

0.1 cm<sup>2</sup>/Vs<sup>[9]</sup> and, thus, correspond to the mobilities of 8.5 × 10<sup>-2</sup> cm<sup>2</sup>/Vs as estimated by Schouten et al. in a crystalline mono-domain of a Pc derivative. This indicates that only for HHTT can the columnar order be preserved over a long range without getting disrupted by disorder or defects.

In conclusion, a further step towards high-mobilities on one hand and processible organic materials on the other has been described by further developing the chemistry of the liquid-crystalline photoconductors. By synthesizing a disctic twin of the triphenylene model compound, it has been possible to obtain charge-carrier mobility data in a glassy columnar phase, in which the charge transport properties of the mesophase are basically maintained. The highest charge-carrier mobilities on the order of 10<sup>-3</sup> cm<sup>2</sup>/V have been obtained in the D<sub>h</sub> mesophase.

The temperature dependence of the charge-carrier mobilities measured in various phase regions from -100 °C up to 165 °C and the influence of different annealing conditions have been rationalized on a qualitative level by assuming a freezing-out of defects at low temperatures, a healing of defects at elevated temperatures, and an additional temperature induced disorder.

### Experimental

2-(10-bromodecyloxy)-3,6,7,10,11-pentapentoxytriphenylene (triphenylenebromide) 15 g (49.98 mmol), 1,10-dibromodecane and 5 g (7.41 mmol) monohydroxypentapentoxytriphenylene, [19], are dissolved in 12 ml 2-pentanone and stirred for 15 h after addition of 6 g (43.31 mmol) potassium carbonate. After filtering and washing with dichloromethane the mixture is subjected to chromatography (silica gel, eluent CH<sub>2</sub>Cl<sub>2</sub>/PE 2:3). Recrystallization from acetonitrile/acetone (1/1) yields 5.21 g (78.8%) pure product as a white solid (m.p. 25 °C). <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.82 (s, 6H, H<sub>arom</sub>), 4.2 (t, 12H, OCH<sub>2</sub>, J = 6.4 Hz), 3.4 (t, 2H, CH<sub>2</sub>Br), 2.0 1.86 (m, 14H, OCH<sub>2</sub>CH<sub>2</sub> + CH<sub>2</sub>CH<sub>2</sub>Br), 1.60–1.34 (m, 32H, OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub> + OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 0.96 (t, 15H, CH<sub>3</sub>, J = 7.0 Hz); FD-MS: m/z: 893.8 (100%) [M]<sup>⊕</sup>.

Dimer **Dit10**: 1.5 g (2.22 mmol) monohydroxypentapentoxytriphenylene and 2.0 g (2.24 mmol) triphenylenebromide are dissolved in 15 ml 2-pentanone under argon atmosphere. The mixture is refluxed for twenty hours after addition of 4 g (28.94 mmol) potassium carbonate and potassium iodide (50 mg). Filtering and chromatography (eluent: CH<sub>2</sub>Cl<sub>2</sub>/PE 1:1) and subsequent recrystallization from acetone yields 2.58 g (76.2%) of the dimer as a white solid. <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>): δ (ppm) = 7.81 (s, 12H, H<sub>arom</sub>), 4.21 (s, 24H, OCH<sub>2</sub>, J = 6.5 Hz), 1.99–1.85 (m, 24H, OCH<sub>2</sub>CH<sub>2</sub>), 1.65–1.35 (m, 52H, OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub> + OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>CH<sub>2</sub>CH<sub>2</sub>O), 0.95 (t, 30H, CH<sub>2</sub>CH<sub>3</sub>, J = 6.9 Hz); EA: C<sub>96</sub>H<sub>142</sub>O<sub>12</sub> (M<sub>w</sub> = 1488.18); Calc: C: 77.48%; H: 9.62%. Found C: 77.19%; H: 9.50%. FD-MS: m/z: 1487.5 (100%) [M]<sup>⊕</sup>.

