Supramolecular Chemistry

DOI: 10.1002/ange.200501467

Conservation of Chirality in a Hierarchical Supramolecular Self-Assembled Structure with Pentagonal Symmetry**

Marie-Christine Blüm,* Elizabeta Ćavar, Marina Pivetta, François Patthey, and Wolf-Dieter Schneider

Molecular and supramolecular chiral recognition governs fundamental processes in living systems.[1] Its importance for disciplines such as biology, pharmaceutics, chemistry, and physics stems from the different properties the two chiral forms exhibit in the presence of chiral phenomena, such as, for example, chiral enzymes and drugs,[2] β-rays,[3] circularly polarized light,[4] and spin-polarized electrons.[5] The differ-

---

[*] M.-C. Blüm, E. Ćavar, Dr. M. Pivetta, Dr. F. Patthey,
Prof. Dr. W.-D. Schneider
Ecole Polytechnique Fédérale de Lausanne (EPFL)
Institut de Physique des Nanostructures
1015 Lausanne (Switzerland)
Fax: (+41) 21-693-0422
E-mail: marie-christine.bluem@epfl.ch

[**] We thank Alessandro de Vita and Massimiliano Stengel for stimulating discussions. This work was supported financially by the Swiss National Science Foundation.

ences in physical and chemical characteristics should become important for the design of molecular electronic and optoelectronic devices.[6] The first steps have been made through the study of the self-organizing behavior of chiral organic molecules by scanning tunneling microscopy (STM) and the determination of the chirality of individual molecules and supramolecular assemblies.[7] Herein we present the first direct observation of all stages of a nested self-assembly of π-conjugated chiral molecules into cyclic supramolecular structures. We have followed by STM the hierarchical self-organization of single molecules into individual pentagonal supermolecules which then act as building blocks for the formation of supramolecular decagons. We show the spontaneous chiral resolution of the racemate into disjointed homochiral complex architectures and demonstrate the possibility to monitor directly the evolution of chiral recognition processes on the molecular and supramolecular level.

The aromatic hydrocarbon 5,6,11,12-tetraphenylnaphthacene (rubrene, $C_{42}H_{28}$) is chiral and nonplanar as a result of intramolecular steric hindrance[8] which causes a twisting of the central tetracene backbone around its axis and forces the four phenyl groups to rotate around their σ bonds (Figure 1 a). Its highly efficient luminescence can be induced by a variety of methods, such as incident light,[9] chemical reactions,[10] and electronic excitation. The latter property established the success of rubrene as a dopant for organic light emitting diodes which led to the improvement of the efficiency and stability of the devices.[11] The high charge carrier mobility measured on the surface of the crystals[12] led to their integration into organic field-effect transistors[13] that can be switched by light[14] as a consequence of the reversible photooxidation behavior of the molecule.[15] Despite this growing interest in the application of rubrene, there have been no investigations of the self-assembly process and the molecular and supramolecular chirality of rubrene at the nanoscale.

