Programmed Helical Phthalocyanine Architectures

een wetenschappelijke proeve op het gebied van de Natuurwetenschappen, Wiskunde en Informatica

Proefschrift

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1.1 Molecular scale electronics

Since 1965, the maximum number of components in a single integrated circuit (IC) has doubled every eighteen months. This observation, (Figure 1.1) often referred to as Moore's Law, is not the result of a law of nature, but rather a self-fulfilling prophecy. Economics and technology drive semiconductor manufacturers to constantly improve the capabilities of electronic devices by means of a continuous increase in their complexity. To be able to cram more and more components on a single IC, these components and interconnecting circuitry will have to become smaller and smaller. In the classical and very successful top-down approach, new generations of lithographic techniques are introduced every few years to continuously decrease the dimensions of functional, bulk semiconductor devices. The

![Figure 1.1 Number of transistors per chip as a function of the year.](image_url)
lithography equipment, which uses a combination of light, stencils, and lenses to transfer circuit patterns onto silicon, determines to which extent the circuitry can be miniaturized; the smallest obtainable dimensions using this approach are roughly of the size of half the wavelength that is used, \( i.e. \sim 0.1 \, \mu m \). It is obvious that this trend can not continue forever.

In the bottom-up approach called "molecular scale electronics", molecules and self-assembled supramolecular structures are designed which have specific electronic functions. The use of molecules as electrical components has several advantages, the most obvious being their extremely small dimensions. Furthermore, molecules are completely identical and can be produced defect-free in large amounts. This, and the possibility of some molecules to either crystallize or self-assemble to form large arrays of identical devices, makes molecular electronics in principle an attractive alternative to classical top-down fabrication.

1.2 Phthalocyanines

Phthalocyanine (1, Pc) is one of the key candidate molecules to be used in a bottom-up approach to assemble miniature devices. It is an 18-electron aromatic molecule with a natural drive to self-assemble in a face-to-face fashion. Since the discovery of the liquid crystalline properties of peripherally-substituted phthalocyanines by Piechocki \textit{et al.} \textsuperscript{4}, these compounds have been among the most intensively investigated molecular materials. Their high thermal stability and relative ease of synthesis, combined with interesting electronic and optical properties, makes them highly attractive for applications in future molecular electronic devices.
1.3 Chirality

The concepts of molecular asymmetry were developed by J. H. van 't Hoff and J. A. Le Bel in 1874 following the resolution by Louis Pasteur of a mixture of tartaric acid salt isomers around 1850. The word 'chiral' (Greek, χειρ = hand), was first introduced into science by Lord Kelvin (William Thomson). His original statement 'I call any geometrical figure, or group of points, chiral, and say it has chirality, if its image in a plane mirror, ideally realized, cannot be brought to coincide with itself' is generally accepted as the definition of chirality.

The importance of chirality is probably the best illustrated with the homo-chirality of the essential building blocks of life, for instance amino acids and sugars, without which life would be unimaginable. The origin of homo-chirality on earth remains an intriguing question. The prime importance of chirality in chemistry was acknowledged with Nobel prices in 1975 for Sir J. W. Cornforth and V. Prelog, and in 2001 for W. S. Knowles, R. Noyori and K. B. Sharpless for their work concerning asymmetric catalysis.

1.4 Aim and outline of this thesis

The work described in this thesis aims at the rational design of phthalocyanine materials whose properties originate at the molecular level. The work concentrates on geometrical control rather than application. More specifically, the work is focused on chirality, the most important reason being the beauty of chirality itself. The highly symmetric phthalocyanine molecule has, unjustly, rarely been modified with chiral components. Another important reason to focus on chirality, is that it allows for the transfer of information from one molecule to another, eventually leading to the stepwise, hierarchical assembly of one-dimensional, two-dimensional and three-dimensional architectures with predicted and well-defined properties, e.g. electron conduction.

From previous work it is known that phthalocyanine derivatives have a natural tendency to aggregate in a more or less face to face fashion. Controlling and applying this property has been the subject of many papers. These, among other interesting studies are introduced in Chapter 2, a literature survey on various phthalocyanine derivatives, focused on studies in the fields of molecular materials, supramolecular chemistry and chirality.

In Chapter 3, a new type of main-chain chirality in polymers is presented, which is demonstrated in a phthalocyaninato-polysiloxane. It is characterized by a basically achiral, linear polysiloxane chain, to which phthalocyanine rings are skewered in a helical fashion. In
Chapter 4, phthalocyanines are presented which contain crown ether moieties and chiral, aliphatic tails. It is shown that secondary interactions can cause the transfer of chirality from simple chiral carbon centers to (super-) helical stacks of phthalocyanines, and how that transfer can be blocked by other secondary interactions, using mechanisms similar to nature. In Chapter 5, an effort is made to take the results of Chapter 4 a step further by incorporating chirality directly into the crown ether ring. It is also described here how hydrogen bonding was deployed at the periphery of the phthalocyanines, aiming at truly programmed helical assemblies. Chapter 6 describes how phthalocyanine derivatives can be visualized and manipulated at the molecular level by means of scanning probe microscopy.

1.5 References and notes

1 Source: http://www.intel.com
8 Lord Kelvin's original definition does not cope very well with dynamic chirality, for instance the left-handed chirality observed for neutrinos. A more recent definition states ‘True chirality is exhibited by systems existing in two distinct enantiomeric states that are interconnected by space inversion, but not by time reversal combined with any proper spatial rotation’. L. D. Barron, True and false chirality, CP violation, and the breakdown of microscopic reversibility in chiral molecular and elementary particle processes, in Physical origin of homochirality in life, 1996, 162-182, D. B. Cline, ed. (New York: Woodbury)
2.1 Introduction

In the last few decades molecular materials have been receiving increased attention as possible components in optical, electronic and magnetic devices.\cite{1,2} Molecular materials are composed of highly ordered molecular units; their construction requires the rational design and synthesis of suitable building blocks, which, in a second step, are organized to form a well-defined structure.\cite{3} Many varieties of building blocks have been utilized; the most common types are amphiphilic molecules, \textit{e.g.} carbohydrates, and rod- and disk-like molecules such as biphenyls, triphenylenes, porphyrins, phthalocyanines, and, more recently, even larger flat molecules.\cite{4-13} Traditionally, covalent synthesis was used to link the molecular units forming the molecular material. More recently, with the advent of supramolecular chemistry, non-covalent assembly approaches have become increasingly popular, utilizing hydrogen bonding, electrostatic, solvophobic, Van der Waals, and $\pi$-$\pi$ interactions as driving forces for the ordered assembly.

2.2 Phthalocyanines

Phthalocyanines 1 (Pcs, derived from the Greek terms naphtha and cyanide, rock oil and dark blue) are flat aromatic dye molecules related to porphyrins 2 and porphyrazins 3, that have been known for many years. An unsubstituted metal-free phthalocyanine was first synthesized accidentally in 1907 by Von Braun,\cite{14} but only in 1934 was the correct structure for iron phthalocyanine elucidated by Linstead.\cite{15} Copper phthalocyanine, a blue pigment which was
first synthesized in 1927 by De Diesbach,\textsuperscript{16} is to date the single largest-volume colorant sold, with an annual production of over 50000 tons.\textsuperscript{17} Since then, numerous metal phthalocyanines have been prepared containing almost every metal ion in the periodic table. Phthalocyanines are extremely stable, both thermally and (photo)chemically, which makes them very useful in numerous industrial applications.\textsuperscript{18} They have been used as photoconducting agents in photocopying machines, as a dye-developer in the color-photography industry,\textsuperscript{19} as a sensitizer in photodynamic cancer therapy\textsuperscript{20-25} and as an anti-scrapie compound.\textsuperscript{26} Recordable compact disks based on phthalocyanine have a life expectancy of up to 200 years, compared to 20 years for other dyes.\textsuperscript{27} Electronic applications include gas sensors, resistors and field effect transistors.\textsuperscript{28-30}
Crown ether functionalized phthalocyanines

The first phthalocyanines peripherally substituted with crown ethers (4-8) were reported in 1986, independently by the groups of Bekâroğlu, Kobayashi, and Nolte. Since then, a large number of other macrocycles have been attached to the periphery of the phthalocyanine core. The self-assembly of these molecules has been studied extensively. It was shown by UV-vis spectroscopy that aggregation can be induced by increasing the polarity of the solvent. In some cases, addition of alkali metal ions has a similar effect. When the diameters of the ions exceed the inner diameters of the crown ether rings, dimeric complexes are formed, in which four ions are sandwiched between two crown ether phthalocyanines. Thus, 4 forms 4:1 guest-host complexes with Li\(^+\) and Na\(^+\) and 4:2 complexes with K\(^+\), Rb\(^+\) and Cs\(^+\). Compound 6 forms 4:1 complexes with Li\(^+\), Na\(^+\) and K\(^+\), and 4:2 complexes with Rb\(^+\) and Cs\(^+\). Phthalocyanine 8 only forms 4:1 complexes, and cannot be induced to form aggregates with alkali metal ions. Using the picrate extraction technique, the free energy of binding (\(\Delta G^0\)) of the various alkali metal ions in the crown ether phthalocyanines was determined. In general, the crown ether phthalocyanines turn out to be better alkali metal ion complexing agent than the corresponding benzo crown ethers (e.g. see the binding profiles for 4 and benzo 5-crown-5 in Figure 2.2). The complexes of 5 with K\(^+\), Rb\(^+\) and Cs\(^+\) picrates were isolated and
characterized, and in all cases, the complexes were stacked in columns, with the cations located in (K⁺) or between (Rb⁺ and Cs⁺) the crown ether moieties.

In an effort to utilize these architectures as synthetic ion channels, a series of crown ether derived phthalocyaninato polysiloxanes (12-14) was synthesized by metal-catalyzed polycondensation of the dihydroxy phthalocyaninato silicons 9-11. The degree of polymerization was calculated by end-group analysis to be 14-18 for 12, 10-15 for 13, and 6-8 for 14, suggesting that the polymerization reaction is sensitive to steric hindrance (vide infra). The occurrence of ion conduction in 12-14 was tested by using these polymers as membranes in concentration cells of the type Na-amalgam(I)|Na picrate-polymer complex|Hg(II), and measuring the decrease of the open-circuit voltage as a function of time. It was observed that only 14, which has 21-crown-7 moieties, was able to conduct Na⁺ ions. However, compared to other synthetic ion channels, the conduction of ions was rather low, probably because the phthalocyanine units within the polymer are in a non-aligned (staggered) arrangement, which distorts the channel structure.

### Electronic conductivity in crown ether phthalocyanines

The electrical properties of 5, its K⁺, Rb⁺, and Cs⁺ picrate complexes and those of the polysiloxane derivatives have also been studied in the solid state by AC impedance spectroscopy. Seebeck measurements showed that the uncomplexed CuPc's are p-type electronic conductors, whereas the metal picrate complexes of 5 exhibit n-type electronic conductivity. Without metal ions complexed in the crown ethers, hole conductivity dominates,

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\sigma_{180^\circ C}/\text{S} \cdot \text{m}^{-1}$</th>
<th>$E_a$/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuPc (180°C)</td>
<td>$6 \cdot 10^{-8}$</td>
<td>1.39</td>
</tr>
<tr>
<td>5 (180°C)</td>
<td>$5 \cdot 10^{-7}$</td>
<td>1.18</td>
</tr>
<tr>
<td>5 · K⁺ (180°C)</td>
<td>$1 \cdot 10^{-5}$</td>
<td>1.33</td>
</tr>
<tr>
<td>5 · Rb⁺ (180°C)</td>
<td>$3 \cdot 10^{-4}$</td>
<td>1.02</td>
</tr>
<tr>
<td>5 · Cs⁺ (180°C)</td>
<td>$7 \cdot 10^{-5}$</td>
<td>1.09</td>
</tr>
<tr>
<td>5 · Iₓ (RT)</td>
<td>$7 \cdot 10^{-3}$</td>
<td>0.12</td>
</tr>
<tr>
<td>5 · K⁺ · Iₓ (RT)</td>
<td>$2 \cdot 10^{-4}$</td>
<td>0.18</td>
</tr>
<tr>
<td>5 · Rb⁺ · Iₓ (RT)</td>
<td>$5 \cdot 10^{-4}$</td>
<td>0.15</td>
</tr>
<tr>
<td>5 · Cs⁺ · Iₓ (RT)</td>
<td>$2 \cdot 10^{-4}$</td>
<td>0.15</td>
</tr>
<tr>
<td>12 (RT)</td>
<td>$7 \cdot 10^{-7}$</td>
<td>0.23</td>
</tr>
<tr>
<td>13 (RT)</td>
<td>$3 \cdot 10^{-7}$</td>
<td>0.29</td>
</tr>
<tr>
<td>14 (100°C)</td>
<td>$1 \cdot 10^{-8}$</td>
<td>0.38</td>
</tr>
</tbody>
</table>
due to $\pi-\pi$ overlap of the macrocyclic rings.\textsuperscript{40,41} Upon the addition of metal picrates this changes to conduction of electrons as a result of interactions between the d-orbitals of the Cu$^{2+}$ centers.\textsuperscript{42-44} The results are summarized in Table 2.1. It can be seen that an increase in conductivity of 2 to 3 powers of ten is achieved when the metal picrates are complexed with the Pcs. This can be explained by the fact that complexation of alkali metal ions results in aggregates with eclipsed phthalocyanine units, and a slight decrease of the interplanar spacing, both resulting in increased orbital overlap between neighboring phthalocyanine units. In the case of the polysiloxane derivatives, the conductivity is also enhanced because of the increased interactions between the neighboring phthalocyanine units. This conductivity is proportional to the length of the polymer, with longer polymers having greater conductivities. Conductivity is further enhanced by doping with iodine\textsuperscript{45} which generates free charge carriers, \textit{i.e.} electron holes. The semi-conductivity of phthalocyanine films also strongly increases in the presence of adsorbed electron-acceptor gases such as NO$_2$. This is a result of the transfer of charge between the electron-donating phthalocyanine molecules and the electron-accepting gas, which reduces the activation energy for charge-carrier (electron holes) generation. The effects of NO$_2$ and NH$_3$ on the conductivity of thin crown ether phthalocyanine films have also been investigated.\textsuperscript{46} It was discovered that saturation of the metal-free 15-crown-5 or 18-
crown-6 phthalocyanine (5 or 7) with KCl gives highly organized molecular materials with excellent gas sensing characteristics at room temperature. Using this material, a hand-held gas sensor was subsequently developed, highlighting the potential of such assemblies.
**Liquid crystalline crown ether phthalocyanines**

For most application purposes, it is necessary to introduce order in the phthalocyanine molecular material. This can be achieved by attaching crown ether functionalities to the phthalocyanine molecules and adding alkali metal ions or by polymerization as was shown above. Another approach, introduced in 1982 by Simon and coworkers, is to attach eight alkoxyethyl tails to the periphery of the Pc molecule which introduces liquid crystalline order. Since then, a large variety of liquid crystalline Pc derivatives has been synthesized containing different aliphatic tails, including alkyl, alkylcarbonyloxy, and alkoxy chains.

A liquid crystalline crown ether functionalized phthalocyanine (15) was prepared which exhibits a mesophase over a large temperature range, i.e. from 148°C until its decomposition at 320°C. In the crystalline phase of this compound, the phthalocyanine molecules are in a tilted, eclipsed conformation, with the crown ether moieties positioned on top of each other. In the mesophase, the molecules are stacked co-facially in a staggered conformation.

Interestingly, in chloroform phthalocyanine 15 self-assembles to form well-defined aggregates of molecular thickness and micrometer length, without the necessity of complexation of alkaline metal ions. Electron micrographs of these aggregates in chloroform (Figure 2.3), revealed very long entangled fibers, the smallest with a diameter matching that of a single phthalocyanine molecule. Such a fiber resembles a multi-wired molecular cable, consisting of an electron conducting stack of phthalocyanines, flanked by four ion channels built from stacked crown ethers, as is schematically shown in Figure 2.4. The resulting fibrous network is capable of gelating the solvent. A fine balance between the solubility of the hydrocarbon chains and the very strong attractive forces between the large phthalocyanine disks is responsible for this behavior. The heat of association was determined to be -125 kJ mol⁻¹, which is exceptionally large for interactions solely based on π-π stacking. The addition of extra aromatic groups at the periphery of the Pc (as in 15) enhances the aggregation process. This effect was also demonstrated by O'Brien et al. using a CuPc peripherally substituted with benzyloxyethoxy groups. Due to the extra π-π interactions, this compound forms well-defined films at the air/water interface.
Chiral phthalocyanines

Chirality is a virtually unexplored parameter in the field of phthalocyanines. Only a few examples of optically pure phthalocyanines$^{50,60-63}$ and analogues$^{64}$ have been published in the literature, some with very interesting superstructures. Van Nostrum et al. prepared Pc 16. It is substituted with eight chiral alkoxy tails derived from (S)-citronellol, and displays a very rich phase behavior.$^{61}$ It appears to be liquid-crystalline from 3°C up to 295°C. Below 111°C, (S)-16 forms a new, chiral D_h* mesophase. This chiral mesophase was investigated with a number of techniques, including X-ray powder diffraction which revealed a helical periodicity of 57Å (corresponding to 16 molecules) along the stacking direction. Circular dichroism studies indicated that the molecules have a left-handed helical structure and solid-state $^{13}$C NMR studies revealed that the aliphatic tails adopt a propeller-shaped arrangement. In contrast to what is expected, the 'racemic' compound rac-16 (which actually consists of a mixture of 43 stereoisomers, composed of 16 pairs of enantiomers and 11 meso compounds) forms a super cooled mesophase at room temperature which, in contrast to the optically pure (S)-16, crystallizes after a few hours.$^{61,65}$

Sub-phthalocyanines are the lower homologues of phthalocyanines, comprising three isoindole units instead of four. When boron is used as a central atom, particularly stable compounds are obtained. The cone-shaped structure allows for the construction of very interesting chiral molecules, very similar to the work of Collet on triveratrilenes two decades ago,$^{66,67}$ as was shown by Torres et al. who synthesized 17, which could be resolved analytically in its enantiomers with the help of HPLC.$^{68}$
Katz et al. have constructed very interesting molecules in which the cores of copper and nickel octaazaphthalocyanines are fused to four non-racemic [7]helicenes. These molecules (18a and 18b) can be self-assembled in LB films that give very large second-order nonlinear optical responses, suggesting that the molecules are organized in large chiral supramolecular arrays. Kimuri et al. have constructed fibrous assemblies in water from copper phthalocyanines peripherally substituted with eight (S)-2,3-dihydroxypropoxy groups (19). CD spectroscopy revealed a left-handed helical arrangement, but unfortunately no helicity was visible with electron microscopy.
Supramolecular chemistry based on phthalocyanine building blocks