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### Lytotropic Polymorphism in Oxovanadium Complexes\*\*

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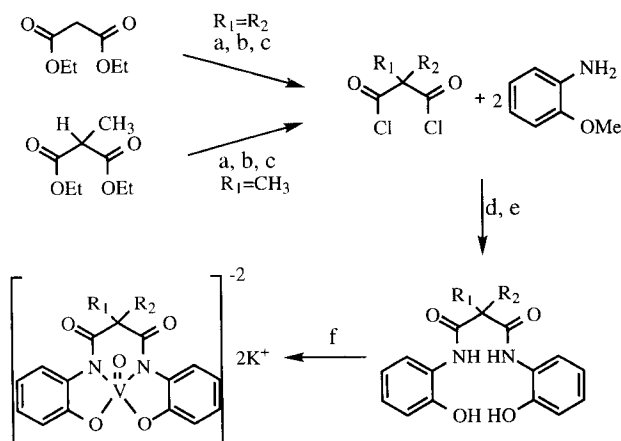
Liquid crystallinity manifested by added solvent, termed lyotropic mesomorphism, offers a great diversity from which to create new materials. Noteworthy features of lyotropics are that they can exhibit low viscosity mesophases at ambient temperature and superstructure dimensions which can range from 10<sup>1</sup>–10<sup>3</sup> Å.<sup>[1]</sup> Although there have been numerous examples of thermotropic transition metal based materials,<sup>[2]</sup> there are few examples of transition metal containing lyotropic systems.<sup>[3, 4]</sup>

The limited number of aqueous lyotropic systems is due in part to the limited stability of coordination compounds in aqueous media.<sup>[3c]</sup> This lack of activity is surprising given that many transition metal complexes are ionic, and are therefore natural building blocks from which to develop lyotropic surfactant molecules. We are interested in transition metal based lyotropic liquid crystals and are endeavoring to develop new classes of these materials with well-defined magnetic anisotropies. As a first step toward this goal, we report herein new types of oxovanadium based surfactants which display binary (surfactant/H<sub>2</sub>O) and ternary (surfactant/H<sub>2</sub>O/decanol) lyotropic mesomorphism.

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Our choice of ligand system is based upon the recent report of Raymond<sup>[5]</sup> that a tetra-anionic diamidate-diphenolate ligand forms dianionic oxovanadium complexes with high stability in aqueous environments. The synthesis of the analogous surfactant molecules (Scheme 1) is similar to that of the previously reported non-mesogenic derivatives ( $R_1 = R_2 = \text{Et}$ ), and this procedure allows for the synthesis of one- and two-tail surfactants.



Scheme 1. **I**:  $R_1 = R_2 = \text{C}_{18}\text{H}_{37}$ . **II**:  $R_1 = R_2 = \text{C}_{10}\text{H}_{21}$ . **III**:  $R_1 = \text{CH}_3$ ,  $R_2 = \text{C}_{12}\text{H}_{25}$ . **IV**:  $R_1 = \text{CH}_3$ ,  $R_2 = \text{C}_{16}\text{H}_{33}$ . (a)  $\text{RBr}$ ,  $\text{NAH/THF}$ , reflux overnight. (b)  $\text{NaOH/H}_2\text{O}$ , reflux, 3 days. (c)  $\text{SOCl}_2$ , warming  $50\text{--}60^\circ\text{C}$ , 3 days. (d)  $\text{NEt}_3/\text{THF}$ , RT. (e)  $\text{BBr}_3/\text{CH}_2\text{Cl}_2$ , RT. (f)  $\text{VO}(\text{acac})/\text{KOH}$ ,  $\text{MeOH}$ ,  $40^\circ\text{C}$ , 4 hours.

The structure of lyotropic phases is related to geometric features which dictate the curvature between the surfactant molecules and solvent.<sup>[6–8]</sup> The critical geometric characteristics are expressed as  $v(la)^{-1}$  in which  $v$  is the molecular volume,  $l$  is the molecular length, and  $a$  is the cross-sectional area of the polar group. A  $v(la)^{-1}$  value of unity provides an optimal condition for a lamellar structure. However, if  $v(la)^{-1} > 1$  then the surfactant layers curve toward the water, and conversely when  $v(la)^{-1} < 1$  the interfacial curvature is in the opposite direction.

