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Thermal and optical behaviour of octa-alkoxy substituted phthalocyaninatovanadyl complexes

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This paper deals with the synthesis of vanadyl phthalocyanines substituted with eight alkoxy chains in the peripheral (2, 3, 9, 10, 16, 17, 23, 24) positions. The alkoxy chain length was varied, and octa-octyloxy ($C_8H_{17}O$), octa-dodecyloxy ($C_{12}H_{25}O$) and octa-hexadecyloxy ($C_{16}H_{33}O$) substituted vanadyl phthalocyanine complexes were prepared. Studies by polarizing optical microscopy and small angle X-ray diffraction (XRD) revealed that all the complexes are liquid crystalline and that these metallomesogens exhibit a columnar phase. The symmetry of the 2D lattice is rectangular, with a *c2mm* space group, as determined by the indexation of the XRD reflections; hence a rectangular columnar phase (Col_r) was assigned. A double periodicity, although weak, along the axis of the columns was found, which indicates some degree of pairing or dimerization. A tentative explanation based on an antiferroelectric stacking is given. Transition enthalpies were determined by differential scanning calorimetry. The compounds start to decompose above 250°C before reaching the clearing temperatures. A significant bathochromic shift of the Q-band in the UV/Vis spectra of the vanadyl complexes compared with the metal-free ligands and other metallophthalocyanines ($M = Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}$) was also observed.

1. Introduction

In 1982, Simon *et al.* reported the first liquid crystalline phthalocyanine copper(II) complex, substituted with eight peripheral alkoxymethyl chains. The metallophthalocyanine displayed a Col_h phase in the range 53 to 300°C, the temperature at which it decomposed without clearing [1]. Many other mesomorphic metal-free and metal-containing phthalocyanine compounds, with alkyl, alkoxy, thioalkoxy and ethyleneoxy chains, have since been synthesized [2–4]. Moreover, amongst the two possible peripheral octa-substitution patterns, i.e. the lateral positions (2, 3, 9, 10, 16, 17, 23, 24) and the radial ones (1, 4, 8, 11, 15, 18, 22, 25) [5, 6], the former have been the most commonly used for liquid crystalline phthalocyanines. In both cases columnar mesophases are formed, and result from the stacking of the flat and rigid phthalocyanine cores into columns, which are themselves arranged into a 2D lattice. These phthalocyanines give mainly hexagonally packed columnar phases and some rare examples of other 2D lattices (such as in rectangular and oblique columnar mesophases) [3, 4]. The melting of the flexible side chains is responsible for the transition from the solid state to the liquid crystalline phase (melting point), while the aromatic cores retain some degree of the crystalline positional and orientational order. The transition from the mesophase to the isotropic liquid (clearing point), which usually takes place at very high temperatures, corresponds to the breakdown of the 2D packing and of the columnar stacking.

Self-assembling of discotic molecules into columnar phases offers the unique possibility of elaborating potential one-dimensional charge carrier systems [7], since electronic interactions, as well as electron and exciton migrations, are strongly favoured within the columns (stacking periodicity $<$ intercolumnar distance). Due to the substantial π–π orbital overlap of the aromatic cores which should ameliorate charge transport along the columns, and to the insulating non-polar medium separating these conducting columns, mesomorphic pthalocyanines appear to be promising candidates for

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one-dimensional semiconductors [8] with applications in the domain of molecular electronics, optoelectronics, photoconductivity, and electro-luminescent devices [9]. In 1998 Shimizu *et al.* reported the first phthalocyanine containing the oxovanadium(IV) ion (= vanadyl ion), namely 2,3,9,10,16,17,23,24-octakis (*n*-octadecylthio) phthalocyaninato-oxovanadium (IV) [10]. This complex showed a Col$_h$ mesophase between 56 and 295°C. It was claimed as the first phthalocyanine to possess a dipolar V=O bond. The same group also reported the analogous Ti=O phthalocyanine complex, again showing two Col$_h$ phases (Cr 59 Col$_{h1}$ 68 Col$_{h2}$ 292 I) [11]. This remarkable stability may be an indication of strong disc-to-disc interaction via the vanadyl groups, as was reported for oxovanadium(IV) Schiffs base complexes by Swager *et al.* [12] and oxovanadium(IV) β-diketonate complexes by Goodby *et al.* [13]. In our attempts to synthesize octa-alkoxy vanadium(II) complexes, we have obtained octa-alkoxy vanadyl phthalocyanines (figure 1) analogous to the compound described in the above mentioned communication [10]. Complexes with three different chain lengths were prepared, namely octa-octyloxy ($C_8H_{17}O$), octa-dodecyloxy ($C_{12}H_{25}O$) and octa-hexadecyloxy ($C_{16}H_{33}O$). The mesophases were characterized by polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and small angle X-ray diffraction (XRD) for three different temperatures (100, 150 and 200°C). The influence of the chain length on the transition temperatures, as well as the variation of the cell parameters with temperature were investigated. The optical behaviour was studied by UV/Vis spectroscopy.

