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Columnar metallomesogens: vanadyl complexes derived from β,δ-triketones

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Two series of vanadyl complexes derived from bis(*o*-hydroxybenzoyl)methane were reported. The mesomorphic properties of the compounds **1** and **2** were studied by differential scanning calorimetry (DSC) and polarizing optical microscopy. Formation of the columnar mesophases was found to be dependent on the sidechain density around the mesogenic core. All the compounds **2** with six alkoxy sidechains exhibited columnar hexagonal ($\mathrm{Col_h}$) phases, however, compounds **1** with two alkoxy sidechains formed crystalline phases. Studies of variable-temperature IR spectra for compounds **2** indicated that linear polymeric structures were observed both in the mesophase and crystalline phase. The crystal and molecular structure of **1** ($n=8$) were determined by means of X-ray single crystal analysis. It crystallizes in the monoclinic space group $P2_1/c$, with $a=14.6581$ (1) Å, $b=14.5933$ (2) Å, $c=21.7985$ (1) Å, $\alpha=90°$, $\beta=100.320$ (1)°, $\gamma=90°$, and $Z=4$. The vanadyl center is bonded in a typical five-coordinate fashion with a solvated tetrahydrofuran molecule sixth-coordinated opposite the axial oxygen. The EPR spectra measured at variable temperatures were also studied.

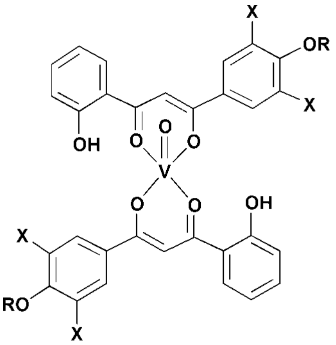
Introduction

Incorporating metal centers to create unique geometric structures has been widely exercised to generate metallomesogenic materials[1] with novel physical properties during the past decade. Numerous metallomesogenic structures exhibiting novel mesomorphic properties have been continuously reported and their physical properties studied. This approach is of particular importance for metal ions with directional local polarity due to the feasible generation of polar materials by proper alignment. Therefore, it is possible to produce achiral ferroelectric structures[2] if the delicate balance of dative interaction is controlled in the solid state. Amongst many inorganic moieties vanadyl is the one that has been applied and investigated most. A few examples of vanadyl[3a–c] and dioxomolybdenum[3d] complexes exhibiting mesomorphic properties have been described, and some of these mesomorphic compounds were also found to assemble in linear chain polymers. In this paper as part of our investigation on bimetallomesogenic complexes[4] we report a new type of vanadyl complex **2** that exhibits columnar hexagonal ($\mathrm{Col_h}$) phases, in which a head-to-tail arrangement of vanadyl groups in a linear chain was also formed. Further, we also found that the formation of linear chain polymeric structures may be controlled by sidechain density attached to the core group.

Results and discussion

Synthesis and characterization

In our previous report[4a] we reported a new type of bicopper complex that exhibited columnar disordered hexagonal phases. The ligand used; β,δ-triketone, is particularly interesting because of its capability of binding two metals in close proximity. The compounds of 1-(2′-hydroxyphenyl)-3-(3′,4′,5′-trialkoxyphenyl)propane-1,3-diones were obtained from 2-(3′,4′,5′-trialkoxybenzoyl)acetophenones by base-catalyzed rearrangement. The base used in this reaction was preheated powder potassium hydroxide. The copper(II) complexes were obtained by reaction of copper(II) acetate and 1-(2′-hydroxyphenyl)-3-(3′,4′,5′-trialkoxyphenyl)propane-1,3-diones in refluxing THF–ethanol. However, all attempts to generate divanadyl complexes by similar procedures gave green solids for complexes **1** or yellow-orange solids for complexes **2**, respectively. Binuclear complexes were initially proposed. However, EPR studies indicated that the complexes were more consistent with mononuclear species. Identical complexes were always isolated regardless of the stoichiometry of vanadyl sulfate or vanadyl acetate used. The metal complexes were characterized and identified by elemental analysis and IR spectra. The X-ray crystal analyses of the isolated plate-like green crystal (**1**; $n=8$) confirmed the structural identity of these vanadyl complexes.†



R = $(CH_2)_nH$
1 X = H
2 X = OR

Variable temperature IR-spectra studies

The IR stretching bands of the V=O group were found to be strongly dependent on the numbers of alkoxy sidechains attached. They appeared at two different regions; 991–999 $\mathrm{cm^{-1}}$ and 891–899 $\mathrm{cm^{-1}}$ for compound **1** and **2**, respectively. This frequency lowering in stretching frequencies for **2** compared with **1** by *ca.* 109 $\mathrm{cm^{-1}}$ implies substantial weaken-

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†CCDC reference number 1145/251. See http://www.rsc.org/suppdata/jm/b0/b005759m for crystallographic files in .cif format.

