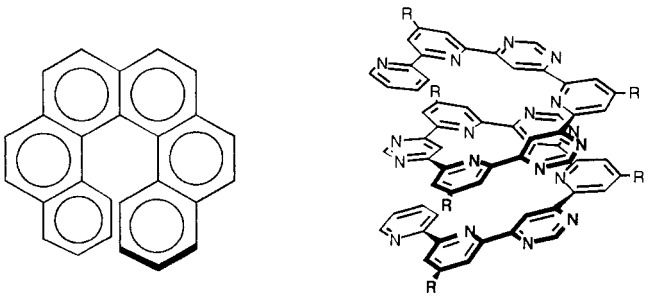
Helical Molecular Programming

Alan E. Rowan and Roeland J. M. Nolte*

The self-organization of molecules into helical and multiple helical architectures can be found throughout nature: from simple α-helical polypeptides and double-helical nucleic acids to more complex helical protein structures, microtubules, and the protein coating of the tobacco mosaic virus.[1] The overall architectural plans required are encoded within the molecular building blocks. Understanding the "programming language" developed and utilized by nature to construct helical structures is of fundamental importance. This knowledge will not only lead to a greater understanding of life, but will also enable the design and construction of new functional helical architectures. The most relevant parameters for controlling the architecture are the molecular size, topology, stereochemistry, and shape. Through processes of self-organization these parameters can be expressed at several hierarchical levels—molecular, macromolecular, and nanomolecular.

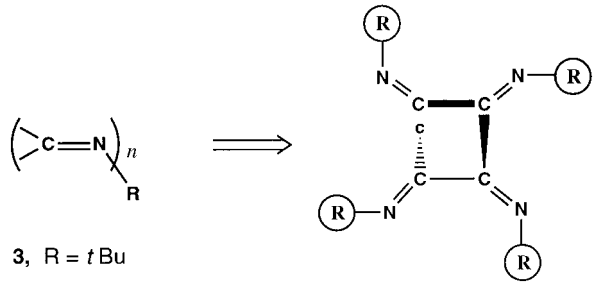
A simple example of molecular programming is the preorganized helical architecture of helicenes.[2] In hexahelicene **1** (Scheme 1) the structural information is encoded in the



1 **2**

Scheme 1. Helicity at a molecular level: Helicene **1** and the oligomeric heteroarene **2** both form helical architectures owing to specific information encoded within the molecules.

geometry of the covalent bonds linking adjacent moieties which, in combination with steric interactions, forces the molecule to adopt a helical geometry. This simple expression of supramolecular helicity was recently further developed by the group of Lehn, who synthesized an achiral polyheterocyclic strand **2** (Scheme 2) which spontaneously organizes to from a two-turn helical structure.[3] This architecture arises as



3, R = *t* Bu

Scheme 2. Polymeric isocyanides **3** form helical rigid rods because of N=C–C=N torsions and steric interactions between the side groups.

a result of several encoded features: an alternating pyridine–pyrimidine sequence, linkage at specific positions, and the preference for a s-*trans* conformation of the single bonds between the alternating units. The resulting helix is adopted both in the solid state and in solution, and is one of the clearest demonstrations of preprogrammed molecular self-organization through specific intramolecular nonbonding interactions. In an alternative approach Moore et al. synthesized oligomers of *m*-phenylacetylene which also spontaneously arrange to give a helical geometry. In this example the helical organization can be readily controlled by solvent and temperature.[4]

The direct linking of aromatic moieties in a *meta* geometry can also give rise to helicity in larger oligomers and polymers. The crystal structure of *m*-deciphenyl revealed an apparently infinite helical chain in which there are five aromatic rings for each turn of the helix.[5] The predicted X-ray powder pattern of this compound, although only a small oligomer, is virtually identical to that of poly(*m*-phenylene) prepared by nickel-catalyzed coupling of *m*-dichlorobenzene. This implies that the larger macromolecule also adopts a similar helical arrangement. Helical polymers are themselves of increasing interest because of their wide variety of possible applications—for example in optical devices, as chiral separation columns, and as components in organic/inorganic hybrid materials. In polymer chemistry the expression of helicity has long been observed since the early work of Natta, Pino, and others.[6] In fact, most isotatic polymers exist as short-range helices in solution. These, however, are dynamic in nature and