Apart from the extensive work done on crown ether functionalized phthalocyanines, a number of groups have reported 'other' supramolecular chemistry based on phthalocyanines. As part of their ongoing research on dimeric capsules based on the self-complementary building block diphenylglycoluril developed by the group of Nolte, Rebek et al. synthesized supramolecular phthalocyanine dimers from which are held together by sixteen hydrogen bonds, as shown in Figure 2.1." \[20\]

In some applications, for instance catalysis and optics, aggregation is not desired. Several groups have shown that aggregation can be effectively prevented by incorporating dendritic substituents in the molecules, even in the solid state. Kimura et al. synthesized hydrophilic phthalocyanines (21, 22) based on Newkome's methodology.\(^{72-74}\) No aggregation of the phthalocyanines is visible in the UV spectra of solutions of these compounds in polar solvents and thin films. McKeown et al. have attached Fréchet's poly(aryl ether) dendrimers around a Pc core, in order to produce glassy solids with the optical properties of solutions.\(^{75}\) Interestingly, even third-generation dendrons attached at the periphery of the phthalocyanine (23) did not prevent co-facial aggregation of the Pc cores in dilute solution.\(^{76}\) This could be achieved however when the dendrons were attached as an axial ligand to silicon phthalocyanine (24).\(^{77}\)
In an effort to mimic the photosynthetic light-harvesting system, Kraus et al. synthesized the small dendrimer 25, which has six phthalocyanine moieties as end groups.\textsuperscript{78} Lindsey's group, as part of their work on multi-porphyrin systems, synthesized light-harvesting arrays based on a phthalocyanine with four (26a) or eight (26b) porphyrins at the periphery.\textsuperscript{79,80} For the free-base and Zn derivatives, very efficient energy transfer from the porphyrins to the phthalocyanine core was observed.
2.3 Helical structures

Helical structures are found throughout nature. Archetypal examples are the $\alpha$-helices in peptides and the A, B and Z-type helices in nucleic acids. In these naturally occurring polymers, the information required for the formation of a specific helical structure is hidden in the chiral centers in the polymer backbone. Many synthetic polymers are also helical. They are sometimes built from achiral monomers and are consequently racemic mixtures of left-handed (M) and right-handed (P) helices, or are characterized by helical reversals within the polymer chain. Polysiloxanes 27 form, as a result of the hindered rotation about the central
Molecular Materials Based on Functionalized Phthalocyanines

C-C bonds, stable helices in solution which can be either left-handed (M) or right-handed (P) in the absence of chiral centers. The racemate of poly-tert-butyl isocyanide can be separated by column chromatography using a chiral support, showing the stability of the helical conformation. The use of optically pure isocyanides, e.g. those based on L-alanine dipeptides, yield helical polymers with specific handedness. The specific helicity of polyisocyanides is prolonged even if the polymerization is continued with achiral monomers.

Polyisocyanates (28) are another class of helical polymers which can be left- or right handed, depending on the chirality of the side chains. In contrast to the polyisocyanides, the helicity is thermodynamically determined. As a result, the polyisocyanates are extremely sensitive to minute chiral forces. The tendency of the monomeric units to determine the handedness of the helical polymer in a cooperative fashion has been shown in many ways, for instance with the help of a polymer built up from a nearly racemic mixture of chiral monomers ("majority rules"), by the copolymerization of an achiral isocyanate with a small amount of chiral monomer ("sergeants and soldiers"), and by chiral solvation or stereo-specific deuterium substitution as in 29.

Nelson et al. showed that phenylene-ethynylene oligomers (i.e., 30) can be driven to fold into (racemic) helical conformations by solvophobic forces. Incorporation of a single chiral binaphthol unit into the backbone induces a bias in the helical twist sense, however not without significant destabilization of the folded conformation. A stable chiral bias could be achieved by introducing chirality into the side chains, as in the polar compound 31, or the
In the group of Lehn, the achiral oligomeric strands 33 of various lengths have been synthesized. These molecules spontaneously organize to form helical structures with six heterocycles per turn. In solution, these oligomers exist as equilibrating mixtures of right-handed and left-handed helices, with a barrier for helical reversal that is independent on the length of the strand. The oligomer comprising 19 heterocycles (n=8) exhibits spontaneous chiral resolution on crystallization. These principles were taken a step further with the synthesis of 34, which again spontaneously organizes into a helical conformation but this time with twelve heterocycles per turn due to the linearity of the pyridazine units. In dichloromethane, because of the doubled π area compared to 33, this compound forms a fibrous network. Electron microscopy revealed both right- and left-handed helical substructures, suggesting that the individual fibers are composed of stacks of helices of compound 34 with the same helical sense. The molecular chirality is consequently translated into supramolecular helicity which is in turn expressed on a nanometer scale.

A nice example of non-polymeric helicity is compound 35a. This disk-like molecule was shown to form helical columnar stacks in alkane solvents. Most interestingly, when 2.5% of 35a was used as a chiral aid to induce helicity in stacks of achiral 35b, the same Cotton effect was obtained as for pure 35a. Helices formed from the achiral molecules seemed to be even more stable than those formed from 35a since the maximum Cotton effect was obtained at 25% of chiral compound added. Also the use of a chiral alkane solvent resulted in a CD effect. These combined results strongly suggest that the molecules adopt a
propeller-like conformation, which could orientate either way but always in the same direction within the same stack.

### 2.4 References and notes


3.1 Introduction

In an earlier study, we reported on the structure and properties of a chiral phthalocyanine (1) with branched aliphatic tails derived from (S)-citronellol. This compound was shown to form a novel chiral columnar mesophase at room temperature, and an achiral D$_r$ mesophase at elevated temperatures. The helical structure that was proposed for the molecules in the chiral mesophase is shown in Figure 3.1C. It represents one of the three possible arrangements of

![Images of helical arrangements](image)

Figure 3.1 Schematic representation of three possible helical arrangements of 1a. The phthalocyanines are represented by disks in A and C and as squares in B to show more clearly the helical packing arrangement.
the phthalocyanine rings. In the first, these rings are arranged in a ‘spiral staircase-like’ manner (Figure 3.1A). In the second (Figure 3.1B), the rings are positioned on top of each other, but the staggering angle between neighboring phthalocyanines is nearly constant and always in the same direction. In the third, the normal of the plane of each phthalocyanine ring is tilted and gradually rotating along the stacking axis. The latter model was in better agreement with X-ray diffraction and circular dichroism studies. We denoted this new mesophase by $D_h^*$. The second arrangement however, could not be completely ruled out, although it is difficult to postulate structures A or B when it is assumed that the molecules rotate around their stacking axis in the mesophase, with a frequency of ca. 5000Hz. In order to differentiate between structures B and C, the polysiloxane analogue 6 of 1 was synthesized in which the center-to-center distance between two neighboring phthalocyanines is fixed at the distance of a Si-O-Si linkage, very close to the Van der Waals distance. The only type of helicity which this polymer can adopt is type B. In order to be able to compare the optical properties of 6 with those of a reference compound we synthesized dimer 7 from hydroxymethylsilicon phthalocyanine 5, which was prepared in an analogous manner to 3.

### 3.2 Results and discussion

#### Synthesis

The synthesis of the monomers is shown in Scheme 3.2. It follows procedures previously developed for other octaalkoxyphthalocyanines. Phthalonitrile 8 was synthesized as described previously, and was subsequently converted into the corresponding diiminoisoindoline 9 with ammonia in THF/MeOH in the presence of sodium methoxide. Reaction of 9 with tetrachlorosilane gave 2 and reaction with trichloro(methyl)silane 4. Both chlorides were found to hydrolyze readily to give the corresponding hydroxides 3 and 5. Polymerization of dihydroxoyde 3 turned out to be more troublesome than expected: at the rather harsh polymerization conditions as described in literature, i.e. heating in vacuo at 200°C, partial thermal decomposition of the alkoxy tails occurred. Lowering the temperature to 170°C resulted in a very slow polymerization reaction, but without any noticeable decomposition of the product 6. Heating 3 in DMF with the aid of microwave irradiation drastically decreased the reaction time to ca. 2 h instead of 48 h, however in this case again no clean reaction took place as was evidenced by the formation of brown side products. We also tried to polymerize dimers of the type HO-(SiPc)-O-(SiPc)-OH which were synthesized
Shish-kebab-like Chirality

Scheme 3.1

1: M=2H
2: M = SiCl₂
3: M = Si(OH)₂
4: M = SiClMe
5: M = Si(OH)Me

6: X = Y = OH, n=26
7: X = Y = Me, n=1

separately. This method has been successfully used by Wegner and co-workers to prepare high molecular weight phthalocyaninato-polysiloxanes. We were not able, however, to increase the molecular weight of 6 by this procedure.

Dimers of the above mentioned type are inseparable from higher oligomers, even with preparative HPLC and therefore cannot be obtained in pure enough form to act as reference compounds for 6. Since the protection of one hydroxyl group with a Me₂BuSi group prior to the condensation, was shown not to prevent the scrambling of the siloxy groups and the formation of higher oligomers, we decided to synthesize monomer 4 in which the silicon
center is protected with a methyl group. Compound 4 could be easily condensed to give dimer 7.

Circular dichroic spectroscopy

In Figure 3.2, the electronic absorption spectra of 3 and 6 are presented. From the exciton shift of the Q-band from 680 nm in monomer 3 to 550 nm in the polymer (a shift of 3519 cm\(^{-1}\)), the degree of polymerization was estimated to be 27, see equation 3.1.\(^9\) For the exciton shift of an infinite polymer, \(\Delta E(N \rightarrow \infty)\), the value of 3609 cm\(^{-1}\) was used, as described

\[
\frac{\Delta E(N)}{\Delta E(N \rightarrow \infty)} = 1 - \frac{1}{N}
\]  

(3.1)

![Electron spectrum graph](image)

**Figure 3.2** Electronic absorption spectra of monomer 3 (A) and polymer 6 (B), and the circular dichroic spectra of 3 (C), 6 at 25°C (D) and 6 at 120°C (E). The spectra of 3 were recorded in chloroform and those of 6 in dodecane.
Shish-kebab-like Chirality

The CD spectra of monomer 3 and polymer 6 at 25°C and 120°C are also presented in Figure 3.2. Monomer 3 did not show a CD signal. In the spectra of 6 some interesting features are present: a bisignate signal emerges around 550 nm, corresponding to the Q-band of the polymer. The z-shape of the signal is typical for an exciton coupled CD signal; the combination of a negative first Cotton effect and a positive second Cotton effect is indicative of negative chirality, i.e. a left-handed helix. It is unclear which absorption band corresponds to the complex CD signals at lower wavelengths; it is impossible, therefore, to assign structural characteristics (such as handedness) to these signals. It is evident, however, that these signals also are the result of the phthalocyanines being positioned in a chiral fashion with respect to each other. Because of the short Si-O-Si distance, i.e. 3.33 Å (compared to an optimal π-π stacking distance of 3.4 Å), the only possible type of helicity for this polymer is that of type B in Figure 3.1.

We would like to call this type of main-chain chirality, which consists of a linear (and therefore non-helical) backbone, to which the side-groups are skewered in a chiral fashion, 'shish-kebab-like chirality'. To the best of our knowledge, this type of chirality is unprecedented in the literature of polymers.

Figure 3.3 Circular dichroic spectra of 1 on quartz (A, 2×10 bilayers [Ref. 1]) and of polymer 6 in solution (B, dodecane) and as a spin-coated film (C). The solid-state spectra have an arbitrary scale.

previously by van Nostrum.

The CD spectra of monomer 3 and polymer 6 at 25°C and 120°C are also presented in Figure 3.2. Monomer 3 did not show a CD signal. In the spectra of 6 some interesting features are present: a bisignate signal emerges around 550 nm, corresponding to the Q-band of the polymer. The z-shape of the signal is typical for an exciton coupled CD signal; the combination of a negative first Cotton effect and a positive second Cotton effect is indicative of negative chirality, i.e. a left-handed helix. It is unclear which absorption band corresponds to the complex CD signals at lower wavelengths; it is impossible, therefore, to assign structural characteristics (such as handedness) to these signals. It is evident, however, that these signals also are the result of the phthalocyanines being positioned in a chiral fashion with respect to each other. Because of the short Si-O-Si distance, i.e. 3.33 Å (compared to an optimal π-π stacking distance of 3.4 Å), the only possible type of helicity for this polymer is that of type B in Figure 3.1.

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In Figure 3.3, the CD spectrum of an annealed LB-film of free-base phthalocyanine 1 is shown, together with the spectrum of an annealed (100°C) spin-coated film of polymer 6 and the solution spectrum of 6 in dodecane. A molecularly dissolved solution of 1 did not

Figure 3.4 A) Circular dichroic spectra of 7 in chloroform (20µM) at temperatures ranging from -10°C to 50°C. The corresponding UV spectrum (20µM, 20°C) is shown in grey. B) Circular dichroic spectra of 7 in toluene (20 µM) at temperatures ranging from 0°C to 80°C. For comparison, the spectrum of 7 in chloroform at 20°C is also shown (grey line). The spike at 637 nm results from noise of the photomultiplier.
show any circular dichroism. The solution and solid-state CD spectra of 6 are identical, which means that no inter-polymer interactions are playing a role, and that all features in the CD spectrum must arise from co-facial Pc-Pc interactions. This is in line with the generally accepted idea that the Pc stacks are well isolated from each other by the alkoxy chains.15 As can be seen in Figure 3.3, the CD spectra of the mesophase of 1 and the polymer 6 are very different. If the helical structure of the mesophase of 1 and that of the polymer 6 would be the same, it is expected that the CD spectra at least qualitatively match. Since this is clearly not the case, structure B (Figure 3.1) seems to be very unlikely for the mesophase of 1.

The circular dichroic spectra of dimer 7 at various temperatures are shown in Figure 3.4A. A pronounced CD effect is visible in the Q-band region, as well as around 400 nm where the oxygen n-\(\pi^*\) CT bands are located. The presence of a CD signal indicates that the phthalocyanine cores have a chiral orientation with respect to each other. Comparison with the polymer spectrum suggests again a left-handed helical orientation. When the temperature is increased from -10°C to 50°C, all signals decrease in intensity, suggesting that the phthalocyanines have more rotational freedom. In order to be able to increase the temperature even further, spectra were also taken in toluene, as is shown in Figure 3.4 B. In this solvent however, only a small CD effect was visible, which hardly altered upon heating from 0°C to 80°C. Hanack et al. have described the synthesis and spectroscopic properties of a range of phthalocyanine dimers very similar to 7, however with achiral or racemic peripheral alkoxy chains.7 They concluded that the conformation of these dimers is strongly solvent-dependent. In aromatic solvents, the dimers have a conformation with a D4d (staggered) or D4h (eclipsed) symmetry and therefore they are achiral (irrespective of chirality in the side chains). These conformations are summarized in Table 3.1. In non-aromatic solvents, the symmetry is lowered to D4, and the phthalocyanine units are at an angle different from 0° or 45°. In the latter case the dimers are chiral, regardless of any chirality of the side chains. These chiral dimers will exist as racemic mixtures if no other chiral centers are present. If the side-chains

<table>
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<th>Conformation</th>
<th>Staggering angle</th>
<th>Symmetry</th>
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<tr>
<td></td>
<td>45°</td>
<td>D4d</td>
</tr>
<tr>
<td></td>
<td>0°</td>
<td>D4h</td>
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<tr>
<td></td>
<td>-25°</td>
<td>m</td>
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<tr>
<td></td>
<td>+25°</td>
<td>D4</td>
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are chiral, the dimers with a positive or negative staggering angle are no longer enantiomers but become diastereomers. It remains unclear whether the structure of dimer 7 in aromatic solvents is fully eclipsed or fully staggered. Space-filling models suggest that in the eclipsed conformation, the aromatic ring of a solvent molecule fits perfectly in the space left between two phenyl rings of one phthalocyanine ring, which will not be possible in the staggered conformation (Figure 3.5). If an aromatic solvent molecule is located in this site, stabilizing edge-to-face \( \pi-\pi \) stacking interactions are likely to occur. We therefore tentatively conclude that the geometry in aromatic solvents is most likely eclipsed and not staggered. In the presence of chiral tails, a small deviation in one specific direction from this eclipsed conformation can cause the observed small CD effect. In non-aromatic solvents, the dimers probably have some 'natural' staggering angle, and the sign of this angle is determined by the chirality of the side-chains, causing a CD effect which is strongly temperature dependent.

**Copolymers of chiral and achiral phthalocyanines**

Often, the physical properties of a two-component system are related to the properties of the unmixed components in a linear fashion. In these cases, a plot of a given measured property as a function of the mole fraction of the components yields a straight line. For instance, the determination of the enantiomeric excess of a compound in a racemic mixture from the optical rotation is based on this principle.\(^{16}\) In 1989, Green showed that in some helical

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*Figure 3.5* Calculated (AM1) space-filling molecular model showing how an aromatic ring of a solvent molecule (benzene) fits in between the phenyl rings of a phthalocyanine molecule.
copolymers, a small amount of a chiral monomer can induce a large excess of one particular helix sense of the polymer main chain. More recently, it was shown that this phenomenon can also take place in some supramolecular aggregates. To test whether this 'sergeants and soldiers' effect would also hold in our case, a small range of copolymers was synthesized (Scheme 3.3), containing 100%, 50%, 20% and 0% of chiral phthalocyanine monomer. The straight chain dihydroxysilicon octadecoxypthalocyanine SiPc(10) was chosen as the achiral monomer. This compound was synthesized as described previously.