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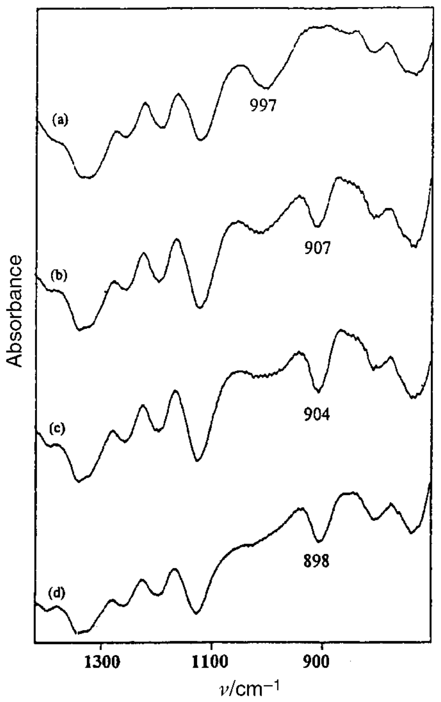

Fig. 1 A plot of V=O stretching frequencies as a function of temperature for vanadyl complexes **2** (n = 12) at: (a) 175 °C (b) 145 °C (c) 140 °C (d) 35 °C.

ing of the V=O bond, and a strong tendency toward linear chain formation[5] in compounds **2** was observed. The IR data showed that the V=O frequency was insensitive (*ca.* 8.0 cm^{-1}) to the carbon length of the alkoxy sidechains. The relative strength in such linear chain structures may be determined qualitatively by the frequency of the V=O stretching mode and the stronger linear chains were observed at a lower frequency. The variable-temperature IR spectra for compound **2** (n = 12) are depicted in Fig. 1. At the isotropics at 175 °C the V=O frequency appeared at 997 cm^{-1} which is characteristic of monomeric structures, and this band was shifted to 907 cm^{-1} when cooled to the mesophase at 145 °C. Upon further cooling to the crystalline state at 25 °C, this band shifted to a slightly higher energy by 9.0 cm^{-1}. The IR data indicated that linear polymeric structures were observed both in the mesophase and crystal phase, only with a slightly different degree of linear-chain strength.

Mesomorphic properties

The mesomorphic behavior of these compounds was studied by DSC thermal analysis and optical polarized microscopy and the phase transitions of the complexes **1** and **2** are summarized in Table 1. Compounds **2** exhibited hexagonal columnar (Col$_h$) mesophases and compounds **1** formed crystalline phases. The DSC analysis of **2** showed typical columnar transition phases, and a larger enthalpy for the mesophase-to-isotropic in complexes **2** indicated that the mesophases were relatively ordered. The temperature range of the mesophases is quite wide (*ca.* 31–170 °C on cooling) and also sensitive to the carbon lengths of the alkoxy sidechains. Some of the compounds with longer carbon lengths (n = 10, 12, 14) are in fact room temperature liquid crystals. When cooled from their isotropic phases, they displayed characteristic optical textures of focal-conic, as shown in Fig. 2, suggesting hexagonal columnar structures. However, all the complexes **1** (n = 8, 16) with two alkoxy sidechains showed crystalline phases. This lack of mesomorphic properties was due to insufficient sidechain density around the larger core group.