2. Experimental

2.1. *Characterization*

Elemental analyses (CHN) were performed on a CE-Instrument EA-1110 elemental analyser. Mass spectra of the organic precursors were recorded on a low resolution electron-impact Hewlett-Packard 5989A instrument for low molecular mass substances. For the phthalocyanines, a Micromass Quattro II (triple quadrupole) instrument was used. MALDI-TOF mass spectra of the vanadyl complexes were measured on a VG Tofspec SE (Micromass, UK) equipped with a N_2-laser (337 nm). UV-Vis spectra were measured on a Shimadzu UV-3100 spectrophotometer, using spectragrade chloroform as the solvent. IR spectra were obtained on a Bruker IFS66 FTIR-spectrometer. The KBr pellet technique was used to mount the samples. DSC measurements were performed on a Mettler-Toledo DSC821e module (scan rate 10°C min^{-1} under a helium flow, aluminum cups). Optical textures of the mesophases were observed with an Olympus BX60 polarizing microscope equipped with a Linkam THMS600 hot stage and a Linkam TMS93 programmable temperature controller. The powder XRD patterns were obtained with two different experimental set-ups, and the neat sample was placed in Lindemann capillaries of 1 mm diameter. A linear monochromatic Cu-K$_{\alpha 1}$ beam (λ = 1.5405 Å) was obtained with a sealed-tube generator (900 W); a Guinier camera and a Debye-Scherrer camera equipped with a bent quartz monochromator and an electric oven were used. In both set-ups the temperature was controlled within ±0.3°C. A first set of diffraction patterns was registered with a curved counter 'Inel CPS 120' associated with a data acquisition computer system; periodicities up to 60 Å could be measured. The other set of diffraction patterns was registered on an image plate; periodicities up to 90 Å could be measured. The phase symmetry was then determined and the cell parameters were calculated from the position of the most intense reflections at the smallest Bragg angle. In each case, exposure times were varied from 1 to 4 h.

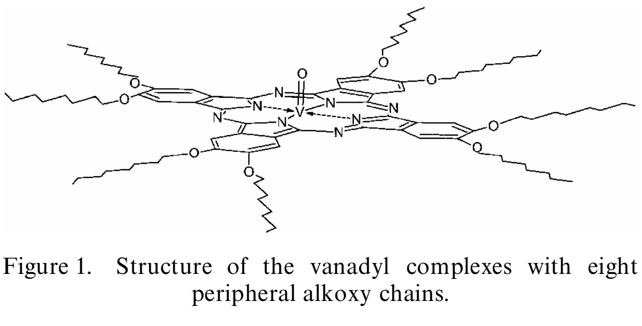


Figure 1. Structure of the vanadyl complexes with eight peripheral alkoxy chains.

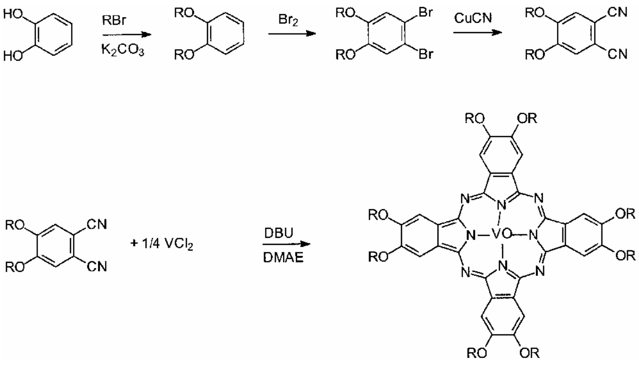
2.2. *Synthesis of the complexes: general procedure*

The 1,2-dicyano-4,5-bis (alkoxy) benzenes were synthesized according to a literature procedure and their purity was checked by CHN elemental analysis and ^{1}H NMR [14–16]. A mixture of 2 mmol 1,2-dicyano-4,5-bis (alkoxy) benzene, 0.54 mmol of vanadium(II) chloride, 5 ml of 2-(dimethylamino) ethanol (DMAE) and 4 drops of 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU) was stirred at 150°C for 48 h under a nitrogen atmosphere. After evaporation to dryness, the green residue was dissolved in a few ml of chloroform and precipitated by adding 50 ml of acetone. The precipitate was filtered off using a Gooch crucible (porosity 4) and washed with acetone, methanol and ethyl acetate. Further purification was carried out by chromatography over neutral alumina (Merck 90) using chloroform as the eluent. After collection and evaporation the product was crystallized from ethyl acetate and dried overnight. The overall yields were 29%, 12% and 4% for the vanadyl complexes with $C_8H_{17}O$, $C_{12}H_{25}O$ and $C_{16}H_{33}O$ chains, respectively. The complexes were characterized by MALDI-TOF mass spectrometry and UV/Vis spectroscopy.

