A Chiral Metal Surface**

Michael Schunack, Erik Lægsgaard, Ivan Stensgaard,
Ib Johannsen, and Flemming Besenbacher*

Chirality is a property commonly associated with organic molecules, biological materials, or inorganic salts. A metal (and its associated surfaces) is normally achiral as a result of the mirror symmetry of its close-packed structures. Chirality can, however, be added to the surface by adsorbing chiral auxiliary molecules onto the substrate surface—a phenomenon often referred to as “chiral modification”. A number of recent studies have reported on the nucleation and growth of such chiral structures within the adsorbed molecular monolayer by the deposition of chiral/prochiral molecules onto the surface of an achiral substrate.[1] Chiral surfaces are generally of great interest in fields such as heterogeneous, asymmetric catalysis and chemical sensors, and for studying the separation of chiral compounds and nonlinear optical materials.[2]

Earlier attempts to create a chiral metal surface tried to exploit the chirality of a homochiral substrate material such as quartz to transfer the chirality to a deposited metal film.[3] Single-crystal metal surfaces with a low Miller index, for example, {100}, {110}, or {111} surfaces, consist of atomically flat terraces that are separated by step edges where one atomic plane meets the next. These step edges contain a certain fraction of so-called kink sites, and it was recently pointed out that such kink sites possess an intrinsic chirality.[4, 5] Surfaces that exclusively contain kink sites of a specific chirality can be formed by cutting single crystals along certain high Miller index directions (see below).[4–6] A recent study indicated that adsorption of L-lysine onto an achiral Cu(100) surface may lead to the partial formation of chiral kink sites at step edges during a step-facetting process.[7]

Herein we report how the adsorption of molecules can bestow chirality onto the extended flat terraces of a single-crystal surface. The chirality is caused by a pronounced surface-restructuring that is induced chemically by the adsorption of chiral molecules. This is revealed directly on the atomic scale by intentionally pushing the molecules aside by means of scanning tunneling microscopy (STM): we find that at full coverage every molecule is associated with a chiral hole in the underlying surface. The observed molecule–hole complexes extend homogeneously over the entire surface and segregate spontaneously into enantiomorphic domains upon gentle annealing, thereby creating a perfectly ordered chiral metal surface.

The molecule–surface system under investigation is 2,5,8,11,14,17-hexa-(*tert*-butyl)decacyclene molecules (HtBDC, $C_{60}H_{66}$) adsorbed on a Cu(110) surface (Figure 1 A). The overall conformation of the molecule in the gas phase is determined by the steric repulsion of the 3/4, 9/10, and 15/16 hydrogen atoms at the peripheral naphthalene groups which leads to a distortion of the molecule. This process results in local conformations, where, for example, the 3-hydrogen atom is located above or below the adjacent 4-hydrogen atom, and is referred to as local A or B conformation, respectively. The three pairs of interacting hydrogen atoms result in the existence of four stereoisomers: AAA, BBB, ABA, and BAB.[8] The two sets AAA/BBB and ABA/BAB are both enantiomers. The first conformation leads to a chiral propeller-shaped molecule with D_3 symmetry (Figure 1 B),[9] whereas the second conformation leads to a boat-shaped molecule that is slightly distorted from the achiral C_s symmetry (Figure 1 C). Simple force-field calculations indicate that the second conformation has a 0.13 eV higher energy than the D_3-symmetric molecule.[10]

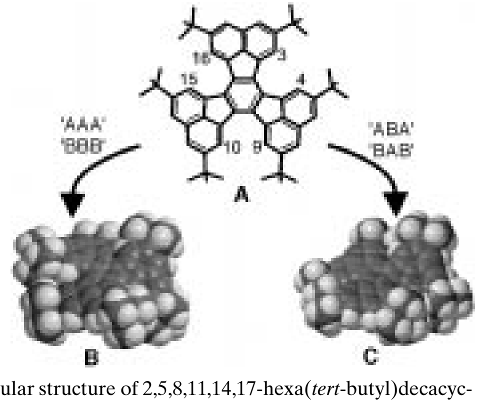

Figure 1. A) Molecular structure of 2,5,8,11,14,17-hexa(*tert*-butyl)decacyclene (HtBDC). Space-filling model of the two low-energy conformations: B) propeller shape of the AAA/BBB conformation, and C) boat shape of the ABA/BAB conformation.[19] The numbers label the positions of the interacting hydrogen atoms that lead to the local A and B conformations (see text for details).