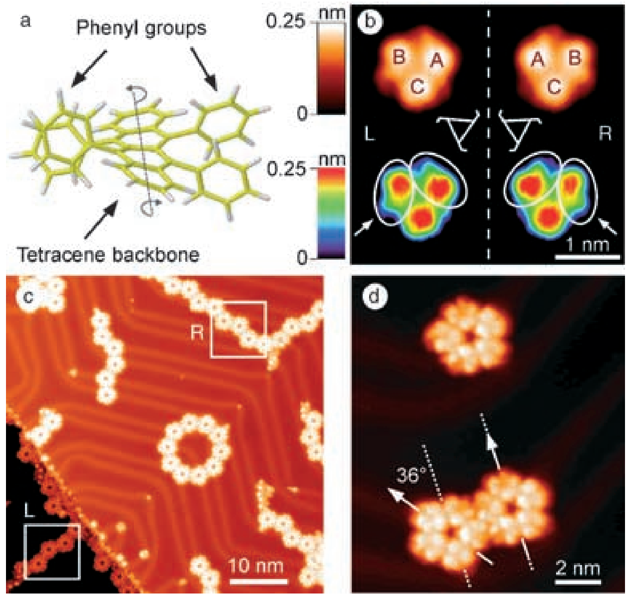

Figure 1. Monomers and self-assembled structures of rubrene on gold. a) Twisted 3D conformation of rubrene in the gas phase. b) STM image of two adsorbed monomers of opposite chirality represented in two different color codings. The arrows indicate the shoulders of feature B for the two enantiomers L and R. c) STM image showing the supramolecular structures on the herringbone-reconstructed Au(111) surface. Two terraces separated by a monatomic step are visible. The squares denoted L and R indicate areas shown in Figure 2 c and d, respectively. d) STM image of an isolated supramolecular pentagon and two interlocked supermolecules resembling gear wheels.

Figure 1 b shows an STM image of two individual molecules of rubrene adsorbed on an Au(111) surface. Three unequally shaped features (denoted by A, B, and C) with an apparent height of approximately 0.25 nm can be detected in each molecule. The monomer on the left has a counterclockwise arrangement of these lobes (BAC), while the one on the right follows a clockwise orientation (ABC), thus the molecules are mirror images of each other and reflect the chiral conformation of the molecule in the gas phase. The same STM image represented in a different color coding in the lower part of Figure 1 b reveals the existence of shoulders (green/blue bulges) belonging to the features A and B which appear either on the left side of each maximum or on the right side, as viewed from the center of the molecule. This characteristic arrangement of asymmetric features determines the molecular chirality and allows the classification of the adsorbed molecules as L or R enantiomers, as shown schematically by the chiral triangles. The independence of these features on an applied voltage between −2 V and +2 V indicates that a modulation of the electronic substrate states by broadened molecular levels gives rise to the observed molecular contrast,[16] thus suggesting that the characteristic appearance of the molecules in the STM images reflects their nonplanar and twisted conformation.

The spontaneous self-assembly of single rubrene molecules results in the formation of complex supramolecular structures (Figure 1 c). The STM image shows disjointed chains and rings which are constructed out of small building blocks. These structures are incommensurate with the hexagonal periodicity of the Au(111) substrate, but are stabilized by the domain walls of the herringbone-reconstructed surface and at step edges. A smaller scale image reveals that the observed building units of the supramolecular chains are molecular assemblies on their own (Figure 1 d). More interestingly, they contain exactly five molecules which are linked into a pentagonal supermolecule with a radius of 1 nm. The appearance of regular pentagons in our experiment is very surprising, given that C_5 symmetries are mainly found in living organisms, but are a rarity in nonliving matter because of the impossibility of a periodic space-filling arrangement with pentagons. Supramolecular self-assembly of adsorbed molecules is the result of a competition between molecule–substrate interactions and noncovalent intermolecular attractions arising from van der Waals forces, hydrogen bonds, and electrostatic interactions. The absence of any permanent dipole in the molecule and the chemical structure of rubrene suggest that the observed self-assembly is the result of an interplay of van der Waals forces and CH⋯π hydrogen bonds. The incommensurability of the structures rules out site-specific bonding to the surface and indicates that the observed supramolecular assembly is determined by intermolecular forces.

A new level of supramolecular self-assembly is reached by a second organization step that follows the first assembly into stable fivefold structures (Figure 1 d). The pentagonal supermolecules diffuse on the surface in a similar manner as the individual molecules and link to each other to form nanometer-sized gearlike wheels. This interlocking of the supermolecules is realized by one pentagonal gear wheel rotating by exactly 36° with respect to the other, which leads to a final distance of approximately 3 nm between their centers. This assembly of two individual supramolecular entities results in a stable individual structure to which other pentagons can join to build supramolecular architectures of higher complexity.

