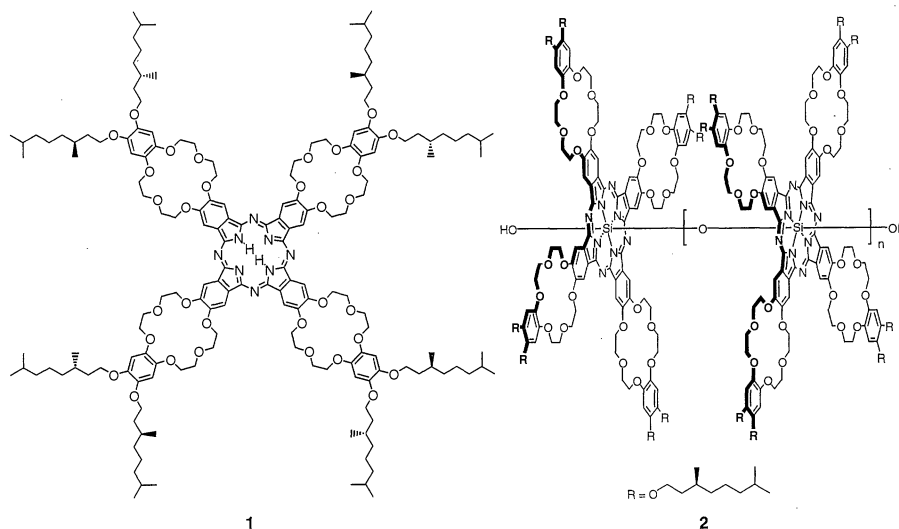


A disk-shaped molecule with chiral tails is shown to form long fibers of molecular diameter and micrometer length by self-assembly in chloroform. The molecules are derived from crown ethers and contain a phthalocyanine ring. In the fibers, they have a clockwise, staggered orientation that leads to an overall right-handed helical structure. These structures, in turn, self-assemble to form coiled-coil aggregates with left-handed helicity. Addition of potassium ions to the fibers leaves their structure intact but blocks the transfer of the chirality from the tails to the cores, leading to loss of the helicity of the fibers. These tunable chiral materials have potential in optoelectronic applications and as components in sensor devices.

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 example, in the fields of catalysis and electronics (4). A great variety of interactions can be exploited, such as hydrogen bonding, van der Waals interactions, π - π stacking, and electrostatic interactions. Recent studies have reported the formation of superstructures driven by π - π -stacking interactions (5), for example, the helical folding of polymers and the formation of helical lyotropic phas-

The molecule (**1**) that forms the superhelix (Fig. 1) contains a phthalocyanine ring to which four benzo crown ether moieties are attached. The peripheral aromatic rings of the molecule are each di-substituted with chiral alkoxy tails. The overall diameter of the disk with extended tails is 60 Å and its thickness is 3.4 Å. The phthalocyanine core in **1** has an extended system of π -electrons. Such π -systems are responsible for the observed conductivity of electrons and excitons in stacked

Electronic absorption spectroscopy could in principle provide information on the type of aggregated structures that are present (6). However, at the very low concentrations ($\sim 10 \mu\text{M}$) required for optical and circular dichroic (CD) spectroscopy studies on phthalocyanines, no aggregation of **1** was observed in chloroform. 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 inferred from the blue-shifted Q-bands of the phthalocyanine rings that appeared at 600 nm (Fig. 3A, top). In nonaggregated **1**, they are located at 630 and 700 nm. This shift is caused by exciton coupling between neighboring phthalocyanines in a stack (6). A couplet (bisignate signal) was present in the CD spectrum at the same wavelength. The sign of this couplet (Fig. 3A, bottom) suggests the presence of a right-handed helical arrangement of the transition dipoles of the phthalocya-



