Shish kebab-like chirality

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The phthalocyanine units in a new optically active phthalocyaninatopolysiloxane are arranged in a rigid helical structure, providing a new kind of main-chain chirality in polymers.

In an earlier paper, we reported on the structure and properties of a chiral phthalocyanine with branched aliphatic tails derived from (*S*)-citronellol **1a**. This compound was shown to form a novel chiral columnar mesophase at room temperature, and an achiral D_r mesophase at elevated temperatures.[1] The helical structure that was proposed for the chiral mesophase is shown in Fig. 1(*c*). It represents one of the three possible arrangements of the phthalocyanine rings. In the first, these rings are arranged in a 'spiral staircase-like' manner [Fig. 1(*a*)]. In the second [Fig. 1(*b*)], the rings are positioned on top of each other, but the staggering angle between neighbouring 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 case was more fully in agreement with our X-ray diffraction and circular dichroism results. We denoted this new mesophase by D_h*. The second arrangement, however, could not be completely ruled out. To resolve this problem we recently synthesised a phthalocyaninatopolysiloxane **2a** with the same chiral side chains as **1a**. We present evidence here that in this polymer the phthalocyanine rings are arranged as depicted in Fig. 1(*b*), which confirms that in the mesophase of **1a** the rings have the previously proposed arrangement [Fig. 1(*c*)]. To the best of our knowledge, polymer **2a** is the first example of an optically active phthalocyaninatopolysiloxane. It displays what we would like to call 'Shish kebab-like chirality'[2] which is a new type of main chain chirality in polymers.

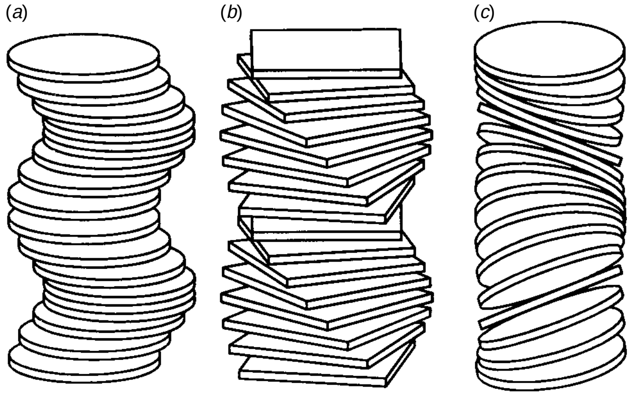
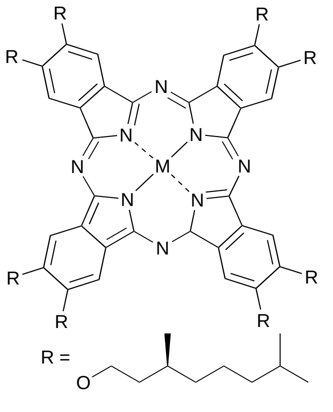


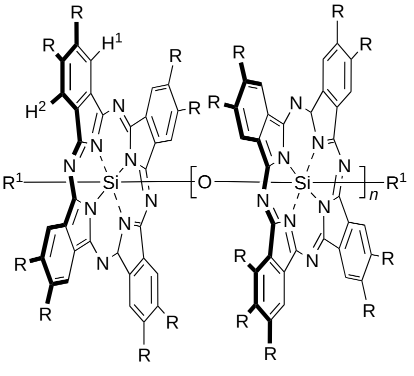
Fig. 1 Schematic representation of three possible helical arrangements of phthalocyanine molecules. The phthalocyanine rings are represented as discs in (*a*) and (*c*) and as squares in (*b*) to show more clearly the helical packing arrangement of the building blocks.

Dihydroxy(phthalocyaninato)silicon **1b** was synthesised following procedures previously developed for other octaalkoxyphthalocyanines.[3] This monomer was polymerised by heating *in vacuo* at 200 °C to give polymer **2a** as a dark blue solid, which was soluble in organic solvents.‡ From the exciton shift of the Q-band, from 680 nm in monomer **1b** to 550 nm in the polymer, the degree of polymerisation (DP) was roughly estimated to be 27.[4] In order to increase the molecular weight of polymer **2a**, we tried to polymerise dimers of the type HO(SiPC)O(SiPC)OH which were synthesised and purified separately. This method has been successfully used by Wegner to prepare high molecular weight phthalocyaninatopolysiloxanes.[3b] We were not able, however, to increase the molecular weight of **2a** by this procedure. We believe that the bulkiness of the aliphatic tails is the reason for this behaviour. In order to be able to compare the optical properties of **2a** with those of a reference compound we synthesised dimer **2b** from hydroxy(methyl)phthalocyaninatosilicon **1c**, which was prepared in an analogous manner to **1b**.‡

The circular dichroism and electronic absorption spectra of **1a**, **1b**, **2a** and **2b** in $CHCl_3$ are presented in Fig. 2. As can be seen, monomer **1b** [Fig. 2(*d*)] does not display any CD effect,



