** indicates that the interaction energies in these MCs respond to a complicate interplay of steric effects and dispersive forces. In fact, the red shifts reflect the strengthening of the dispersion (polarization and charge transfer) forces in the corresponding excited adducts. However, the observation that the larger red shift is associated with the less stable complex **Rs** (Table 1) indicates a dual effect of the HOMO →LUMO electron transition in the chromophoric moiety of **Rr** and **Rs**. This not only enhances the attractive dispersion forces, but also alters to a different extent the repulsive forces arising from steric congestion in the complexes.

The values for D_0^+ in Table 1 qualitatively parallel the corresponding D_0'' energies. The homochiral complex **Rr**$^+$ is more stable toward dissociation than the heterochiral adduct **Rs**$^+$. However, comparison of $\Delta = 1.1 \pm 0.4\ \mathrm{kcal\,mol^{-1}}$ and $\Delta^+ = 1.6 \pm 0.4\ \mathrm{kcal\,mol^{-1}}$ reveals that extra stabilization due to ionization is larger for the more stable homochiral complex **Rr** (Table 1). These findings are consistent with the hypothesis of a homochiral complex **Rr**, wherein steric hindrance between the two moieties is less demanding, and therefore tightening between them after chromophore ionization is easier.

In conclusion, the 2cR2PI/TOF technique has been applied for the first time to measure the energetics of neutral and ionic diastereomeric complexes between a chiral aromatic alcohol and a chiral aliphatic alcohol in a supersonic beam. The homochiral **Rr** complex is more stable than the heterochiral **Rs** diastereomer in both the ground and excited states. The same is true for the corresponding ionic adducts. The difference in stability for the neutral adducts is attributed to different steric requirements.

Experimental Section

The experimental setup for the generation of MCs and their spectral analysis was described previously.[8] Supersonic beam production of the MCs was obtained by adiabatic expansion of a carrier gas (Ar), seeded with the corresponding alcohols **R** and **r** or **s** (Aldrich Chemical Co.), through a pulsed 400-μm nozzle kept at 85 °C. The molecular beam was allowed to pass through a 1-mm skimmer into a second chamber equipped with a TOF spectrometer. The laser system consisted of a Nd:YAG doubled in frequency ($\lambda = 532$ nm) which pumps two dye lasers. The dye frequencies were doubled and, when necessary, mixed with residual 1064-nm radiation. The ions formed by 2cR2PI ionization in the TOF source are mass-discriminated and detected by a channeltron after a 50-cm flight path. The photoionization results are corrected for the effect of the electric field strength (200 V cm^{-1}) produced by the extraction plates of the TOF spectrometer.

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Monodisperse Poly(triacetylene) Rods: Synthesis of a 11.9 nm Long Molecular Wire and Direct Determination of the Effective Conjugation Length by UV/Vis and Raman Spectroscopies**

Rainer E. Martin, Thomas Mäder, and
François Diederich*

*Dedicated to Professor Armin de Meijere
on the occasion of his 60th birthday*

The study of oligomers with precisely defined length and constitution has become an important tool for providing specific information concerning the structural, electronic, and optical properties of the corresponding polydisperse, long-chain polymeric analogues.[1, 2] A second interest in monodisperse, π-conjugated rod-like oligomers arises from their potential to function as molecular wires in molecular scale electronics and nanotechnological devices.[3] Recently, we described the synthesis of a series of monodisperse Me$_3$Si-endcapped poly(triacetylene) oligomers (PTA oligomers) that ranged from a 0.96 nm long monomeric to a 4.61 nm long hexameric rod.[4] By extrapolative evaluation of linear optical and third-order nonlinear optical data we predicted an effective conjugation length (ECL) in the range of 7 to 10 monomer units for poly(triacetylenes). The ECL[5, 6] defines the number of repeat or monomer units in a π-conjugated