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nines within a stack of phthalocyanine molecules in an aggregate (10). Three types of helicity can be imagined (Fig. 3B). First,

the crown ether phthalocyanine rings may be arranged in a "spiral staircase-like" manner. Second, the rings may be posi-

tioned 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-phthalocyaninosilicon derivative of **1**, which was polymerized to give phthalocyaninato-polysiloxane **2** (11) (Fig. 1). Polymer **2** has a polysiloxane backbone, to which the crown ether phthalocyanine units are attached in a skewed fashion, giving a shish kebab-like structure. The CD spectrum of the covalent polymer in chloroform shows the same couplet in the Q-band region (Fig. 3A, bottom, blue line) as the self-assembled noncovalent polymer (Fig. 3A, bottom, red line), again indicative of a right-handed helical structure. For steric reasons, the only possible helical structure for the polysiloxane polymer is type 2 in Fig. 3B (12). X-ray powder diffraction revealed that in the noncovalent stack of **1**, the phthalocyanine cores are at a distance of 3.4 Å, which would be very short if structures of type 1 or 3 had been 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 2 in Fig. 3B.

A fiber with a right-handed twist and a type 2 structure has a "grooved" exterior. In order to maximize the van der Waals contact between two fibers twisted around each other (Fig. 3C), each of them has to bend over in order to fit into the groove of the other fiber. The tilting angle between the two fibers is called the crossing or cross-over angle. This angle is double the angle of the groove with respect to the stacking axis, which in turn depends on the dimensions of the monomer, and the staggering angle between two monomers according to

$$\alpha = 2 \arctan \left(\frac{D\phi}{2d} \right) \quad (1)$$

where α is the crossing angle, d the interplanar stacking distance, D the diameter, and ϕ the staggering angle in radians. In the case of our crown ether phthalocyanine rings, with $D = 60$ Å and $d = 3.4$ Å, we calculate using Eq. 1 that for staggering angles larger than 6.5°, the crossing angle becomes larger than 90°, and a supercoiled structure is formed that has a helical sense opposite to that of the original helix. From the crossing angle measured in the electron micrographs (125°), a staggering angle of 12° could be estimated.

The experiments described above indicate that chiral information is transferred from the (*S*)-chiral centers in the tails of **1** to the cores,

Scheme 1. Synthesis of crown ether phthalocyanine **1**. (i) Br₂, CH₂Cl₂, 0°C (80%); (ii) chloroethoxyethanol, NaI, Na₂CO₃, acetonitrile, 80°C (61%); (iii) *p*-toluenesulfonyl chloride (Tos = *p*-toluenesulfonyl), pyridine, -10°C (80%); (iv) 3,4-dihydroxybenzaldehyde, K₂CO₃, *N,N*-dimethylformamide (DMF), 120°C (59%); (v) H₂O₂, H₂SO₄, methanol, 20°C (65%); (vi) (KSO₃)₂NO, *N*(*n*-butyl)₄Cl, KH₂PO₄, H₂O, tetrahydrofuran, room temperature (98%); (vii) Zn, acetic acid, acetic anhydride, 80°C (80%); (viii) (*S*)-3,7-dimethyloctyl bromide, NaOH, *n*-butanol, 118°C (59%); (ix) CuCN, pyridine, DMF, 153°C (60%); and (x) *N,N*-dimethylaminoethanol, 135°C (20%).