[*] Prof. R. J. M. Nolte, Dr. A. E. Rowan
Department of Organic Chemistry, NSR Center
University of Nijmegen
Toernooiveld, NL-6525 ED Nijmegen (The Netherlands)
Fax: Int. code + (31) 24-365 2929
e-mail: rowan@sci.kun.nl

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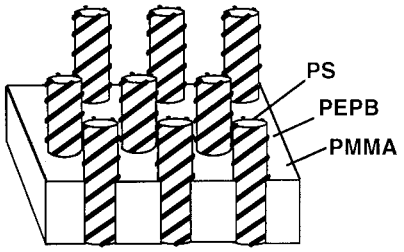
highly dependent on the solvent or slight changes in the polymer side chains. To date only a very limited number of stable, helical, synthetic macromolecules are known—for example polyisocyanides, poly(chloral), and poly(triphenylmethyl methacrylate). The helicity in polyisocyanides is determined by the torsional angle of the N=C–C=N bonds and the steric interactions of the side groups attached to the nitrogen atoms. Upon polymerization of *tert*-butyl isocyanide (**3**) two resolvable left- and right-handed helices were obtained (Scheme 2) with a turn at about every 3.9 units.[7] Unlike with helical biopolymers such as nucleic acids and proteins, the absence of chiral information in the basic building block leads in principle to an equal preference for either left- or right-handed helices. In practice, however, an enantiomeric excess of one helix can be obtained by using a chiral catalyst. The helical sense of the polymer can also be controlled by including chirality in the side group. Polymerization of homochiral isocyanides gives diasteroisomers in unequal amounts; polymerization of (*R*)-$(CH_3)_2CHCH_2CH(CH_3)NC$ preferentially gives a left-handed helix, whereas (*S*)-$CH_3CO_2CH_2$ $CH(CH_3)NC$ gives a right-handed helix. Takahashi et al. recently showed that by using a chiral isocyanide oligomer as an initiator subsequent polymerization with an achiral isocyanide monomeric unit gives a helical polymer with the same sense as the small oligomer.[8]

The subtlety of the parameters which induce chiral expression were clearly demonstrated by Green et al.[9] for polymeric isocyanates **4** (Scheme 3). These stiff helical polymers have no predetermined sense, and in long polymer chains helical reversals may occur. The cooperative stereochemistry of the side groups is so large that only a very small chiral bias in the monomeric unit is magnified and controls the helical sense of large portions of the macromolecule. Upon polymerization of a mixture of *R* and *S* enantiomers of **4a**—in which a 2% excess of the *R* enantiomer exists—the resulting polymer has similar chiral properties as the homochiral polymer made from enantiomerically pure (*R*)-**4a**. The chiral sense of the resulting polymer is determined by the major component. The reaction is so sensitive that even isotopic substitution of the side group results in a preference for one form (**4b**). This phenomenal positive cooperativity can be considered to be a form of molecular amplification. The two polymers discussed already possess a helical backbone whose helical preference can be modified by the size and stereochemistry of the side groups. The induction of helicity into nonhelical polymers is being studied in a very elegant way by Percec et al.[10] Inspired by the behavior of the tobacco mosaic virus, which induces a helical conformation in RNA, they synthesized a series of large, bulky "monodendron" side groups. When these large, tapered moieties are covalently attached to a polymer backbone, the conformation of the backbone is altered from a random coil to a helix. The size and shape encoded in the large side groups which pack on the outside of the polymer induce the chirality. The group of Stadler took one step further on the hierarchical ladder and synthesized a triblock copolymer: polystyrene(55)-*block*-polybutadiene(26)-*block*-poly(methyl methacrylate)(137) (**5**).[11] By a process of controlled phase separation this polymer forms an incredible self-organized system in which helices of polybutadiene microphases are wound around columns of polystyrene, which themselves are embedded in a matrix of poly(methyl methacrylate) (Scheme 4).