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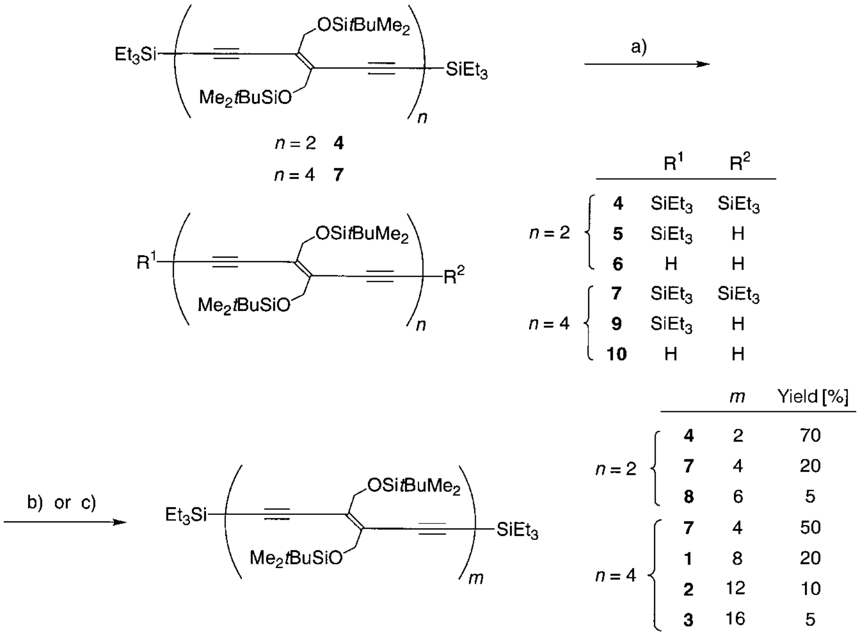
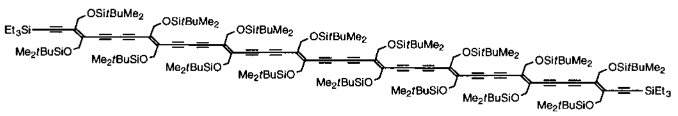
polymer that are required to furnish size-independent optical, redox, or other properties, and this concept has been quite useful in the theoretical and experimental understanding of π-conjugated polymers.



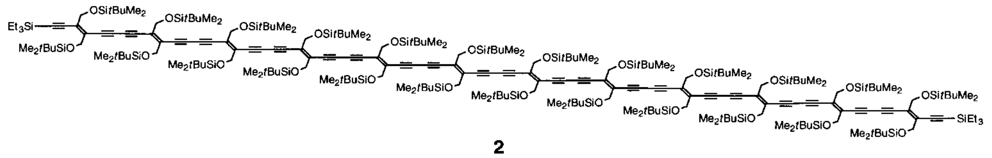
Scheme 1. Synthesis of PTA oligomers by statistical deprotection–oligomerization sequences. a) NaOH, THF/MeOH 1/1, 20 °C, 20 min. b) (for $n = 2$): CuCl, *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), CH_2Cl_2, 4-Å molecular sieves, air, RT, 2 h. c) (for $n = 4$): CuCl, TMEDA, toluene, 4-Å molecular sieves, dry O_2 atmosphere, reflux, 1 h.

To determine directly the ECL of poly(triacetylenes) experimentally[5, 7] we have now dramatically extended the oligomeric series by preparing a 6.07 nm long octameric (**1**), a 8.99 nm long dodecameric (**2**), and a 11.9 nm long hexadecameric PTA rod (**3**).[8] With its linearly conjugated 16 double and 32 triple bonds between the terminal Si atoms hexadecamer **3** is currently the longest linear, fully π-conjugated molecular wire without aromatic repeat units.[9] We also show that the direct determination of the ECL from the saturation of linear optical properties and the Raman frequency[10] of the acetylenic C≡C stretch with increasing oligomeric length is in good agreement with the initial predictions.

