CHEMISTRY of MATERIALS

VOLUME 1, NUMBER 3 MAY/JUNE 1989

Communications

Molecular Assemblies in Discotic Mesophases and Langmuir–Blodgett Films of 1,4,8,11,15,18,22,25-Octasubstituted Phthalocyanines

Michael J. Cook,* Neil B. McKeown, and
Andrew J. Thomson

School of Chemical Sciences
University of East Anglia, Norwich, NR4 7TJ, UK

Kenneth J. Harrison

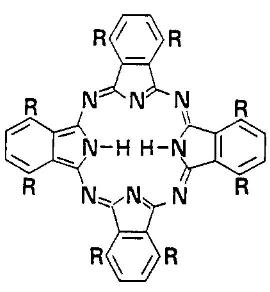
Royal Signals and Radar Establishment
St. Andrews Road, Great Malvern
Worcs. WR14 3PS, UK

Robert M. Richardson, Antony N. Davies, and
Stephen J. Roser

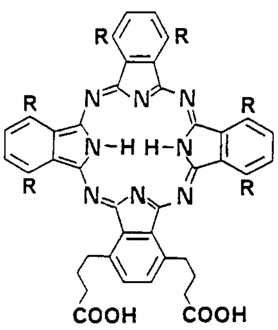
School of Chemistry, University of Bristol
Cantock's Close, Bristol, BS8 1TS, UK

Received August 12, 1988

Several classes of hexa- or octasubstituted polybenzoannelated aromatic systems exhibit thermotropic liquid-crystalline behavior.[1] These essentially planar disk-like molecules may either stack cofacially in a discotic columnar mesophase or show orientational order in a discotic nematic mesophase. Recently, we described some novel discotic liquid crystalline phthalocyanines of which 1 is an example.[2] A feature of 1 is that it forms three distinct mesophases. The first, D_1, is formed on cooling the isotropic liquid to 152 °C. At 101 °C a new mesophase, denoted as D_3 in our earlier paper, is formed, which on cooling to 73.5 °C undergoes a transition to mesophase D_4. The latter temperature is below the crystal-D_3 transition (84.5 °C) and the material crystallizes on standing.



1, R = *n*-octyl



2, R = *n*-octyl

There are two aspects to the present paper. First, we report the X-ray structural characterization and visible-region absorption spectrum of mesophases D_1 and D_3. We then show how the phase changes relate to the molecular reorganization that occurs on warming a Langmuir–Blodgett (LB) film of the structurally similar phthalocyanine 2, a study of which we described recently.[3,4]

Results and Discussion. X-ray diffraction measurements were performed for D_1 and D_3 using a conventional flat-plate camera with copper Kα radiation. No data could be obtained for D_4 because the material crystallized within the time scale of the experiment. The X-ray diffraction peaks for D_1 measured at 115 °C correspond to Miller indices of 200/110 and 310 (using indices based on a rectangular cell). The absence of a peak corresponding to the 210 plane suggests the lattice is *c* centered. This and the fact that the 200 and 110 peaks are coincident, which implies that $a = 3^{1/2}b$ (Figure 1), indicate that D_1 comprises columnar stacks of cofacial molecules arranged with hexagonal lattice symmetry. The fan texture observed under the polarizing microscope is consistent with this conclusion.[5] The unit cell dimensions are $a = 39.3 \pm 0.2$ Å and

---

[1] Destrade, C.; Foucher, P.; Gasparoux, H.; Tinh, N. H. *Mol. Cryst. Liq. Cryst.* **1984**, *106*, 121.

[2] Cook, M. J.; Daniel, M. F.; Harrison, K. J.; McKeown, N. B.; Thomson, A. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1086.

[3] Cook, M. J.; Daniel, M. F.; Harrison, K. J.; McKeown, N. B.; Thomson, A. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1148.

[4] McKeown, N. B.; Cook, M. J.; Thomson, A. J.; Daniel, M. F.; Harrison, K. J.; Richardson, R. M.; Roser, S. J. *Third International Conference on Langmuir-Blodgett Films*; Gottingen, July 1987; *Thin Solid Films*, **1988**, *159*, 469.