Initial investigations over a range of concentrations were performed by observing contact preparations between the complexes and solvents with a polarizing microscope. For two-tail surfactants **I** and **II**,  $v(la)^{-1}$  is close to unity and lamellar phases dominate. For **I** and **II** the introduction of liquid crystalline behavior requires the addition of  $\text{H}_2\text{O}$ , and neither complex exhibits thermotropic mesomorphism and they decompose when heated to  $175^\circ\text{C}$  and  $215^\circ\text{C}$  respectively.

The position of the  $\text{V}=\text{O}$  stretching bands in solid state ( $942\text{ cm}^{-1}$  for **I** and  $934\text{ cm}^{-1}$  for **II**), and the green color in both solid and solution are indicative of monomeric structures. Compound **I** was only briefly investigated and exhibited a lamellar mesophase at a concentration of 12% (weight percentage) and at temperatures above  $38^\circ\text{C}$  (Krafft point). In this material, the elevated temperatures were necessary to overcome the tendency of the  $\text{C}_{18}$  chains to crystallize.

To generate mesomorphic behavior at ambient temperature, we synthesized a shorter tail analogue compound, **II**, which displays a binary aqueous lamellar phase throughout the concentration range of 14%–50% (**II** weight percentage, Fig. 1a). The lamellar phase was recognized with the use

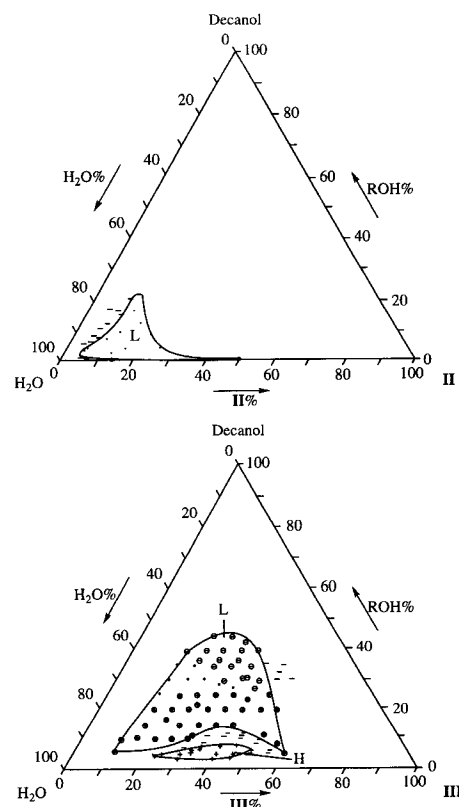


Fig. 1. The room-temperature ternary phase diagrams (surfactant/ $\text{H}_2\text{O}$ /decanol) of **II** (top) and **III** (bottom). The symbols represent experimental data points and  $(-)$  indicates biphasic regions,  $(\oplus)$  and  $(\ominus)$  indicate optically positive and negative regions respectively, and  $(\odot)$  indicates a lamellar phase with very low birefringence. Lamellar phases are labeled as  $(L_x)$ , the hexagonal phase is indicated by  $(H_x)$ .

of a polarizing microscope, and viscous samples at concentrations above 26% display focal conic textures. Decreased percentages of compound **II** provide a more fluid lamellar phase, and a classic oily streak pattern appears as bright bands separating the homeotropic regions (Fig. 2). The introduction of a decanol co-surfactant into the binary system stabilizes the mesomorphism in the oil-rich region in the phase diagram and allows the lamellar phase to exist at concentrations as low as 6% of **II** (Fig. 1a). At still lower concentrations of **II**, the phase diagram shows biphasic behavior.