In Figure 3.6, the CD spectra of the copolymers measured in various solvents are shown. In benzene, unusual features appear in the spectra at higher wavelength (500-650 nm, Q band area). Also in the other solvents the spectra have an irregular shape in this region. It is known that the shape, location and intensity of the Q-bands are very dependent on the solvent, the temperature, the Pc staggering angle, and the degree of polymerization of the polymers. These bands, therefore, can not be used as a probe of helicity in the present case. In the region at 400 nm, however, (the O-n-π* region), all spectra displayed the same type of bisignate signals with isosbestic points. Because of this feature it was decided to use the CD intensity in this region as the helicity probe. In Figure 3.7, the normalized CD intensity (ε+ - ε-) at 400 nm is plotted as a function of the fraction of chiral monomer. At first glance, in every solvent a non-linear behavior is observed, however, one has to take into account that the monomer itself is not helical, but the interaction between two neighboring monomers. In a random [CxA1-x]n copolymer (C=chiral, A=achiral), three types of interactions between pairs of monomers

\[ \text{R} = \text{O} \]
\[ \text{R'} = \text{O} \]
\[ x = 1, 0.5, 0.2, 0.0 \]
(dimers) can occur: CC, CA and AA. If the polymer is truly random and of sufficient length
(to be able to ignore end group effects), one can calculate the relative amounts of these
dimers: \([CC] = x^2\), \([AA] = (1-x)^2 = 1-2x+x^2\) and \([CA] = 2x(1-x) = 2x-2x^2\). If only one chiral
monomer is needed for a 'dimer' to be helical, the total helical content in a \([C_xA_{1-x}]_n\)
copolymer amounts to \([CC] + [CA] = x^2+2x-2x^2 = 2x-x^2\). This function is also plotted in
Figure 3.7. It is clearly visible that in both hexane and THF this theoretical curve is followed.
The AA pairs do not contribute at all to the total helicity. In benzene and chloroform, the CA
dimer apparently contributes less to the helicity than the CC dimer (about 65%). Solvent
effects are known for phthalocyanine dimers, as was pointed out by Kleinwachter et al. who
showed that the staggering angle in phthalocyaninato disiloxanes is largely dependent on the
solvent.7

Figure 3.6 CD spectra of phthalocyaninato polysiloxanes (SiPc(10)) containing 20%, 50% or
100% chiral monomers (SiPc(8,2)*) in various solvents. A: tetrahydrofuran, B: hexane, C:
chloroform, D: benzene.
3.3 Conclusions

The polymers described above exhibit an unusual kind of helicity. They consist of an achiral main chain to which the monomers are skewered in a helical fashion. This helicity is caused by the interaction between neighboring phthalocyanines and not by some natural helicity in the polymer backbone, as was shown with a so-called 'sergeants and soldiers' experiment. Not to observe any cooperativity in a rigid helical polymer is extremely rare.\(^20\)

3.4 Experimental section

General procedures

All chemicals were commercial products and were used as received, unless stated otherwise. Thallous triflate (\(\text{TiSO}_3\text{CF}_3\)) was prepared as described by Caseri et al.\(^4\) \(^1\)H-NMR spectra were recorded on Bruker AC-100 and Bruker AC-300 instruments. Chemical shifts are reported in ppm relative to tetramethylsilane (\(\delta=0.00\)) as an internal standard. Optical spectra were recorded using a Bio-Rad FTS-25 instrument for FT-IR, a Varian Cary 50 spectrophotometer for UV/Vis and a Jasco J-810 spectropolarimeter for CD. MS spectra were recorded on a VG 7070E or a Finnigan MAT900S instrument. Melting points were
determined on a Jeneval polarization microscope equipped with a Linkam THMS 600 hot stage and a Linkam TMS92 temperature programmer, and are reported uncorrected. Elemental analyses were determined with a Carlo Erba EA 1108 instrument. Semi-empirical (AM1) calculations were performed on a Silicon Graphics Challenge computer running the MOPAC 93 package.

Synthesis

(S,S)-1,2-Dicyano-4,5-bis(3,7-dimethyloctoxy)benzene (8).

This compound was synthesized as described for the racemic compound.21

(S,S)-5,6-Bis(3,7-dimethyloctocy)isoindoline-1,3-diimine (9).

Compound 8, (2.63 g, 6.0 mmol) and sodium methoxide (0.80 g, 15 mmol) were placed in a three-necked flask, which was flushed with anhydrous ammonia for 10 minutes. Methanol (30 ml) and THF (40 ml) were added, and the mixture was stirred for 30 minutes and then refluxed for 4 h. During these periods a stream of anhydrous ammonia was continuously bubbled through the solution. The complete conversion was confirmed with FT-IR by the disappearance of the C≡N stretch frequency at 2228 cm⁻¹. The solvents were removed in vacuo, CHCl₃ and MgSO₄ were added, and the mixture was filtered over celite and concentrated until dryness. Yield: 2.12 g (77%) of a light green solid. FT-IR (KBr) \( \tilde{\nu} \) [cm⁻¹] = 1033 (N-H), 1295 (Ar-O-C), 1499, 1599 (Ar), 1631 (C=N), 2844, 2927, 2954 (CH₂), 3245-3365 (N-H) cm⁻¹. \( \delta \) (ppm) 0.84-0.90 (d, 12H, CH₃), 0.91-0.98 (d, 6H, CH₃), 1.25 (m, 12H, CH₂), 1.3-2.1 (m, 6H, CH₂, CH), 4.08 (t, 4H, OCH₂), 7.12 (s, 2H, Ar-H).

Dihydroxy (2, 3, 9, 10, 16, 17, 23, 24 – octa [(S)-3, 7-dimethyloctoxy] phthalocyaninato) silicon (3).

In a Schlenck vessel under a stream of anhydrous nitrogen, diiminoisoindoline 9 (2.12 g, 4.6 mmol) was dissolved in freshly distilled quinoline (1.75 ml). The vessel was closed with a septum and SiCl₄ (1 ml) was added through a syringe. The mixture was immediately brought to 170°C in a pre-heated oil bath, and kept at this temperature for 2 h. After cooling, CHCl₃ (2 ml) and water (10 ml) were added and the mixture was stirred for 2 h. The layers were separated and the organic layer was washed with water (3×75 ml), dried over MgSO₄ and concentrated in vacuo. The product was purified with column chromatography (SiO₂/CHCl₃ followed by Al₂O₃ (act. III)/CHCl₃). Yield: 366 mg (17%) of a dark green solid. FT-IR (KBr)
Shish-kebab-like Chirality

\[ \Lambda^{-1} [\text{cm}^{-1}] = 743, 754, 823 (\text{Si-OH}), 914, 1101 (\text{Ar-H}), 1010, 1063, 1205, 1282 (\text{Ar-O-C}), 1365 (\text{Si}), 1390, 1425, 1501, 1606 (\text{Ar}), 1465, 2843, 2869, 2926, 2954 (\text{CH}_2, \text{CH}_3), 3455 (\text{SiO-H}) \text{ cm}^{-1}. \]

\(^1\)H NMR (CDCl\(_3\), 300MHz) \(\delta\) (ppm) 0.90-0.94 (d, 48H, CH\(_3\)), 1.15-1.50 (m, 72H, CH\(_2\), CH\(_3\)), 1.53-1.62 (m, 8H, CH), 1.95 (m, 16H, OCH\(_2\)CH\(_2\)), 2.18 (m, 8H, CH), 4.64 (t, 16H, OCH\(_2\)), 9.95 (s, 8H, ArH). UV/Vis (CHCl\(_3\), 25°C), \(\lambda_{\text{max}}\) (nm) 677, 650, 612, 361, 343, 300. Anal. \((\text{C}_{112}\text{H}_{178}\text{N}_8\text{O}_8\text{Si})_n\) found (calcd.) C: 72.57 (73.72), H: 9.85 (9.83), N: 5.87 (6.14).

**Polymer (6)**

Dihydroxy Pc 3 (121 mg, 66\(\mu\)mol) was placed in a Schlenck vessel and brought under high vacuum. The solid was heated at 170°C for 8 days in vacuo, yielding a dark blue polymer. Anal. \((\text{C}_{112}\text{H}_{176}\text{N}_8\text{O}_9\text{Si})_n\) Found (Calcd.): C: 74.45 (74.46); H: 9.86 (9.82); N: 6.16 (6.20).

**Preparation of copolymers**

For the preparation of copolymers, the monomers were first mixed in chloroform solution and evaporated in vacuo. After this, the same procedure as for the homopolymer was used.

**Hydroxy(methyl) \((\mbox{2, 3, 9, 10, 16, 17, 23, 24 – octa [(S)-3, 7-dimethyloctoxy] phthalocyaninato}) silicon (5).**

This compound was synthesized identically to 3, using 500 mg of 9 in 5 ml of quinoline and 1 ml of methyltrichlorosilane as the silylating agent. Yield: 297 mg (60%). \(^1\)H-NMR (CDCl\(_3\), 300MHz) \(\delta\) (ppm) -6.3 (s, 3 H, SiCH\(_3\)), 0.7-2.5 (m, 152 H, CH\(_2\), CH\(_3\)), 4.0-4.8 (b, 16 H, OCH\(_2\)), 9.0 (s, 8 H, ArH).

**Disiloxane (7)**

A solution of 180 mg (0.1 mmol) of hydroxy(methyl) phthalocyaninato silicon 5 and 35 mg (0.1 mmol) of TlSO\(_3\)CF\(_3\) in 50 ml of freshly distilled pyridine was refluxed for 5 h. in a nitrogen atmosphere. After cooling, a mixture of water (25 ml) and methanol (25ml) was slowly added to the solution. The mixture was filtered over celite, and the filter cake was washed with methanol until the filtrate was colorless. The product was obtained with dichloromethane, concentrated in vacuo and purified with column chromatography (Al\(_2\)O\(_3\) act. III, MeOH/CHCl\(_3\) 0-1%). Yield: 134 mg of a dark blue sticky powder (75%). \(^1\)H-NMR
(CDCl₃, 300 MHz) δ -8.35 (s, 6 H, SiCH₃) 0.8-2.5 (m, 304 H, CH₂, CH₃), 4.1-4.9 (b, 32 H, OCH₂), 8.26 (s, 8 H, ArH), 8.64 (s, 8 H, ArH).

3.5 References and notes

13. Zhou et al. have reported chiral shish-kebab type polymers, however in their case neither the backbone was linear nor the 'kebabs' were skewered to the 'shish'. Q. F. Zhou, R. Xie and Y. T. Zhu, Macromol. Symp. 1997, 118, 183.
14. This spike resulting from noise was shown by recording several spectra at slower recording speeds in the area 630 nm - 650 nm.


20 M. M. Green, personal communication.

4.1 Introduction

Helical architectures are very common throughout nature. The best studied examples are the double helices formed by deoxyribose nucleic acid (DNA) and the $\alpha$-helical motifs found in proteins. The latter biopolymers can spontaneously adopt helical conformations because of the molecular information present in the amino acid building blocks. In many cases, proteins assemble further to form hierarchical superstructures which are also helical, and often have opposite handedness. Collagen, for instance, is composed of three left-handed helices, which wind around each other to give a right-handed superhelical coil.\(^1\) Other examples of helices are the so-called heavy chains of myosin which self-assemble to generate extended $\alpha$-helical coiled coils composed of six polypeptide chains which have a rod-like structure with an overall length of more than 100 nm.\(^2\) An inspirational self-assembled helical structure is also formed by the tobacco mosaic virus. The individual protein molecules of this virus spontaneously self-organize around the viral DNA molecule to give a right-handed helical structure.\(^3\)

One of the goals of chemistry is to achieve control over the structure of synthetic molecules and macromolecules, opening the way for new applications, for instance in the fields of catalysis and electronics.\(^4\) A great variety of interactions can be exploited, such as hydrogen bonding, Van der Waals interactions, $\pi$-$\pi$-stacking, and electrostatic interactions. Recent studies have shown that the formation of superstructures can be driven by $\pi$-$\pi$-stacking interactions exclusively,\(^5\)\(^-\)\(^10\) for example, in the case of the helical folding and the formation of helical lyotropic phases of m-phenylene ethynylene oligomers.\(^11\)
One of the objectives of the research described in this thesis was to study the self-assembly of helical architectures, using molecular building blocks that self-organize due to $\pi-\pi$ interactions. Phthalocyanine 2 has been developed previously in our group, and was designed to exhibit thermotropic liquid-crystalline properties, but was found to possess lyotropic liquid-crystalline properties as well. In chloroform solution, this compound forms very large linear strands, of molecular thickness and micrometer length, as was visualized by electron microscopy. These strands, which consist of more than $10^4$ molecules, can be considered to be multi-wired molecular cables. They contain a central electron wire composed
of stacked phthalocyanine units, and four ion channels formed by crown ether rings that are placed on top of each other, surrounded by an insulating hydrocarbon mantle.

In this Chapter, an unusual example of helix and superhelix formation is presented, based on the self-assembly of chiral phthalocyanine molecules. The helicity in these superstructures is controlled by chiral centers remote from the areas of intermolecular interaction, and can be tuned by the addition of potassium ions. The molecule (1) that forms the superhelix is presented in Chart 4.1. It contains a phthalocyanine ring to which four benzo crown ether moieties are attached. The peripheral aromatic rings of the molecule are each substituted with two chiral alkoxy tails derived from citronellol. The overall diameter of the disc is 60 Å if the tails and crown ethers are fully stretched, and has a thickness of 3.4 Å. The phthalocyanine core in 1 has an extended system of \( \pi \)-electrons, which are known to be responsible for the observed conductivity of electrons and excitons in stacked phthalocyanines.\(^{12}\) The crown ether moieties have potential to behave as ion conductors,\(^{13}\) and the chiral tails can induce liquid-crystalline behavior.\(^{14}\) Compound 3, which also contains chiral aliphatic tails, was synthesized for comparison with 1. However, the tails in this compound are expected to be too short for inducing liquid-crystalline properties and serve only as a source of chirality. In addition, polysiloxane 6 was synthesized, to serve as a macromolecular analogue for the supramolecular 'polymer' formed by 1.

4.2 Results and discussion

Synthesis

The route that was used for the synthesis of 1 is presented in Scheme 4.1. It is a modification of the route applied by van Nostrum for the synthesis of the non-chiral analogue 2.\(^{15}\) By introducing the alkyl tails in a later stage, not only less reaction steps involving expensive chiral materials are required, but it is also more convenient to access a variety of compounds based on the benzocrown ether phthalocyanine skeleton. The key intermediate, dibromo diacetyl dibenzocrown ether 11, can be conveniently alkylated by deprotecting the acetyl groups \textit{in situ}, \textit{viz.} by a transesterification reaction in basic butanol in the presence of an alkyl halide. If both acetyl groups are removed before an ether linkage is formed, a very unstable diphenolate intermediate is generated. This can be circumvented by using 4-methyl-2-pentanone in the presence of base as reagent, in which case the acetyl group is very slowly removed in a Claisen-type condensation. In the latter method, always at least one of the
Scheme 4.1

(i) 3,4-Dihydroxybenzaldehyde, $K_2CO_3$, DMF, 120°C (59%); (ii) $H_2O_2$, $H_2SO_4$, MeOH, 20°C (65%); (iii) $K(SO_3)_2NO$, N(n-butyl)$_4$Cl, $K_2HPO_4$, $H_2O$, THF, 20°C (98%); (iv) Zn, AcOH, Ac$_2$O, 80°C (80%); (v) (S)-3,7-dimethyloctylbromide, NaOH, n-BuOH, 118°C (59%) or (R)-2-methylbutylbromide, 4-methyl-2-pentanone, $K_2CO_3$, 118°C, (60%); (vi) CuCN, pyridine, DMF, 153°C (50-80%); (vii) N,N-dimethylaminoethanol, 135°C (20-25%); (viii) NH$_3$, NaOMe, MeOH, THF (100%), and (ix) (1) SiCl$_4$, quinoline, 190°C (2) $H_2O$, MeOH, CHCl$_3$, 20°C (39%).
oxygen atoms is protected with either an acetyl group or an alkyl tail. Interestingly, this condensation reaction is catalyzed by crown ethers,\textsuperscript{16} which means that we are dealing with an interesting kind of autocatalysis in the present case. Polysiloxane 6 was synthesized using standard procedures.\textsuperscript{17} Phthalonitrile 14 was converted to the corresponding diiminoisoindoline 16 in THF/MeOH. This compound was subsequently reacted with tetrachlorosilane in quinoline to give dichlorophthalocyaninato silicon 4 which was readily hydrolyzed with water. The resulting dihydroxypthalocyaninato silicon 5 was polymerized by quickly heating \textit{in vacuo} at 190°C. The resulting polymer was readily soluble in

\textbf{Figure 4.1} Transmission electron micrographs (platinum shadowing) of gels formed in chloroform. Top: left-handed helical aggregates of 1. Bottom: Achiral aggregates formed by 3.
chloroform, unlike the analogous polymer containing unbranched alkoxy tails previously prepared by van Nostrum, which was only soluble at low degrees of polymerization.18

**Aggregation in solution**

When 1 was heated in an organic solvent, i.e. chloroform at concentrations >5 mg/ml, and then cooled down slowly, strong aggregation of the molecules to an organogel took place. Electron micrographs (Figure 4.1) showed that this gel was composed of long, left-handedly twisted fibers, which had nanometer diameters and micrometer lengths. The bundles typically contained up to 25 fibers, each with the diameter of one single phthalocyanine molecule (60 Å). Compound 3 also formed an organogel, however, this gel was far less stable than the gels formed by 1 or 2. This poor gelation behavior is attributed to the fact that 3 is less soluble in hot chloroform. It should be noted that no fibers and no helical features were visible in the electron micrograph of 3.

Electronic absorption spectroscopy can in principle provide information about the type of aggregated structures that are present in the gels of 1 and 3. However, at the very low concentrations (~10 µM) required for optical and circular dichroic (CD) spectroscopy, no aggregation of 1 was observed in chloroform. It was found, however, that aggregation could
be induced by increasing the polarity of the solvent. In a mixture of chloroform and methanol (1:1 v/v), 1 was partly aggregated even at very low concentrations as could be concluded from the blue-shifted Q-bands of the phthalocyanine rings which appeared at 600 nm (Figure 4.2, bottom). In non-aggregated 1 they are located at 660 and 700 nm, as can still be seen in Figure 4.2. This shift is caused by exciton coupling between neighboring phthalocyanines in a stack. A couplet (bisignate signal, Figure 4.2, top) was present in the CD spectrum at the same wavelength. The combination of a positive first Cotton effect and a negative second Cotton effect suggests the presence of a right-handed helical arrangement of the transition dipoles of the phthalocyanines within a stack.\(^{19}\) Again, three types of helicity can be imagined, see Figure 3.1 (Chapter 3). First, the crown ether phthalocyanine rings may be arranged in a ‘spiral staircase-like’ manner. Second, the rings may be positioned on top of each other, but with a staggering angle between neighboring phthalocyanines that is nearly constant and always in the same direction. Third, the normal of the plane of each phthalocyanine ring may be tilted and gradually rotated along the stacking axis. In order to differentiate between these structures, we synthesized the dihydroxy-phthalocyaninato silicon derivative of 1, which was polymerized to give phthalocyaninato-polysiloxane 6.\(^{17}\) Polymer 6 has a polysiloxane backbone, to which the crown ether phthalocyanine units are attached in a skewered fashion, giving a shish-kebab-like structure. The CD-spectrum of the covalent polymer in chloroform shows a very similar couplet in the Q-band region as the self-assembled non-covalent polymer, again indicative of a right-handed helical structure. In this type of polymers, because of the small Si-O-Si distance (3.33 Å, compared to an optimal \(\pi-\pi\) stacking distance of 3.4 Å\(^{20}\)) the only possible helical structure is type B in Figure 3.1.\(^{21}\) X-ray powder diffraction revealed that in the non-covalent stack of 1, the phthalocyanine cores are at a distance of 3.4 Å, (vide infra) which would be too short if structures of type A or C were formed. These combined results suggest that the arrangement of the molecules within the self-assembled stack, as well as in the classical polymer, is most likely that of type B in Figure 3.1.