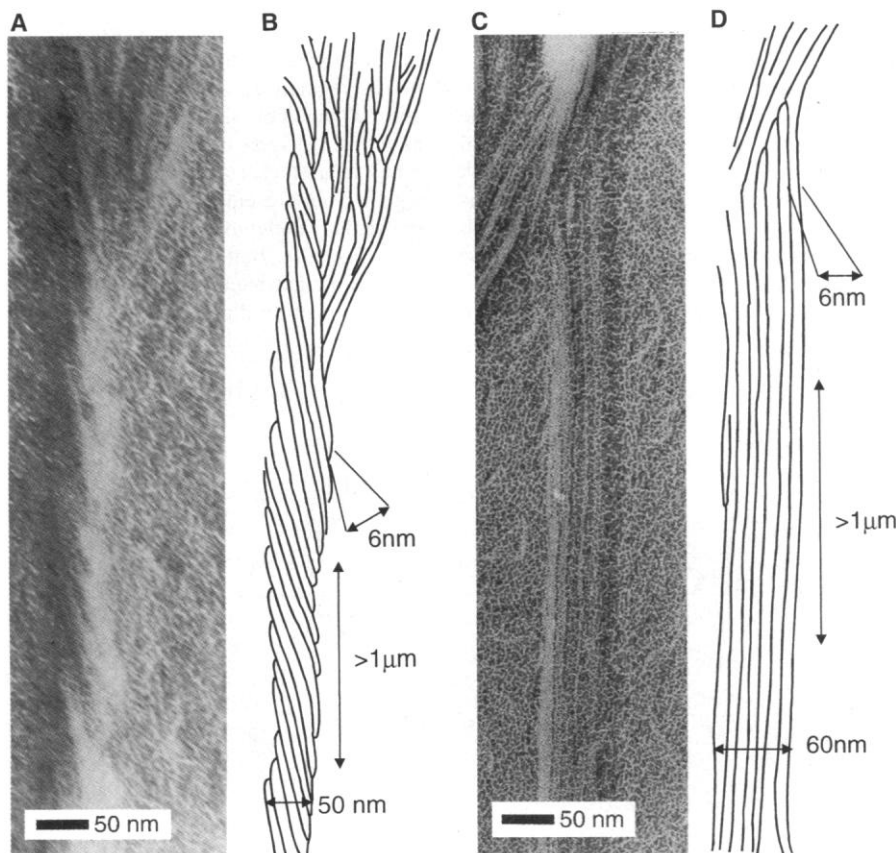
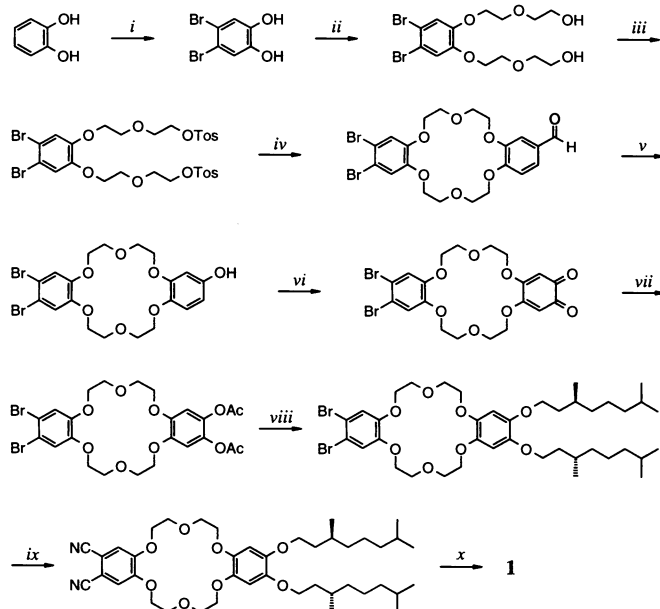


Fig. 2. Transmission electron micrographs (platinum shadowing) of gels from compound **1**. (A) Left-handed coiled-coil aggregates in chloroform. (B) Schematic representation of the helices in (A). (C) Nonhelical rods formed in chloroform in the presence of KCl. (D) Schematic representation of the rods in (C).

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where it is amplified to give right-handed helical fibers, which then further pack into left-handed supercoils. If this analysis is correct, it should be possible to block the chirality transfer by forcing the molecular disks into an eclipsed (face to face) conformation instead of a staggered one, in which case the helical structure should be lost.