The single-tail compounds **III** and **IV** are also monomeric light green salts which exhibit  $\text{V}=\text{O}$  stretching bands at  $947\text{ cm}^{-1}$  in the solid state. Similar to **I** and **II**, they do not display thermotropic mesomorphism and decompose when heated above  $190^\circ\text{C}$ . The presence of only a single tail lowers  $v(la)^{-1}$  enough that we find no evidence of mesomorphism

in binary mixtures with H<sub>2</sub>O. However, ternary compositions with decanol are mesomorphic for **III** and **IV**, and depending upon the composition, both hexagonal and lamellar phases are observed by optical microscopy for **III**. As expected, the lamellar and hexagonal phases are separated by a biphasic region. The hexagonal mesophase is recognized by its linear birefringent defects and fan shaped domains (Fig. 2).

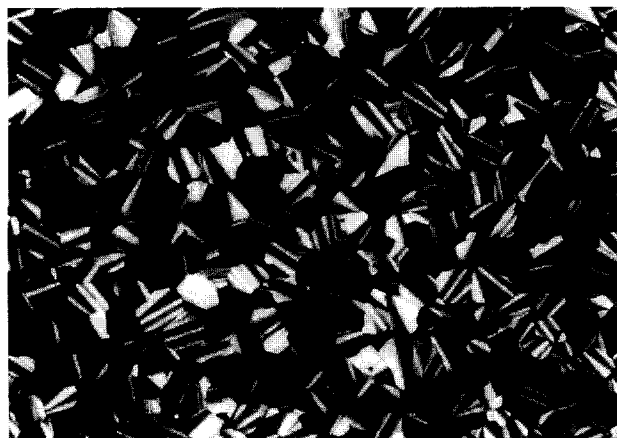
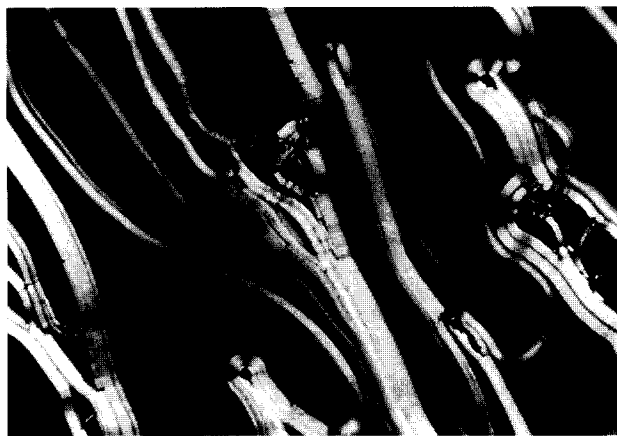
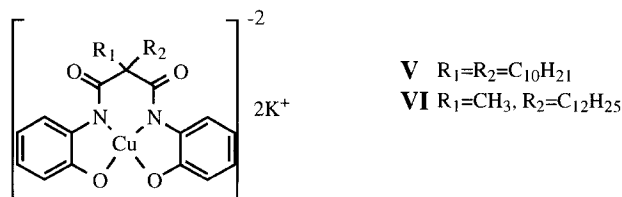


Fig. 2. Top) The oily streak texture of **II**'s lamellar phase in the binary system. Bottom) The fan-shaped texture indicative of a hexagonal phase for **III** in ternary system.

The lamellar phase is very large and extends to decanol concentrations as high as 45% (Fig. 1b). The interference colors vary gradually throughout the lamellar region, and at intermediate concentrations, the samples display very low birefringence. Investigations with compensators indicate a change in the optical sign with composition. At low decanol concentrations the lamellar phase is optically positive, and at high decanol concentrations the samples are optically negative. This behavior may be the result of changes in **III**'s polarizability due to hydrogen bonding with decanol or a result of a double refraction index effect. Large crystals appear in the sample rich region of the phase diagram, and we find that **III** has limited stability in large concentrations of decanol. As a result, the lamellar phase is only stable for a

period of several days. On the other hand, the hexagonal phase is stable for more than a month. Compound **IV** was investigated only briefly and similar to **III** we observed a lamellar phase in the ternary system which is stable over a broad range.

In principle the tetra-anionic ligand used herein can produce other surfactants upon combination with other transition metal ions, however, our initial attempts in this direction have been limited by the low chemical stability. For example, the one- and two-tail copper analogues (**V** and **VI**) display lamellar ternary phases (surfactant/H<sub>2</sub>O/decanol), but these compounds could not be studied in detail due to decomposition in ternary system.