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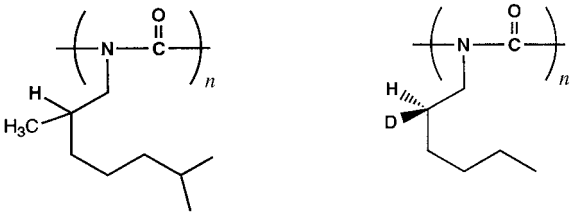
Scheme 4. Schematic representation of the self-organized architecture formed by phase separation of the triblock copolymer **5** (PS = polystyrene, PEPB = polybutadiene, PMMA = poly(methyl methacrylate)).



4a 4b

Scheme 3. The helical preference of polymeric isocyanates **4** can be controlled by isotopic substitution.

Intermolecular interactions between individual polymers chains can also lead to helical induction. Meijer and coworkers synthesized chiral, conjugated polythiophenes which show remarkable optical properties.[12] The helicity present in each polymer unit is only expressed upon cooling, when the polythiophene chains pack to form a helical aggregate. The helical sense of the assembled macromolecule can be easily controlled by varying the rate of cooling; rapid cooling gives one helical sense, and slow cooling the other. Another approach to the construction of chiral polymers was the elegant work by Ito et al., who prepared a variety of 2,3-quinoxalines from a chiral precursor.[13] The optical activity in these macromolecules could be easily tuned and results from the helicity in the backbone of the polymer and not the helical aggregated species.[14] An interesting recent development is the method for constructing double-helical polymer chains designed by Nozaki et al.[15] Condensation of (*S*)-1,1′-binapthyl-2,2′-dicarbonyl dichloride with biphenyl-2,2′,6,6′-tetrol generates oligomeric esters in which the chirality of the starting binapthyl is carried throughout the oligomer. Although only oligomers have been synthesized so far, polymeric chains can be expected to have interesting properties.

In nature numerous helical architectures result from self-assembly of small building blocks into larger molecular assemblages. This process of self-organization through noncovalent interactions is recognized as crucially important in the construction of biological systems. One approach to mimicking the helical arrays found in nature, in particular the double-stranded helix of DNA, has been the design and study

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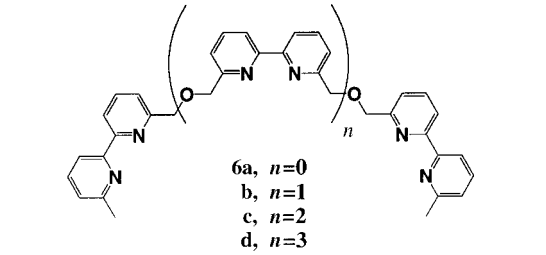
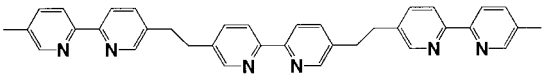
of metal–ligand complexes known as "helicates".[16] This area was investigated as early as the late 1970s by the group of Saenger, who constructed helical metal–polyether complexes,[17] but has rapidly expanded since the inspirational early work by Lehn and co-workers, who showed that oligobidentate ligands **6a** and **6b** (Scheme 5) form double-helical





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Scheme 5. Oligopyridine ligands **6** and **7** self-assemble in the presence of metal ions to form a variety of helical arrays.

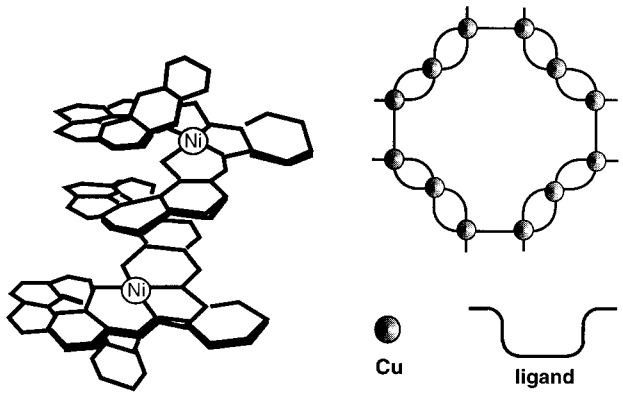
complexes.[18] These helicates possess many features seen for self-organizing biological systems. The binding of Cu^{I} ions is cooperative, and the oligoligands display self-selection. This means that for a mixture of ligands **6a**–**6d**, helical-forming species will only selectively bind a second ligand of the same size.[19] This phenomenon was described as "instructed system paradigm". Using this self-assembly to form a well-defined scaffold, Lehn et al. synthesized a helix with five copper ions and pendant nucleoside units, a "deoxyribonucleohelicate".[20] With possible applications as a complimentary ligand for the DNA double helix this nanometer-sized architecture highlights the possibilities for creating functional assemblies. The helical sense can also be controlled by a variety of means: introducing chirality in the oxymethylene linker,[21] using chiral bipyridine ligands,[22] or, as shown by Siegel et al., linking two strands of **6c** through a chiral spacer. The resulting helical sense of the copper–ligand helix is controlled by the chirality of the spacer at one end.[23]