3. Results and discussion

3.1. *Synthesis*

The octa-alkoxy substituted phthalocyaninatovanadyl complexes **1**–**3** were synthesized via a template reaction between one equivalent of vanadium(II) chloride and four equivalents of 1,2-dicyano-4,5-bis(alkoxy)benzene using 2-dimethylaminoethanol as solvent, in the presence of one half equivalent of the sterically hindered base 1,8-diazobicyclo[5.4.0]undec-7-ene (DBU) (see the scheme). The reaction mixture turned black, after a few minutes, probably due to oxidation of the vanadium(II) chloride to the oxovanadium(IV) (VO^{2+}) cation. After a few hours, the colour of the reaction mixture changed to green, once the phthalocyanine complex was formed. The presence of the vanadyl cation, rather than the vanadium(II) ion in the complexes was confirmed by IR spectroscopy by the presence of the V=O stretching frequency ($992\,cm^{-1}$ for the octa-octyloxy compound, $993\,cm^{-1}$ for the octa-dodecyloxy compound and $995\,cm^{-1}$ for the octa-hexadecyloxy compound). MALDI-TOF mass spectrometry was used to characterize the compounds. The purity was checked by UV/Vis spectroscopy, because the spectrum of the vanadyl phthalocyanine is markedly different from the spectrum of the corresponding metal-free phthalocyanine (different splitting of the Q-band). A summary of the complexes and the mass spectrometry data is given in table 1.



Scheme. Synthesis of the phthalonitrile precursors and of the octa-substituted vanadyl phthalocyanine complexes.

Table 1. MALDI-TOF data for the oktakis(alkoxy) substituted vanadyl phthalocyanines

	Compound	Formula	*M* (isotopic)	*M* (found)
1	$(C_8H_{17}O)_8PcVO$	$C_{96}H_{144}N_8O_9V$	1604.05	1605.16
2	$(C_{12}H_{25}O)_8PcVO$	$C_{128}H_{208}N_8O_9V$	2052.55	2054.01
3	$(C_{16}H_{33}O)_8PcVO$	$C_{160}H_{272}N_8O_9V$	2501.05	2502.86

3.2. *Mesomorphism*

The vanadyl complexes **1**–**3** are liquid crystals with a wide mesophase temperature range. The mesophase behaviour was investigated by POM, DSC and small-angle XRD. The melting points are nearly chain length independent, since the three compounds melt at around 60°C (table 2). Neither did repeated heating runs up to 175°C affect the position of the peaks (onset). For all three compounds, the clearing temperature could not be reached before decomposition of the sample took place in the high temperature domain of the mesophase (onset of decomposition was around 250°C for all the complexes).

As a representative example, the DSC thermogram of the VO compounds is shown in figure 2 for $n = 12$, $(C_{12}H_{25}O)_8PcVO$. Only one peak was seen, corresponding to the melting of the crystal into the mesophase. Note that enthalpy increases lightly with chain length.

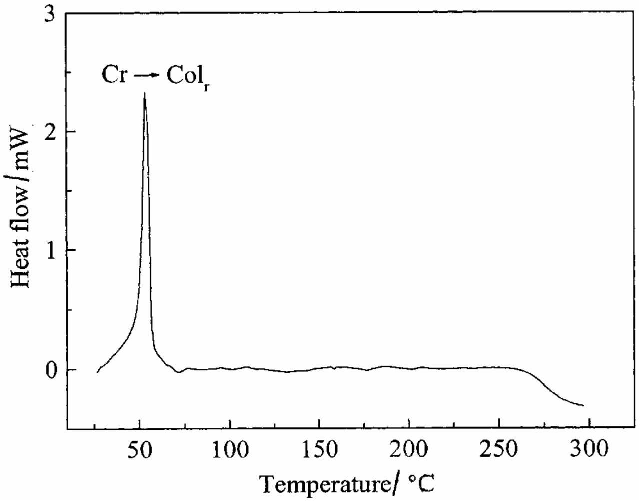


Figure 2. DSC thermogram (first heating run) of the complex $(C_{12}H_{25}O)_8PcVO$. Endothermic transitions point upwards. The peak in the thermogram corresponds to the transition from the crystalline state (Cr) to the rectangular columnar mesophase (Col$_r$).