In summary, we have reported new types of ionic transition metal compounds which exhibit mesomorphism at room temperature in water and water/decanol systems. The phase behavior of the ternary systems was studied and both hexagonal and lamellar phases were identified. Our ongoing investigations will focus on developing lyotropic materials with large magnetic anisotropies,<sup>[9,10]</sup> and this area is promising considering recent results which show the facile orientation of a magnetically doped lyotropic phase by small magnetic fields.<sup>[11]</sup> Additionally, lyotropic behavior has recently been demonstrated in Chervel phases,<sup>[12]</sup> suggesting that other anisotropic inorganic materials can be incorporated into lyotropic phases. New transition metal based lyotropic systems may provide for yet unknown properties and future technological opportunities in surfactant science.

### Experimental

**Two-tail ligands:** A mixture of 44.2 g (0.2 mole) 1-bromodecane (C<sub>10</sub>H<sub>21</sub>Br) and 15.2 ml (0.1 mole) diethylmalonate in 200 ml dried tetrahydrofuran (THF) was added dropwise into 6.0 g NaH under nitrogen atmosphere. The mixture was refluxed overnight and the product was concentrated under vacuum to give 40.8 g substituted diethylmalonate as an oil in 92% yield. This product was then suspended in a 250 ml aqueous solution containing 23 g NaOH and refluxed for three days. HCl was carefully added to the solution with stirring until the pH was 1. The mixture was cooled and the resulting solid was filtered. This solid was then dissolved in THF, filtered to separate it from insoluble salts and concentrated in vacuum to afford 22.8 g of the malonyl diacid in 64% yield. The malonyl dichloride was obtained by heating the diacid in excess SOCl<sub>2</sub> at 50 °C–60 °C for three days. After evaporation of the SOCl<sub>2</sub>, 22.4 g product was isolated (90% yield). The final two steps in the ligand synthesis were performed exactly as in [5].

The R<sub>1</sub> = R<sub>2</sub> = C<sub>18</sub> ligand was synthesized by the same method and the one-tail ligands were made by the analogous procedure except that 0.2 mole diethylmethylmalonate was used. The additional steps to **I**, **II**, **III**, and **IV** were performed by straightforward adaptation of the procedures described in [5]. Compound **I**: C<sub>51</sub>H<sub>82</sub>N<sub>2</sub>O<sub>5</sub>VK<sub>2</sub>: C, 66.67 (66.24); H, 8.86 (8.79); N, 3.00 (3.46). Compound **II**: C<sub>35</sub>H<sub>50</sub>N<sub>2</sub>O<sub>5</sub>VK<sub>2</sub>·2H<sub>2</sub>O: C, 56.50 (55.90); H, 7.31 (7.11); N, 3.76 (3.86); V, 6.85 (6.97). Compound **III**: C<sub>28</sub>H<sub>36</sub>N<sub>2</sub>O<sub>5</sub>VK<sub>2</sub>·3H<sub>2</sub>O: C, 50.67 (50.97); H, 6.33 (6.30); N, 4.22 (4.50); V, 7.86 (8.03). Compound **IV**: C<sub>32</sub>H<sub>44</sub>N<sub>2</sub>O<sub>5</sub>VK<sub>2</sub>·3H<sub>2</sub>O: C, 53.39 (53.94); H, 7.00 (6.79); N, 3.89 (4.03). Com-

pounds V and VI: A stirred  $N_2$ -saturated methanol solution of 0.5 mmole of the diamidate-diphenolate ligand was treated with 2 mmole KOH in ethanol and stirred for 15 min. 0.5 mmole solid cupric acetate was then added to this solution in one portion and after heating for 4 hours at  $50^\circ\text{C}$ – $60^\circ\text{C}$ , the solvent was removed under reduced pressure to yield the black solid which was dried under vacuum overnight. The complex was dissolved in ethylacetate, filtered and the filtrate was reduced under vacuum to provide black crystals in 60% yield. Anal. Calcd.(found) for: Compound V:  $C_{35}H_{50}N_2O_4CuK_2 \cdot H_2O$ : C, 58.18 (58.38); H, 7.25 (7.57); N, 3.88 (3.43); Cu, 8.79 (7.96). Compound VI:  $C_{28}H_{36}N_2O_4CuK_2 \cdot H_2O$ : C, 53.86 (53.82); H, 6.13 (6.99); N, 4.48 (4.50).