At room temperature (RT) individual HtBDC molecules are highly mobile on the planar Cu(110) surface and diffuse rapidly at the timescale of STM imaging (seconds). The molecules primarily decorate the steps at low coverages, but linear islands of molecules nucleate randomly on the terraces above a certain coverage (Figure 2 A). The islands consist of double rows of molecules aligned along the symmetry-equivalent $[\bar{1}1\bar{2}]$ and $[\bar{1}12]$ directions of the Cu(110) surface and fluctuate in size, as seen from STM movies.[11] The diffusion of the molecules is frozen out at low sample temperatures (< 150 K), and individual molecules are imaged as six lobes arranged in a distorted hexagon with threefold rotational symmetry. Each lobe corresponds to a tunnel-current contribution of the *tert*-butyl groups, as confirmed by elastic-scattering quantum chemistry calculations (Figure 2 A).[12]

---

[*] Prof. Dr. F. Besenbacher, M. Schunack, Dr. E. Lægsgaard,
Prof. Dr. I. Stensgaard
CAMP and Institute of Physics and Astronomy
University of Aarhus
Ny Munkegade, 8000 Aarhus C (Denmark)
Fax: (+45) 86120740
E-mail: fbe@ifa.au.dk

Dr. I. Johannsen
The Danish Polymer Centre
Risø National Laboratory, 4000 Roskilde (Denmark)

[**] We would like to acknowledge fruitful discussions with Trolle Linderoth as well as the financial support from the Danish National Research Foundation through the Center for Atomic-scale Materials Physics (CAMP), from the VELUX Foundation, and from the EU networks “Manipulation of individual atoms and molecules” and “Bottom up Nanomachines”.

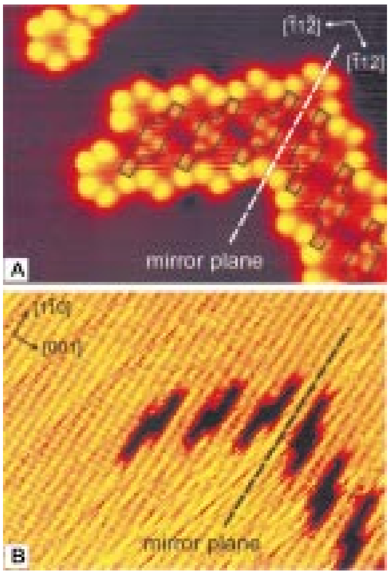

Figure 2. A) Constant current images (110×82 Å^2) of the HtBDC double-row structure and immobilized single molecules at 25 K ($V = 1250$ mV, $I = 0.42$ nA). Holes in the restructured surface are framed black. B) Holes underneath the molecules after pushing the molecules aside. The holes consist of approximately 14 Cu atoms expelled from the surface in two adjacent [$1\bar{1}0$] rows ($V = 10$ mV, $I = 1.78$ nA).

We have recently shown that molecules can be pushed away by operating the STM tip in manipulation mode.[13] This enabled us to directly examine the underlying Cu(110) surface, which revealed a pronounced restructuring into a characteristic trench-base structure: 14 Cu atoms are dug out of the surface to which the molecules are anchored (Figure 2B). These holes explain the variation in the intensity of the six lobes of the molecules within the molecular double rows: the dimmer lobes correspond to *tert*-butyl groups located on top of a hole.[13]

The holes formed in the surface contain kink sites and are therefore chiral, as explained in the following. The chirality of kink sites and the nomenclature according to Ahmadi et al. are shown in Figure 3A and B.[5] When the surface is viewed from above, a kink site is of *R* configuration if the sequence of the surface orientations meeting at the kink site runs clockwise in the order {111}-{100}-{110} (corresponding to a decreasing density of atoms in the topmost layer) and of *S* configuration if the orientation runs counter-clockwise.[14] As shown in Figure 3C the holes contain either two *R* or two *S* kinks, which in the following are referred to as *RR* and *SS* holes, and are consequently chiral, that is, nonsuperimposable by simple translation or rotation.