Table 2. Mesophase behaviour of the oktakis(alkoxy) substituted vanadyl phthalocyanine complexes.[a]

	Compound	Transition temperatures/°C	Melting enthalpy $\Delta H_m/kJ\,mol^{-1}$
1	$(C_8H_{17}O)_8PcVO$	Cr 63 Col$_r$[b] 250 dec[c]	33
2	$(C_{12}H_{25}O)_8PcVO$	Cr 51 Col$_r$ 250 dec	53
3	$(C_{16}H_{33}O)_8PcVO$	Cr 60 Col$_r$ 250 dec	57

[a] The melting point (T_m) and melting enthalpy (ΔH_m) were determined by DSC. The reported temperatures are peak temperatures; the complexes decompose above 250°C.

[b] Col$_r$ = rectangular columnar mesophase.

[c] dec = decomposition.

Figure 3. Mesophase texture of the complex $(C_{12}H_{25}O)_8$PcVO as seen between crossed polarizers at 240°C.

The texture observed between crossed polarizers in the microscope is depicted in figure 3 for the same compound, and is characteristic of a columnar mesophase. Before the start of decomposition some textural changes could be observed, although it was not possible to assign such changes to the transition to another mesophase.

In order to clarify the exact nature of the mesophase, XRD experiments were carried out for the three complexes at three different temperatures. The XRD patterns for the compounds **1**–**3** at 100°C are shown in figure 4 as representative examples. The wide angle X-ray patterns consist of: (*a*) a diffuse scattering halo at *c.* 3.5 Å which is the inter-disc stacking periodicity of the phthalocyanine cores along the columns; (*b*) another, broader halo at around 4.5 Å, corresponding to the liquid-like order of the aliphatic chains, and (*c*) a less broad peak at about 7 Å, which may indicate the formation of dimers along the axis of the column. In the small angle region, two intense fundamental reflections and three higher order reflections were observed. The *h k l* indexation is characteristic of a two-dimensional rectangular packing of columns, and of a rectangular columnar phase (Col_r), with the *c2mm* 2D space group. Tables 3–5 list the indexation of the X-ray reflections for compounds **1**–**3** at three temperatures. The phase is disordered since there is no long range correlation order within the columns as evident from the broadness of the peak at 3.5 Å. No modification of the columnar phase structure with temperature could be observed.

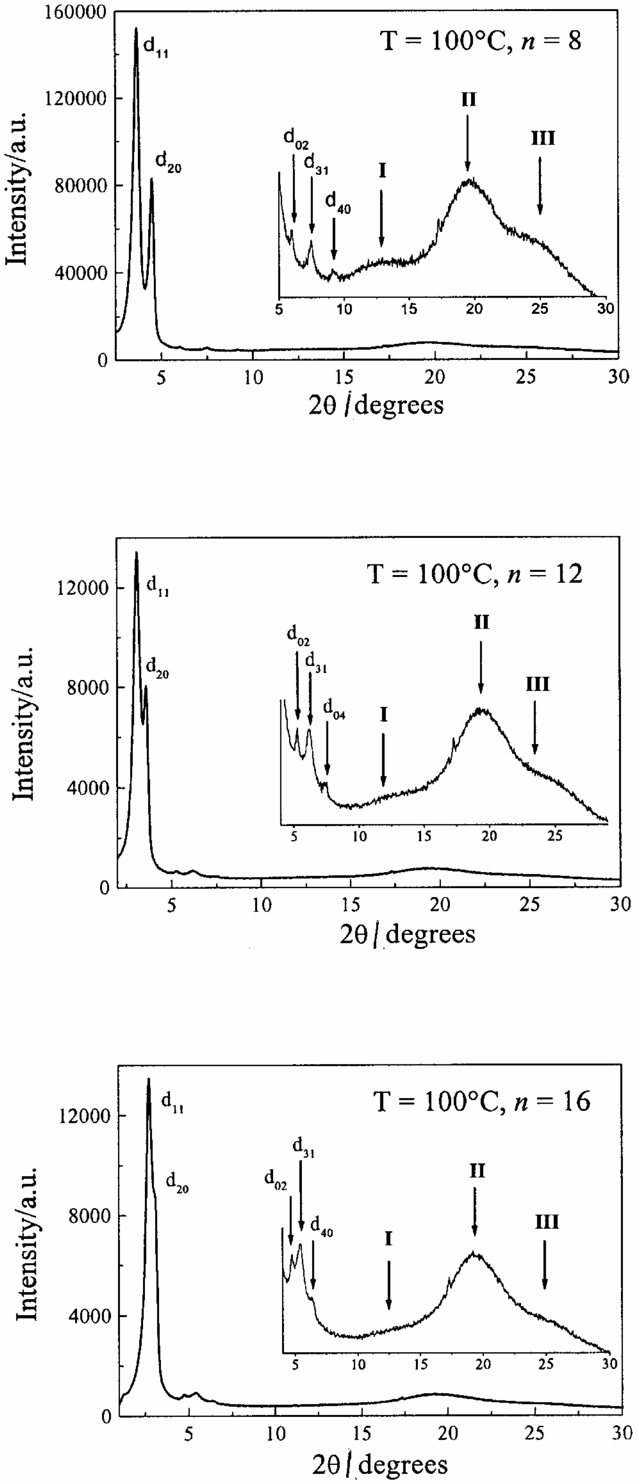


Figure 4. X-ray diffractograms for compounds **1** (top), **2** (middle), **3** (bottom) at 100°C: The magnified inset shows details of the diffraction peaks of low intensity.