The above-mentioned helical arrays can be considered as consisting of three basic components: a binding site, a metal, and a ligand linking this binding site to another. All three components can be programmed with specific information which spontaneously gives a defined final architecture upon mixing. The coordination preference of metal can be controlled by using the appropriate metal ions, and the ligand properties can be varied by altering the denticity (bidentate, tridentate). The spacer linking the ligand units must be sufficiently flexible to allow the molecule to wrap around but rigid enough to prevent the second binding site from coordinating to the first metal. The size and geometry of the spacer in part controls the pitch and also the sense of the resulting helix.

Using these structural parameters Williams et al. and Constable et al. demonstrated control over the resulting helical architectures by using different metal ions.[24] Upon adding Cu ions with a tetrahedral coordination geometry to a bidentate ligand a di-copper double helix is generated, whereas a triple helix is formed upon the addition of a metal ion with octahedral geometry. The latter, in which the metal centers are lanthanide ions, are currently being investigated as possible light-conversion devices.[25]

This process of spontaneous self-organization is also highly dependent on the data encoded within the ligand. Because of the 6,6′ linkage in ligands of type **6** (Scheme 5) octahedral metals cannot be accommodated due to steric hindrance if three strands were to bind to two metals; in the 4,4′ linkage in ligand **7** there would be no steric hindrance. When **6b** and **7** are mixed in the presence of Ni^{II} and Cu^{I} **6b** binds only to Cu and **7** only to Ni ions.[19] In the presence of Fe^{II} ions **7** forms an even more complex array. This bipyridine ligand self-assembles with the Fe^{II} ions around a chloride ion template to form a circular double-helicate architecture.[26]

Bell et al chose a slightly different approach to construct double-helical arrays.[27] Instead of using the coordination preference of the metal as a major driving force for assembly, a double helix was constructed by emphasizing the geometrical preference of the ligand. With a heterohelicene which already has a helical geometry enforced due to covalent bonds, it was demonstrated that with the correct ligand even Group 1 metal ions such as sodium may control the assembly of double-helical supermolecules. When sodium salts are added two types of double helices can be formed: one in which two helices wrap around one metal ion and one in which they wrap around two metal ions. Katz et al. took the combination of metals and helicene molecules a step further by constructing a helicene possessing a salicylaldehyde functionality at both ends. In combination with nickel acetate and a phenyldiamine ligand, a beautiful, helical, conjugated ladder polymer (**8**, Scheme 6) is formed.[28] The planarity of the "nickel salophene" connections not only results in a conjugated system but also induces the polymer to wind in just one direction.



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Scheme 6. Salicylaldehyde-functionalized helicenes complex nickel ions to form a helical polymeric assemblage (**8**). Schematic representation of the cyclic dodecacopper helicate from Lehn et al. which forms spontaneously in a preprogammed way.