The imaging of the double-row structures seems to reflect the molecules' different conformations (Figure 4). All molecules along the [$\bar{1}1\bar{2}$] rows are imaged identically and reflect a certain conformation, whereas the molecules along the [$\bar{1}12$] rows have the enantiomorphic conformation—the molecules within a given double row are superimposable by a 180° rotation. Hence, the two molecule conformations are chiral and nonsuperimposable. If we tentatively assume that the STM images of the molecules can be interpreted as simple geometric height corrugations, then the molecules along the rows correspond to the AAA and BBB conformations: three bright and three dim lobes of the molecules reflect the two sets of three *tert*-butyl groups lying in two parallel planes, as seen in the propeller conformation model in Figure 1B. Within this interpretation the molecules at the elbows interconnecting the rows thus correspond to the (achiral) ABA conformations: The four bright and two dim lobes (or two bright and four dim lobes) reflect the two sets of four and two *tert*-butyl groups lying in two parallel planes (see the model of the boat conformation in Figure 1C). We must, however, keep in mind that, in principle, STM images do not simply reveal geometrical height contours.[15]

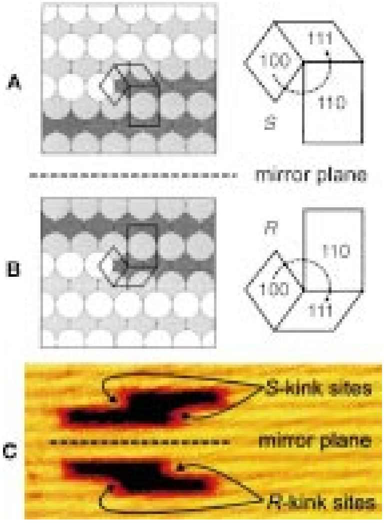

Figure 3. Illustration of chirality and nomenclature of kink sites on an fcc{110} surface.[5] The black frames in the ball models mark the unit cells of the three surface orientations—(100), (110), and (111)—involved in the kink formation, as labeled in the enlarged drawings (see text for details). A) *S* configuration; B) *R* configuration; C) STM image of the two hole types which demonstrates the positions of the kink sites.

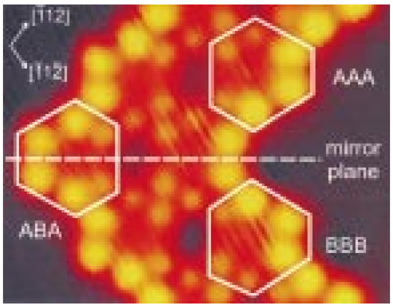

Figure 4. STM images of the double-row structure. Chiral AAA and BBB conformations along the rows and achiral ABA conformation in the elbows are indicated.

We speculate that the chirality of the Cu surface is imprinted into the surface by the chiral molecules: the adsorption of chiral molecules on top of chiral holes leads to diastereomeric complexes with different interaction energies. The AAA (BBB) conformation may, for example, have a lower interaction energy with an *RR* (*SS*) hole than with an *SS* (*RR*) hole. Accordingly, one type of enantiomeric hole will be decorated with one and only one enantiomeric conformation of the molecule. It would therefore be very interesting to perform theoretical STM simulations of the different conformations and compare them with the experimental findings.

1433-7851/01/4014-2624 $ 17.50+.50/0

Figure 5 depicts the growth of HtBDC molecules on the Cu(110) surface at increasing coverage (measured in monolayers (ML), where 1 ML is defined as the number of atoms per unit area in the unreconstructed Cu surface layer). Since the HtBDC molecules are fairly large (diameter ≈ 15 Å), a saturated molecular overlayer only corresponds to a coverage of approximately 0.03 ML (see below).

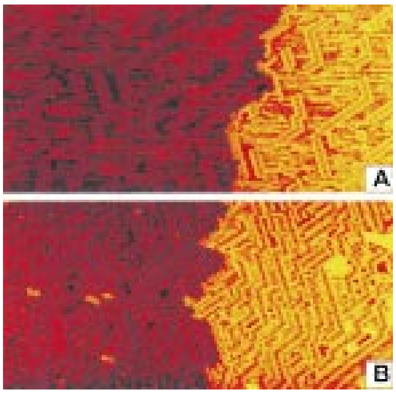

Figure 5. Constant current STM images at RT with increasing coverages of zigzagged HtBDC rows (1000×500 Å^2, $V = 1250$ mV, $I = 0.55$ nA): A) approximately 0.01 ML; B) approximately 0.03 ML.

The molecular rows grow in length and density with increasing coverage, and the zigzag rows, which alternate irregularly along the $[\bar{1}1\bar{2}]$ and $[\bar{1}12]$ direction, eventually cover the entire surface (Figure 5). If this unordered saturated overlayer is annealed at 410 K for around 10 min, uniform domains with diameters in the range of 100–1000 Å build up. Each of these domains consists of densely packed rows along the $[\bar{1}1\bar{2}]$ or $[\bar{1}12]$ direction exclusively (Figure 6 A), which demonstrates that the straight double-row structure is indeed thermodynamically stable and energetically preferred over the zigzagged rows.