It is remarkable that the present vanadyl phthalocyanines display a columnar phase with a rectangular 2D symmetry, a rather rare example in phthalocyanine compounds [3]. Indeed, due to their almost perfect disc-shape, octa-alkoxy substituted phthalocyanine compounds mainly stack into cylindrical columns which self-organize to form the hexagonal columnar phase. A regular stacking along the columnar axis favoured by means of V=O interactions was also expected due to the net dipole moment along the molecular small axis, as in

Table 3. XRD data for the oktakis(octyloxy) substituted vanadyl phthalocyanine complex. a and b are the fundamental cell parameters and S is the unit cell area.

Temperature/°C	d_{meas}/Å	$h\,k$	I^{a}	d_{calc}/Å	Parameters
100	23.0	1 1	VS	23.0	$\mathrm{Col_r}$-$c2mm$
	19.5	2 0	S	18.9	$a = 39.0$ Å
	14.2	0 2	W	14.25	$b = 28.5$ Å
	11.95	3 1	S	11.8	$S = 1111$ Å^2
	9.8	4 0	S	9.75	
	7.0	broad	halo I		
	4.5	broad	halo II		
	3.5	broad	halo III		
150	23.3	1 1	VS	23.3	
	19.5	2 0	S	19.5	$\mathrm{Col_r}$-$c2mm$
	7.0	broad	halo I		$a = 39.0$ Å
	4.6	broad	halo II		$b = 29.0$ Å
	3.5	broad	halo III		$S = 1133$ Å^2
200	23.35	1 1	VS	23.35	$\mathrm{Col_r}$-$c2mm$
	19.9	2 0	S	19.9	$a = 39.8$ Å
	7.1	broad	halo I		$b = 28.8$ Å
	4.6	broad	halo II		$S = 1148$ Å^2
	3.5	broad	halo III		

[a] Intensities I: VS = very strong, S = strong, W = weak.

Table 4. XRD data for the oktakis(dodecyloxy) substituted vanadyl phthalocyanine complex. a and b are the fundamental cell parameters and S is the unit cell area.

Temperature/°C	d_{meas}/Å	$h\,k$	I^{a}	d_{calc}/Å	Parameters
100	27.55	1 1	VS	27.55	$\mathrm{Col_r}$-$c2mm$
	23.85	2 0	S	23.85	$a = 47.7$ Å
	16.9	0 2	W	16.9	$b = 33.75$ Å
	14.3	3 1	S	14.4	$S = 1610$ Å^2
	11.8	4 0	M	11.9	
	7.0	broad	halo I		
	4.5	broad	halo II		
	3.5	broad	halo III		
150	27.3	1 1	VS	27.3	$\mathrm{Col_r}$-$c2mm$
	23.7	2 0	S	23.7	$a = 47.4$ Å
	14.3	3 1	S	14.3	$b = 33.4$ Å
	7.1	broad	halo I		$S = 1583$ Å^2
	4.6	broad	halo II		
	3.5	broad	halo III		
200	27.2	1 1	VS	27.2	$\mathrm{Col_r}$-$c2mm$
	23.85	2 0	S	23.85	$a = 47.7$ Å
	16.4	0 2	W	16.55	$b = 33.1$ Å
	14.4	3 1	S	14.35	$S = 1580$ Å^2
	7.1	broad	halo I		
	4.6	broad	halo II		
	3.5	broad	halo III		

[a] Intensities I: VS = very strong, S = strong, W = weak.

the case of the structurally related alkylthio complexes, 2,3,9,10,16,17,23,24-octakis(octadecylthio)phthalocyaninato-oxovanadium(IV) [10] or -oxotitanium(IV) [11], which showed a hexagonal columnar mesophase only. In the present case, it is clear that the presence of the dipole strongly affects the packing, since it is the only structural difference, with respect to other metallophthalocyanines with alkoxy chains [3].

In order to propose a suitable packing mode taking into account both the molecular shape and the phase

Table 5. XRD data for the oktakis(dodecyloxy) substituted vanadyl phthalocyanine complex. a and b are the fundamental cell parameters and S is the unit cell area.