Powder XRD diffraction was used to confirm the structures

Table 1 Phase behavior[a] of vanadyl complexes **1** and **2**

Complex	n	Phase
2	5	$K_1 \underset{87.7\ (2.14)}{\overset{92.0\ (1.81)}{\rightleftharpoons}} K_2 \underset{160.7\ (0.51)}{\overset{178.2\ (1.05)}{\rightleftharpoons}} Col_{ho} \underset{191.7\ (2.33)}{\overset{199.3\ (4.42)}{\rightleftharpoons}} I$
	6	$K_1 \underset{36.5\ (1.17)}{\overset{72.6\ (3.08)}{\rightleftharpoons}} K_2 \underset{117.1\ (0.38)}{\overset{142.9\ (0.24)}{\rightleftharpoons}} Col_{ho} \underset{190.0\ (2.62)}{\overset{199.6\ (3.33)}{\rightleftharpoons}} I$
	7	$K_1 \underset{48.8\ (0.25)}{\overset{43.3\ (1.23)}{\rightleftharpoons}} K_2 \underset{104.3\ (0.23)}{\overset{124.3\ (0.42)}{\rightleftharpoons}} Col_{ho} \underset{184.2\ (3.33)}{\overset{191.2\ (3.36)}{\rightleftharpoons}} I$
	8	$K \underset{54.2\ (0.13)}{\overset{82.5\ (0.28)}{\rightleftharpoons}} Col_{ho} \underset{185.8\ (3.87)}{\overset{190.8\ (3.88)}{\rightleftharpoons}} I$
	10	$K \underset{9.1\ (4.49)}{\overset{18.5\ (6.77)}{\rightleftharpoons}} Col_{ho} \underset{178.8\ (2.47)}{\overset{182.2\ (3.61)}{\rightleftharpoons}} I$
	12	$K \underset{21.9\ (9.46)}{\overset{34.8\ (11.0)}{\rightleftharpoons}} Col_{ho} \underset{156.5\ (2.70)}{\overset{169.8\ (3.71)}{\rightleftharpoons}} I$
	14	$K \underset{30.5\ (21.7)}{\overset{49.5\ (21.0)}{\rightleftharpoons}} Col_{ho} \underset{148.3\ (1.26)}{\overset{159.8\ (1.63)}{\rightleftharpoons}} I$
1	8	$K_1 \underset{87.0\ (0.18)}{\overset{178.2\ (2.12)}{\rightleftharpoons}} K_2 \underset{141.7\ (11.7)}{\overset{220.0\ (14.1)}{\rightleftharpoons}} I$
	16	$K_1 \underset{45.7\ (4.17)}{\overset{61.0\ (4.67)}{\rightleftharpoons}} K_2 \underset{159.8\ (5.54)}{\overset{185.5\ (6.08)}{\rightleftharpoons}} I$

[a] n represents the number of carbons in the alkoxy chain. K_1, K_2 = crystal phases; Col$_h$ = columnar hexagonal ordered phase; I = isotropic. The transition temperature (°C) and enthalpies (in parentheses, KJ mol^{-1}) are determined by DSC at a scan rate of 10.0 °C min^{-1}.

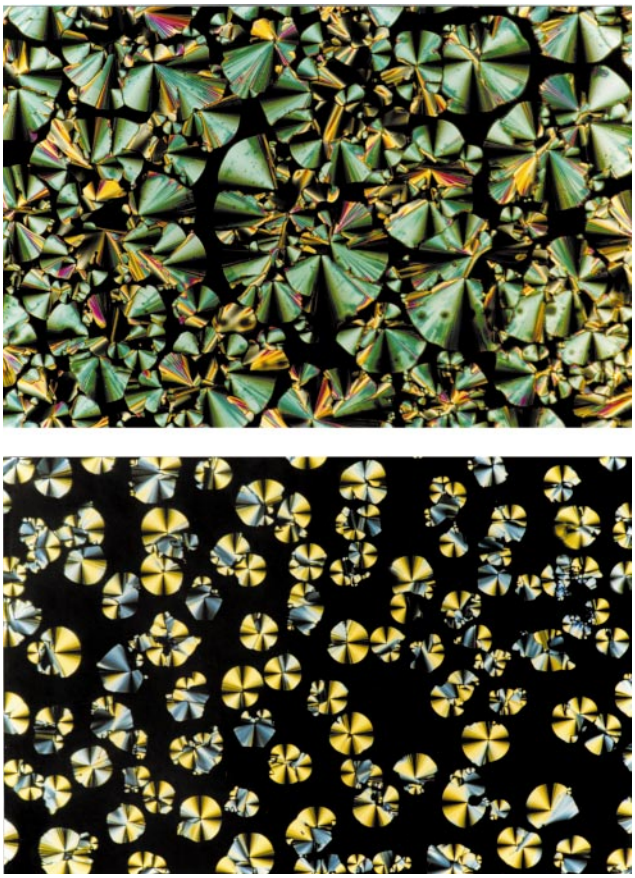

Fig. 2 Optical textures (100 ×) observed by complex **2** ($n = 12$). The Col_{ho} phase at 162.0 °C (top: thick sample) and 159.0 °C (bottom: thin sample).