Compound 3, as opposed to 1, does aggregate in chloroform at very low concentrations. The CD spectrum (Figure 4.2) is almost a mirror image of that of 1, indicating a left-handed orientation of the phthalocyanines. Although the aggregation is not as well-defined as that of 1, as was shown with electron microscopy, it is expected that also in this case only exciton coupling between co-facially stacked phthalocyanines results in the CD effect.
As is shown above, the phthalocyanines in the stacks are arranged in a right-handed helical fashion (CD spectroscopy), whereas the super helices formed from them adopt a left-handed helix (electron microscopy). This paradoxical result can be understood by the following model. A fiber with a right-handed twist and a type B structure (Figure 3.1) has a ‘grooved’ exterior. In order to maximize the van der Waals contact between two fibers twisted around each other, each of them has to bend in order to fit into the groove of the other fiber, as is shown in Figure 4.3. The tilting angle between the two fibers is called the ‘inter-axial’, ‘crossing’ or ‘crossover’ angle. If only steric interactions are taken into account, this angle is double the angle $\beta$ of the groove with respect to the stacking axis. The crossing angle $\alpha$ depends on the diameter $D$ of the molecule, and the staggering angle $\phi$ and the stacking distance $d$ between two monomers. From Figure 4.4 it follows that $\tan(\beta)=a/d$, $\phi=a/r$ ($\phi$ in radians) and $r=D/2$. Combining these, gives equation 4.1. In Figure 4.5, the crossing angle $\alpha$

$$\alpha = 2 \arctan \left( \frac{D\phi}{2d} \right)$$

**Figure 4.3** Suggested mechanism for the self-assembly of 1 (represented by squares): (i) Right-handed stacking of mono- and oligomeric phthalocyanines into a linear helical stack. Due to the helicity, a groove is formed at an angle $\beta$ with respect to the stacking direction; (ii) two stacks meet at double angle $\beta$; (iii) the stacks bend towards each other; (iv) this bending continues along the chains resulting in a superhelix.

**Helical interactions**

As is shown above, the phthalocyanines in the stacks are arranged in a right-handed helical fashion (CD spectroscopy), whereas the super helices formed from them adopt a left-handed helix (electron microscopy). This paradoxical result can be understood by the following model. A fiber with a right-handed twist and a type B structure (Figure 3.1) has a ‘grooved’ exterior. In order to maximize the van der Waals contact between two fibers twisted around each other, each of them has to bend in order to fit into the groove of the other fiber, as is shown in Figure 4.3. The tilting angle between the two fibers is called the ‘inter-axial’, ‘crossing’ or ‘crossover’ angle. If only steric interactions are taken into account, this angle is double the angle $\beta$ of the groove with respect to the stacking axis. The crossing angle $\alpha$ depends on the diameter $D$ of the molecule, and the staggering angle $\phi$ and the stacking distance $d$ between two monomers. From Figure 4.4 it follows that $\tan(\beta)=a/d$, $\phi=a/r$ ($\phi$ in radians) and $r=D/2$. Combining these, gives equation 4.1. In Figure 4.5, the crossing angle $\alpha$

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**Figure 4.3** Suggested mechanism for the self-assembly of 1 (represented by squares): (i) Right-handed stacking of mono- and oligomeric phthalocyanines into a linear helical stack. Due to the helicity, a groove is formed at an angle $\beta$ with respect to the stacking direction; (ii) two stacks meet at double angle $\beta$; (iii) the stacks bend towards each other; (iv) this bending continues along the chains resulting in a superhelix.
Self-assembly of Disk-shaped Molecules to Coiled-coil Aggregates with Tunable Helicity

**Figure 4.4** Definitions of groove-angle $\beta$, stacking distance $d$, staggering angle $\phi$, radius $r$ and arc $a$ in a helically arranged stack.

**Figure 4.5** Plot of the crossing angle $\alpha$ as a function of the staggering angle $\phi$, according to equation 4.1. The three points (○, □, △) represent cases A, B and C (Figure 4.6) respectively. Crossing angles $\alpha$ exceeding $90^\circ$ correspond to helices with opposite handedness and crossing angles of $180^\circ - \alpha$, as indicated by the gray line.

**Figure 4.6** Three typical cases to show how the staggering angle determines the relative handedness of a superhelix. (A) A small staggering angle (<6.5°) results in a superhelix with the same handedness. (C) A large staggering angle (>6.5°) gives a superhelix with opposite handedness. (B) Borderline case: 'achiral' superhelix.
Chapter 4

is plotted as a function of the staggering angle $\phi$ according to this equation, with $D = 60$ Å and $d = 3.4$ Å. In this graph, three cases are shown. At staggering angles smaller than $6.5^\circ$, the crossing angle is smaller than $90^\circ$, which results in a superhelix with the same handedness (Figure 4.6A). At larger staggering angles, the crossing angle $\alpha$ exceeds $90^\circ$, which corresponds to a superhelix of opposite helicity and a crossing angle of $180^\circ - \alpha$ (Figure 4.6C). When the crossing angle is close to $\pm 90^\circ$ (at the intersections of the dotted lines), the superhelix can go either way as can be seen in Figure 4.6B. Of all staggering angles possible, 86% will result in a superhelix with an opposite handedness.

This analysis is very similar to that developed by Gottarelli et al. to explain the observed handedness of lyotropic liquid crystalline phases formed by guanisino quartets. They derived that an opposite handedness for the cholesteric phase is formed when $p / D < \pi$ ($p = $ helical pitch, $D = $ diameter) and a like handedness when $p / D > \pi$, which seems to be opposite to our theory. This paradox can be explained with the help of Figure 4.7: if the helix is extended in the direction of the bisector of the crossing angle as in the fibers (A), it will be left-handed; if it is extended in the direction of the normal to the crossing angle as in a cholesteric phase (B), it will be right-handed.

Sergeants and soldiers: Mutiny

An intriguing question is how the liquid-like tails in 1 are able to induce the helicity in the phthalocyanine aggregates. Two possibilities can be envisaged: (i) the phthalocyanines form

Figure 4.7 A) Left-handed superhelix. B) Schematic representation of a right-handed cholesteric discotic phase obtained with exactly the same crossing angle ($+60^\circ$).
Self-assembly of Disk-shaped Molecules to Coiled-coil Aggregates with Tunable Helicity

helical stacks even without the presence of a chiral center. Introduction of chirality leads to a helical bias; (ii) the phthalocyanines do not stack in a helical fashion if chiral centers are absent. The molecules are eclipsed (as was shown to be the case in the solid state of achiral \( \text{2} \) by van Nostrum\(^2\)), and the chiral tails cause the phthalocyanines to deviate from this achiral state. In the first case, a racemic mixture of helices is intrinsically present. The formation of the helical stacks may or may not be cooperative, \textit{i.e.} the helicity of two neighboring phthalocyanines may or may not be translated throughout the stack. Possibility (i) was initially expected to be the most likely one, since molecular mechanics calculations and a crystallographic database search\(^2\) had revealed that the two benzene rings in a metal-free dibenzo 18-crown-6 molecule are never in the same plane, but are often at an angle. This would suggest that also in a phthalocyanine fused with four dibenzo 18-crown-6 moieties, the four peripheral benzene rings are not in the plane of the phthalocyanine core but at an angle. If this is the case, the molecule can readily adopt a propeller-shape. A stack of propeller-shaped molecules is likely to be intrinsically helical.

To test the presence of an intrinsic helix in stacks of dibenzo crown phthalocyanines, a so-called sergeants and soldiers experiment was performed.\(^{26,27}\) Compound \( 3 \) was used as a chiral 'sergeant', and compound \( 2 \) as achiral 'soldier' since both had been shown to aggregate at low concentrations in chloroform without the need of adding a polar solvent such as methanol. In Figure 4.8, the relative CD intensities of solutions containing varying concentrations of \( 2 \) and \( 3 \) in chloroform, are plotted as a function of the percentage of chiral monomer present. Analysis of the data indicates that the 'soldiers' are only slightly influenced

\( \text{Figure 4.8 Normalized CD intensity as a function of the percentage of chiral phthalocyanine present. The curve is the statistical amount of pairs of neighboring chiral molecules.} \)
by the presence of the 'sergeants'. If no cooperative effects play a role the CD intensity must be the result of pairs of chiral monomers which are located next to each other. The statistical amount of pairs of chiral monomers in a random mixture of the type \( C_x A_{(1-x)} \) (\( x = \text{fraction of chiral monomer} \)) is proportional to \( x^2 \), hence also the CD intensity will be proportional to \( x^2 \) if only these pairs possess a specific handedness. This theoretical curve is plotted in Figure 4.8, from which it can be seen that the data points and the calculated curve coincide. This indicates that the observed CD intensity almost entirely originates from the chiral phthalocyanines themselves; the mixed (achiral-chiral) pairs of neighboring molecules do not adopt a specific helical orientation. Interestingly, in the mixed chiral-achiral polymers shown in Chapter 3, the mixed pairs had a similar helicity as the chiral-chiral pairs, depending on the solvent.

It was also attempted to induce helicity in the stacks of achiral phthalocyanines by adding a chiral alkali metal salt (potassium tartrate) and by using a solvent mixture composed of chloroform and ethyl (S)-lactate. However, no induced CD effect could be observed. These data strongly indicate that the aggregates have no intrinsic helix structure but that this structure is induced by the chiral centers in the tails. (possibility (ii), see above)

**Interaction with alkaline metal ions**

Crown ethers are known to form stable complexes with alkaline metal ions and unsubstituted dibenzo-18-crown-6 has been reported to give 1:1 complexes with potassium ions.\(^{28}\) In order to investigate what type of complexes are formed between compound 1 and potassium ions, titration experiments were performed in chloroform. The changes in the Q band regions of the absorption spectra of a dilute solution of compound 1 in chloroform revealed that two successive processes take place as the amount of potassium picrate is varied. During the first process, which occurs upon the addition of 0-1.7 equivalents of potassium ions (Figure 4.9A), the intensities of the Q bands at 685 and 700 nm decrease while at 630 nm a new band arises. The second process which occurs in the range of 1.5-8 equivalents of potassium ions is characterized by the fact that the Q bands at 685 and 700 nm increase while the band at 630 decreases (Figure 4.9B). The spectrum of pure 1 and the spectrum of 1 saturated with potassium ions was found to be nearly identical, whereas the spectrum of 1 with approximately two equivalents of \( K^+ \) was completely different. The characteristic absorption at 630 nm is indicative of the presence of co-facial phthalocyanine dimers. The direct interconversion process between the dimers and the free monomers is evident from the fact that several isosbestic points are observed.\(^{29}\) These results suggest that at low concentrations, potassium ions are shared between two crown ether units of two different phthalocyanines. In
this way, four ions can be accommodated by two phthalocyanines, in a similar fashion as lawn bowling balls are held in a container (Figure 4.10). This process is expected to be facilitated by attractive π–π interactions between the aromatic rings. When more than 2 equivalents of potassium picrate are added, the crown ether ring start to complex additional potassium ions, which eventually leads to separation of the sandwich-like complexes. It is interesting to note that the dimer complex did not show any CD activity, suggesting that the phthalocyanine molecules in the dimers are stacked in an eclipsed conformation.

The largest spectral differences that occur upon the addition of K⁺ ions can be seen at 700 nm.(Figure 4.9) Also the effect of other metal ions on the UV spectrum of 1 in chloroform was investigated. In Figure 4.11, the absorbance at 700 nm is plotted as a function of the ion/Pc ratio. It is clearly visible that all metal ions have an appreciable effect on the

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**Figure 4.9** Electronic absorption spectra (Q-band region) of 1 (10 µM) in chloroform in the presence of increasing amounts of potassium picrate. A) 0-1.5 equivalents. B) 1.5-8 equivalents. Arrows denote increasing K⁺/Pc ratio.
spectral properties, but not all to the same extent. In the case of Na⁺ ions, only very small quantities of dimer are formed. This is because sodium fits comfortably inside one crown ether unit and no energy is gained from complexing a second crown ether ring. However, as was also observed for K⁺ (Figure 4.9), the shape of the Q band of the non-aggregated phthalocyanine is slightly different (broader and less intense) when metal ions are present in the crown ether units than when these ions are not present, causing a decrease of the absorbance at 700 nm which is not related to dimer formation. In the presence of Rb⁺, very stable dimers are formed which do not break apart at higher metal ion concentrations. This phenomenon is related to the radius of the Rb⁺ ion which has the perfect dimension to give a

![Figure 4.10 Schematic representation of the formation and breakdown of the sandwich-type complexes between alkaline metal ions and 1. (A) Non-aggregated 1. (B) Dimer 1₂·4M⁺. (C) Non-aggregated 1·4M⁺.](image)

![Figure 4.11 Normalized absorbance at 700 nm as a function of the ratio metal ion / phthalocyanine 1 for different alkali and earth alkali metal ions: Na⁺ (■), K⁺ (□), Rb⁺ (Δ), Cs⁺ (●) and Ba²⁺ (○) picrate.](image)
complex in which four ions are accommodated by two co-facially stacked phthalocyanines. In the case of Cs\(^+\), the fit between the ion and crown ether ring is no longer perfect, which results in a system in which dimeric and monomeric phthalocyanine complexes are in equilibrium. The effect of Ba\(^{2+}\) is similar to that of K\(^+\), in the sense that dimers are formed which break apart at higher ion concentrations. This result was not unexpected, since the ionic radii of potassium and barium are very similar. Due to the higher charge of Ba\(^{2+}\), the equilibrium lies more towards the side of the dimer and less towards the monomeric species, which explains why the minimum in the curve is closer to the theoretically expected value of \([M^{2+}]/[1] = 2\), and closer to that of the curve of Rb\(^+\).

**Figure 4.12** Transmission electron micrographs (platinum shadowing) of gels from compound 1, showing the effect of KCl on the formation of the aggregates. (A) and (B) Left-handed coiled-coil aggregates without KCl. (C) and (D) Nonhelical rods formed in the presence of KCl.
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Blocking of chirality transfer

When 1 was heated in chloroform in the presence of solid KCl, and allowed to cool down to room temperature, a gel was formed similar to 1. Close inspection by electron microscopy (Figure 4.12 C) revealed that fibers were still formed but that they had no helical character. This lack of helicity can be understood if it is assumed that the ions are located between the crown ether units of neighboring phthalocyanines, and force the molecules in an eclipsed orientation as in Figure 4.10B. This is well possible, since it was shown that K+ can form sandwich-type 4:2 complexes as well as 4:1 complexes. Interestingly, no well-defined fiber structures were observed when 1 was treated in chloroform with RbClO₄, suggesting that in that case, the complex 1₂ · 4RbClO₄ can not aggregate any further. This is probably due to the size of the ions, which causes the crown ethers to bend away from the phthalocyanine plane, prohibiting a well-defined co-facial aggregation.

In an effort to obtain more detailed structural information of the structures of the helical and non-helical gels formed by 1 with and without the presence of KCl, small angle X-ray diffraction studies on the dried-in gels of 1 were carried out. The results are summarized in Table 4.1. Interestingly, the structure of 1 in the dried-in lyotropic phase showed remarkable similarities with the thermotropic phase of 2 with linear alkoxy tails, also shown in Table 4.1.¹⁸ In all cases, the peaks could be assigned to a hexagonal columnar lattice. The (100) and (210) reflections could be analyzed using the Scherrer formula \( \xi = \lambda / (\omega \sqrt{2} - \cos \theta) \), with \( \omega \sqrt{2} \) being the band width at half height in radians. For 1, a value of \( \xi = 64.5 \text{ Å} \) was obtained, which corresponds to a single column as an ordered domain, typical for a columnar mesophase.

Table 4.1 d-spacings (Å), assigned Miller indices (hkl) and calculated inter-columnar distances D derived from X-ray diffraction experiments on various crown ether phthalocyanines

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>1</th>
<th>1 · x KCl</th>
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<tbody>
<tr>
<td>(100)</td>
<td>33.2</td>
<td>36.52</td>
<td>35.3</td>
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<tr>
<td>(200)</td>
<td>16.8</td>
<td>-</td>
<td>17.3</td>
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<tr>
<td>(210)</td>
<td>13.3</td>
<td>14.22</td>
<td>13.4</td>
</tr>
<tr>
<td>(001)</td>
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<td>3.36</td>
<td>3.34</td>
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<tr>
<td>D</td>
<td>38.3</td>
<td>42.17</td>
<td>40.76</td>
</tr>
</tbody>
</table>

² Data taken from ref.18.
The influence of alkaline metal ions on polymer phthalocyanine 6

Due to the breakdown of the sandwich-type complexes of 1 and alkali metal ions at the very low concentrations required for the optical experiments, even in the presence of methanol, it was impossible to follow the disruption of the helicity of the fibers by potassium ions with the help of CD spectroscopy. This is not a problem in the case of polymer 6, since in this macromolecule the phthalocyanine cores are covalently linked. In Figure 4.13, the CD spectra of 6 in the presence of various amounts of potassium picrate are shown. Upon increasing the ratio $[K^+]/[Pc]$, remarkable changes in the CD spectra occurred, both in the shape and the intensity of the CD bands. Initially, at low concentrations of potassium ions, the intensity of the spectrum decreases, accompanied with a small blue-shift of the bands. At higher concentrations, the spectrum regained its intensity, and the bands became even stronger than without any ions present, and also the original shapes of the bands returned. These results can be explained in a similar way as discussed above for the supramolecular polymers (See Figure 4.14). At low concentrations of potassium ions, sandwich-type complexes are formed, forcing the phthalocyanines that bind an ion into an eclipsed conformation. At higher concentrations, each crown ether ring hosts one ion, and electrostatic repulsion drives the crown ethers apart.