0897-4756/89/2801-0287$01.50/0 © 1989 American Chemical Society

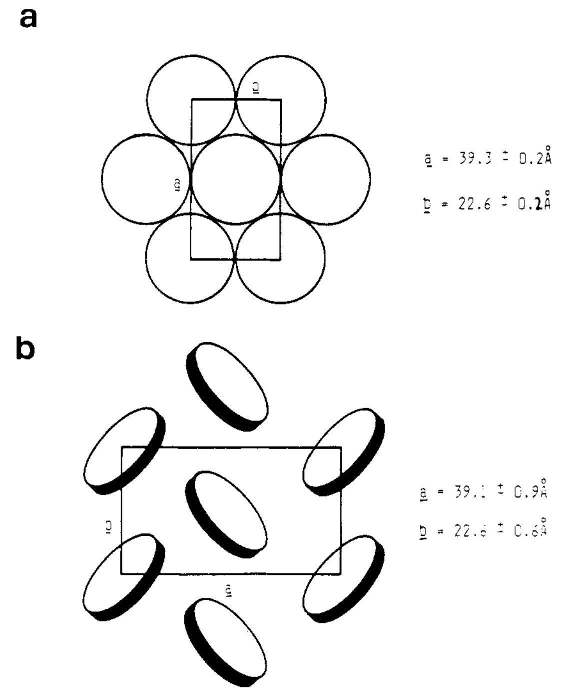


Figure 1. Schematic representation showing the c face within a rectangular unit cell and lattice parameters for (a) the hexagonal mesophase, D_1, of **1** and (b) the rectangular mesophase, D_3, of **1**.

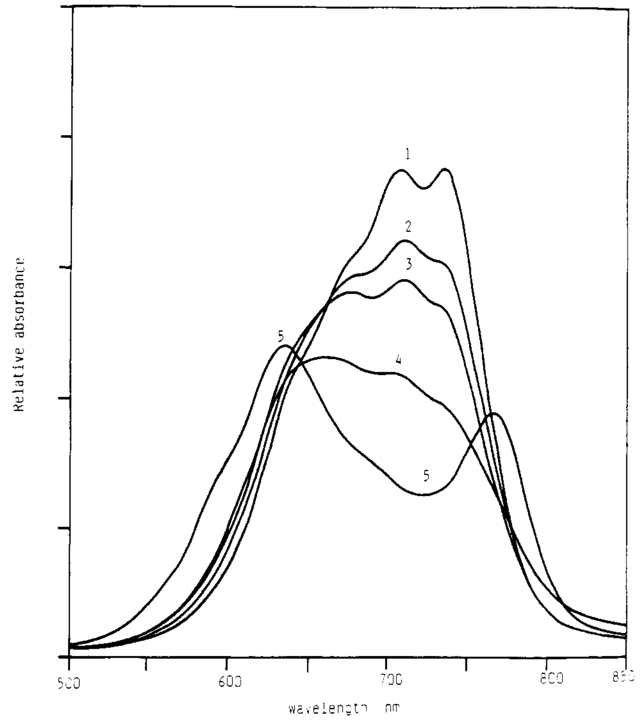


Figure 2. Visible region spectra of **1** on a silica slide. Line 1 at 155 °C, isotropic liquid; line 2 at 147 °C, D_1; line 3 at 105 °C, D_1; line 4 at 92 °C, D_3; line 5 at 40 °C, crystallized material.

$b = 22.6 \pm 0.2$ Å (Figure 1). An additional band corresponding to a spacing of 4.4 Å is diffuse and indicates that there is no long-range translational ordering of the molecules along the axis of the stack. We therefore categorize the structure of D_1 as disordered hexagonal (D_{hd}) after Destrade[1] et al., where D indicates a discotic, h that the lattice is hexagonal, and d that there is disordered spacing within the column.

The observed diffraction peaks for the D_3 mesophase (90 °C) have indices 200/110, 210, and 310. Diffraction arising from the 210 plane indicates that the lattice is not c centered and that the symmetry of the columns is therefore likely to be rectangular. The expected splitting of 200/110 was not apparent at the resolution of the diffractometer. Values for the lattice parameters $a = 39.1 \pm 0.9$ Å and $b = 22.6 \pm 0.6$ Å are similar to those for D_1. Three types of rectangular lattice have been identified hitherto in columnar mesophase systems, viz., $D_{rd}(C2/m)$, $D_{rd}(P2/a)$, and $D_{rd}(P2_1/a)$, where D and d are as above, r denotes rectangular, and $C2/m$, $P2/a$, and $P2_1/a$ are the planar space groups. The $C2/m$ space group normally has a larger difference in specific area per molecule than the hexagonal lattice in the same discotic compound. Also, $C2/m$ should give a significant 200/110 and 400/220 splitting which is not observed. Data for D_3 are therefore inconsistent with this space group. The similar textures of D_3 and D_4 (observed under the polarizing microscope)[2] suggests that D_4 does not belong to this space group either, and we suggest that they be assigned as $D_{rd}(P2_1/a)$ and $D_{rd}(P2/a)$ mesophases, respectively, distinguishing them on the basis that the latter is generally found at lower temperatures than the former.

