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Preliminary communication

Novel dipolar metallomesogen: an octa-substituted vanadyl phthalocyanine with low clearing temperature

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A novel dipolar metallomesogen, the 2,3,9,10,16,17,23,24-octakis(*n*-octadecylthio)phthalocyanatoxovanadium(IV) complex was synthesized and its phase transition behaviour investigated. This complex showed a Col_h mesophase between the melting and clearing points, 56 and 295°C, respectively. This is the first phthalocyanine metallomesogen possessing a dipolar V=O bond and it shows a relatively low clearing temperature which is attractive for investigation of physical and/or chemical properties related to the dipolar part.

Phthalocyanine has a largely extended π -conjugation system, which makes it very attractive as a candidate for novel advanced materials such as electric conductors, photovoltaic materials, catalytic materials, gas-sensors, etc. [1]. On the other hand, metallomesogens have been

extensively studied with respect to their mesomorphic nature within this decade [2]. In particular, a variety of phthalocyanine metallomesogens have been synthesized and exhibit mesomorphic phase transition behaviour with interesting physical and/or chemical properties [3-7]. Dipolar liquid crystals are an especially interesting category for novel advanced materials in relation to dipolar switching [8], ferroelectricity [9] and nonlinear optics [10].

In this communication, the mesomorphic phase transition behaviour of the first vanadyl phthalocyanine

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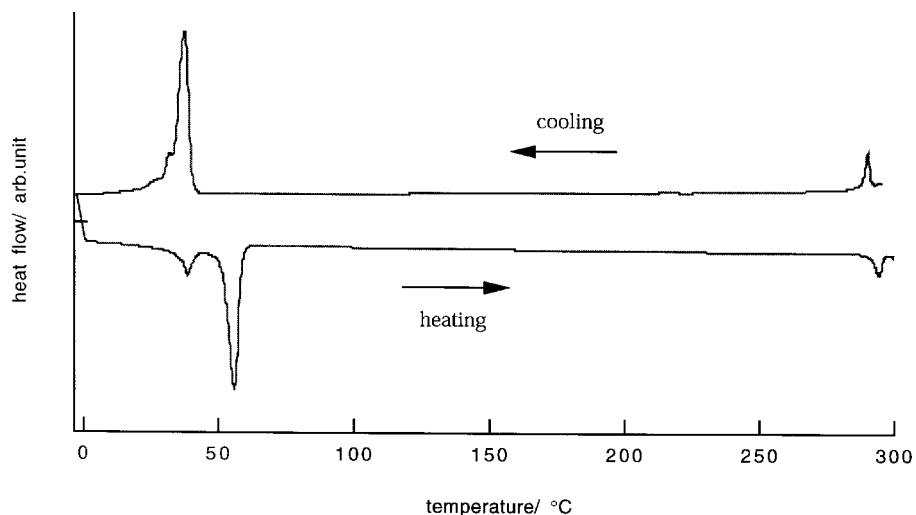
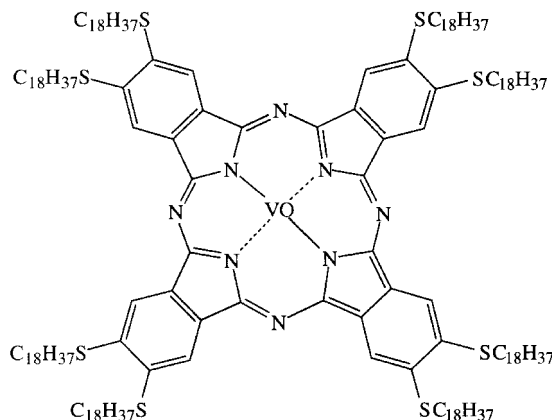


Figure 1. DSC traces of the vanadyl complex. Heating and cooling rate 5°C min⁻¹.

metallomesogen, 2,3,9,10,16,17,23,24-octakis(*n*-octadecylthio)phthalocyanatooxovanadium(IV) is reported.



The compound was synthesized according to a literature method, with slight modifications [11]. Bis(octadecylthio)phthalonitrile given by the reaction of 4,5-dichlorophthalonitrile with octadecylmercaptan in $K_2CO_3/DMSO$ was used for synthesis of the phthalocyanine complex. The crude product was recrystallized from chloroform–acetone solution to give a dark green fine crystalline powder. The characterization of this compound was carried out using infrared and electronic spectroscopy, and the elemental analysis showed very good agreement with theoretical values. ν_{max} (cm^{-1}): 999 (V=O). λ_{max} (nm, $CHCl_3$): 461, 662, 704, 737. Elemental analysis (%):

found (calculated): C 74.03 (74.02), H 10.74 (10.73), N 4.07 (3.92).

Figure 1 shows DSC traces of the compound. The microscopic observation of texture revealed that the phase appearing between 56 and 295°C is a mesophase, of which the texture is typical for a columnar mesophase, as shown in figure 2.