In contrast to the supramolecular polymer this repulsion does not cause the breakdown of the complex because now a stable polymer backbone is present. The phthalocyanines are forced to adopt a more staggered conformation, resulting in a higher staggering angle and a larger

Figure 4.13 CD spectrum of 6 as a function of the amount of potassium picrate per Pc monomer.
CD effect than when no potassium ions are bound in the crown ether rings. The staggering angle does not reach 45°, since in that case the structure would be achiral (apart from the chirality of the tails) and the CD effect would be expected to disappear, which is not the case. Addition of sodium picrate to the polymer was found to hardly alter the CD signal. Rubidium behaved in a similar way as potassium but the observed effects were much smaller. Unlike in the case of monomeric crown ether phthalocyanine, the effect of the addition of barium ions was different from that of potassium and only a small decrease in intensity was observed. The reason for this difference might be that polymer 6 does not bind barium ions very well because of the very strong repulsive forces between these doubly charged ions, preventing the complexation of two ions at close proximity.

4.3 Conclusions

The results presented here provide insight into the way chiral information is transferred and expressed in synthetic supramolecular systems. An interesting mechanism is proposed by which chirality is amplified in a non-linear fashion from point chirality to supramolecular (helical) chirality. The $S$-chiral centers in the tails of the crown ether phthalocyanine molecules induce a clock-wise orientation of the molecular discs, which, aided by strong $\pi-\pi$ stacking, leads to the formation of fibers with right-handed helicity. Side-on aggregation of the fibers subsequently yields super-coiled structures with left-handed helicity in a hierarchical self-assembly process. Such a control over chirality may be valuable in designing
new materials for opto-electronic applications. The present chiral fibers are attractive candidates for use as non-linear optical materials and as components in sensor devices, for instance in the detection of alkali metal ions.

4.4 Experimental section

General procedures

All chemicals were commercial products and were used as received, unless stated otherwise. $^1$H-NMR spectra were recorded on Bruker AC-100 and Bruker AC-300 instruments. Chemical shifts are reported in ppm relative to tetramethylsilane ($\delta=0.00$) as an internal standard. Optical spectra were recorded using a Bio-Rad FTS-25 instrument for FT-IR, a Varian Cary 50 spectrophotometer for UV/Vis and a Jasco J-810 spectropolarimeter for CD. MS spectra were recorded on a VG 7070E or a Finnigan MAT900S instrument. Melting points were determined on a Jeneval polarization microscope equipped with a Linkam THMS 600 hot stage and a Linkam TMS92 temperature programmer, and are reported uncorrected. Elemental analyses were determined with a Carlo Erba EA 1108 instrument. Transmission electron micrographs were recorded on JEOL-100CX II and Philips EM 201c electron microscopes. Samples were prepared by applying a small amount of a gel to a carbon-coated copper grid; excessive material was shaken off after 5 seconds. After drying, the samples were stained by platinum shadowing at an angle of approximately 45°.

Synthesis

1,2-(4-Methylphenyl)sulfonyloxyethoxy]ethoxy]benzene (7)

This compound was synthesized according to a literature procedure.$^{15}$

13, 14-Dibromo-6, 7, 10, 17, 18, 20, 21-octahydrodibenzo[b, k][1, 4, 7, 10, 13, 16] hexaoxacyclooctadecine-2-carbaldehyde (8)

3,4-Dihydroxybenzaldehyde (4.76 g, 34.4 mmol), 7 (25.92 g, 34.4 mmol) and K$_2$CO$_3$ (10.5 g, 75.7 mmol) were mixed together in 400 ml of freshly distilled acetonitrile, and refluxed for 16 h. After cooling, the mixture was acidified with conc. hydrochloric acid, and concentrated in vacuo. Water (200 ml) and chloroform (300 ml) were added. The organic layer was washed with water (3×200 ml) and concentrated in vacuo. The product was purified by crystallization from chloroform, yielding 13.67 g of a white solid, mp 190°C. FT-IR (KBr) $\Lambda \text{ [cm}^{-1}]$ =
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1236, 1279 (Ar-O-C), 1498 (Ar), 2725, 1693 (H-C=O). $^1$H NMR (CDCl$_3$): $d$ 3.90-4.33 (m, 16H, CH$_2$), 7.05 (s, 2H, BrArH), 6.9-7.5 (m, 3H, CHOArH) 9.78 (s, 1H, H-C=O). MS (EI): m/z 546 (M$^+$). Anal. found (Calcd.) for C$_{21}$H$_{22}$O$_7$Br$_2$: C 46.25 (46.18), H 3.90 (4.06).

13, 14-Dibromo-6, 7, 9, 10, 17, 18, 20, 21-octahydrodibenzo [b, k] [1, 4, 7, 10, 13, 16] hexaoxacyclooctadecin-2-ol (9)

A mixture of H$_2$O$_2$ (6.7 g, 58.8 mmol), 1 ml H$_2$SO$_4$ and 150 ml of methanol was added to a suspension of 9 (21.43 g, 39.2 mmol) in 150 ml chloroform. After 18 hours of stirring at room temperature, water (150 ml) was added. The precipitate was filtered off and kept separately. The layers were separated, and the water layer was extracted with chloroform (3×50 ml). The combined organic layers were washed with water, and concentrated in vacuo. The resulting solid was combined with the collected precipitate and crystallized from a mixture of THF and chloroform (1:1 v/v). Yield: 13.10 g (65%) of a white powder (mp 176°C). FT-IR (KBr) $\Lambda^{-1}$ [cm$^{-1}$] = 1253, 1223 (Ar-O-C), 1356 (Ar-O-H), 1493 (Ar), 3347 (OH), MS (EI): m/z 546 (M$^+$).

13, 14-Dibromo-2, 3, 6, 7, 9, 10, 17, 18, 20, 21-decahydrodibenzo [b, k] [1, 4, 7, 10, 13, 16] hexaoxacyclooctadecine-2, 3-dione (10)

K(NO)(SO$_3$)$_2$ (6.63 g, 25.4 mmol) and a solution of KH$_2$PO$_4$ (0.86 g, 6.36 mmol) in 100 ml water are added quickly to a vigorously stirring solution of tetrabutylammonium chloride (1.12 g, 4.04 mmol) in 200 ml water. This mixture is added quickly to a solution of 9 in 200 ml of THF, and stirred vigorously for 2 hours at room temperature. The solution was saturated with NaCl, and stirred for one more hour. The organic layer was separated, and the THF was removed in vacuo. The resulting solid was dissolved in chloroform (100 ml), washed with water (3×50 ml) and concentrated in vacuo. Yield: 4.94 g (90%) of an orange solid, mp 190°C. $^1$H NMR (CDCl$_3$): $d$ 3.56-4.33 (m, 16H, CH$_2$), 5.69 (s, 2H, H-C-C=O), 7.05 (s, 2H, ArH). MS (EI): m/z 534 (M$^+$).

13, 14-Dibromo-2, 3, 6, 7, 9, 10, 17, 18, 20, 21-decahydrodibenzo [b, k] [1, 4, 7, 10, 13, 16] hexaoxacyclooctadecine-2, 3-diacetate (11)

Compound 10 (6.35 g, 12.02 mmol) and powdered zinc (3 g) were refluxed in a mixture of 60 ml of acetic acid and 60 ml of acetic anhydride for 3 hours. After removal of the solvents in vacuo, chloroform (100 ml) was added. The suspension was filtered to remove the insoluble salts. The residue was washed with chloroform, and the combined filtrates were concentrated to yield 6.02 g (79%) of a yellowish solid, mp 193°C. $^1$H NMR (CDCl$_3$): $\delta$ 2.255 (s, 6H,
CH₃), 3.95-4.14 (m, 16H, CH₂), 6.690 (s, 2H, AcOArH), 7.055 (s, 2H, BrArH). MS (FAB) m/z 635 (M+). Anal. found (Calcd.) for C₂₄H₂₆O₁₀Br₂: C 45.81 (45.45), H 4.09 (4.13).

2, 3-Dibromo-13, 14-di[(S)-3, 7-dimethyloctyloxy]-6, 7, 9, 10, 17, 18, 20, 21-octahydrodibenzo [b, k] [1, 4, 7, 10, 13, 16] hexaoxacyclooctadecine (12)
A mixture of diacetate 11 (1.26 g, 1.99 mmol), K₂CO₃ (1.65 g, 12.0 mmol) and (S)-1-bromo-3,7-dimethyloctane (0.92 g, 4.18 mmol) in degassed butanol was refluxed for 40 h. After cooling, the mixture was acidified with 3N aqueous HCl and concentrated. Water (200 ml) was added, and the mixture was extracted with chloroform (2×100 ml). The combined organic layers were washed with water (3×100 ml) and concentrated. The product was purified with column chromatography (silica, 2% methanol/chloroform), yielding 0.97 g (59%) of a white solid, mp 113°C. ḳH-NMR (CDCl₃, 300MHz): δ 0.85-0.94 (m, 18H, CH₃), 1.10-1.82 (m, 20H, CH₂, CH), 3.92-4.12 (m, 20H, OCH₂), 6.58 (s, 2H, ArH), 7.06 (s, 2H, BrArH). Anal. found (Calcd.) for C₄₀H₆₂O₈Br₂: C 57.78 (57.83), H 7.48 (7.52).

2, 3-Dibromo-13, 14-di[(R)-2-methylbutoxy]-6, 7, 9, 10, 17, 18, 20, 21-octahydrodibenzo [b, k] [1, 4, 7, 10, 13, 16] hexaoxacyclooctadecine (13)
A mixture of diacetate 11 (1 g, 1.58 mmol), K₂CO₃ (1 g, 7.2 mmol) and (R)-1-bromo-2-methylbutane (6 g, 40 mmol) in 20 ml freshly distilled methyl isobutyl ketone was refluxed for 18 h. After cooling, the mixture was acidified with 3N aqueous HCl and concentrated. Water (200 ml) was added, and the mixture was extracted with chloroform (2×100 ml). The combined organic layers were washed with water (3×100 ml) and concentrated. The product was purified with column chromatography (silica, 2% methanol/chloroform), yielding 0.65 g (60%) of a white solid.

13, 14-Di[(S)-3, 7-dimethyloctyloxy]-6, 7, 9, 10, 17, 18, 20, 21-octahydrodibenzo [b, k] [1, 4, 7, 10, 13, 16] hexaoxacyclooctadecine-2, 3-dicarbonitrile (14)
A solution of dibromocrown ether 12 (0.148 g, 0.179 mmol), CuCN (80 mg, 0.89 mmol) and 0.5 ml pyridine in 10 ml DMF was refluxed under nitrogen for 60 h. After cooling, the mixture was poured into 50 ml of 25% aqueous ammonia. Chloroform (25 ml) was added and air was bubbled through the mixture for 2 h. The mixture was extracted with chloroform (3×25 ml), the organic layer was washed with ammonia, water, and brine, dried over MgSO₄, and concentrated. The product was purified by column chromatography (silica gel, 0.5% methanol/chloroform) and finally crystallized from ethanol, yielding 77.4 mg (60%) of a
white solid. Mp: 96°C. \(^1\)H-NMR (CDCl\(_3\), 300MHz): \(\delta\) 0.85-0.94 (m, 18H, CH\(_3\)), 1.10-1.85 (m, 20H, CH\(_2\), CH), 3.92-4.24 (m, 20H, OCH\(_2\)), 6.57 (s, 2H, ArH), 7.12 (s, 2H, CNArH). MS (FAB) m/z 723 (M\(^+\)).

13, 14-Di{(R)-2-methylbutoxy} -6, 7, 9, 10, 17, 18, 20, 21-octahydrodibenzo [b, k] [1, 4, 7, 10, 13, 16] hexaoxyoctadecine-2, 3-dicarbonitrile (15)

A solution of dibromocrown ether 13 (0.6 g, 0.87 mmol), CuCN (0.4 g, 4.4 mmol) and 0.5 ml pyridine in 10 ml DMF was refluxed under nitrogen for 60 h. After cooling, the mixture was poured into 50 ml of 25% aqueous ammonia. Chloroform (25 ml) was added and air was bubbled through the mixture for 2 h. The mixture was extracted with chloroform (3\(\times\)25 ml), the organic layer was washed with ammonia, water, and brine, dried over MgSO\(_4\), and concentrated. The product was purified by column chromatography (silica gel, 0.5% methanol/chloroform), yielding 230 mg (45%) of a white solid.

Tetrakis(13, 14-di-(S)-3, 7-dimethyloctyloxy-6, 7, 9, 10, 17, 18, 20, 21-octahydrodibenzo [b, k] [1, 4, 7, 10, 13, 16] hexaoxyoctadecine)-[2, 3]-phthalocyanine (1)

Dicyanocrown ether 14 (33.9 mg, 0.046 mmol) was refluxed in freshly distilled 2-(dimethylamino)-1-ethanol (0.5 ml) for 60 h under nitrogen. After cooling, acetonitrile (10 ml) was added and the mixture was filtrated. The residue was dissolved in a very small amount of chloroform and precipitated in methanol (20 ml). This procedure was repeated (alternating with acetonitrile and methanol) until a colorless filtrate remained. The product was finally obtained by freeze-drying from benzene. Yield: 9.9 mg (30%) of a dark green solid. \(^1\)H-NMR (CDCl\(_3\), 300MHz): \(\delta\) 0.75-1.00 (m,72H, CH\(_3\)), 1.00-1.85 (m, 80H, CH\(_2\), CH), 3.75 (t, 16H, OCH\(_2\) tail), 3.90-4.80 (m, 64H, OCH\(_2\) crown), 6.64 (s, 8H, ArH), 8.35 (s, 8H, PcH). Anal. found (Calcd.) for C\(_{168}\)H\(_{250}\)N\(_8\)O\(_{32}\)·8H\(_2\)O: C 66.44 (66.42), H 8.86 (8.82) N 3.65 (3.69).

Tetrakis(13, 14-di-(R)-2-methylbutoxy-6, 7, 9, 10, 17, 18, 20, 21-octahydrodibenzo [b, k] [1, 4, 7, 10, 13, 16] hexaoxyoctadecine)-[2, 3]-phthalocyanine (3)

Dicyanocrown ether 15 (230 mg, 0.39 mmol) was refluxed in freshly distilled 2-(dimethylamino)-1-ethanol (1 ml) for 60 h under a nitrogen atmosphere. After cooling, chloroform (2 ml) was added and the mixture was filtrated. The residue was dissolved in toluene, concentrated, and refluxed in chloroform (4 ml) for 5 minutes. After cooling, the resulting floppy gel was filtered in a Soxhlet container. The product was purified by Soxhlet
Self-assembly of Disk-shaped Molecules to Coiled-coil Aggregates with Tunable Helicity

extraction with acetone (2 h) and methanol (2 h), and finally obtained with toluene. The solution was concentrated and freeze-dried from benzene to yield 50 mg (22%) of a dark green solid. MS (FAB) m/z 2355 (M·Na⁺).

13, 14-Di [ (S)-3, 7-dimethyloctyl] oxy-2, 3, 6, 7, 9, 10, 17, 18, 20, 21-decahydro-1H-benzo [11, 12] [1, 4, 7, 10, 13, 16] hexaoxacyclooctadecino [2, 3-f] isoindole-1, 3-diimine (16)

Dicyanocrown ether 14 (39.7 mg, 0.055 mmol), NaOMe (5.6 mg, 0.1 mmol), 10 ml THF and 10 ml MeOH were placed in a three-necked flask equipped with a gas inlet. Anhydrous ammonia was bubbled through the solution, first 1 h at room temperature and subsequently during reflux for 4 h. The crude product was concentrated in vacuo, dissolved in chloroform, and filtrated over celite. Removal of the solvent in vacuo afforded 37 mg (91%) of a light green solid, mp 150°C (dec. to give 1) ¹H-NMR (CDCl₃,100MHz): δ 0.8-1.0 (m, 18H, CH₃), 1.1-1.9 (m, 20H, CH₂ + CH), 3.8-4.3 (m, 20H, OCH₂), 6.575 (s, 2H, RÖArH), 6.983 (s, 2H, CArH). MS (FAB) m/z 740 (M⁺).

Tetrakis(13, 14-di-(S)-3, 7-dimethyloctyloxy-6, 7, 9, 10, 17, 18, 20, 21-octahydrodibenzo [b, k] [1, 4, 7, 10, 13, 16] hexaoxacyclooctadecine)-[2, 3]-phthalocyaninato silicon dihydroxyde (5)

To a solution of 16 (42.5 mg, 0.057 mmol) in 1.5 ml quinoline was added tetrachlorosilane (1.5 g, 8.8 mmol) under a nitrogen atmosphere. The solution was stirred at 150°C for three days. After cooling, water (1 ml) was added and the mixture was stirred for 1 h, and taken up in 20 ml CH₂Cl₂. The organic layer was washed with H₂O (3×20 ml) and concentrated to a volume of ca. 10 ml. The product was precipitated repeatedly from acetonitrile and methanol, and finally obtained by a Soxhlet-extraction with acetone. Yield: 16.5 mg (39%) of a dark green solid.

¹H-NMR (CDCl₃, 300 MHz): δ 0.6-1.0 (m, 72H, CH₃), 1.0-1.9 (m, 80H, CH₂ + CH), 3.91 (m, 16H OCH₂), 3.8-4.5 (m, 64H, CH₂ crown), 6.55 (s, 8H, ArH).

Poly [tetrakis(13, 14-di { [ (S)-3, 7-dimethyloctyl] oxy} -6, 7, 9, 10, 17, 18, 20, 21-octahydrodibenzo [b, k] [1, 4, 7, 10, 13, 16] hexaoxacyclooctadecine)-[2, 3]-phthalocyaninato] siloxane (6)

Dihydroxy phthalocyaninato silicone 5 (60.0 mg, 0.02 mmol) was heated at 200°C in vacuo for 3 h. Yield: 60 mg (100%) of a purple solid.

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1H-NMR (CDCl3, 300 MHz): \( \delta \) 0.6-0.9 (m, 72H, CH3), 0.9-1.9 (m, 80H, CH2 + CH), 3.749 (t, 16H, OCH2) 3.5-4.7 (b, 64H, CH2 crown), 6.0-6.5 (b, 8H, ArH), 7.5-8.2 (b, 8H, PcArH).