1a M = 2H
b M = $Si(OH)_2$
c M = Si(Me)OH



2a R^1 = OH, $n \approx 26$
b R^1 = Me, $n = 1$

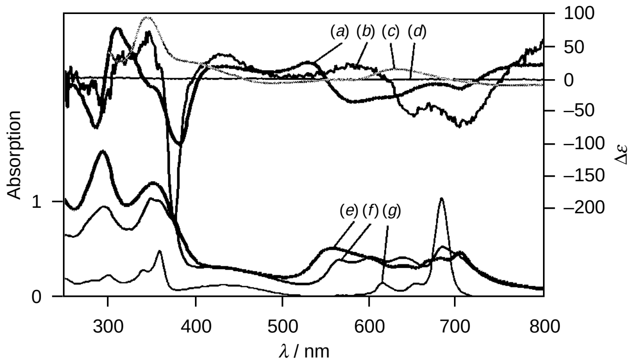


Fig. 2 Circular dichroism spectra of (*a*) **2a**, (*b*) **2b**, (*c*) **1a** and (*d*) **1b**, and electronic absorption spectra of (*e*) **2a**, (*f*) **2b** and (*g*) **1b**. All spectra are in $CHCl_3$ (10 μM) except for the mesophase of **1a**. In the latter case, the spectrum is of a film of 20 bilayers on a quartz plate; the scale is arbitrary.

indicating that its tails do not have a chiral influence on the electronic transitions of the aromatic core of this compound. The polymer **2a** [Fig. 2(*a*)] however, is strongly CD active. The negative couplet at 550 nm corresponds to the Q-band of the polymerised species, suggesting that its phthalocyanine rings are arranged in a left-handed helix.[5] This helicity is caused by the chiral side chains. Again, one could propose for the helical structure the three arrangements that are shown in Fig. 1. However, the silicon–silicon distance in phthalocyaninato-polysiloxanes is 3.3 Å (*vide infra*),[3] which is too short for the structures in Fig. 1(*a*) and 1(*c*) to be formed. This leaves only the structure of Fig. 1(*b*) as the possible helical arrangement for polymer **2a**. In the spectrum of **2a** recorded in dodecane at 120 °C (not shown), the intensity of the CD effect was only slightly decreased (by about 25%) suggesting that even at high temperatures the helical structure of **2a** is retained. The CD spectrum of dimer **2b** [Fig. 2(*b*)] shows the same features as that of polymer **2a**, but the couplet corresponding to the Q-band in the dimer is red-shifted with respect to the polymer. In the ^1H NMR spectrum of dimer **2b**, two resonances were present for the phthalocyanine protons (shown as H^1 and H^2 in the structure of **2**, confirming the asymmetry of the molecule. Increasing the temperature caused broadening of these resonances, but no coalescence could be observed below 120 °C. This result shows that the structure is very rigid. The CD spectrum of the mesophase of **1a** is also presented in Fig. 2(*c*). This spectrum is completely different from that of the polymer, eliminating the structure in Fig. 1(*b*) and therefore confirming the previous structural model for this mesophase [Fig. 1(*c*)]. If the polymer and the columnar mesophase had the same helical arrangement of molecular units, the CD spectra should be similar. The spectrum of an LB multilayer of **2a** (not shown) was very similar to the solution spectrum, which implies that effects due to orientational order or intercolumnar effects cannot explain the differences between the spectra of **1a** and **2a**.

X-Ray diffraction experiments were carried out, but did not provide any information about the periodicity or the pitch of the helix in **2a**. This negative result may be due to the rather low degree of polymerisation of **2a**. For such a pitch to be visible by X-ray, it should persist over extended length, *i.e.* several helical turns. This is easily accomplished in a liquid crystalline phase, *e.g.* in that of **1a**,[1] but probably not in a polymer with a degree of polymerisation of 25–30. In the X-ray diffraction pattern, the reflection corresponding to the intracolumnar Pc–Pc spacing was rather broad, probably as a result of the limited degree of polymerisation. A value of 3.3 Å could be calculated, which is in line with literature values.[3]

In summary, we have provided evidence that the stacked phthalocyanine molecules in the mesophase of **1a** and in polymer **2a** have a different helical arrangement. Current studies are aimed at the use of polymers of type **2a** as nonlinear optical materials and as optical switches.

Notes and References

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‡ Polymer **2a** was synthesised starting from (*S*,*S*)-1,2-dicyano-4,5-bis(3,7-dimethyloctoxy)benzene (ref. 1). The latter compound was converted quantitatively into the diiminoisoindoline derivative with NH_3 and NaOMe in MeOH [ref. 3(*a*)]. After subsequent reaction with $SiCl_4$ in quinoline at 190 °C, followed by hydrolysis with water, a dark green crude product was formed. After repeated precipitation in MeOH and acetone, the dihydroxy(phthalocyaninato)silicon **1b** was obtained (40%), which was polymerised *in vacuo* at 200 °C to give the violet–blue polymer **2a**. *Selected data* for **1b**: δ_H($CDCl_3$, 300 MHz) 0.7–2.8 (br, 152 H, aliph. H), 3.8–5.0 (m, 16 H, OCH_2), 6.5–9.0 (br, 8 H, ArH) ($C_{112}H_{176}N_8O_9Si$): Found (%) (Calc.): C, 74.45 (74.46). H, 9.86 (9.82); N, 6.16 (6.20).

Dimer **2b** was synthesised from hydroxy(methyl)phthalocyaninatosilicon **1c**, which was synthesised in a similar manner to **1b** using $MeSiCl_3$ instead of $SiCl_4$ as the silylating agent (yield 60%). Dimerisation with TlOTf in pyridine gave **2b** in 75% yield. *Selected data* for **1c**: δ_H($CDCl_3$, 300 MHz) −6.3 (s, 3 H, $SiCH_3$), 0.7–2.5 (m, 152 H, aliph. H), 4.0–4.8 (br, 16 H, OCH_2), 9.0 (s, 8 H, ArH). For **2b**: δ_H($CDCl_3$, 300 MHz) −8.35 (s, 6 H, $SiCH_3$) 0.8–2.5 (m, 304 H, aliph. H), 4.1–4.9 (br, 32 H, OCH_2), 8.26 (s, 8 H, ArH), 8.64 (s, 8 H, ArH).

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