Temperature/°C	d_{meas}/Å	$h\,k$	I^{a}	d_{calc}/Å	Parameters
100	31.7	1 1	VS	31.7	Col$_r$-$c2mm$
	27.8	2 0	S	27.8	$a = 55.6$ Å
	19.0	0 2	W	19.3	$b = 38.6$ Å
	16.5	3 1	S	16.7	$S = 2141$ Å^2
	13.9	4 0	M	13.9	
	7.0	broad	halo I		
	4.5	broad	halo II		
	3.5	broad	halo III		
150	31.4	1 1	VS	31.4	Col$_r$-$c2mm$
	28.0	2 0	S	28.0	$a = 47.4$ Å
	18.9	0 2	W	19.0	$b = 33.4$ Å
	16.8	3 1	S	16.7	$S = 1583$ Å^2
	7.1	broad	halo I		
	4.6	broad	halo II		
	3.6	broad	halo III		
200	30.9	1 1	VS	30.9	Col$_r$-$c2mm$
	28.1	2 0	S	28.1	$a = 56.2$ Å
	18.6	0 2	W	18.5	$b = 37.0$ Å
	16.8	3 1	S	16.7	$S = 2080$ Å^2
	7.1	broad	halo I		
	4.6	broad	halo II		
	3.6	broad	halo III		

[a] Intensities I: VS = very strong, S = strong, W = weak.

symmetry, the cell parameters a and b and the rectangular lattice area, $S = ab$, were studied as a function of both the chain length n and the temperature T.

Figure 5 shows, as expected, the increase of both parameters a and b with chain length, although the variation of a is somewhat more pronounced than that of b (the a/b ratio increases). The rectangular lattice, in the temperature range studied, does not evolve towards a pseudo-hexagonal symmetry i.e. the a/b ratio does not converge to $\sqrt{3}$. Moreover, a and b are almost constant with temperature. Consequently, S increases with n, figure 6(a), in agreement with the incremental increase of the chain lengths, but is also almost temperature independent, figure 6(b). The two stacking periodicities do not change either with T or with n. These results support the idea that the thermal expansion of the chains occurs on average in the plane perpendicular to the columnar axis, with a tendency for the chain lengthening to occur preferentially along the a-direction.

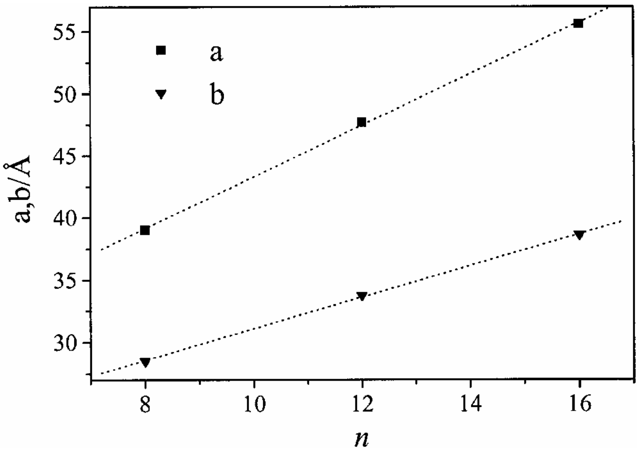


Figure 5. The variation of the lattice parameters a and b as a function of the alkoxy chain length n at 100°C.

It is also interesting to compare the values found for the rectangular columnar cross-section ($S/2$), with the values of the cross-sections of the hexagonal columnar phases calculated for related octa-alkoxyphthalocyanine complexes. On average, the columnar cross-section is 800 Å^2 for $n = 8$, 900–1000 Å^2 for $n = 12$, and 1200 Å^2 for $n = 16$ [15–19]. These values are slightly higher than those found here (tables 3–5), therefore suggesting a tilt. This tilt should occur along the b direction in order to keep the ellipitical shape of the column, in agreement with the symmetry of the two-dimensional rectangular lattice. The formation of the latter may thus be explained by the antiparallel stacking of two molecules, and by the subsequent tilt of the core with respect to the columnar axis along the short elliptical axis as shown in figure 7.

Such a dimeric structure has already been determined in the case of the phthalocyanine of lead(II) [20], and demonstrated by EXAFS spectroscopy on a related platinum(II) phthalocyanine complex [21]. Furthermore, the stacking periodicity of about 7 Å is observed in phthalocyanine complexes of the trivalent lanthanides, which are known to possess a double-decker structure. It is clear that the dipole moment will contribute to such an antiferroelectric stacking, although the reason for favouring such an arrangement with respect to the alkylthio analogues is not clear. This may result from the differences in the electronic behaviour of the terminal chains: the alkoxy groups are electron-donating to the phthalocyanine ring, whereas the alkylthio groups are to a first approximation neither electron-donating nor electron-withdrawing. The position of the V=O stretching vibrations in the IR spectrum (992–995 cm^{-1}) indicates that no linear chains of vanadyl groups arising from V=O … V=O interactions are present. Linear chain formation produces shifts to lower wavenumbers (*c.* 850–870 cm^{-1}) [12].