A fascinating aspect of this progression of supramolecular structures is that the molecular chirality is conserved and transferred to the next higher organizational level. A detailed analysis of the pentagonal supermolecules from the first assembly step reveals the existence of two different types of fivefold structures. Pentagons are found that consist of five L-type molecules (Figure 2 a), while others are made out of five R-type molecules (Figure 2 b). This observation shows that the spontaneous self-assembly of the individual chiral molecules is enantioselective, and results in two versions of homochiral pentagons. Furthermore, each molecule in the structures is rotated by approximately 14° around its center to optimize the interlocking between the molecules (Figure 2 a,b). The direction of rotation is dependent on the molecular chirality: counterclockwise for the L-type molecules and clockwise of the R-type species. This rotation of the molecules, together with the homochirality of the whole assembly, results in the creation of L-type and R-type pentagons (Figure 2 a, Figure 2 b). The impact of this chiral property on the second step of self-assembly results in the formation of nested chiral structures. STM images of supramolecular chains (Figure 2 c,2 d) clearly demonstrate that chirality is conserved in the spontaneous interlocking of pentagonal supermolecules. This observation proves that the two enantiomers of the molecule, as well as the pentagonal supermolecules, are not acting equally in the bonding process as this would result in chirally mixed supramolecular architectures. On the contrary, chiral recognition is of decisive importance for the supramolecular self-assembly and results in a spontaneous self-resolution of the original racemic mixture into nanometer-sized homochiral architectures.

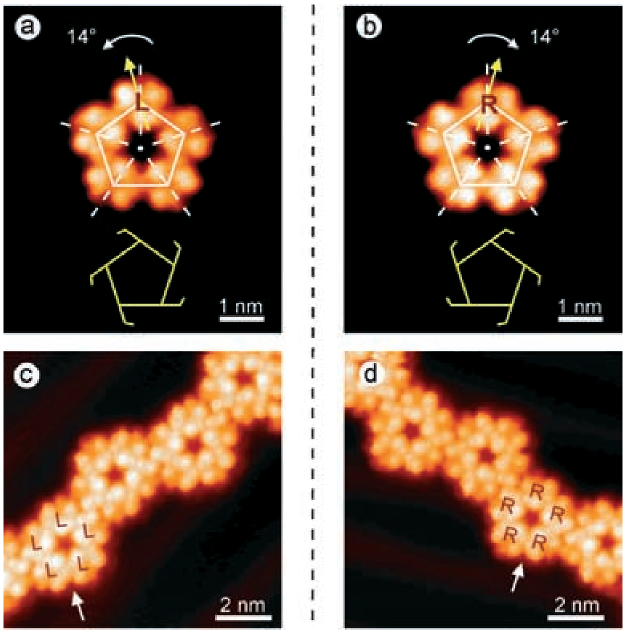

Figure 2. STM images of the enantioselective self-assembly into left- and right-handed supramolecular structures that are mirror images. a, b) Chiral pentagons formed by L-type (a) and R-type (b) molecules, rotated into opposite directions around their centers. c, d) Magnified image of the areas indicated in Figure 1 c. Self-assembled chiral chains of interlocked L-type (c) and R-type (d) pentagons.

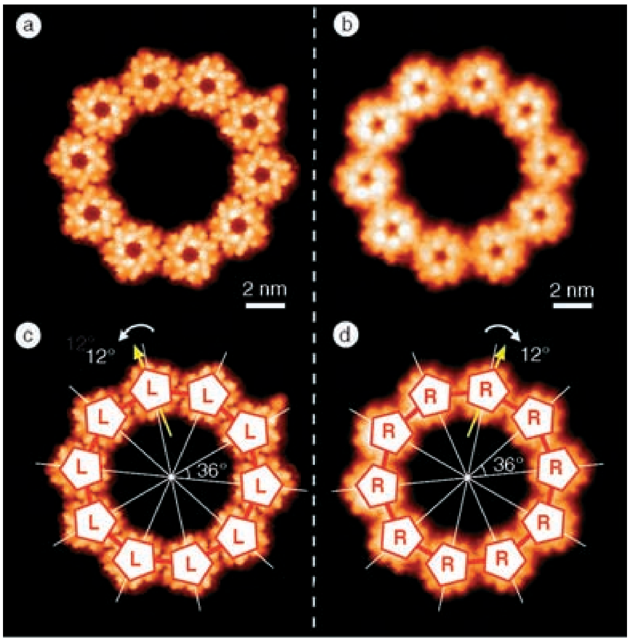

Figure 3. Formation of chiral supramolecular decagons of pentagonal supermolecules. a, b) STM images of a left-handed (a) and a right-handed (b) homochiral decagon. c, d) Construction of the decagons out of ten counterclockwise rotated L-type pentagons (c) and clockwise rotated R-type pentagons (d).