Figure 2 shows the visible region spectra obtained of the compound at various temperatures during cooling from the isotropic liquid phase, the material having been heated on a glass slide by using a Mettler FP82 hot stage located in the chamber of a Perkin-Elmer Lambda 9 spectrophotometer. Lines 2 and 3 correspond to the hexagonal phase D_1 at different temperatures and show λ_{max} 674, 710, and 732(s) nm. Small differences in band shape presumably reflect reorganization in the disordered regions of the columns. Line 5 shows the spectrum of the crystallized material and is characterized by two relatively sharp bands at 634 and 766 nm.

We now turn attention to our recent investigation of Langmuir–Blodgett (LB) films of compound **2**.[3,4] This material, purpose designed for deposition by the LB technique, gives highly ordered films by Y-type deposition affording an assembly of bilayers with the two component monolayers H bonded together. The bilayer spacing, measured by low-angle X-ray diffraction, is 41 Å.[4] Compound **2** does not itself show mesophase behavior, but on heating the film to 127.5 °C there is a significant and irreversible change and the bilayer spacing is lowered to 36 Å. The spectra of the unheated and heated film are reproduced here as Figure 3. Polarized absorption spectra of the unheated film are consistent with the presence of "herring bone" columns of molecules.[4] This is a characteristic packing of simple unsubstituted phthalocyanine molecules in the crystalline state.[6]

The results obtained for compound **1** provide further insight into the structure of the films of **2**. There is a close similarity between the absorption bands of the crystalline phase of the former, line 5 of Figure 2., with those of the unheated film of the latter (λ_{max} 636 and 762 nm). This provides excellent confirmation of the high degree of order within the LB film. Furthermore, the X-ray data for **1** show that its effective molecular diameter is 22.6 Å; see Figure 1. This will also correspond to the longest distance from one side of **2** to the other. The distance from the carboxylic acid residues to the opposite side will be shorter and perhaps nearer 20 Å.[7] The measured bilayer spacing

---

(5) Gasparoux, H.; Destrade, D.; Fug, G. *Mol. Cryst. Liq. Cryst.* **1980**, *59*, 109.

(6) Lyons, L. E.; Walsh, J. R.; White, J. W. *J. Chem. Soc.* **1960**, 167.

(7) This value is less than that suggested by us earlier[4] on the basis of molecular models.

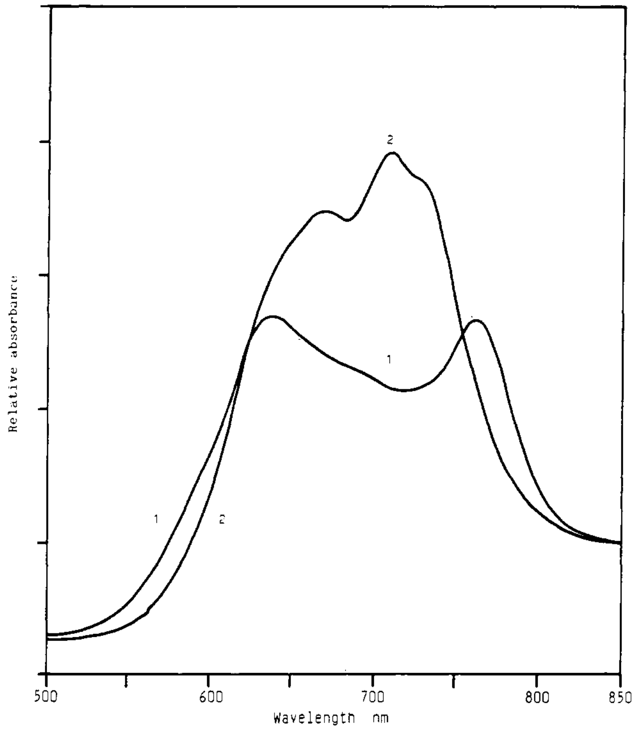


Figure 3. Visible region spectra of a Langmuir–Blodgett film of **2**. Line 1 at 25 °C; line 2 at 130 °C.

of 41 Å in the unheated film is about twice this value, suggesting that the molecules are standing essentially perpendicular to the substrate surface.

The spectrum of the heated LB film of **2**, λ_{max} 672, 710, 732 (s) nm, shows a close similarity to the spectrum of the D_1 mesophase of **1**. This implies that when the film is heated the columnar packing is reorganized, the herringbone packing being replaced by one that mimics the hexagonal packing shown in Figure 1. We postulate, therefore, that on heating the film the molecules within a column become fully cofacial and that a cross section of the columnar packing within a bilayer can be broadly represented by the lower two rows of circles in Figure 1. On this basis and because of the shorter distance from the carboxylic acid residues to the other side of the molecule, the bilayer spacing in the heated film should be somewhat lower than the distance a = 39.3 Å, as is indeed the case.