4.5 References and notes


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This thesis, Chapter 3.


In the presence of methanol and potassium picrate, no aggregates are observed.
5.1 Introduction

Thus far in this thesis, several crown ether-functionalized phthalocyanines have been described, each displaying different behavior in solution. Compound 1, with non-functionalized 18-crown-6 ether rings (Chart 5.1), is fairly soluble in non-polar solvents. In contrast, Pc 2, with linear alkoxy chains attached to the crown ethers via benzene linkers, is only soluble in hot chloroform and gels upon cooling. The same is true for compound 3, however the solubility of this phthalocyanine is less and the resulting gel is not very firm. Compound 4 is soluble in chloroform at low concentrations; at higher concentrations, a gel can be formed by heating and subsequent cooling. Compound 5 does not dissolve in any organic solvent, whereas the phthalocyanines substituted peripherally with alkoxy tails, which were prepared in the late 1980’s (not shown), are very well soluble. From these simple gel studies, it is apparent that the benzene rings tend to render the phthalocyanine insoluble as a result of a strong exo-recognition, whereas the alkoxy chains tend to solubilize them. The gel state can be considered to be a compromise of these two opposing forces; a) a solid in the stacking direction as a result of the (enthalpic) tendency of the central core to aggregate, and b) a solution in the directions orthogonal to the stacking direction which is a result of the entropy gained by the highly soluble aliphatic chains. A gel such as that formed from 2 can therefore be considered to be a one-dimensional solid and a two-dimensional solution. If this assumption is correct, it opens the possibility to tune the gel-formation not only by changing the nature of the aliphatic tails, as shown in Chapter 4, but also by altering the stacking of the rest of the molecule. Previously, Van Nostrum et al. argued that the very strong self-assembly of 2 is the result of intermolecular exo-recognition of the phthalocyanine units and the four
benzene units. If this assumption is correct, it should be possible to tune the self-assembling properties by varying the nature of the linker. For example, if the peripheral aromatic rings would be replaced by fully saturated linkers as in 6, weaker exo-recognition will be expected and the overall interactions will be decreased. Such a compound should, in principle, not form extended aggregates in organic solvents. On the other hand, if the peripheral benzene rings were replaced by functional groups that are known for their strong interactions in organic solvents, such as amides (for instance compound 7), strong recognition is expected, which then might result in very large aggregates.

Replacing the benzene linkers by either saturated groups or amide functions will inevitably change the \( sp^2 \)-centered carbon atoms that are fused with the crown ethers into \( sp^3 \) centered atoms. This automatically introduces chirality into the molecule, which can be dealt with in two ways. If optically pure starting materials are used and no racemization occurs during the synthesis, well-defined optically pure compounds will be obtained. If racemic starting materials are used, or any racemizing synthetic steps occur then a mixture of isomers will be obtained. The first approach will be slightly more expensive and will require more care during the synthesis, whereas the latter one may render any purification or characterization steps more difficult. Chirality has shown to be an excellent tool to characterize supramolecular structures by means of circular dichroic spectroscopy.
Furthermore, bringing chiral centers closer to the core of the phthalocyanine molecule might be an excellent opportunity to investigate in more detail the hierarchical way in which chirality is transferred from the chiral centers to the superstructure as was shown for 4. For these reasons, the obvious choice was to aim for optically pure compounds, in preference to the synthesis of mixtures of stereoisomers.

Optically active compounds of the type of 6 and 7 can be synthesized starting from the natural tartaric acid, a widely used precursor for the synthesis of esters, ethers and amides. Already in the mid-seventies it was established that L-(+)-tartaric acid is a highly suitable structural unit for incorporation into a crown ether system, since it is a substituted ethylene glycol of known absolute configuration and it is readily available in optically pure form.

5.2 Results and discussion

Synthesis

The route for the synthesis of the crown ether phthalocyanines with alkyl tails connected via aliphatic spacers is shown in Scheme 5.1. First, catechol was converted into diol 8, which was obtained in almost pure form by extraction with ethyl acetate, followed by washing with water. This product was chlorinated with thionyl chloride in pyridine, yielding dichloride 9, which could be purified by Kugelrohr distillation. Quantitative bromination with molecular bromine in chloroform followed by substitution of the chlorine atoms in a Finkelstein exchange with sodium iodide in acetonitrile, yielded diiodide 11, which was purified by crystallization from methanol. For the preparation of this compound, a route via the chloride instead of the corresponding ditosylate, which was described previously was chosen, in order to avoid column chromatography. Protected threitol 12 was synthesized from L-(+) tartaric acid following literature procedures. This compound was reacted in KOH/DMSO with decyl bromide and the resulting product was deprotected in situ with trifluoro acetic acid. Subsequent crystallization from diethyl ether yielded diol 13. Reaction of 13 with diiodide 11 using thallous ethoxide as a base in DMF gave crown ether 15 in poor yield (22%). Other attempts to achieve ring closure using different bases, templates, and leaving groups resulted almost exclusively in elimination reactions. Cyanation of 15 with CuCN in DMF directly yielded copper phthalocyanine 6a. It is known that in some cases, a dinitrile cannot be isolated and is directly converted into the corresponding copper phthalocyanine. It was not investigated, however, whether this could have been prevented in the present case.
It is clear that it would be very laborious to synthesize a homologues series of phthalocyanines with alkyl tails of different lengths following the route of Scheme 5.1, since these tails are introduced in a too early stage of the synthesis. In order to be able to introduce
the aliphatic tails in a later stage, phthalocyanine 6b containing benzyl protected peripheral hydroxyl groups was synthesized from the diol 14, see Scheme 5.1. Unfortunately, not enough material could be obtained to use this compound as a precursor for the synthesis of phthalocyanine derivatives with different chain lengths.

Crown ether phthalocyanines 7a and 7b, both containing amide linkers, were synthesized following the route described in Scheme 5.2. A related route has been used by Fyles et al to prepare lipophilic crown ethers.11 Commercially available (+)-N,N,N',N'-tetramethyl-L-tartaramide (19) was reacted with diiodide 11 in DMF using thallous ethoxide as a base to yield crown ether 20. This dibromide was cyanated using standard methods to give 21, which was converted into the corresponding phthalocyanine 22 by refluxing in
dimethyl aminoethanol. Refluxing in acidic methanol converted this octa-amide substituted phthalocyanine into the octa-ester 23, which in turn was converted into amides 7a and 7b by heating this compound in n-hexyl amine and n-dodecylamine, respectively.

Molecular modeling

Prior to the actual synthesis of the amide-containing phthalocyanines, some initial molecular modeling experiments were performed. For these experiments, compound 24 was used as a model since it is more simple than compounds 7a and 7b, which facilitates computation. In 24, the central hydrogen atoms have been omitted to leave an anti-aromatic dehydro-phthalocyanine. Most force fields do not include anti-aromaticity and will just regard the molecule as a flat, conjugated system, whereas including the central hydrogen atoms results in unrealistic rotation around the two 'single' bonds in the phthalocyanine core (indicated by arrows in Figure 5.1), as a result of repulsive electrostatic forces between the two nitrogen hydrogen atoms. Furthermore, in compound 24, only two peripheral amide crown ethers are present instead of four to simplify the computation. This has obviously an enormous impact on the energies involved; however, because the two-fold symmetry axis of 24 coincides with the pseudo-four-fold symmetry axes of 7a and 7b, and the crown ether units can be considered independently, it is expected that the modeled geometry will be quantitatively comparable. In consequence, any conclusions drawn for the two fold symmetrical 24 will also hold for the four-fold symmetrical analogues. In Figure 5.2, a typical result obtained with the MM3 force field is shown.13-15 Initially, four molecules of 24 were placed on top of each other in a fully eclipsed geometry and this system was then extensively minimized. Two conclusions can be made: firstly, due to the chirality of the molecules, the phthalocyanines adopt a staggered conformation; secondly and most importantly, the calculations show that, as
a result of hydrogen bonding, the amide groups prefer a longer stacking distance than the aromatic core. This difference is somehow compensated by an increased staggering angle but not entirely.
Aggregation behavior

The aggregation behavior of compounds 6a, 6b, 7a, and 7b was studied by investigating their gel forming properties in various solvents. Phthalocyanine 6a was found to dissolve very well in apolar solvents including chloroform and hexane, but did not form any gel upon cooling. This result is in line with the idea that the benzene rings in 2, 3 and 4 are responsible for the tendency of these molecules to gelate. Since these rings are absent in 6a, no such gels can be formed. Amide phthalocyanine 7a only dissolved in polar solutions, e.g. DMF or a mixture of methanol and chloroform. Compound 7b, on the other hand, was found to be soluble in chloroform but did not aggregate upon cooling. For these compounds, no solvents could be found in which aggregation and solvation are in such a balance that a gel is generated as was apparently the case for 4. Various CD measurements on 7b confirm the absence of even small chiral aggregates in solution, since no CD signal could be observed. These results can be explained by the misfit in stacking distance between the amide groups on the one hand and the phthalocyanine core on the other hand, as was suggested by the calculations (see above).

Surprisingly, when compound 6b was dissolved in hot aromatic solvents (10 mg/ml) and subsequently cooled to room temperature, a gel was obtained. This gel was studied by electron microscopy (TEM). As can be seen in Figure 5.3, it consists of well-defined needle-shaped structures all having micrometer length. The diameter of the smallest needles is 30 nm, approximately eight times the diameter of the individual molecules. So, in contrast to

Figure 5.3 Transmission electron micrographs (platinum shadowing) of gels from compound 6b in benzene.
compounds 2 and 4, the fibers are not single stacks of molecules. In the pictures, unfortunately no clear chirality could be observed. In addition circular dichroic spectroscopy on a diluted gel did not show any optical activity. The most plausible explanation for these results is that the molecules are stacked in a columnar fashion. In the long direction of the aggregates the molecules are well-ordered, whereas in the perpendicular directions no long-range order is present, which accounts for the small lateral dimensions. An explanation for the lack of chirality in these aggregates could be the role of the solvent. Since the aggregates are only observed in aromatic solvents, it is tentatively proposed that the solvent molecules take positions between the benzene rings of the phthalocyanine molecules (in an orientation as indicated in Figure 3.5), thereby not only stabilizing the aggregates by edge-to-face \( \pi-\pi \) interactions but also blocking non-eclipsed orientations of the phthalocyanine molecules.

5.3 Conclusions

In this chapter, experiments are described aimed at exploring the possibilities to form linear aggregates from rationally designed phthalocyanines, inspired by the results reported in Chapter 4. Starting from compound 2, which is to date the best-gelating phthalocyanine, first the peripheral benzene rings were formally removed. This resulted in a predicted complete loss of aggregation power. Secondly, it was attempted to re-introduce interacting groups at the periphery by implementing amide functions containing alkyl tails. In the case of short alkyl tails the compound (7a) was poorly soluble. In the case of long alkyl tails (compound 7b) no aggregation could be observed. It might be possible that intermediate chain lengths still can give well-defined aggregates, but this has not been investigated yet. Molecular modeling studies clearly indicate that the stacking distance at the periphery of the phthalocyanine molecules should be complimentary to that at the phthalocyanine core. This hypothesis was substantiated by the surprising aggregation behavior of the benzyl derivative 6b, whose peripheral groups stack at the same distance as the phthalocyanine core itself.

5.4 Experimental section

General procedures

Catechol was recrystallized from CHCl₃ prior to use. DMF was distilled from BaO at reduced pressure and kept under an inert atmosphere. Merck silica gel (60H) was used for column
chromatography. Acetonitrile was distilled from CaH₂. All other chemicals were commercial products and were used as received, unless stated otherwise. ¹H-NMR spectra were recorded on Bruker AC-100 and Bruker AC-300 instruments. Chemical shifts are reported in ppm relative to tetramethylsilane (δ=0.00) as an internal standard. Optical spectra were recorded using a Bio-Rad FTS-25 instrument for FT-IR, a Varian Cary 50 spectrophotometer for UV/Vis and a Jasco J-810 spectropolarimeter for CD. MS spectra were recorded on a VG 7070E or a Finnigan MAT900S instrument. Melting points were determined on a Jeneval polarization microscope equipped with a Linkam THMS 600 hot stage and a Linkam TMS92 temperature programmer, and are reported uncorrected. Elemental analyses were determined with a Carlo Erba EA 1108 instrument. Transmission electron micrographs were recorded on JEOL-100CX II and Philips EM 201c electron microscopes. Samples were prepared by applying a small amount of a gel to a carbon-coated copper grid; excessive material was shaken off after 5 seconds. After drying, the samples were stained by platinum shadowing at an angle of approximately 45°. Molecular modeling experiments were carried out using the MacroModel 5.0 package running on a Silicon Graphics Challenge computer.

**Synthesis**

1,2-Di[2-(2-hydroxyethoxy)ethoxy]benzene (8)

A mixture of 50 g (0.4 mol) 2-(2-chloroethoxy)-1-ethanol and 21 g (0.19 mol) catechol and 20 g NaI (0.13 mol) in 300 ml freshly distilled acetonitrile was refluxed for 15 minutes under a nitrogen atmosphere, whereupon 43 g (0.4 mol) Na₂CO₃ was added. The mixture was refluxed for another 18 h, and, after cooling, carefully acidified with concentrated hydrochloric acid. The mixture was concentrated \textit{in vacuo}, taken up in 500 ml of H₂O and extracted with ethyl acetate (3 × 200 ml). The combined organic fractions were washed (brine, 200 ml), dried (MgSO₄), filtered, and concentrated. Yield: 45 g (82%) of crude 8 as a clear oil.

1,2-Di[2-(2-chloroethoxy)ethoxy]benzene (9)

To compound 8 (40 g, 0.14 mol) in 50 ml of chloroform were added 25.5 ml (0.35 mol) of SOCl₂ and 32 ml (0.4 mol) of pyridine. The mixture was stirred for 18 h and subsequently washed with aqueous hydrochloric acid (3 N, 300 ml) and brine, passed through a short column of Al₂O₃ (act III), and concentrated. The product was purified by distillation in a Kugelrohr at 220°C, yielding 22 g (49%) of a clear viscous oil. ¹H NMR (CDCl₃, 300MHz) δ
Crown Ether Phthalocyanines Derived from Tartaric Acid

(ppm) 6.92 (b, 4H, ArH), 4.17 (t, J=4.8Hz, 4H, ArOCH2), 3.89 (t, J=4.8Hz, 4H, ArOCH2CH2), 3.85 (t, J=5.9Hz, 4H, CH2CH2Cl), 3.66 (t, J=5.9Hz, 4H, CH2Cl).

1,2-Dibromo-4,5-di[2-(2-chloroethoxy)ethoxy]benzene (10)
A mixture of 26 g of bromine (0.16 mol) in 100 ml of chloroform was slowly dropped into a solution of 21.5 g (66.5 mmol) 9 in 100 ml of chloroform in an ice bath. The escaping HBr gas was led into 500 ml of aqueous NaOH (4 N). The mixture was stirred for 18 h during which the ice bath was allowed to warm to ambient temperature. The solution was washed with aqueous NaOH (200 ml, 1 N), aqueous NaHSO3 (200 ml, 1 N) and brine (200 ml) and concentrated. Yield: 33 g (100%) of a yellowish oil. 1H NMR (CDCl3, 300MHz) δ (ppm) 7.13 (s, 2H, ArH), 4.13 (t, J=4.7Hz, 4H, ArOCH2), 3.87 (t, J=4.7Hz, 4H, ArOCH2CH2), 3.83 (t, J=5.8Hz, 4H, CH2CH2Cl), 3.65 (t, J=5.8Hz, CH2Cl).

1,2-Dibromo-4,5-di[2-(2-iodoethoxy)ethoxy]benzene (11)
A mixture of 32.6 g of 10 (68 mmol) and 25 g of NaI (0.17 mol) in 250 ml of acetonitrile was refluxed for 18 h under a nitrogen atmosphere. The mixture was concentrated and taken into 300 ml of chloroform, washed with water (200 ml) and NaHSO3 (100 ml, 1 N) and concentrated. Finally, the product was crystallized from methanol, yielding 38 g (84%) of a white solid. 1H NMR (CDCl3, 300MHz) δ (ppm) 7.14 (s, 2H, ArH), 4.14 (t, J=4.8Hz, 4H, ArOCH2), 3.88 (t, 4.8Hz, 4H, ArOCH2CH2), 3.84 (t, J=6.9Hz, 4H, OCH2CH2I), 3.28 (t, 6.9Hz, 4H, CH2I).

(2S, 3S)-1, 4-Di(decyloxy)butane-2, 3-diol (13)
A mixture of powdered KOH (30 g, 0.53 mol) in 260 ml of DMSO was stirred for 5 min. Diol 12 (10.65 g, 66 mmol) and 1-bromodecane (58 g, 0.26 mol) were added and stirring was continued for 2 h., after which the mixture was kept at -18°C for 10 h. The mixture was taken into 1L of H2O and extracted with CH2Cl2 (3×200 ml). The organic layer was washed with H2O (3×200 ml), dried (MgSO4) and concentrated in vacuo. Residual 1-bromodecane and 1-decene were removed through distillation at reduced pressure (135°C, 0.8 Torr). TFA (35 ml) and H2O (1 ml) were added and the resulting mixture was stirred for 5 minutes, after which CH2Cl2 (100 ml) and H2O (100 ml) were added. The layers were separated, the organic layer was washed with H2O (2×100 ml) and brine (100 ml), and concentrated in vacuo. The resulting solid was crystallized from ice-cold diethyl ether, yielding 24g (90%) of a white
solid. $^{1}$H NMR (CDCl$_3$, 300 MHz) $\delta$ (ppm): 3.8-3.9 (b, 2H, HOCH), 3.5-3.6 (b, 4H, CH$_2$C(H)OH), 3.47 (m, 4H, OCH$_2$CH$_2$), 2.87 (s, 1H, OH), 2.86 (s, 1H, OH), 1.5-1.6 (m, 4H, OCH$_2$CH$_2$), 1.15-1.4 (b, 14H, CH$_2$), 0.88 (t, J=6.7Hz, 6H, CH$_3$).