An entirely new and especially beautiful result of the enantiomerically pure self-organization is the creation of a second generation of cyclic size-defined structures (Figure 3). These planar decagons are composed of ten pentagonal supermolecules of the same chirality and rotated by approximately 12° around their centers. The orientation of the rotation depends on the chirality of the pentagonal building blocks and determines the chirality of the decagons (Figure 3 a, Figure 3 b). The overlaid picture in Figure 3 c describes the finding that the decagon shown is a homochiral assembly of exclusively L-type pentagonal supermolecules. Since each pentagon is constructed out of five L-type molecules, we obtain a hierarchically organized architecture of 10 × 5 = 50 molecules of the same chirality. This fact, together with the counterclockwise orientation of each pentagon, yields an L-type chirality of the tenfold supramolecular structure. The creation of the mirror image of this chiral pattern, namely the R decagon made out of clockwise-rotated R pentagons, is the result of analogous but mirrored building rules as the L-type structure (Figure 3 d). The rotation of neighboring pentagonal supermolecules by 36° illustrates that the chiral supramolecular decagons are a special result of the formation of supramolecular chains. The white arrows in Figure 2 c and d indicate the docking sites the last pentagons of the chains would have to take to continue the arclike arrangement of the three previous ones. If ten such chirally selected pentagons join together in this way, their assembly leads to the construction of a supramolecular decagon with a diameter of 10 nm. In contrast to the combination of the first three pentagons, which always construct the basis for a cycle, the arriving supermolecules from the forth unit on have only a 50 % chance of occupying the "correct" site. This reduces the probability for the development of a complete decagon to less than 1 %, a value which explains the rarity of these nested patterns.

Our results demonstrate the surprising hierarchical complexity of the two-dimensional supramolecular assembly of rubrene on gold (Figure 4 a). We have identified its three successive generations: single molecules, pentagonal supermolecules, and supramolecular decagons. The chirality of the individual molecules is conserved in both assembly steps, and both resulting generations of the progression are chiral as a result of the chirality-dependent rotation of the building blocks (Figure 4 b). Since this self-organization of increasing complexity is enantioselective on the molecular and supramolecular level, we obtain a spontaneous resolution of the original racemic mixture of individual molecules into homochiral architectures. Our findings on the conservation and recognition of chirality at all stages of the supramolecular self-assembly of rubrene may have an impact on the development of chiral molecular electronic and optoelectronic devices, and exemplify the working principle of basic processes in nature.

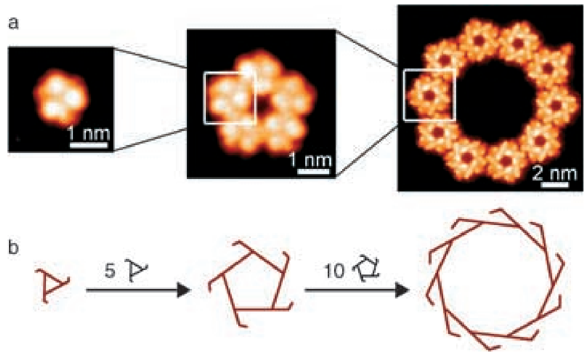

Figure 4. Hierarchy and conservation of chirality in the spontaneous two-dimensional supramolecular assembly. a) STM images representing the three generations of the nested two-staged self-organization. b) Enantioselective assembly from L-type monomers to L-type pentagons and further on to L-type decagons.

Experimental Section

Experiments were performed using a home-built scanning tunneling microscope in an ultrahigh vacuum system at a base pressure of 2×10^{-11} mbar and a temperature of 5 K. Typical tunneling parameters were: $I_t = 20$ pA and $V_S = -0.8$ V. The rubrene molecules were deposited at low coverage (0.3 monolayers) in situ by sublimation from a home-built evaporator onto a clean Au(111) substrate at room temperature.