A model of the ordered, saturated structure is sketched in Figure 6 B, and shows the commensurable superstructure of the molecules. A unit cell contains two HtBDC molecules and 64 Cu atoms, that is, the saturated coverage is $2/64 \approx 0.031$ ML. We conclude from the unequivocal correlation between the row direction and the hole type underneath,[16] that the holes within a given domain are all alike and hence the domains are homochiral. Moreover, *every* molecule is connected with a chiral kink site. This occurrence demonstrates how the molecules induce chirality to the extended terraces of the metal crystal surface.

Since a domain contains molecules of one enantiomeric conformation exclusively, an explanation of how the two conformations separate into domains, namely, how the adsorbate layer rearranges from unordered zigzag rows (=racemic conglomerate) into large chiral domains (=racemic compounds), is necessary. Separation by diffusion seems rather unlikely because of the dense packing. A local rearrangement seems, however, possible as a result of the low inversion energy between the HtBDC conformations AAA and BBB.[17] At the same time the holes underneath the molecular layer in the Cu surface can easily be converted from *RR* into *SS* by diffusion of Cu atoms. The overall surface is racemic, because of the conformational flexibility of the HtBDC molecules, and consists of equal amounts of both domains. We propose that an overall homochirally restructured surface may be obtained by using slightly modified HtBDC molecules where, for example, surrounding groups larger than *tert*-butyl groups force the molecule to be conformationally fixed in the AAA or BBB form.

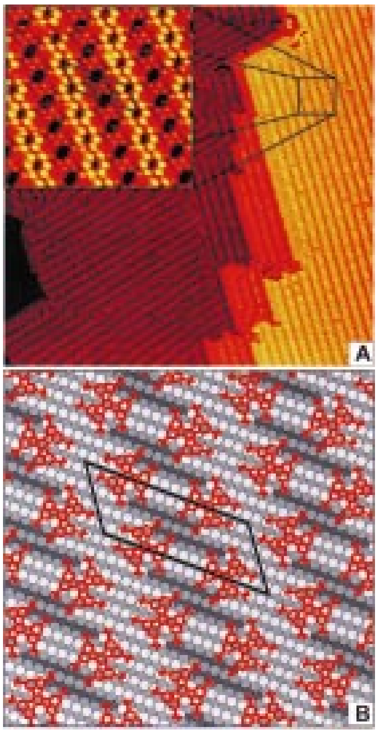

Figure 6. Constant-current STM image at RT after annealing the fully covered surface (see Figure 5 B) at 410 K. A) Domains of densely packed molecules along the $[\bar{1}1\bar{2}]$ and $[\bar{1}12]$ directions (1000×1000 Å^2, $V = 1250$ mV, $I = 0.51$ nA). The inset shows a close-up of a domain (100×100 Å^2, $V = 1768$ mV, $I = 0.30$ nA): the $\left(\begin{smallmatrix} 4 & 4 \\ 16 & 0 \end{smallmatrix}\right)$ unit cell and the hole contour are framed black. B) Ball model of the double-row structure—the substrate atoms are shaded darker whenever the layers lie deeper. The molecules are shown in red and the unit cell is framed black.

In conclusion, we have shown that the adsorption of chiral molecules can bestow chirality onto the extended, flat metal terraces. Previously, chiral surfaces have mainly been formed by adsorbing chiral molecules onto an (unreconstructed) achiral surface, thus forming molecular overlayer domains which are chiral. Our finding of chirality in a metal surface itself may shed new light on the mechanistic understanding of the catalytic behavior of chirally modified surfaces. Catalytic surfaces are generally considered as a static checkerboard providing adsorption sites for the chiral auxiliary and the reactants, while we have shown that a chiral restructuring of the substrate surface may have to be taken into account.

Experimental Section

The experiments were performed in an ultrahigh vacuum (UHV, base pressure $< 10^{-10}$ mbar) chamber equipped with a home-built low- and variable-temperature STM capable of operating at 25–400 K.[18] The Cu(110) surface was cleaned by cycles of 2.0 keV Ne ion bombardment followed by annealing at 820 K.

The HtBDC powder was degassed in UHV at 400 K for several hours prior to use. The molecules were dosed in UHV onto the clean Cu(110) surface by organic molecular beam deposition out of a resistively heated glass crucible at 450 K with a deposition rate of around 0.0001 ML s^{-1}. The substrate was kept at RT. The amount of dosed HtBDC molecules on the surface was controlled by keeping the crucible temperature constant and varying the exposure time (5 – 600 s). The STM images at low temperatures were obtained by cooling the sample down to the desired temperature after the deposition of the molecules at RT.