The synthesis of oligomers **1**–**3** started from dimer **4**, which was prepared in 97 % yield by an oxidative Hay coupling of mono-Et_3Si-protected (*E*)-3,4-bis[{(*tert*-butyl)dimethylsilyloxy}methyl]hex-3-ene-1,5-diyne (Scheme 1).[4, 11] Statistical deprotection of **4** under kinetic control with NaOH in THF/MeOH 1/1 at room temperature afforded mono-deprotected **5** and bis-deprotected **6**, besides recovered **4**, and this mixture was oligomerized directly under Hay conditions. This protocol avoided the handling and purification of the rather unstable unprotected alkynes. Reaction times for the cleavage of the Et_3Si groups in **4** were typically and reproducibly around 10 min, and product formation was monitored by thin-layer chromatography. After workup the concentrated solution was diluted with dry CH_2Cl_2 containing 4-Å molecular sieves and then TMEDA and CuCl were added. After vigorously stirring the reaction mixture (2 h) under an atmosphere of air followed by workup, the oligomers formed were purified by preparative size exclusion chromatography (SEC; 5 × 180-cm glass column filled with Bio-Beads SX-1 (Bio-Rad), CH_2Cl_2). This strategy permitted the synthesis of predominantly tetrameric **7** together with minor amounts of hexameric **8** and traces of unseparable polymers (<5 %).[11] Recovered dimer **4** was then used in the next deprotection–oligomerization cycle, thus making this route very efficient.



1



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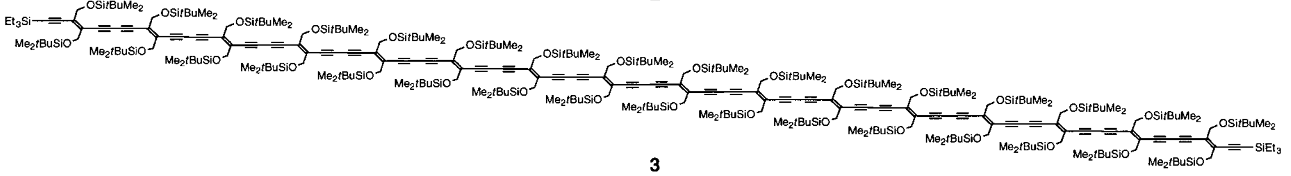

3

The same procedure starting from tetrameric **7** to produce a mixture of **7**, mono-deprotected **9**, and bis-deprotected **10** by statistical deprotection, followed by oligomerization, yielded monodisperse octameric **1**, dodecameric **2**, and hexadecameric **3** as the main products besides recovered **7**. The reaction conditions were only slightly changed, and the oligomeriza-

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tion was performed in toluene under reflux in an atmosphere of dry O_2 (see experimental section). Purification of all oligomers up to dodecameric **2** was achieved by preparative SEC as described above, whereas the isolation of pure hexadecameric **3** required preparative SEC on a commercial TosoHaas TSKgel G3000 HR column (5μm; 2.15 × 60 cm).[12] A final purification of the oligomers was achieved in each case by precipitation from MeOH followed by centrifugation. An improved synthesis of hexadecameric **3** (20% yield) used octameric **1** as the starting material in the statistical deprotection–oligomerization sequence. The larger molecular weight difference between the various oligomers obtained in this conversion greatly facilitated the SEC separation and purification of **3**.

The oligomers exhibit an increasingly deep yellow color with growing chain length; they are readily soluble in aprotic solvents such as toluene and CH_2Cl_2 but insoluble in protic solvents. The pure oligomers are highly stable for months under standard laboratory conditions, and their melting points increase in the order 69 °C (**4**), 151 °C (**7**), 183 °C (**8**), 202 °C (**1**), 219 °C (**2**), and >220 °C (**3**).

The purity of the oligomers was clearly revealed by MALDI-TOF mass spectrometry in the positive ion and linear detection mode. When using 3-(3-indolyl)acrylic acid as a matrix the hexadecameric rod **3** only displayed the molecular ion $[M+\mathrm{Na}]^+$ as the parent ion at *m/z* 6056 (6055.5 is calculated for the most abundant isotope in the molecular ion cluster, $^{12}C_{329}{}^{13}C_3H_{574}O_{32}{}^{28}Si_{31}{}^{29}Si_2{}^{30}Si^{23}Na^+$, Figure 1). No trace of the octameric starting material **1** was detected in the spectrum.