The lower thermal stability of the alkoxy substituted phthalocyanines compared with that of the alkylthio substituted analogue, for which the clearing point could be observed, may be attributed to this less efficient packing (although it should be mentioned that the higher thermal stability of the compound of ref. [10] can be related to the longer chain length, i.e. octadecylthio).

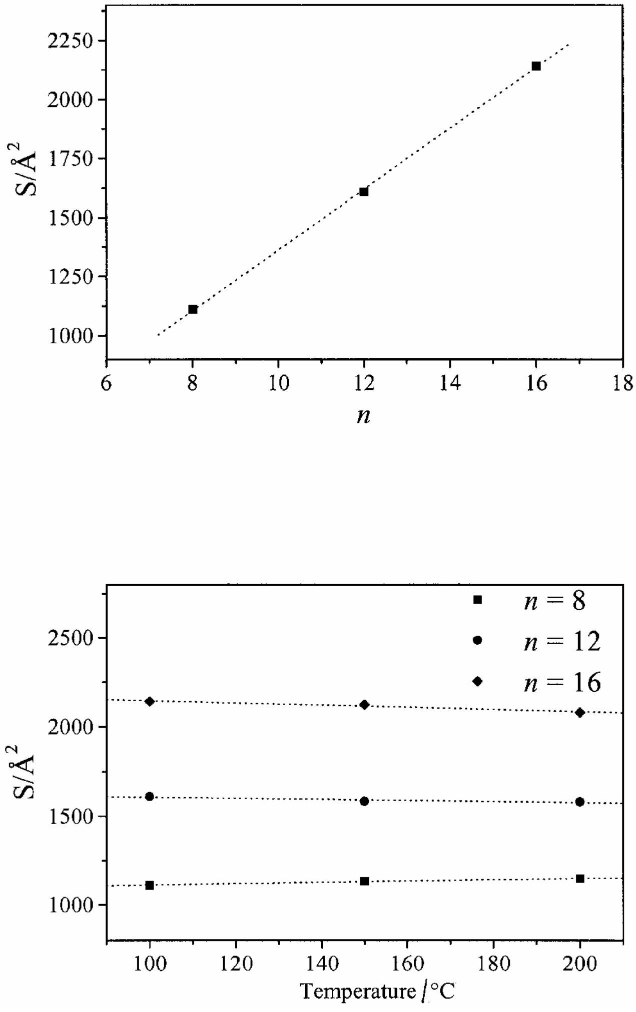


Figure 6. The variation of the rectangular lattice area S with the chain length n (top) and the temperature T (bottom).

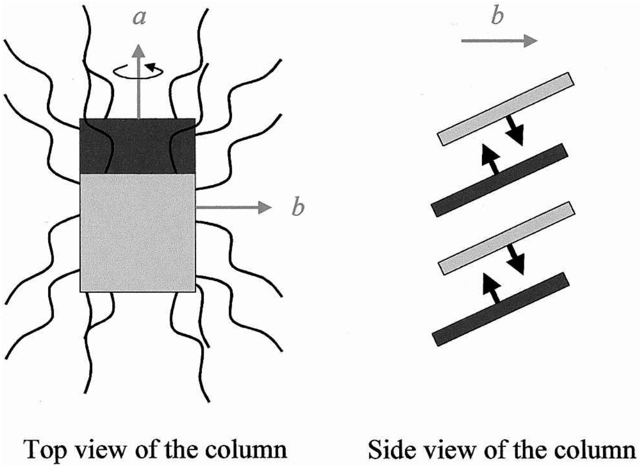


Figure 7. Schematic representation of the stacking of the phthalocyanine molecules along the columnar axis.

3.3. *Optical properties*

The purity and depth of the blue and green colours of phthalocyanine compounds arise from the unique property of these molecules in having an isolated, single absorption band located in the far red end of the visible spectrum near 670 nm, with a molar absorptivity ε often exceeding 10^5 $\mathrm{mol}^{-1}\,\mathrm{cm}^{-1}$. This absorption band is called the *Q-band* and is responsible for the colour of the compound. Unlike many other molecules, the next most energetic set of transitions is generally much less intense, lying just to the blue side of the visible region near 340 nm. The absorption at about 340 nm is called *B-band*. The *Q-band* as well as the *B-band* involve $\pi \rightarrow \pi^*$ transitions. The *Q*-band absorption is assigned to a transition from the HOMO of a_{1u} symmetry to the LUMO of e_g symmetry. The first excited state is a doubly dengerate ^1E_u. The Q- and the B-bands are similar for different metal phthalocyanines though there can be differences in the peak positions and the fine structure. The fine structure occurs due to vibronic couplings.