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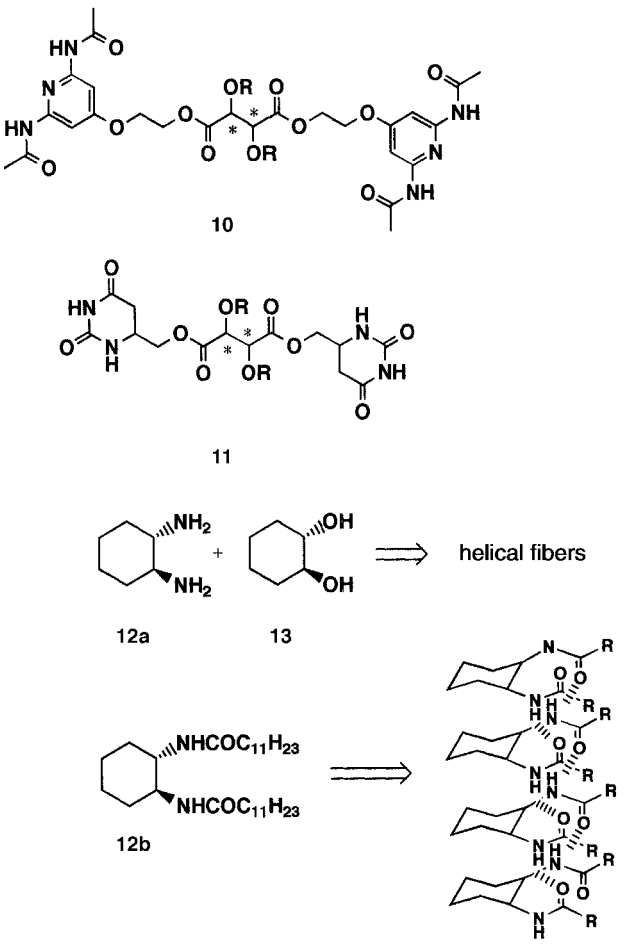
Lehn et al. recently demonstrated that by using the molecular information encoded in the metal–ligand components it is possible to program the spontaneous assembly of even more highly complex, helical architectures. One of the most recent examples is the nanocyclic dodecanuclear Cu helicate **9**[29] (Scheme 6). In this assemblage twelve Cu ions and four multifunctional ligands spontaneously self-assembly in a two-step process to give a specific inorganic nanomolecule.

A variety of other approaches have also been investigated for the controlled construction of helical nanometer-sized architectures. The uracil and pyridine derivatives **10** and **11** based on tartaric acid assemble by complementarity of the base pairs to form helical superstructures. Species based on L-tartaric acid give right-handed helices, and those based on D-tartaric acid left-handed helices.[30] If a mixture of L-uracil and D-pyrimidine derivatives—or of D-uracil and L-pyrimidine derivatives—is used, no helicity is observed. Only configurationally compatible units assemble if all four possible species are mixed. This chiral resolution was also observed in the aggregation of chiral 1,2-diaminocyclohexanes by Hanessian et al.[31] When the (*R*,*R*) and (*S*,*S*) derivatives of **12a** were mixed with equimolar amounts of (*S*,*S*)-1,2-cyclohexanol **13**, two triple-helical supramolecular structures were generated (Scheme 7). The (*S*,*S*)-diamine of **12a** formed a homochiral left-handed helix with **13**, whereas **13** and the (*R*,*R*)-diamine of **12a** gave a heterochiral right-handed architecture. The group of Hanabusa modified the packing ability of *trans*-1,2-diaminocyclohexane by adding amide functionalities and long alkyl chains to give **12b**.[32] The (*R*,*R*) and (*S*,*S*) enantiomers of **12b** gelate in a variety of solvents to give right-and left-handed helical fibers, respectively, with a diameter of 40–70 nm. They result from cooperative, chiral self-organization.



Scheme 7. Chiral tartaric acid derivatives **10** and **11** self-assemble to helical architectures. (*R*,*R*)- and (*S*,*S*)-diaminecyclohexanes **12a** assemble with **13** to give helical arrays. Cyclohexanediamides **12b** aggregate through a network of hydrogen bonds and packing to form gels consisting of helical fibers.