X-ray diffraction (XRD) measurements assigned the mesophase to be a hexagonal columnar mesophase (Col_h phase). Three reflection peaks in the narrow angle

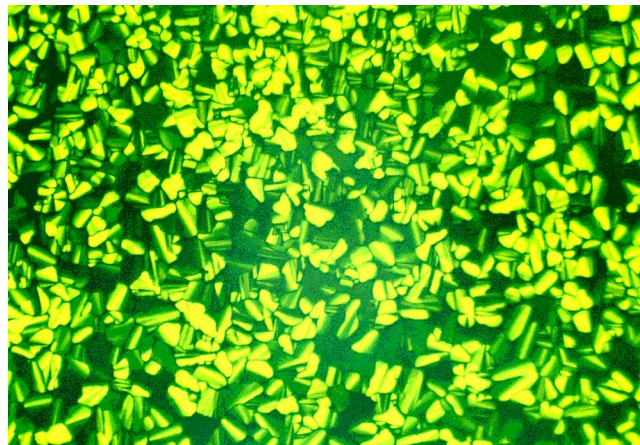


Figure 2. A typical texture of the Col_h phase at 230°C. Magnification x200.

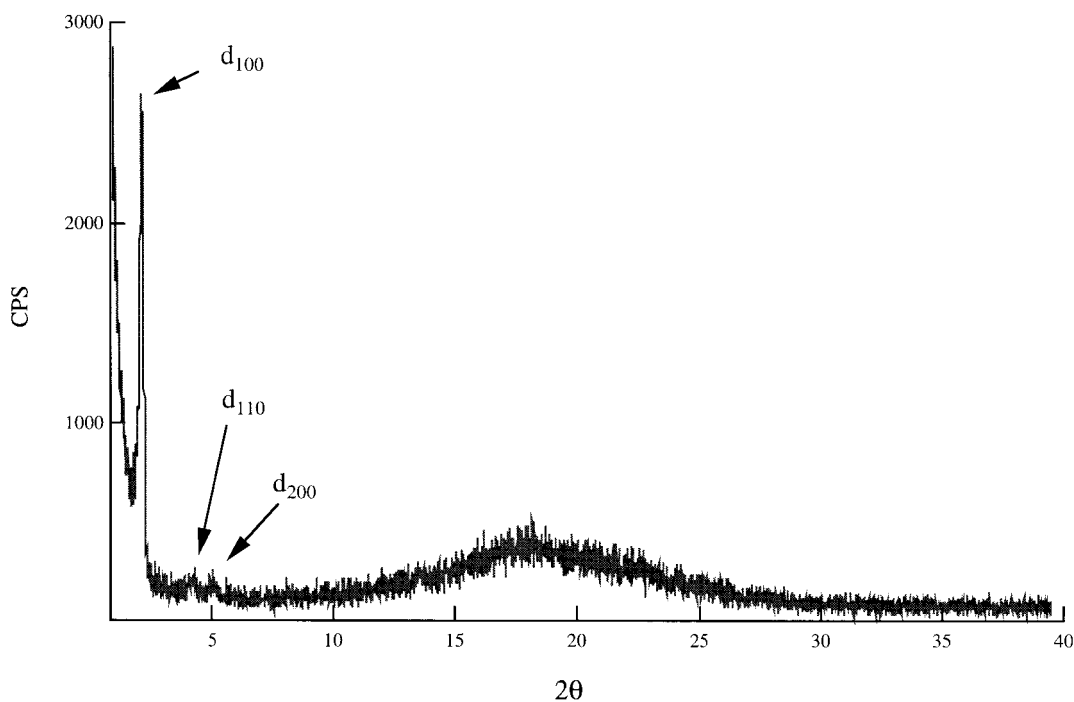


Figure 3. An XRD pattern of the Col_h phase at 230°C (powder sample, CuK_{α}).

region could be recognized and the spacing ratio was $1:1/\sqrt{3}:1/2$, which corresponds to a hexagonal arrangement of columns. In the wider angle region no marked peaks were detected and only one broad halo centred around $2\theta=20^\circ$ ($c. 4.5 \text{ \AA}$) is observed which is derived from the molten alkyl chains. The XRD pattern for the powder sample is shown in figure 3.

The phase transition enthalpies (ΔH) of the melting and clearing points were estimated to be 180 and 11.5 kJ mol^{-1} , respectively, obtained by DSC measurements. The large value of ΔH for the melting point is comparable with that of the alkoxy analogue and is reasonable considering the number and the length of the alkyl chains. However, the ΔH value of 11.5 kJ mol^{-1} for clearing point from the Col_h mesophase is distinctively larger than the value for the Col_{hd} -I and smaller than the value for Col_{ho} - Col_{hd} -I phase transitions of the analogous metal-free phthalocyanine mesogen [12].

It has been reported that discotic mesogens having a V=O moiety are likely to show columnar mesophases relating to V=O—V=O interaction [13, 14]. Such an intermolecular specific interaction could stabilize a columnar structure. As for this compound, therefore, the large ΔH value of the clearing point may indicate the contribution of such an interaction to the stability of the columnar structure. However, it would probably be so weak, considering the evidence that no marked reflections corresponding to the intracolumnar periodicity were detected. Further studies of this question are in progress.

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