Received: April 28, 2005

Keywords: chirality · enantioselectivity · scanning probe microscopy · self-assembly · supramolecular chemistry

---

[1] J. Cohen, *Science* **1995**, *267*, 1265.
[2] J. M. Brown, S. G. Davies, *Nature* **1989**, *342*, 631.
[3] W. J. Meiring, *Nature* **1987**, *329*, 712.
[4] D. H. Metcalf, S. W. Snyder, S. Wu, G. L. Hilmes, J. P. Riehl, J. N. Demas, F. S. Richardson, *J. Am. Chem. Soc.* **1989**, *111*, 3082.
[5] K. Ray, S. P. Ananthavel, D. H. Waldeck, R. Naaman, *Science* **1999**, *283*, 814.
[6] a) E. W. Meijer, A. P. H. J. Schenning, *Nature* **2002**, *419*, 353; b) V. Percec, M. Glodde, T. K. Bera, Y. Miura, I. Shiyanovskaya, K. D. Singer, V. S. K. Balagurusamy, P. A. Heiney, I. Schnell, A. Rapp, H.-W. Spiess, S. D. Hudson, H. Duan, *Nature* **2002**, *419*, 384; c) Y. Wada, M. Tsukada, M. Fujihira, K. Matsushige, T. Ogawa, M. Haga, S. Tanaka, *Jpn. J. Appl. Phys.* **2000**, *39*, 3835.
[7] a) G. P. Lopinski, D. J. Moffatt, D. D. M. Wayner, R. A. Wolkow, *Nature* **1998**, *392*, 909; b) M. Böhringer, K. Morgenstern, W.-D. Schneider, R. Berndt, F. Mauri, A. De Vita, R. Car, *Phys. Rev. Lett.* **1999**, *83*, 324; c) M. Ortega Lorenzo, C. J. Baddeley, C. Muryn, R. Raval, *Nature* **2000**, *404*, 376; d) A. Kühnle, T. R. Linderoth, B. Hammer, F. Besenbacher, *Nature* **2002**, *415*, 891; e) R. Fasel, M. Parschau, K.-H. Ernst, *Angew. Chem.* **2003**, *115*, 5336; *Angew. Chem. Int. Ed.* **2003**, *42*, 5178; f) J. Weckesser, A. De Vita, J. V. Barth, C. Cai, K. Kern, *Phys. Rev. Lett.* **2001**, *87*, 096101; g) Q. Chen, D. J. Frankel, N. V. Richardson, *Langmuir* **2002**, *18*, 3219; h) S. M. Barlow, S. Louafi, D. Le Roux, J. Williams, C. Muryn, S. Haq, R. Raval, *Langmuir* **2004**, *20*, 7171.
[8] a) N. Sato, K. Seki, H. Inokuchi, *J. Chem. Soc. Faraday Trans. 2* **1981**, *77*, 1621–1633; b) P. U. Biedermann, A. Levy, J. J. Stezowski, I. Agranat, *Chirality* **1995**, *7*, 199.
[9] I. B. Berlman, *Handbook of fluorescence spectra of aromatic molecules*; Academic Press, New York, **1971**.
[10] D. M. Hercules, *Science* **1964**, *145*, 808.
[11] Z. Zhi-lin, J. Xue-yin, X. Shao-hong, T. Nagatomo, O. Omoto, *J. Phys. D* **1998**, *31*, 32.
[12] V. Podzorov, E. Menard, A. Borissov, V. Kiryukhin, J. A. Rogers, M. E. Gershenson, *Phys. Rev. Lett.* **2004**, *93*, 086602.
[13] V. C. Sundar, J. Zaumseil, V. Podzorov, E. Menard, R. L. Willett, T. Someya, M. E. Gershenson, J. A. Rogers, *Science* **2004**, *303*, 1644.
[14] V. Podzorov, V. M. Pudalov, M. E. Gershenson, *Appl. Phys. Lett.* **2004**, *85*, 6039.
[15] Y. Harada, T. Takahashi, S. Fujisawa, T. Kajiwara, *Chem. Phys. Lett.* **1979**, *62*, 283.
[16] A. J. Fisher, P. E. Blöchl, *Phys. Rev. Lett.* **1993**, *70*, 3263.