The expression of molecular information at the macroscopic level by self-organization is a topic of great interest since it may lead to a more thorough understanding of the construction processes used by nature. The assembly of surfactants and amphiphilic molecules is of particular interest, as chirality within the individual molecule can be expressed in the suprastructure by the formation of helices and twisted bilayers. A wide variety of chiral amphiphiles based on amino acids (glutamate,[33] alanine[34]), phospholipids,[35] and carbohydrates[36] form chiral architectures. In the case of the glutamate derivatives the sense of the resultant helix is related to the molecular chirality: An L derivative of glutamate gives a right-handed helix, whereas a D enantiomer yields a left-handed helix. The encoded molecular data is expressed at the macroscopic level. The groups of Fuhrhop,[36] Pfannemüller,[37] and O'Brien[38] studied the assembly behavior of chiral amphiphiles—in particular gluconamides—which assemble to create micellar helical and multihelical superstructures. *N*-*n*-Octyl-D-gluconamide (**14a**, Scheme 8) forms ropelike architectures with a length to width ratio of up to 104. These structures are believed to consist of a helix of six intertwined micellar strands.[39] As in the glutamates the pure enantiomers form helices with enantiomorphology (i. e., in the case of **14a** only right-handed helices are formed), whereas racemic mixtures crystallize. The expression of chirality at the macroscopic level is a result of strong hydrogen bonds between adjacent molecules and efficient packing of the alkyl chains. The group of Nolte has varied the head group of these gluconamides (e. g. **14b**, **14c**) and found that the molecules self-assemble even in organic solvents to form organogels. Closer examination of these gels showed that they consist of well-defined micrometer-sized helical fibers.[40]

The self-assembly process required to form such highly complex nanomolecular architectures consists of numerous processes which are hierarchical in nature. Modified gluconamide **15** (Scheme 8), which possesses an imidazole head group, has also been fully investigated by Nolte et al. Although the hydrogen-bonding OH groups are protected, this molecule still readily self-assembles. In the presence of Cu^{II} ions **15** forms a 4:1 ligand–copper complex, which in turn self-assembles to generate a bilayer; in a stepwise fashion this further organizes to yield a nanometer-sized "molecular braid" consisting of four strands.[40] The sensitivity of the resultant architecture to the molecular geometry is highlighted by the phospholipid analogues **16** and **17** (Scheme 9).[41] Although both have an *R* configuration they are structurally different and give dramatically different expressions of chirality. Phospholipid **16** gives platelike aggregates, whereas **17** forms left-handed helical strands with a diameter of 22 nm, which themselves further assembly to give large ropelike architectures (Figure 1). The helicity is the

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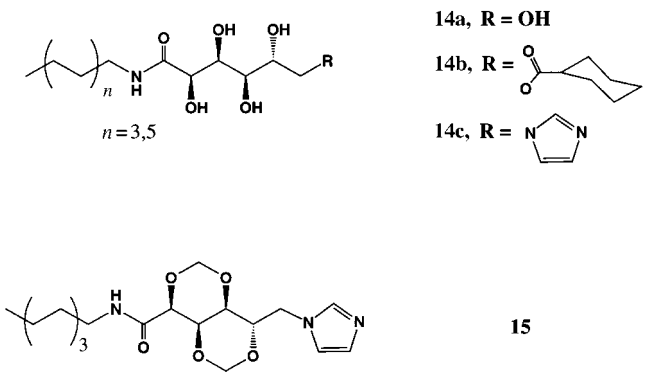
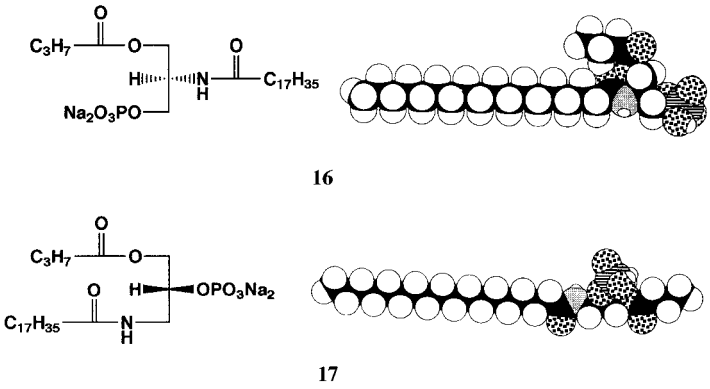


Scheme 8. *N*-*n*-Octyl-D-gluconamides **14** self-assemble in a variety of solvents to form complex intertwined architectures in which the chirality of the simple building blocks is expressed at a macromolecular level. Protected imidazole gluconamide **15** assembles in the presence of copper ions in a hierarchical fashion to give nanometer-sized molecular braids.



Scheme 9. Phospholipids **16** and **17** (and their space-filling representations).