Received: February 13, 2001
Revised: April 20, 2001 [Z 16608]

---

[1] a) F. Stevens, D. J. Dyer, D. M. Walba, *Angew. Chem.* **1996**, *108*, 955; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 900; b) G. P. Lopinski, D. J. Moffatt, D. D. M. Wayner, R. A. Wolkow, *Nature* **1998**, *392*, 909; c) M. O. Lorenzo, C. J. Baddeley, C. Muryn, R. Raval, *Nature* **2000**, *404*, 376; d) F. C. De Feyter, P. C. M. Grim, M. Rücker, P. Vanoppen, C. Meiners, M. Sieffert, S. Valiyaveettil, K. Müllen, F. C. De Schryver, *Angew. Chem.* **1998**, *110*, 1281; *Angew. Chem. Int. Ed.* **1998**, *37*, 1223; e) M. Böhringer, K. Morgenstern, W.-D. Schneider, R. Berndt, *Angew. Chem.* **1999**, *111*, 832; *Angew. Chem. Int. Ed.* **1999**, *38*, 821; f) J. V. Barth, J. Weckesser, C. Cai, P. Günther, L. Bürgi, O. Jeandupeux, K. Kern, *Angew. Chem.* **2000**, *112*, 1285; *Angew. Chem. Int. Ed.* **2000**, *39*, 1230.

[2] a) *Chiral Reactions in Heterogeneous Catalysis* (Eds.: G. Jannes, V. Dubois), Plenum, New York, **1995**; b) H. U. Blaser, *Tetrahedron: Asymmetry* **1991**, *2*, 843; c) A. Baiker, H. U. Blaser in *Handbook of Heterogeneous Catalysis, Vol. 5* (Eds.: G. Ertl, H. Knözinger, J. Weitkamp), Wiley-VCH, Weinheim, **1997**, p. 2422; d) L. Hecht, L. Barron, *Chem. Phys. Lett.* **1994**, *225*, 525.

[3] a) G. M. Schwab, L. Rudolph, *Naturwissenschaften* **1932**, *20*, 363; b) G. M. Schwab, F. Rost, L. Rudolph, *Kolloid Z.* **1934**, *68*, 157; c) K.-H. Ernst, M. Böhringer, C. F. McFadden, P. Hug, U. Müller, U. Ellerbeck, *Nanotechnology* **1999**, *10*, 355.

[4] C. F. McFadden, P. S. Cremer, A. J. Gellman, *Langmuir* **1996**, *12*, 2483.

[5] A. Ahmadi, G. Attard, J. Feliu, A. Rodes, *Langmuir* **1999**, *15*, 2420.

[6] a) D. S. Sholl, *Langmuir* **1998**, *14*, 862; b) T. D. Power, D. S. Sholl, *J. Vac. Sci. Technol. A* **1999**, *17*, 1700; c) G. Attard, A. Ahmadi, J. Feliu, A. Rodes, E. Herrero, S. Blais, G. Jerkiewicz, *Phys. Chem. B* **1999**, *103*, 1381.

[7] X. Zhao, *J. Am. Chem. Soc.* **2000**, *122*, 12584.

[8] Permutations of ABA and BAB reproduce the same molecule rotated by ±120°.

[9] D. M. Ho, R. A. Pascal, Jr., *Chem. Mater.* **1993**, *5*, 1358.

[10] K. Zimmermann, R. Goddard, C. Krüger, M. W. Haenel, *Tetrahedron Lett.* **1996**, *37*, 8371.

[11] See movie at http://www.ifa.au.dk/camp/movies/htbdc.mpg. General remarks about STM movies can be found in F. Besenbacher, *Rep. Prog. Phys.* **1996**, *59*, 1737.

[12] J. K. Gimzewski, C. Joachim, R. R. Schlittler, V. Langlais, H. Tang, I. Johannsen, *Science* **1998**, *281*, 531.

[13] M. Schunack, L. Petersen, A. Kühnle, E. Lægsgaard, I. Stensgaard, I. Johannsen, F. Besenbacher, *Phys. Rev. Lett.* **2001**, *86*, 456.

[14] This terminology is in analogy with the Cahn – Ingold – Prelog sequence rule for chiral substances, see, for example, F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry*, *Part A*, 3rd ed., Plenum, New York, **1990**, chap. 2.