$(8S, 9S)$ -18, 19-Dibromo-8, 9-di [ (decyloxy) methyl] -2, 3, 5, 6, 8, 9, 11, 12, 14, 15-decahydro-1, 4, 7, 10, 13, 16-benzohexaoxacyclooctadecine (15)
A solution of 4.03 g of 13 (10 mmol) in 125 ml of DMF under nitrogen was treated with 1.4 ml of TIOEt (4.8 g, 19 mmol). The mixture was stirred at ambient temperature for 30 min. and then warmed to 60°C, whereupon 6.64 g of 11 (10 mmol) was added. The mixture was stirred at 60°C for 18 h, cooled and filtered through Celite. The filter cake was washed with CH$_2$Cl$_2$, and the combined filtrates were concentrated. Column chromatography (silica, eluent: ethylacetate/heptane, 1:4 v/v) yielded 1.8 g (22%) of a viscous colorless oil. $^{1}$H NMR (CDCl$_3$, 300 MHz) $\delta$ (ppm): 7.06 (s, 2H, ArH), 4.09 (m, 4H, ArOCH$_2$), 3.9-3.3 (m, 22H, OCH), 1.51 (m, OCH$_2$CH$_2$), 1.25 (b, 14H, CH$_2$), 0.88 (t, J=6.7Hz, 6H, CH$_3$).

Tetrakis$(8S, 9S)$-8, 9-Di(decyloxy)methyl)-2, 3, 5, 6, 8, 9, 11, 12, 14, 15-decahydro-1, 4, 7, 10, 13, 16-benzohexaoxacyclooctadecine)-18,19-phthalocyaninato copper (6a)
A mixture of 1.8 g of 15 (2.22 mmol), 1 g of CuCN (11 mmol) and 0.5 ml of pyridine in 50 ml of DMF was refluxed for 42 h under a nitrogen atmosphere. The mixture was cooled to ambient temperature and poured into 250 ml of 25% aqueous ammonia containing 50 ml of chloroform. Air was bubbled slowly through the solution for 2 h. The layers were separated and the aqueous layer was extracted with chloroform (2×100 ml). The combined organic layers were washed with aqueous ammonia (100 ml) and water (2×100 ml), dried over MgSO$_4$, filtered and concentrated in vacuo. The solid was washed in a Soxhlet apparatus with methanol (24 h) and collected with chloroform. Finally, the dark green product was obtained by column chromatography (silica, ethylacetate/heptane 1:4 v/v). FAB-MS: m/z = 2871 (M+).

$(2S,3S)$-1,4-Di(benzyloxy)butane-2,3-diol (14)
This compound was synthesized as described in literature.$^{16}$

$(8S,9S)$-8,9-Di[(benzyloxy)methyl]-18,19-dibromo-2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecine (16)
To a solution of diol 14 (1.5 g, 5.0 mmol) in 20 ml of DMF under a nitrogen atmosphere was slowly added 2.5 g of TIOEt (9.9 mmol). The mixture was heated to 65°C and 3.3g (5.0
mmol) of 11 was added, after which the mixture was stirred at 65°C for 16 h. After cooling, the mixture was treated with water (0.5 ml) and filtered through Celite. The filter cake was washed with CH₂Cl₂, and the combined filtrates were concentrated. Column chromatography (silica, eluent: ethyl acetate/hexane 1:1 v/v, followed by Al₂O₃, eluent: ethyl acetate/hexane 1:2 v/v) yielded 0.88 g (25%) of a white solid. ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 7.3 (m, 10H, ArH), 7.08 (s, 2H, ArH), 4.5-4.4 (dd, 4H, CH₂Ar), 4.1-3.5 (m, 22H, OCH).

(8S,9S)-8,9-Di[(benzyloxy)methyl]-2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecine-18,19-dicarbonitrile (18)

A mixture of dibromide 16 (0.9 g, 1.27 mmol), CuCN (0.34 g, 3.8 mmol) and 0.2 ml of pyridine in 50 ml of DMF was stirred at reflux for 40 h under a nitrogen atmosphere. After cooling, the mixture was poured into aqueous ammonia (200 ml) and air was bubbled through the solution for 2 h. The mixture was extracted with chloroform (4×10 ml) and the combined organic layers were washed with water (2×20 ml), concentrated and chromatographed twice (silica, eluent: chloroform followed by silica, eluent: ethyl acetate/hexane 1:2 v/v). The product was finally purified by crystallization from ethanol, yielding 0.33 g (43%) of a white solid. ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 7.3 (m, 10H, ArH), 7.00 (s, 2H, ArH), 4.5-4.4 (dd, 4H, CH₂Ar), 4.1-3.5 (m, 22H, OCH). FT-IR (KBr) Λ⁻¹ [cm⁻¹] = 2230 (C≡N).

Tetrakis((8S,9S)-8,9-Di[(benzyloxy)methyl]-2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecine)-18,19-phthalocyanine (6b)

A solution of dicyano crown ether 18 (0.45 g, 0.75 mmol) in 1.3 ml 2-(dimethylamino)-1-ethanol was stirred at reflux for 40 h under a nitrogen atmosphere. After cooling, chloroform (0.1 ml) was added and the product was precipitated from acetonitrile and filtered over Celite. The filter cake was washed with methanol until the filtrate was colorless. The product was obtained with chloroform, concentrated in vacuo and purified with column chromatography (NaBr-impregnated silica, eluent: 10% methanol/chloroform), yielding 0.1 g (25%) of a dark green solid. ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 8.86 (s, 8H, PcH), 7.3 (m, 40H, ArH), 4.7 (m, 16H, CH₂OPc), 4.4-4.5 (dd, 16H, CH₂Ar), 4.2-3.6 (m, 72H, OCH), -4.67 (s, 2H, NH).
A solution of 1.54 g of 19 (7.5 mmol) in 75 ml of DMF under nitrogen was treated with 1.1 ml of TlOEt (3.8 g, 15 mmol). The mixture was stirred at ambient temperature for 30 min. and then warmed to 60°C, whereupon 5 g of 11 (7.5 mmol) was added. The mixture was stirred at 60 °C for 18 h, cooled, and filtered through Celite. The filter cake was washed with CH₂Cl₂, and the combined filtrates were concentrated. Column chromatography (silica, eluent: 2% methanol/chloroform) yielded 0.80 g (17 %) of a white solid. ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 7.08 (s, 2H, ArH), 4.80 (s, 2H, CHC=O), 4.12 (t, J=4.3Hz, 4H, ArOCH₂), 3.88 (t, J=4.3Hz, 4H, CH₂OCH), 3.80 (m, 8H, CH₂OCH₂), 3.16 (s, 6H, NCH₃), 2.92 (s, 6H, NCH₃).

A mixture of 800 mg of 20 (1.31 mmol), 0.6 g of CuCN (6.7 mmol) and 0.5 ml of pyridine in 30 ml of DMF was refluxed for 42 h under a nitrogen atmosphere. The mixture was cooled to ambient temperature and poured into 150 ml of 25% aqueous ammonia containing 50 ml of chloroform. Air was bubbled slowly through the solution for 2 h. The layers were separated, the aqueous layer was extracted with chloroform (2×100 ml). The combined organic layers were washed with aqueous ammonia (100 ml) and water (2×100 ml), dried over MgSO₄, filtered and concentrated in vacuo. Column chromatography (silica, eluent: 2% methanol/chloroform) yielded 0.25 g (38 %) of a white solid. ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 7.13 (s, 2H, ArH), 4.79 (s, 2H, CHC=O), 4.21 (t, J=5.1Hz, 4H, ArOCH₂), 3.88 (m, 8H, CH₂OCH), 3.80 (m, 8H, CH₂OCH₂), 3.16 (s, 6H, NCH₃), 2.92 (s, 6H, NCH₃). FT-IR (KBr) Λ⁻¹ [cm⁻¹] = 2207 (C≡N), 1703 (C=O).

Dicyno crown ether 21 (200 mg, 0.4 mmol) was refluxed in freshly distilled 2-(dimethylamino)-1-ethanol (2 ml) for 40 h under nitrogen. After cooling, acetonitrile (15 ml) was added and the mixture was filtrated. The residue was dissolved in a very small amount of chloroform and precipitated from acetonitrile (20 ml). This procedure was repeated until a
colorless filtrate remained. The product was purified by column chromatography (silica, eluent: 10% methanol/chloroform), yielding 20 mg (10%) of a dark green solid. FT-IR (KBr) $\Lambda^{-1}$ [cm$^{-1}$] = 1698 (C=O).

Tetrakis(dimethyl-(8$R$, 9$R$)-2, 3, 5, 6, 8, 9, 11, 12, 14, 15-decahydro-1, 4, 7, 10, 13, 16-benzohexaoxacyclooctadecine-8, 9-dicarboxylate)-18, 19-phthalocyanine (23)

A solution of 20 mg of Pc 22 (0.010 mmol) in a mixture of 20 ml methanol and 4 ml of concentrated aqueous hydrochloric acid was refluxed for 4 h. The mixture was cooled and poured dropwise into 50 ml of saturated aqueous NaHCO$_3$, which was subsequently extracted with chloroform (3×50 ml). The combined organic layers were washed with water (2×50 ml), evaporated, and dried in vacuo. Yield: 15 mg (80%) of a dark green solid. FT-IR (KBr) $\Lambda^{-1}$ [cm$^{-1}$] = 1744 (C=O).

Tetrakis(N8, N9-dihexyl- (8$R$, 9$R$)-2, 3, 5, 6, 8, 9, 11, 12, 14, 15-decahydro-1, 4, 7, 10, 13, 16-benzohexaoxacyclooctadecine-8, 9-dicarboxamide)-18, 19-phthalocyanine (7a)

A mixture of 6 mg 23 (3 µmol) and 2 ml hexylamine (15 mmol) was stirred at reflux under a nitrogen atmosphere for 16 h. The mixture was concentrated at reduced pressure and redissolved in a mixture of chloroform and methanol. This procedure was repeated three times, after which the product was kept in vacuo for 20 h. Yield: 7 mg (90%) of a dark green solid. FT-IR (KBr) $\Lambda^{-1}$ [cm$^{-1}$] = 3205 (NH), 1469, 1706 (C=O).

Tetrakis(N8, N9-didodecyl- (8$R$, 9$R$)-2, 3, 5, 6, 8, 9, 11, 12, 14, 15-decahydro-1, 4, 7, 10, 13, 16-benzohexaoxacyclooctadecine-8, 9-dicarboxamide)-18, 19-phthalocyanine (7b)

A melt of 9 mg 23 (5 µmol) and 1 g of dodecylamine (5 mmol) was stirred at 120°C under a nitrogen atmosphere for 16 h. Dodecylamine was distilled off at reduced pressure. Chloroform (20 ml ) was added, and the solution was washed with 1N aqueous hydrochloric acid (2×50 ml) and finally with water. Yield: 5 mg (34%) of a dark green solid.
5.5 References and notes


2. Not to be confused with a smectic phase, which can be considered to be a two-dimensional liquid and a one-dimensional solid.


14. *ibid.* 8566

15. *ibid.* 8576

6.1 Introduction

Nanotechnology, or as it is sometimes called, molecular manufacturing\textsuperscript{1}, is the branch of science which deals with the design and construction of extremely small devices, close to the molecular level of matter. As was shown previously in this thesis, the construction of well-defined architectures whose dimensions and tolerances are in the range of 0.1 - 100 nanometers, can easily be accomplished by hierarchical self-assembly processes, as long as all the information needed for the self-assembly is contained within the molecular building blocks. A nice example of such an architecture is the multi-stranded helical fiber that is built up from phthalocyanine \textsuperscript{1}, as was described in Chapter 4. The actual construction of the superstructure from \textsuperscript{1} is done by heating and cooling in chloroform; the self-assembled structure obtained in this way is dictated by the programmed properties of the phthalocyanine building block, such as shape, aspect ratio, (local) solvophobicity, chirality and aromaticity. The major source of inspiration for the generation of artificial nano-sized systems is the biological world, where the same programmed properties and instructions, amongst others, are used to create very elegant and well-organized biological architectures.\textsuperscript{2} Unlike the many chemical examples of self-assembly,\textsuperscript{3,4} the biological structures are assembled and disassembled in space and time, generating viruses, cells and entire organisms. The studies described in the previous chapters dealt with the rational design of the properties of phthalocyanine building blocks in order to control the resulting superstructure. Although it was shown that these structures are formed, it is still a long way to obtain actual nanodevices, due to the lack of positional and chronological control during the assembly process.
One of the ways to achieve positional control in nanotechnology is by means of nanomanipulation using an SPM (scanning probe microscope) tip. Previous research has shown that it is possible to position atoms, molecules, nanoparticles, and liquid droplets with an SPM instrument. Scanning force microscopy (SFM) and scanning tunneling microscopy (STM), the two main techniques within the SPM family, have been extensively used previously to visualize ordered architectures of phthalocyanines molecules. These architectures were processed either from solution with the help of Langmuir-Blodgett techniques or by sublimation in ultra high vacuum. To the best of our knowledge, no scanning probe experiments have been carried out to visualize molecules at the gel-solid interface. In this chapter, the first attempts in that direction are described, as well as the manipulation of these structures. Furthermore, experiments are described in which scanning force microscopy is used to visualize a phthalocyaninato polysiloxane polymer.

6.2 Results and discussion

STM on monomeric phthalocyanines

In Figure 6.1, the experimental setup for the STM experiments is schematically drawn. The operation of a scanning tunneling microscope (STM) is based on the so-called tunneling
Figure 6.2 Top: sub-molecularly resolved STM micrograph of phthalocyanine 2 at the gel-HOPG interface. Bottom: Schematic representation of the proposed arrangement of the phthalocyanines at the interface.
current, which starts to flow when a sharp tip (a) approaches a conducting surface (b) at a distance of approximately one nanometer. The tip is mounted on a piezoelectric tube, which allows tiny sub-nanometer movements by applying a voltage at its electrodes. Thereby, the electronics (c) of the STM system control the tip position in such a way that the tunneling current and, hence, the tip-surface distance is kept constant, while at the same time a small area of the sample surface is scanned. This movement is recorded and can be displayed as an image of the surface topography. In another mode of operation, the vertical movement of the tip is following the surface more slowly; in that case, the current is plotted as an image.

The molecules used for the STM experiments are compounds 1 and 2, shown in Chart 4.1 (Chapter 4). These phthalocyanines are functionalized by four benzocrown ether rings, and the peripheral aromatic rings are each di-substituted with either branched chiral (1) or linear achiral (2) alkoxy chains. In organic solvents, these molecules form a gel. Figure 6.2 shows sub-molecularly resolved current STM images of a gel of 2 at the interface with the substrate, highly oriented pyrolitic graphite (HOPG). The molecules are self-assembled in an "edge-on" fashion, forming lamellae consisting of π–π stacked phthalocyanines. The intracolumnar periodicity, or stacking distance, as calculated from the STM profiles, amounted to d = 4.2±0.2 Å, the inter-columnar periodicity was calculated to be 45±2 Å. The rather large stacking distance, considering a typical π–π stacking distance between two phthalocyanine disks of s = 3.4 Å, suggest that the phthalocyanine cores are tilted from the normal to the surface by an angle γ, which (using cos(γ) = s/d) could be calculated to be 36°. The values previously obtained in the crystalline phase by van Nostrum et al. are d = 4.3 Å and γ = 38°, which is nicely in agreement with those presented here. In Figure 6.2, also the individual crown ether moieties can be observed, which is especially clear in the lower right area. This automatically leads to the conclusion that in this arrangement, the phthalocyanines are completely eclipsed with all crown ethers lined up. Such an ordered array of crown ethers could well serve as an ion channel, as suggested earlier by Van Nostrum. The aliphatic tails are not visible because of their liquid-like nature and their limited impact on the conductivity. Their presence is only indicated by the space left between the stacks. The proposed molecular arrangement is also shown in Figure 6.2, bottom. These lamellar architectures are similar to the tubular nanostructures monitored by SFM on LB films of other phthalocyanine derivatives.

In Figure 6.3a, STM images of phthalocyanine 1 are shown. Several coexisting phases can be observed: two "face-on" phases (1 and 2 in Figure 6.3a), and an "edge-on" lamellar
Figure 6.3 STM images of 1 at the gel-HOPG interface: a) current image (U$_1$=0.58V, average I$_1$=53 pA). Four main features are shown: a thermodynamically stable, relatively loosely packed hexagonal lattice (1), a metastable, more densely packed hexagonal lattice (2), lamellae (3) and lamellae which have been induced by the STM tip. b) height image (U$_1$=0.58V, average I$_1$=53 pA) showing that the 'large' hexagonal lattice is aligned along the main axes of the lamellae which are marked by the white arrows. c) Zoom-in of area 4 revealing lamellae of π-π stacked Pcs.

The "edge-on" lamellae, which, similar to those observed for 2 are made up of π-π stacked phthalocyanine molecules, exhibit widths of 47±2 Å and lengths in the micrometer range. The stacking distance amounts to 4.4 Å, corresponding to a slightly larger angle with the normal of the plane of 40°. The reason for this difference is caused by the branched aliphatic tails, which occupy more space close to the phthalocyanine core. For a molecular structure of the loosely packed hexagonal phase (see below) having an average unit cell vector of $a = 35±2$ Å, the total area occupied by a molecule amounts to $a^2\sin(60°) = 1060±120$ Å$^2$. Given the lamellar widths, in the approximation of a rectangular shaped
molecule packed "edge-on", the thickness of the lamellae self-assembled on HOPG can be calculated to be 23 Å. Since the conjugated core has a diameter of about 10 Å, the remaining part of the lamellae, which consists of aliphatic moieties, has a thickness of roughly 13 Å. It is worth noting that the possibility of tunneling electrons through such a 23 Å-thick layer of the lamellar phase indicates a remarkable conductivity of the hybrid saturated-unsaturated molecule in the direction parallel to the disk.