of the mesophases. A summary of the diffraction peaks and lattice constants for the complexes **2** is given in Table 2. They all displayed a diffraction pattern of two-dimensional hexagonal lattice with a strong peak and two weak peaks, which are characteristic of columnar (Col_h) phases with a *d*-spacing ratio of 1, $(1/3)^{1/2}$ and $(1/4)^{1/2}$. However, liquid-like correlations occurred at wider angle regions of 4.66–4.93 Å. In addition, observation of a distinct weak peak at 3.67–3.73 Å indicated a relatively ordered mesophase. This relatively sharp peak corresponded to core–core correlation and referred to a more regular period within the columns. We also found that the low-angle reflections shifted to a smaller *d*-spacing at lower temperature (*i.e.* $d = 39.79$ Å at 130 °C and $d = 39.24$ Å at 100 °C for complex **2**; $n = 12$). The hexagonal lattices correlated well with increasing side chain lengths.

EPR studies

The X-band EPR spectra of **2** ($n = 12$) measured at different temperatures are depicted in Fig. 3. In CH_2Cl_2 (Fig. 3a) at room temperature this compound exhibits a resolved eight-line hyperfine band (^{51}V; $I = 7/2$) of the characteristic d^1 vanadyl center; part of the parallel region overlapped with the perpendicular region. The spectrum in Fig. 3b corresponds to the *as-received* sample taken at room temperature, in which one broad shoulder (if any) is barely observable in the low-field region. When the sample was heated to the clearing point at 175 °C the spectrum in Fig. 3c consisted of an unresolved hyperfine structure. The EPR data also indicated that the spectra were independent of the aliphatic chain length. The absence of a spectrum consisting of 15 lines due to exchange by two vanadyl centers additionally confirmed the mononuclear nature of these complexes.

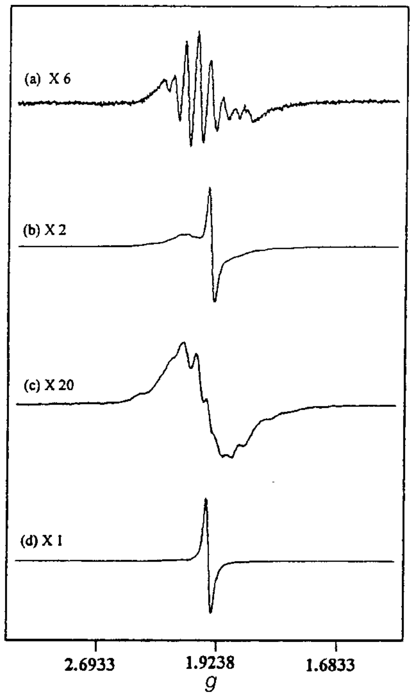

Fig. 3 EPR spectra of complex **2** ($n = 12$) measured at: (a) room temperature in CH_2Cl_2 (a) room temperature of *as-received* samples (c) 175 °C; isotropic phase (d)140 °C; columnar phase.

Crystal and molecular structures†

While a few nonmesomorphic divanadyl complexes have been reported[6] and the structures resolved by single-crystal X-ray analyses, the two vanadyl centers in these known systems were not bonded in such close structural proximity. Larger bond strain might prohibit the formation of two vanadyl centers in such a tight structural cavity. Single-crystal X-ray structural analysis was performed on a vanadyl complex **1** ($n = 8$). The single crystal was grown from a THF solution, and this compound showed only a crystalline phase. Fig. 4 shows the molecular structure with the atomic numbering scheme, and Table 3 shows the crystallographic data and structure refinement for the molecule. The coordination geometry at the vanadium center can be described as a typical square pyramid. In addition, a tetrahydrofuran molecule of solvation was coordinated opposite the axial oxygen. The axial V=O distance of 1.605 Å is in the normal range of 1.52–1.68 Å reported for vanadyl groups,[6] and the four equatorial V–O distances are slightly different; but all in the range 1.971–1.978 Å (Table 4). In the crystal structure the vanadium is bonded at the $[O_2O_2]$-