Acknowledgment. We thank the SERC for financial support and research studentships. This paper is reproduced by permission of the Controller of Her Majesty's Stationary Office.

Registry No. **1**, 110962-72-6; **2**, 111749-41-8.

Growth of Polycrystalline CaF_2 via Low-Temperature Organometallic Chemical Vapor Deposition

Michael J. Benac, Alan H. Cowley,*
Richard A. Jones,* and Al F. Tasch, Jr.†

Departments of Chemistry and
Electrical and Computer Engineering
The University of Texas at Austin
Austin, Texas 78712

Received August 19, 1988

Silicon-on-insulator (SOI) material structures are of considerable interest in integrated circuit technology. This type of structure, if successfully developed, allows the fabrication of three-dimensional integrated circuits. It also allows the fabrication of memory and logic circuits that are immune to both soft errors due to α particles and single-particle upset events caused by high-energy particles.[1] Almost all of the current research and development activity in SOI is focused on the use of a layer of amorphous SiO_2 of thickness 1500–5000 Å as the insulator. The 1000–5000-Å single-crystal overlying silicon layer is then formed by various approaches involving the recrystallization of amorphous or polycrystalline silicon from seed locations in the underlying silicon substrate or the use of very high dose ($\sim 10^{18}$ ions/cm^2) ion implantation of oxygen to form an amorphous SiO_2 layer below the surface of silicon substrate. These approaches all have numerous obstacles to overcome due to the difficulty in obtaining low-defect density, high-quality single-crystal silicon on the amorphous SiO_2 layer.

An alternative approach to the formation of the SOI structure is the use of a single-crystal, lattice-matched insulator. This then allows the possibility for the growth of the single-crystal overlying silicon layer directly on the insulator. Calcium fluoride (CaF_2) is an excellent candidate for SOI because it has a wide bandgap and a cubic structure similar to that of silicon, and it is lattice matched to silicon to within 0.6% at room temperature. SOI insulator based on CaF_2 has been demonstrated by using molecular beam epitaxy (MBE).[2] The source of CaF_2 for this growth process is CaF_2 itself, evaporated from tungsten or graphite crucibles at very high temperatures (1200–1400 °C) onto silicon substrates at temperatures of 550–700 °C.[3,4] However, much work remains to be done to achieve high electrical quality SOI structures and interfaces and topographically smooth layers of uniform thickness.

We have initiated a program aimed at achieving high-quality CaF_2 on silicon at lower temperatures (200–400 °C) since this should prevent layer mixing, wafer warpage, and film stresses, which are problems associated with high-temperature depositions. The new approach is based on the combination of an organometallic chemical vapor deposition (OMCVD) reaction to form CaF_2 and a remote plasma-enhanced chemical vapor deposition (RPCVD) materials growth technique.

One key requirement for the success of this approach has been to identify and develop appropriate volatile precursors and CVD reactions that will produce CaF_2. Unlike other well-documented OMCVD processes such as those employed for the fabrication of thin films of III/V compound semiconductors,[5] there appears to be no previous reports of CVD growth on CaF_2. This may be due to the lack of suitable volatile calcium compounds.[6] Earlier work on organocalcium chemistry tended to focus on the use of small ligands such as methyl and ethyl. This lack of steric saturation often resulted in intractable oligomeric materials or decomposition products (typically via hydrogen abstraction). The use of bulkier groups has resulted in the isolation of stable organocalcium deriva-

---

† Supported by ONR/SDIO Contract No. N00014-87-K-0323.

(1) Lam, H. W.; Tasch, A. F.; Pinizzotto, R. F. *VLSI Electron.: Microstruct. Sci.* **1982**, *4*, 1.

(2) Schowalter, L. J.; Fathauer, R. W. *J. Vac. Sci. Technol.* **1986**, *A4*, 1026.

(3) Schowalter, L. J.; Fathauer, R. W.; Goehner, R. P.; Turner, L. G.; DeBlois, R. W.; Hashimoto, S.; Peng, J.-L.; Gibson, W. M.; Krusius, J. P. *J. Appl. Phys.* **1985**, *58*, 302.

(4) Reichelt, K.; Rey, M. *J. Vac. Sci. Technol.* **1973**, *10*, 1153.

(5) Ludowise, M. J. *J. Appl. Phys.* **1985**, *58*, 231.

(6) Lindsell, W. E. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 1.