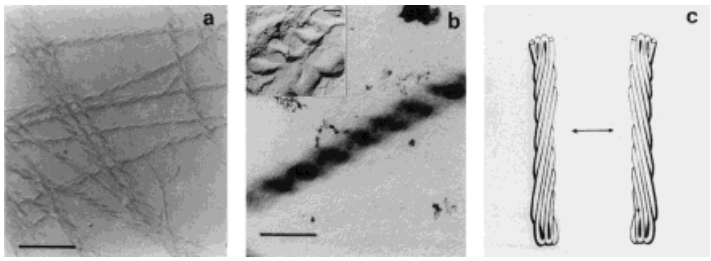


Figure 1. Electron micrographs of helices formed by **17** (2 wt %) in water (bar = 500 nm): a) left-handed helices (Pt shadowed), b) right-handed super helix (Pt shadowed; inset: image after freeze fracturing), c) schematic representation of supercoiled DNA.

result of the chirality within the molecular units and also the specific complementarity of intermolecular interactions, which carries this information through to the macroscopic level. Owing to its more linear shape **17** can pack more tightly, and hence the chiral molecular information is not lost upon self-assembly. The resultant nanomolecules themselves seem to be tunable by small changes in salt concentration or pH, which induces the left-handed helices to coil up and form large right-handed superhelices in a manner analogous to the formation of supercoiled DNA.[42]

Helicity in macromolecular and supramolecular systems can be obtained by a variety of methods. The principle of molecular programming is clearly demonstrated in the case of helicate structures resulting in the spontaneous self-assembly of, for example, large helical nanocycles. The rules governing the construction of helical nanosized arrays from amphiphlic building blocks are far more complex and are only now being elucidated. To mimic more closely the ability of nature to construct complex multicomponent helical architectures, a combination of many processes in a hierarchical assembly line will be required. The first steps in this direction are currently being taken. These helical assemblies and polymers are expected to have interesting physical and material properties, in particular as optical devices, that is, chiral light-emitting and nonlinear optical materials.[43] The ultimate goal is not just to mimic nature but to go a step further and be able to preprogram molecules to give not only specific architectures but also defined functionality.

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Conjugated π Systems with Heavy Main Group Elements— A Stable Neutral Silaarene and the First Tetrasilabutadiene**

Thomas Müller*

The question of conjugation and aromaticity in organosilicon compounds has recently attracted considerable interest. For instance, the influence of cyclic conjugation on the stability of aminosilylenes has aroused controversy.[1] However, even simple stable neutral silaarenes like derivatives of silabenzene have been elusive until very recently. This is in sharp contrast to the successful synthesis of kinetically stabilized silenes and 1-silaallenes.[2] In addition calculations predict for silabenzene a resonance stabilization of about 75% of that calculated for benzene.[3] Early fundamental investigations showed that silaarenes can be produced as short-lived intermediates in the gas phase or in the matrix at low temperatures and that they can be characterized by IR, UV, or PE spectroscopy.[4] None of these compounds could be however investigated in solution or even isolated in substance. Investigations by Märkl and co-workers[5] revealed the extraordinary reactivity of silaarenes. Even the with bulky groups substituted silabenzene **1** is at $-100^{\circ}C$ only of limited stability.

On the other hand the search for anionic silaarenes has been more successful during the last years. Almost simultaneously the groups of Boudjouk, Tilley, and West[6] reported the synthesis of silolyl anions **2**, analogues of the cyclopentadienyl anion, and silole dianions **3**. Surprisingly, the silicon in **2** is pyramidalized and the anions have localized C=C bonds. Cyclic conjugation with involvement of the silicon atom seems to play only a minor role in **2**. In contrast, silole dianions **3** as well as germole dianions[7] have delocalized π electron systems with almost identical CC bond lengths. The silicon atom in **3** is markedly deshielded relative to tetracoor-

[*] Dr. T. Müller
Fachinstitut für Anorganische und Allgemeine Chemie der Humboldt Universität
Hessische Strasse 1-2, D-10115 Berlin (Germany)
Fax: Int. code + (49) 30-2093 6966
e-mail: h0443afs@joker.rz.hu-berlin.de

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