[15] a) P. S. Weiss, D. M. Eigler, *Phys. Rev. Lett.* **1993**, *71*, 3139; b) P. Sautet, M.-L. Bocquet, *Phys. Rev. B* **1996**, *53*, 4910; b) P. Sautet, *Chem. Rev.* **1997**, *97*, 1097.

[16] The correlation was confirmed by manipulating several molecular double-row structures and checking the restructuring underneath. Attempts to push molecules away from densely packed domains did not succeed in resolving the underlying restructured surface directly.

[17] The activation energy for the inversion of the closely related decacyclene molecule was calculated to be only 0.13 eV; see ref. [9].

[18] L. Petersen, M. Schunack, B. Schaefer, T. R. Linderoth, P. B. Rasmussen, P. T. Sprunger, E. Lægsgaard, I. Stensgaard, F. Besenbacher, *Rev. Sci. Instrum.* **2001**, *72*, 1438.

[19] The conformations in Figure 1 B and C are derived from molecular-mechanics force-field calculations using the Titan software from Wavefunction, Inc.

Organophosphorus Dendrimers as New Gelators for Hydrogels

Christelle Marmillon, Fabienne Gauffre, Tadek Gulik-Krzywicki, Christophe Loup, Anne-Marie Caminade,* Jean-Pierre Majoral,* Jean-Pierre Vors, and Elmar Rump

Owing to their numerous applications in different fields (cosmetics, health care, textile, paper, packaging, oil field, photographic industry, etc) gels continue to attract considerable attention.[1] They can be considered as composite materials made of a three-dimensional (3D) supramolecular network imprisoning a large quantity of liquid. The driving force for the formation of gels can be van der Waals, hydrophobic, fluorophobic, $\pi-\pi$ stacking, dipole – dipole, weak coordination interactions, or hydrogen bonds. A number of small molecules are able to form gels such as steroids, fatty acids, copper chelates, fluorinated alkanes, peptides, cyclic dipsipeptides, anthracene derivatives, amino pyridines, calixarenes. More sophisticated macromolecules such as bisarborols (bidirectional molecules with a lipophilic central chain substituted on the end with polyalcohol groups) were found to act also as gelators in water[2] or in hot solvent mixtures such as ethanol/water or dimethylformamide/water.[3] Very recently Aida et al.[4] described the formation of physical gels in acetonitrile with peptide core dendrimers.

Herein we report the first examples of the use of hydrosoluble dendrimers as new gelators in water that allow the confinement of a variety of organic and organometallic substances under very mild conditions.

Polycationic dendrimers **3-[G$_0$]** – **3-[G$_4$]** (P(S) core, generation 0 to 4, pyridinium chloride as terminal groups), **4-[G$_0$]** – **4-[G$_4$]** (P(S) core, ammonium chloride as terminal groups), **6-[G$_2$]** (P_3N_3 core, pyridinium chloride as terminal groups) are prepared in quantitative yield by reacting the corresponding dendrimers **1-[G$_0$]** – **1-[G$_4$]** or **2-[G$_2$]**[5] (terminal aldehyde groups) with either Girard-P reagent or Girard-T reagent in methanol (Scheme 1). The polycationic dendrimer **5-[G$_1$]** (P(S) core, pyridinium acetate as terminal groups) is obtained by anion exchange from **3-[G$_1$]** and sodium acetate. All dendrimers are characterized as a mixture of isomers around the terminal CH=N–NH–C(O)–CH$_2$ linkage as shown by ^{13}C NMR spectroscopy. Indeed two signals are detected at $\delta = 61.8-63.0$ for the terminal CH$_2$ groups and at $\delta = 162.3-168.1$ for the carbonyl groups. ^{1}H NMR spectra confirm the

---

[*] Dr. A.-M. Caminade, Dr. J.-P. Majoral, Dr. C. Marmillon,
Dr. F. Gauffre, C. Loup
Laboratoire de Chimie de Coordination, CNRS
205 route de Narbonne, 31077 Toulouse cedex 04 (France)
Fax: (+33) 5-61-55-30-03
E-mail: caminade@lcc-toulouse.fr, majoral@lcc-toulouse.fr

Dr. T. Gulik-Krzywicki
Centre de Génétique Moléculaire, CNRS
91198 Gif-sur-Yvette (France)

Dr. J.-P. Vors, Dr. E. Rump
Aventis Crop Science
14-20 rue Pierre Baizet, BP 9163, 69263 Lyon cedex 09 (France)

Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.