We tested this possibility by adding K^+ ions to the fibers. Crown ethers form stable complexes with alkaline metal ions (13). In order to investigate what type of complexes are formed between compound **1** and K^+ ions, a titration experiment was performed in chloroform. Unsubstituted 18-crown-6 forms solely 1:1 complexes with K^+ ions. The Q-band regions of the electronic absorption spectra of a dilute solution of compound **1** in chloroform with different amounts of potassium picrate (Fig. 4A, left) show that the spectrum of pure **1** and the spectrum of **1** saturated with K^+ ions are nearly identical (red lines), whereas the spectrum of **1** with approximately two equivalents of K^+ (dark blue line) is rather different. The latter spectrum is that of a mixture of cofacial phthalocyanine dimers (characteristic absorption at 630 nm) and nonaggregated phthalocyanines. The direct conversion of these two species follows from the intersection points (isosbestic points) in the series of spectra (Fig. 4A, right) (14). The largest difference in the spectra occurs at 700 nm, where the Q-band of nonaggregated phthalocyanine is located. These results suggest that at low concentrations, K^+ ions are shared between two crown ether units of two different phthalocyanines. In this way, four ions can be accommodated by two crown ether phthalocyanine rings, similar to the way lawn bowling balls are held in a container (Fig 4B). This process will be facilitated because attractive π - π interactions occur between the aromatic rings. When more than two equivalents of potassium picrate are added, the crown ethers start to take up one K^+ ion in each ring, which leads to separation of the sandwichlike complexes. We found that the dimer complex did not show any CD activity, suggesting that the crown ether phthalocyanines within it have an eclipsed conformation.

A solution of **1** in chloroform was heated in the presence of solid KCL, filtered, and then cooled, which again resulted in the formation of an organogel. Electron micrographs of this gel show that almost no helical structures are present (Fig. 2C). The fibers look remarkably similar to those formed by an achiral liquid crystalline crown ether phthalocyanine (15). The disappearance of helicity can be explained by assuming that the metal ions are located dynamically in, or between, the crown ether

rings. In this way, the transfer of chirality is blocked because the phthalocyanines are forced to adopt an eclipsed conformation,

as outlined above.

The results presented here provide insight into how chiral information can be trans-

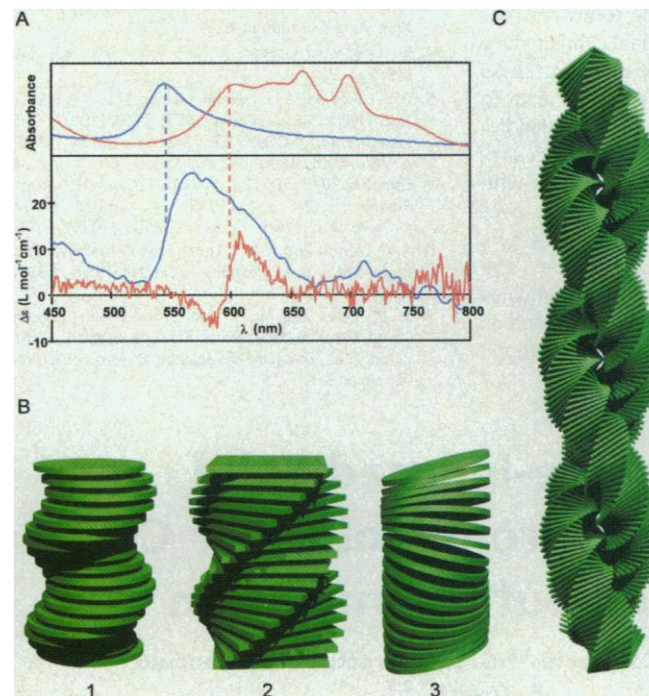


Fig. 3. (A) Electronic absorption spectra in arbitrary units (top) and CD spectra (bottom) of **1** (red line) and polymer **2** (blue line). (B) Three types of helical aggregates that may be formed by **1**. The molecules are represented as disks in **1** and **3** and as squares in **2** to show more clearly the helical packing arrangement of the building blocks. (C) Calculated model (16) of a coiled-coil from **1** reproducing the observed handedness of the single fibers and the superstructure. For the calculation the following parameters (Eq. 1) were used: $\phi = 12^\circ$, $d = 3.4$ Å, $D = 60$ Å.