The UV/Vis spectra of complexes **1**–**3** in chloroform were compared with those of analogous complexes with other transition metals as the central ion ($\mathrm{M} = \mathrm{Co^{II}}, \mathrm{Ni^{II}}, \mathrm{Cu^{II}}, \mathrm{Zn^{II}}$) [22]. The vanadyl complexes clearly exhibit a bathochromic shift (red shift) of the Q- and B-bands judged against the other transition metals. Table 6 shows the Q-band absorption maxima for complexes **1**–**3** and

Table 6. Q-band absorption maxima for complexes **1**–**3** and the Co^{II}, Cu^{II}, Zn^{II} and Ni^{II} complexes with the same chain lengths [22].

Compound		log ε	λ_{max}/nm
$(C_8H_{17}O)_8$PcZn		5.19	679.0
$(C_8H_{17}O)_8$PcCu		5.29	681.5
$(C_8H_{17}O)_8$PcNi		5.25	672.5
$(C_8H_{17}O)_8$PcCo		5.01	672.0
$(C_8H_{17}O)_8$PcVO	**1**	5.33	702.5
$(C_{12}H_{25}O)_8$PcZn		5.18	679.0
$(C_{12}H_{25}O)_8$PcCu		5.34	681.5
$(C_{12}H_{25}O)_8$PcNi		5.24	673.0
$(C_{12}H_{25}O)_8$PcCo		5.10	672.0
$(C_{12}H_{25}O)_8$PcVO	**2**	5.36	703.0
$(C_{16}H_{33}O)_8$PcZn		5.16	680.5
$(C_{16}H_{33}O)_8$PcCu		5.28	681.5
$(C_{16}H_{33}O)_8$PcNi		5.10	672.5
$(C_{16}H_{33}O)_8$PcCo		5.01	672.0
$(C_{16}H_{33}O)_8$PcVO	**3**	5.34	702.5

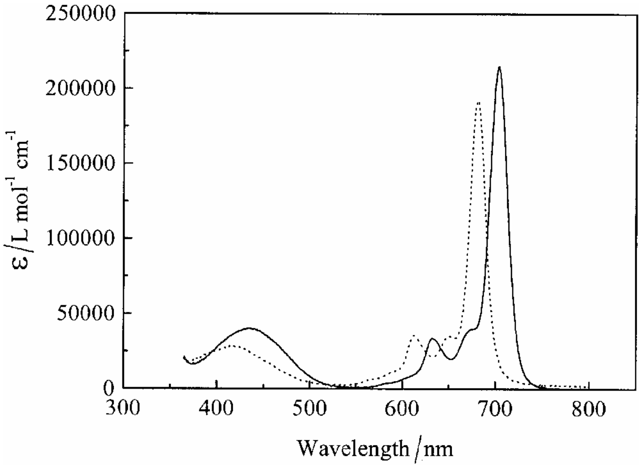


Figure 8. UV/Vis spectra of vanadyl complex **3** (solid line) and of the corresponding copper(II) compound (dotted line). The spectra have been recorded using chloroform as solvent.

the Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} complexes with the same chain lengths. The spectra for the octa-hexadecyloxy compounds are depicted in figure 8.

The vanadyl phthalocyanines have a C_{4h} symmetry in contrast to the D_{4h} symmetry of the other metallophthalocyanines and the D_{2h} symmetry of the metal-free phthalocyanines. Due to the C_{4h} symmetry, the Q-band of vanadyl phthalocyanine is not split just as in the case of the D_{4h} metallophthalocyanines (and in contrast to the PcH_2 compounds).

4. Conclusions

Vanadyl phthalocyanines substituted with eight alkoxy chains in the peripheral (2, 3, 9, 10, 16, 17, 23, 24) positions have been synthesized. The alkoxy chain length was varied: octa-octyloxy ($C_8H_{17}O$), octa-dodecyloxy ($C_{12}H_{25}O$) and octa-hexadecyloxy ($C_{16}H_{33}O$) complexes were prepared. Studies by POM and small angle XRD revealed that all the complexes are liquid crystalline and that the symmetry of the 2D lattice is rectangular, with a *c2mm* space group; hence a rectangular columnar mesophase (Col_r) was assigned. Clearing points could not be observed before the decomposition of the samples (>250°C). The double periodicity along the axis of the columns points to an antiferroelectric stacking of the Pc cores, due to the net dipole moment. A significant bathochromic shift of the Q-band in the UV/Vis solution spectra of the vanadyl complexes was observed compared with the metal-free ligands and to the transition metal analogues (Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}).

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