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## Charge Transport and Molecular Dynamics in Columnar Stacks of Liquid Crystalline Phthalocyanine Derivatives\*\*

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Broadband dielectric spectroscopy ( $10^{-2}$ – $10^9$  Hz) has been employed to study the electric charge transport and molecular dynamics in the columnar stacks of liquid crystalline phthalocyanine derivatives. The conductivity contribution is a thermally activated process and it originates from

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hopping charge transport of ionic and electronic defects in the discotic stacks. Three dielectric relaxation processes are observed, covering a broad dynamic regime from  $10^{-1}$  Hz up to  $10^{10}$  Hz. Phthalocyanine derivatives substituted with eight alkyl or alkoxy side chains may display a discotic columnar mesophase over a broad temperature range.<sup>[1, 2]</sup> In the mesophase the macrocycles are stacked to form columns while the hydrocarbon chains are liquid-like. The special properties of phthalocyanine-like molecules displaying highly mobile electronic charge carriers on band-gap photoexcitation,<sup>[3]</sup> or the possibility of forming metal complexes, and the columnar arrangement make these discotic liquid crystals interesting as one-dimensional semiconductors or as photoconductors.<sup>[4–6]</sup> Broadband dielectric spectroscopy is ideally suited for the study of the molecular dynamics and the charge transport in these materials.<sup>[7]</sup> The results are discussed with respect to recent microwave measurements limited to the frequency range from 26.5 to 38 GHz.<sup>[8, 9]</sup>

The dielectric measurements were carried out on the compounds  $H_2Pc(OC_9H_{19})_8$  and  $H_2Pc(CH_2OC_{12}H_{25})_8$ . Figure 1 shows the chemical structure of the two phthalocyanine derivatives. To cover the frequency regime from  $10^{-2}$  to  $10^9$  Hz three different measurement systems were com-

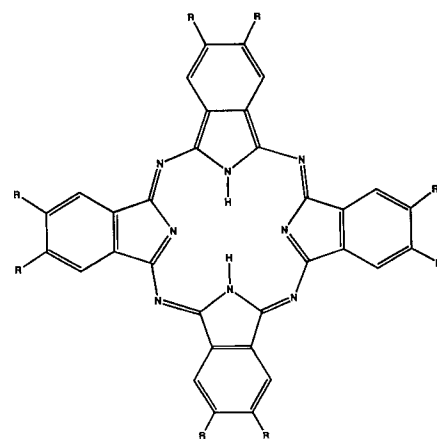


Fig. 1. Chemical structure of the two investigated compounds.  $H_2Pc(OC_9H_{19})_8$ : R =  $CH_3(CH_2)_8O-$ .  $H_2Pc(CH_2OC_{12}H_{25})_8$ : R =  $CH_3(CH_2)_{11}OCH_2-$ .

bined:<sup>[10]</sup> i) a frequency response analyzer Solartron Schlumberger FRA1260 which was supplemented with a high-impedance preamplifier of variable gain ( $10^{-2}$  to  $10^6$  Hz). ii) a Hewlett Packard Impedance analyzer HP4291A ( $10^2$  to  $10^7$  Hz). iii) a Hewlett Packard coaxial reflectometer HP4191A ( $10^6$  to  $10^9$  Hz). The samples were kept between two gold plated brass electrodes with glass fibers as spacers. In the frequency range from  $10^{-2}$  to  $10^6$  Hz the capacitor was 50  $\mu\text{m}$  thick and 20 mm in diameter. The capacitor used in the coaxial line at  $10^6$  to  $10^9$  Hz had a thickness of 20  $\mu\text{m}$  with a diameter of 5 mm.