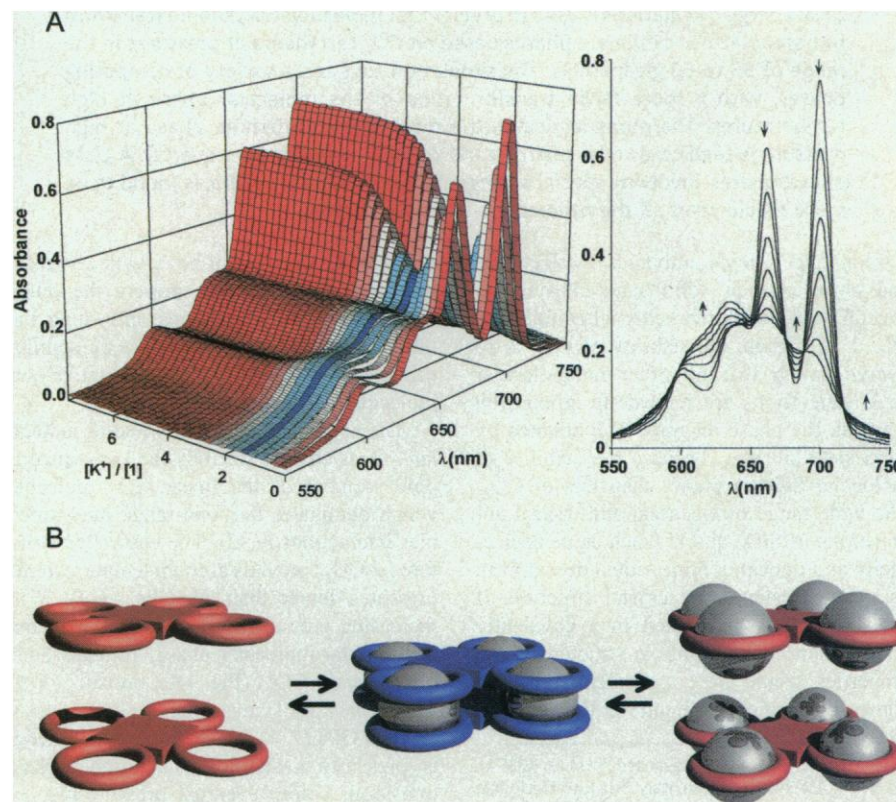


Fig. 4. (A) (Left) Electronic absorption spectra of **1** in chloroform (concentration 10 μ M) as a function of the ratio of potassium picrate and **1**. (Right) Isosbestic points at 597, 650, 675, 688, and 717 nm that appear when the $[K^+]/[1]$ ratio is increased from 0 to 2. The arrows indicate increasing potassium picrate concentration. (B) Schematic representation of the formation and breakdown of the sandwich-type complexes between K^+ ions and **1**.

ferred and expressed in synthetic systems in a way similar to nature. An interesting mechanism is suggested by which chirality is amplified to give supramolecular (helical) chirality, namely through the following processes: The S-chiral centers in the tails induce a clockwise orientation of the molecular disks which, aided by strong π - π stacking, leads to the formation of fibers with right-handed helicity. Side-on aggregation of the fibers subsequently yields supercoiled structures with left-handed helicity. Such a control over chirality may be valuable in designing new materials for optoelectronic applications. The present chiral fibers are attractive candidates for use as nonlinear optical materials and as components in sensor devices, for example, for the detection of alkali metal ions.