Interestingly, the lamellar phase coexists with two different hexagonal phases (1 and 2 in Figure 6.3a): A metastable phase with a cell of \( a = 18.3\pm0.2 \) Å and \( \alpha = 60^\circ \), which disappears after a couple of hours (2 in Figure 6.3a), and a more loosely packed, almost hexagonal structure with \( a = 34\pm2 \) Å and \( b = 37\pm2 \) Å, and \( \beta = 56\pm4^\circ \), which is more stable and lasts for at least several days (1 in Figure 6.3a). In both these arrangements the conjugated disks are oriented "face-on" on the basal plane of the graphite substrate. The dimensions of these crystal lattices indicate that in both "face-on" packings the lateral substituents (crown ethers and aliphatic chains) are not fully extended, thus adopt a coiled conformation. This is not unlikely, since it is expected that the aromatic core of the molecule has more affinity to the graphite substrate than the aliphatic tails. The main lattice axis of the thermodynamically stable phase is aligned along the main lamella direction (white arrow in Figure 6.3b) whereas the spacings of the two structures in the \( xy \) plane are not in registry. By raising the average tunneling current and decreasing the applied voltage one can increase substantially the forces exerted by the STM tip on the organic film. This process allowed us to manipulate the film of 1 at the molecular level. A structural rearrangement from the small hexagonal lattice ("face-on") to the lamellae ("edge-on") could be induced. After returning to the standard imaging condition of the adsorbate, the manipulation was visible in area 4 in Figure 6.3a and at larger magnification in Figure 6.3c, which indicated the occurrence of electromechanical switching. The "face-on" oriented molecules are present both as packed crystals with sizes of hundreds of square nanometers and as isolated objects embedded where defects in the lamellar structures are located, \( i.e. \) at lamella boundaries. This unusual type of molecular inclusion in a tightly packed array, together with the high viscosity of the gel phase, may be the reason for the markedly low mobility of the single molecules, which differs from previous studies on Pc films grown and characterized in ultra high vacuum.\(^{14}\)

In STM height imaging (Figure 6.3b) a feedback loop controls the vertical position of the tip in such a way that a preset tunneling current flowing between the substrate and the tip is maintained constant while the tip scans horizontally above the sample; the vertical position \( z = f(x,y) \) is plotted. In the case of a conducting sample, this would correspond to the
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topography. In samples with poor conductivity, the heights obtained are largely dependent on the resistance of the material. In Figure 6.3b, the molecules in the "face-on" phase appear as bright spots, corresponding to a small substrate-tip distance, whereas the "edge-on" phase appears darker, indicating a larger substrate-tip distance. Given the roughly estimated layer thickness of the lamella of 23 Å and the thickness of the "face-on" layer of ca. 3.4 Å, this means that the conductivity perpendicular to the plane of the phthalocyanine is much larger than the conductivity parallel to the plane. This is nicely in agreement with previous observations that the conductivity of stacks of phthalocyanines is much higher in the stacking direction than between neighboring stacks.25

SFM on phthalocyaninato-polysiloxanes

A scanning force microscope (SFM) probes the surface of a sample with a sharp tip. The tip is located at the free end of a cantilever that is 100 to 200µm long. Forces between the tip and the sample surface cause the cantilever to bend, or deflect. A detector measures the cantilever deflection as the tip is scanned over the sample, or the sample is scanned under the tip. The measured cantilever deflections allow a computer to generate a map of surface topography. An advantage of SFM with respect to STM, is that it can be used to study all kinds of materials at all kinds of layer thicknesses, because it does not depend on tunneling currents. Unfortunately, we were not able to visualize gels of phthalocyanines 1 and 2 with this technique. In earlier studies it was shown that it is possible to visualize by AFM individual phthalocyaninato-polysiloxanes embedded in an LB monolayer of insulating isopentyl-cellulose.26 For this reason, we attempted to visualize phthalocyaninato-polysiloxane 6 (see Chapter 4).

A highly diluted (micro molar regime) solution of 6 in chloroform was spin-coated on a freshly cleaved HOPG substrate. In Figure 6.4, a molecularly resolved imaging attained with tapping mode SFM on a film with a thickness in the monolayer regime is shown; macromolecular cylinders with a diameter of (4.1±0.3) nm, as determined from topographical profiles, are clearly visible throughout the sample. The length of the rods extend to hundreds of nanometers; it is difficult to say however whether the rods are individual polymers, or if they consist of multiple polymers which are packed in a head-to-tail motif. In either case, these nanostructures exhibit the properties to act in the future as a nanowire in a molecular scale electronic device. As was pointed out in Chapter 4, the phthalocyanine monomers in polymer 6 are skewered to the polysiloxane backbone in a helical fashion. Unfortunately, this
helicity is not observed in Figure 6.4, as it would irrefutably show the handedness of the helicity.

6.3 Conclusions

The low mobility of the phthalocyanine molecules at the gel-solid interface allows them to be studied with great precision, which is of particular interest for future scanning tunneling investigations on phthalocyanines. Moreover, STM experiments at the solid-gel interface have a great advantage over the well-established method of performing studies at the solid-liquid interface, because of the greater stability of the former gel phase (up to several days). We
believe that this approach can be extended to a large variety of low molecular mass gel-forming molecules.

As was shown in this chapter, the interplay of intra-molecular, inter-molecular and interfacial forces can be used to construct highly organized two and three-dimensional structures from phthalocyanine building block at the gel-HOPG interface. The switching between different nanostructures co-existing at the surface can be stimulated with the STM tip and a resolution on the molecular scale can be achieved. These results may be of interest for future applications of phthalocyanines in areas such as molecular electronics, optoelectronics, and sensor development.

6.4 Experimental section

Scanning tunneling microscopy
The STM investigations were carried out with a home-made beetle-type, low-current STM. A drop of an almost saturated solution of 1 or 2 in a mixture (50:1) of CHCl₃ and 1,2,4-trichlorobenzene (Aldrich) was applied to a freshly cleaved HOPG substrate. Evaporation of some solvent occurred slowly and gave rise to the slow (on a time scale of several hours) formation of a stable gel phase adsorbed on HOPG, which was visible to the naked eye. By varying the tunneling parameters, namely decreasing the voltage and increasing the average tunneling current, it was possible to visualize the HOPG lattice underneath and therefore to calibrate the piezo in situ. This procedure was also used to induce a structural rearrangement in Figure 6.3c. The tunneling tips were mechanically cut from a 0.25 mm Pt/Ir (80:20) wire. Unit cells and backbone spacings were averaged on several images after their correction for the piezo drift (using SPIP Scanning Probe Image Processor, Version 1.720, Image Metrology ApS, Lyngby, Denmark).

Scanning force microscopy
The Tapping Mode Scanning Force Microscopy study was performed with a Digital Instruments E-scanner. A range of scan lengths from 12 μm to 0.1 μm was explored using commercial Si cantilevers with a spring constant between 36 and 50 N/m and a resonance frequency of 285-318 kHz (Olympus Optical Co, LTD, Japan). Thin films were processed from highly diluted solutions of phthalocyaninato-polysiloxane 6 in chloroform by spin
coating on a freshly cleaved HOPG substrate, followed by thermal annealing for 1-3 h at 100°C. The sizes of the visualized cylinders were determined from topographical profiles.

### 6.5 References and notes

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27 Digital Instruments, Santa Barbara, CA, USA.
Summary

This thesis describes experiments in the areas of macro- and supramolecular chemistry that have been performed with phthalocyanine derivatives. Phthalocyanines are flat and highly symmetric dye molecules. They are both (photo)chemically and thermally very stable, and exhibit unique optical and electrical properties which have been utilized in the application of phthalocyanines in pigments, as components in electrical devices and in optical storage media. Most phthalocyanine molecules investigated to date have high symmetry and consequently it is of great interest to explore the field of chiral derivates. The synthesis and properties of chiral derivatives, therefore, are the central theme of this thesis.

Chapter 1 is a brief introductory chapter in which it is attempted to place the concepts and aims of the research which is described in this thesis in a broader perspective. Chapter 2 presents a literature survey on the discovery and application of phthalocyanines in chemistry, with particular emphasis on supramolecular aspects.

In Chapter 3 a novel polymeric phthalocyanine is presented, which is synthesized from phthalocyanine monomers that are peripherally substituted with eight chiral alkoxy tails and contain a central dihydroxysilane function. Upon heating, a chiral phthalocyaninato-polysiloxane is formed, in which the phthalocyanine units are tightly stacked on top of each other, skewered by a central polysiloxane backbone. The chirality present in the side chains induces each phthalocyanine unit to rotate with respect to its neighbor. This rotation is always in the same direction, and as a result, the polymer has a left-handed helical conformation. We call this new type of chirality in polymers, in which the side chains are skewered in a helical fashion to a linear polymer backbone, 'shish-kebab-like chirality'. By synthesizing copolymers from mixtures of chiral and achiral phthalocyanines, it was shown that the helicity of the polymer only persists over short length scales, i.e. in the immediate neighborhood of the chiral monomers. This total absence of cooperativity is unique in the area of rigid, helical polymers.

The principles described in Chapter 3 for covalent phthalocyanine polymers can also be applied to supramolecular 'polymers', which are the subject of Chapter 4. Here, a phthalocyanine molecule of which the chiral chains are linked to the phthalocyanine core via four crown ether units is reported. In organic solvents, these molecules spontaneously form large columnar stacks of micrometer length and molecular thickness, in a similar way as the
non-chiral analogue which was described previously by our group. The resulting stacks form a tangled network which is capable of gelating the solvent. Circular dichroic spectroscopy revealed that the stacks possess a right-handed helical twist. Interestingly, electron microscopy showed the presence of left-handed helical fibers. These observed left and right handed helicities are the result of the chirality present in the aliphatic side chains which is expressed at different hierarchical levels. As a consequence of the chirality of the tails, the phthalocyanine molecules are oriented at a specific angle with respect to each other which results in a right handed helix. Subsequently, the right-handed helices form left-handed superhelices by a process of molecular recognition. The presence of crown ether moieties in the phthalocyanine allows for manipulation of the structure of the aggregates with the help of alkali metal ions. Potassium ions are able to simultaneously complex two crown ether rings in a sandwich type arrangement, and as a result, the phthalocyanine molecules are forced in an eclipsed conformation with respect to each other, which leads to the formation of linear aggregates instead of helical ones. These linear aggregates strongly resemble the aggregates that are formed from the corresponding achiral phthalocyanine. Not only it is possible to hardware program the phthalocyanine derivatives in such a way that helical aggregates are formed instead of linear stacks, but also this process can be reversed by software programming, viz. with the help of metal ions.

The very strong aggregation of the crown ether phthalocyanines equipped with aliphatic chains is the result of two opposite processes, namely the tendency of the side chains to become solvated and dissolve, and the propensity of the flat part of the molecule to crystallize. The benzene rings that connect the aliphatic tails to the crown ether rings play an essential role in the aggregation process. In Chapter 5, the interactions between these benzene rings are investigated by replacing them, on the one hand by non-interacting aliphatic linkers and on the other hand by strongly interacting amido groups. Removal of the benzene rings increases the solubility dramatically, whereas the introduction of amide groups leads to a decrease in the solubility. Unfortunately, no well-defined aggregates could be formed in the latter case, probably because of the mismatch between the optimal distance between the amide groups and the optimal distance of the $\pi-\pi$ stacking of the phthalocyanine cores.

Finally in Chapter 6, experiments using the scanning-probe techniques STM and AFM to visualize supramolecular and macromolecular phthalocyanine structures at the gel-graphite interface are described. The possibility to induce a phase transition with an STM-tip, viz. from a phase in which the phthalocyanine molecules are ordered parallel to the substrate to a phase in which the molecules are ordered perpendicular to this substrate is also demonstrated. To the
best of our knowledge, the investigation of a gel-solid interface by STM is unprecedented, as opposed to the liquid-solid interface which has been extensively studied. Due to the presence of the gel, the interface remains stable for an extremely long period of time, which opens the way for a wide variety of materials stabilized with gels to be investigated by STM in the future.
Samenvatting

In dit proefschrift worden experimenten beschreven op de gebieden van de macromoleculaire en de supramoleculaire chemie, meer in het bijzonder gericht op derivaten van ftalocyanine. Ftalocyanine is een zeer symmetrisch en vlak kleurstofmolecuul. Het is thermisch en (foto)chemisch zeer stabiel en bezit unieke optische en elektrische eigenschappen die toegepast worden in ondermeer verven maar ook in de elektronica en in optische opslagmedia. Juist vanwege de hoge symmetrie van het molecuul is het bijzonder interessant om chirale derivaten te synthetiseren en te onderzoeken, vandaar dat chiraliteit de rode draad vormt in dit proefschrift.

Na een korte inleiding in hoofdstuk 1, waar geprobeerd is het onderzoek in een breder kader te plaatsen, wordt in hoofdstuk 2 een literatuuroverzicht gegeven van de toepassingen van ftalocyaninen, met name op het gebied van de supramoleculaire chemie.

In hoofdstuk 3 wordt een nieuw en bijzonder polymeer beschreven. Het wordt gevormd uit monomeren van ftalocyanine die chirale zijketens en een centrale dihydroxysilaangroep bezitten. Door verhitting ontstaat hieruit een chiraal ftalocyaninatopolysiloxaan, waarin de ftalocyanine-eenheden zeer strak op elkaar gestapeld zijn, als het ware gespietst aan de centrale polysiloxaanketen. Als gevolg van de chiraliteit van de zijgroepen zijn de ftalocyanineschijven iets ten opzichte van elkaar gedraaid en wel steeds in dezelfde richting. Hierdoor heeft het polymeer de vorm van een linkshandige schroef. Deze nieuwe vorm van chiraliteit in polymeren, waarbij de hoofdketen geen chirale centra bezit en ook geen chirale conformatie heeft, maar waar de zijgroepen wel steeds in dezelfde richting zijn gedraaid ten opzichte van elkaar, hebben we 'shish-kebabchiraliteit' genoemd. Door copolymeren te maken van het chirale ftalocyaninemonomeer en een ander achiraal ftalocyaninemonomeer, kon worden aangetoond dat bij ftalocyaninatopolysiloxanen de helixrichting alleen vastligt in de directe omgeving van een chirale eenheid en dat het van het oplosmiddel afhankt in hoeverre een achiraal monomeer zich voegt naar de wil van een chiraal buurmonomeer. Deze totale afwezigheid van coöperativiteit in een rigide, schroefvormig polymeer is opmerkelijk te noemen.

De resultaten en principes beschreven in hoofdstuk 3 voor covalente polymeren blijken ook grotendeels geldig te zijn voor supramoleculaire 'polymeren'. Dit laatste is het onderwerp van hoofdstuk 4. Hier is een ftalocyanine beschreven dat is voorzien van
Samenvatting

kroonethers, waaraan via benzeenringen chirale paraffinestaarten zijn gekoppeld. De moleculen blijken in organische oplosmiddelen spontaan te stapelen tot kolommen van micrometerlengte en een breedte van één ftalocyaninemolecuul, op een vergelijkbare manier als het achirale analogon, dat reeds eerder beschreven is door onze groep. Deze kolommen zijn in staat het oplosmiddel te binden tot een gel. Bundels van deze kolommen zijn onder de elektronenmicroscoop zichtbaar als linkshandig gedraaide kabels, terwijl circulair-dichroismemetingen aantonen dat binnen een enkele kolom een rechtshandige draaiing aanwezig is. De oorsprong van deze tegengestelde draaiingen moet worden gezocht in de chiraliteit van de zijgroepen, die op diverse hiërarchische niveaus tot expressie komt. Het gebruikte ftalocyaninemolecuul zelf is chiraal en de stapeling van deze moleculen op elkaar vindt onder een hoek plaats die steeds dezelfde is, waardoor een rechtshandige helix wordt gevormd. Vervolgens assembleren verschillende rechtshandige helices met elkaar waardoor de linkshandige superhelix ontstaat die zichtbaar is met een elektronenmicroscoop. Deze chirale structuren zijn extra interessant omdat de aanwezigheid van de kroonetherringen het mogelijk maakt om de structuur van de aggregaten te beïnvloeden met behulp van metaalionen. Kaliumionen blijken uitstekend in staat om de vorming van chirale structuren te blokkeren, doordat deze ionen telkens twee kroonetherringen tegelijk kunnen complexeren in een sandwich-achtige structuur, die daardoor gefixeerd wordt. Hierdoor worden de ftalocyaninemoleculen gedwongen om recht op elkaar te stapelen in plaats van onder een hoek, zodat er vervolgens geen schroefvormige maar lineaire aggregaten ontstaan. Deze aggregaten lijken weer zeer sterk op de aggregaten die gevormd worden door het eerder genoemde achirale ftalocyaninederivaat. Enerzijds is het mogelijk om de bouwstenen van lineaire aggregaten zodanig hardwarematig te programmeren dat er gedraaide aggregaten ontstaan, anderzijds is het ook mogelijk om de draaiing van deze aggregaten softwarematig weer te blokkeren door metaalionen toe te voegen.

De oorzaak voor de zeer sterke aggregatie van de ftalocyaninen met kroonethers en alifatische zijketens moet gezocht worden in de balans die bestaat tussen enerzijds de neiging van de zijketens om op te lossen en anderzijds de neiging van de kern van het molecuul om dat juist niet te doen. Hierbij zijn de benzeengroepen die de verbinding vormen tussen de kroonethers en de zijketens van wezenlijk belang. In hoofdstuk 5 is de interactie die bestaat tussen de benzeenringen van aangrenzende ftalocyaninen onderzocht en wel door deze te vervangen door enerzijds alifatische groepen waartussen geen of zeer zwakke interactie te verwachten is en anderzijds door amidogroepen, die doorgaans juist zeer sterke onderlinge interacties ondergaan in organische oplosmiddelen. Het blijkt inderdaad dat het weglaten van
de benzeenringen de oplosbaarheid sterk verhoogt en dat de introductie van zeer sterk interacterende amidogroepen de verbindingen juist moeilijk oplosbaar maakt. Het is niet gelukt om met deze derivaten lange, goed gedefinieerde supramoleculaire systemen te construeren. In het geval van de amidoverbindingen was dit wel verwacht, maar is dit waarschijnlijk niet mogelijk omdat de optimale bindingsafstand tussen de amides groter is dan de optimale afstand tussen de ftalocyaninekernen.

In hoofdstuk 6 ten slotte is beschreven hoe met behulp van de technieken STM (scanning-tunneling-microscopy) en AFM (atomic-force-microscopy) supramoleculaire en macromoleculaire ftalocyaninestructuren zichtbaar gemaakt kunnen worden aan een grafietoppvlak. Tevens wordt in dit hoofdstuk getoond dat het mogelijk is om met een STM-tip faseovergangen te induceren en wel van een fase waar de ftalocyaninemoleculen vlak liggen naar een fase waarin deze moleculen loodrecht op het vlak geordend zijn. Dit is de eerste keer dat geprobeerd is het grensvlak van een gel en een substraatoppervlak te onderzoeken met behulp van STM; het grensvlak vloeistof-substraatoppervlak werd al eerder bestudeerd. Het blijkt dat dankzij de aanwezigheid van een gel het grensvlak zeer lang stabiel blijft, hetgeen voor STM-onderzoek aan andere materialen in de toekomst goede perspectieven biedt.
List of Publications


Dankwoord

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Curriculum Vitae