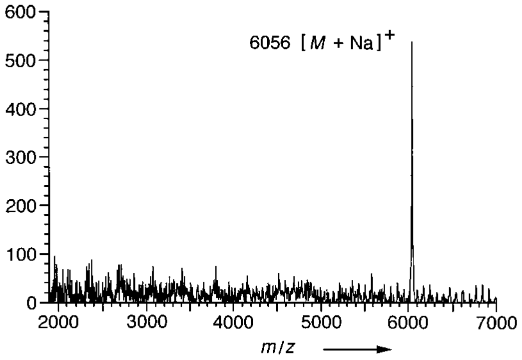

Figure 1. MALDI-TOF mass spectrum of **3** (intensity in arbitrary units, matrix: 3-(3-indolyl)acrylic acid).

The excellent solubilities of the oligomers, largely a consequence of the laterally appended $Me_2tBuSiOCH_2$ groups, allowed full characterization of the molecular rods by ^1H and ^{13}C NMR spectroscopy. Whereas the ^{13}C NMR spectrum of octameric **1** depicted 24 separate resonances for the C atoms of the conjugated backbone (8 C(sp^2) resonances between $\delta = 129$ and 133, 2 outer alkyne C(sp) resonances at $\delta = 102$ and 107, and 14 interior alkyne C(sp) resonances between $\delta = 81$ and 88), the C(sp^2) and inner alkyne C(sp) resonances in dodecameric **2** and hexadecameric **3** showed severe overlap in the expected spectral regions. This suggests that individual C(sp^2) and C(sp) atoms, respectively, begin to resemble each other electronically. The information at which point a single monomer in a conjugated polymer loses its electronic individuality is important for the determination of the chain length at which a polymer can delocalize charge carriers without that carrier experiencing end effects.[13] It is noticeable that the ^{13}C NMR resonance overlap starts at an oligomeric length (between octamer and dodecamer), which corresponds to the predicted ECL for poly(triacetylenes) by UV/Vis spectroscopy. Both NMR and IR spectra do not provide any indication for photochemical *trans*→*cis* isomerization of the molecular rods **1**–**3**;[14] we therefore have high confidence that these compounds are present in the all-*trans* configuration shown. Furthermore, X-ray crystal structure analyses on PTA oligomers revealed a preference of the planar backbones for the depicted s-*trans* conformation of the double bonds;[15] such geometry also accommodates best the bulky, lateral silyl groups.

The UV/Vis spectra of the new oligomers in $CHCl_3$ are shown in Figure 2a. The deconvoluted[16] longest-wavelength absorption maximum (λ_{max}) shifts bathochromically with increasing chain length for the shorter oligomers up to octameric **1**,[4] whereas for the higher oligomers this shift vanishes. Thus $\Delta\lambda_{max}$ upon changing from hexameric **8** to