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Pressure-Induced Solid Carbonates from Molecular CO₂ by Computer Simulation

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A combination of ab initio molecular dynamic simulations and fully relaxed total energy calculations is used to predict that molecular CO₂ should transform to nonmolecular carbonate phases based on CO₄ tetrahedra at pressures in the range of 35 to 60 gigapascals. The simulation suggests a variety of competing phases, with a more facile transformation of the molecular phase at high temperatures. Thermodynamically, the most stable carbonate phase at high pressure is predicted to be isostructural to SiO₂ α -quartz (low quartz). A class of carbonates, involving special arrangements of CO₄ tetrahedra, is found to be more stable than all the other silica-like polymorphs.

Carbon and silicon, although isoelectronic and close in their solid state behavior in several ways, differ markedly when fully oxidized. In carbon, the stability of CO₂ is so overwhelming that no other nonmolecular solid state forms are known. In silicon, by contrast, the phase diagram is dominated by solid state silicates, because the stability of molecular SiO₂ is poorer than that of CO₂. The wide range of electrical and optical applications of SiO₂ quartz (such as piezoelectricity and optical nonlinearities) derive from its noncentrosymmetric crystal structure. If CO₂ could be synthesized in a covalently bonded noncentrosymmetric structure, these properties would be complemented by the higher mechanical strength of the less de-

formable C–O covalent bond with respect to the Si–O one. Here we present theoretical calculations and simulations, indicating that ultrahigh pressures should reduce the stability of molecular CO₂ in favor of quartzlike nonmolecular solid state carbonates.

The crystalline structure of solid molecular CO₂ is characterized by the large quadrupole moment of the linear CO₂ molecule, which dominates the long-range intermolecular interactions (1, 2). The cubic Pa3 structure (α -CO₂) prevails at room temperature for pressures lower than 11 GPa (3–5). With increasing pressure above 11 GPa, a second quadrupolar molecular phase, an orthorhombic *Cmca* (β -CO₂) (Fig. 1A), prevails (5, 6). This *Cmca* molecular phase persists to at least 50 GPa (7, 8), but no further knowledge is presently available of additional phase transition, before eventual pressure-induced chemical decomposition (9).

We have explored this unknown pressure region by constant pressure molecular dynamics (MD) simulations based on the variable-cell method (10). The first-principles

density functional nature of the method and the variable cell dynamics are effective for simulating pressure-induced solid-solid phase transformations in a variety of systems (11), including the characterization of the pressure-induced polymerization of carbon monoxide (12). The density functional scheme used is based on the Becke-Lee-Yang-Parr generalized gradient-corrected local density approximation (LDA/GGA) (13), and nonlocal (14) pseudopotentials for ion cores (15). Wavefunctions for MD simulations were expanded in plane waves with an energy cutoff of 80 Ry and Γ point sampling of the Brillouin zone (BZ). Final electronic and structural refinements were obtained by fully converged k-point sampled calculations and 100 Ry cutoff.

The validity of the computational scheme was initially checked by comparing our optimized β -CO₂ molecular lattice structure with the x-ray data at 12 GPa (5). Our calculated structures are consistent with the experimentally derived structure, especially in the fully converged k-points calculations [256 k-points in the full BZ], where errors in the lattice constants are less than 0.3%. Moreover, the tilt angle of the molecules relative to the *c* axis, usually difficult to reproduce because of its weak energy dependence, is calculated to be 52.5°, consistent with the experimental value of 52°. We also confirm, as already found by Gygi (6), that molecules lie in the plane identified by the *c* axis and the shorter axis of the basal plane. These results show that the LDA/GGA description of solid molecular CO₂ can be used to explore the high-pressure phase diagram of solid CO₂.

The first MD simulation was started with an orthorhombic simulation box containing 16 CO₂ molecules initially in the β -CO₂ phase at 12 GPa, with a time step of 0.3 fs. The temperature was equilibrated (16) at 300 K for 3 ps, during which the β -CO₂ structure remained stable. Pressure was then increased

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