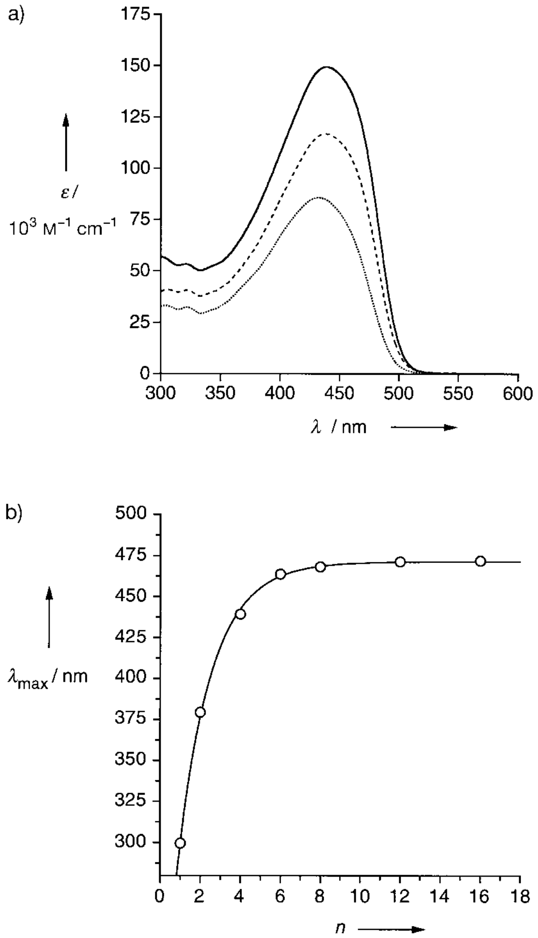

Figure 2. a) Electronic absorption spectra of the PTA oligomers in $CHCl_3$ at 20 °C. b) Convergence of the deconvoluted λ_{max} values (from the monomeric to hexadecameric rod: $\lambda_{max} = 299.6 \pm 0.1$; 379.4 ± 0.1 (**4**); 439.2 ± 0.2 (**7**); 463.7 ± 0.8 (**8**); 468.1 ± 0.8 (**1**); 471.2 ± 0.6 (**2**); 471.8 ± 0.6 (**3**)) with an overlaid exponential fit.

octameric **1** is 4 nm, from octameric **1** to dodecameric **2** is 3 nm, and finally from dodecameric **2** to hexadecameric **3** no additional increase in λ_{max} was observed (Figure 2b). From these data, the ECL in a PTA backbone can now be determined to occur around $n = 10$, thus verifying the previously estimated value of $n = 7-10$ monomeric units.[4] A more elaborated determination of the ECL by using an exponential equation[5] provided the same ECL of $n = 10$ and $b_1 = 0.594$, a parameter that indicates how "fast" the limit of convergence is reached.

Raman scattering studies of the PTA oligomers in $CHCl_3$ solutions[17] at 20°C showed an exponential decrease in the frequencies of the triple and double bond stretches $\nu_{(C\equiv C)}$ and $\nu_{(C=C)}$ with lengthening of the π-conjugated backbone. The two resonances also increase significantly in intensity with increasing chain length. From the plotted data for the acetylenic stretch (Figure 3) the ECL can be directly estimated to lie in the range of 10 monomer units, which is in excellent agreement with the UV/Vis data.

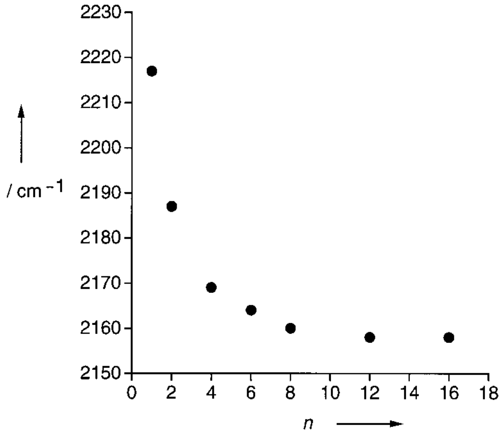

Figure 3. Plot of the Raman-active stretches $\nu_{(C\equiv C)}$ for the PTA oligomers as a function of the oligomeric length. The wavenumbers are (from the monomeric to the hexadecameric rod): $\tilde{\nu} = 2217$, 2187 (**4**), 2169 (**7**), 2164 (**8**), 2160 (**1**), 2158 (**2**), 2158 (**3**) cm^{-1}.

The SEC traces of the product mixture obtained by deprotection–oligomerization of **8** indicated that even higher monodisperse PTA oligomers, such as a 24-mer, should be stable and isolable; attempts to prepare such molecular rods of unprecedented length using the fast and efficient statistical synthetic protocol described in this communication are now under way.

Experimental Section

Synthesis of **1**–**3** from **7**: A solution of 1 M aqueous NaOH (1 mL) at 20°C was added to a solution of **7** (0.10 g, 0.059 mmol) in THF/MeOH 1/1 (30 mL). After TLC (SiO_2, n-hexane/AcOEt 40/1) indicated the appearance of bis-deprotected **10** (approximately 10 min), the reaction was immediately quenched by addition of saturated aqueous NH_4Cl (100 mL). After extraction with CH_2Cl_2 (4 × 50 mL), the collected organic phases were dried ($MgSO_4$), and concentrated at water aspirator pressure to about 10 mL. Dry toluene (20 mL) containing 4-Å molecular sieves was added followed by TMEDA (0.01 g, 0.01 mL, 0.083 mmol) and CuCl (0.002 g, 0.024 mmol). Dry O_2 was passed directly over the solution while it was heated to reflux for 1 h. After addition of a solution of EDTA (EDTA = ethylenediaminetetraacetic acid, pH 8, 100 mL), the mixture was exhaustively extracted with CH_2Cl_2, the organic phase washed with saturated aqueous NaCl (100 mL), and dried ($MgSO_4$). Concentration at water aspirator pressure, preparative SEC, and precipitation from MeOH followed by centrifugation yielded **7** (0.050 g, 50%), **1** (0.018 g, 20%), **2** (0.009 g, 10%), and **3** (0.005 g, 5%).

Analytical data for **3**: Deep yellow solid, m.p. > 220°C. UV/Vis ($CHCl_3$): λ_{max} [nm] (ε [cm^{-1}M^{-1}]): 270 (61300), 281 (61200), 301 (*sh*, 56800), 321 (53300), 439 (149400); FT-IR ($CHCl_3$) [cm^{-1}]: 2956(s), 2933(s), 2856(s), 2417(w), 2383(w), 2348(w), 1667(m), 1645(m), 1600(m), 1495(m), 1461(m), 1367(m), 1261(s), 1183(m), 1168(m), 1100(s), 1072(m), 1041(m), 1017(m), 922(w), 839(m), 811(m); Raman ($CHCl_3$): [cm^{-1}]: 3017(m), 2925(w), 2398(w), 2158(w), 1555(w), 1496(w), 1214(m), 761(m), 665(s), 364(s), 259(s); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.069$ (s, 12H), 0.075 (s, 12H), 0.083 (s, 168H), 0.62 (q, $J = 7.9$ Hz, 12H), 0.89–0.90 (m, 288H), 0.99 (t, $J = 7.9$ Hz, 18H), 4.40 (s, 4H), 4.44 (s, 56H), 4.48 (s, 4H); ^{13}C NMR (125.8 MHz, $CDCl_3$ + 20 mM [Cr(acac)$_3$]): $\delta = -5.42$, 4.03, 7.21, 18.09, 25.60, 63.59, 63.81, 81.52, 82.60–83.15 (large overlap), 84.93, 86.81, 87.10 (large overlap), 87.18, 87.40, 102.35, 107.25, 129.49, 131.69–132.19 (large overlap), 132.35, 133.08; MALDI-TOF-MS: see Figure 1; elemental analysis calcd for $C_{332}H_{574}O_{32}Si_{34}$ (6033.16): C 66.10, H 9.59; found: C 66.20, H 9.52.

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[11] All new compounds were fully characterized by their melting points, UV/Vis, IR, Raman, ^{1}H and ^{13}C NMR spectroscopies, and MALDI-

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**).

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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[**]

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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]

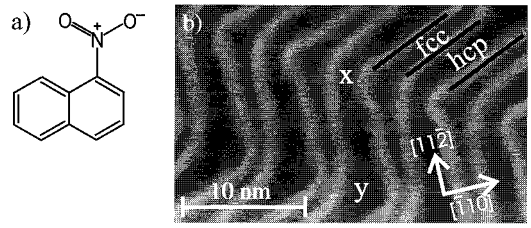

Figure 1. a) Structural formula of 1-nitronaphthalene (NN). b) STM topograph of the reconstructed Au(111) surface. Broad/narrow dark stripes correspond to domains with surface atoms in fcc/hcp positions. Two domain orientations rotated by 120° alternate and form a herringbone pattern. Two inequivalent 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 2a). 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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