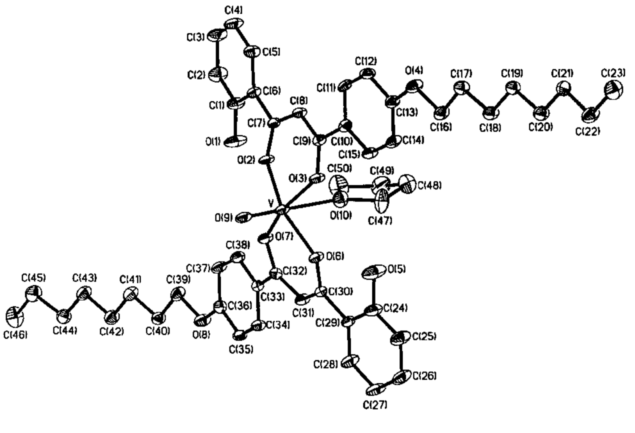

Fig. 4 An ORTEP drawing for vanadyl complexes **1** ($n = 8$) with the numbering scheme, and thermal ellipsoids of the non-hydrogen atoms are drawn at the 50% probability level.

Table 2 Variable-temperature XRD diffraction data for vanadyl complexes **2**

Complex		Mesophase	Lattice spacing /Å	*d*-Spacing /Å obs. (calcd.)	Miller indices
2	$n=7$	Col$_{ho}$ (150 °C)	30.95	26.80 (26.80)	(100)
				13.62 (13.41)	(020)
				8.47 (7.74)	(220)
				4.83 (br)	
				3.73 (br)	
		Col$_{ho}$ (130 °C)	30.35	26.28 (26.28)	(100)
				13.46 (13.14)	(020)
				4.93 (br)	
				3.72 (br)	
	10	Col$_{ho}$ (130 °C)	36.39	31.52 (31.52)	(100)
				15.61 (15.76)	(020)
				13.22	
				4.87 (br)	
		Col$_{ho}$ (60 °C)	35.74	30.95 (30.95)	(100)
				24.51	
				15.46 (15.48)	(020)
				4.73 (br)	
				3.70	
	12	Col$_{ho}$ (130 °C)	39.79	34.46 (34.46)	(100)
				16.91 (17.23)	(020)
				14.32	
				4.88 (br)	
				3.70 (br)	
		Col$_{ho}$ (100 °C)	39.24	33.98 (33.98)	(100)
				16.99 (16.99)	(020)
				14.73	
				4.66 (br)	
				3.70(br)	
	14	Col$_{ho}$ (130 °C)	43.17	37.39 (37.39)	(100)
				18.38 (18.69)	(020)
				15.50	
				4.78 (br)	
				3.71 (br)	
		Col$_{ho}$ (90 °C)	42.46	36.77 (36.77)	(100)
				28.23 (21.23)	(110)
				18.06 (18.39)	(020)
				15.20	
				4.75 (br)	
				3.67 (br)	

coordination site of the β-diketonate moiety leaving the phenolic-oxygen atom unbonded. The vanadium atom is 0.373 Å from the average plane of the four equatorial oxygen atoms defined by O2, O3, O6 and O7. The two angles of O(2)–V–O(3) and O(2)–V–O(7) are 88.84(8)° and 87.18(8)°, respectively, which show a slight deviation from the ideal angle of 90° expected for a flat square-planar complex. The overall molecular shape is nearly flat, and the perpendicular molecular length and width of the molecule viewed as a rectangle is measured *ca.* 31.71 Å and 10.94 Å, respectively. A side view of the crystal packing showing the layered structures are presented in Fig. 5, in which the two shortest distances between two layers and two adjacent V–O bonds were

Table 3 Crystallographic data and structure refinement for bis[1-(2′-hydroxyphenyl)-3-(4′-octyloxyphenyl)propane-1,3-dionato]oxovanadium†

Empirical formula	$C_{50}H_{62}O_{10}V$
Formula weight	873.94
Temperature	120 (1) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a=14.6581$ (1) Å, $\alpha=90°$
	$b=14.5933$ (2) Å, $\beta=100.320$ (1)°
	$c=21.7985$ (1) Å, $\gamma=90°$
Volume, *Z*	4587.48 (7) Å^3, 4
Density	1.265 Mg m^{-3}
Crystal size	0.45 × 0.18 × 0.15 mm
θ range for data collection	1.41 to 26.40°
Reflections collected	21509
Independent reflections	9281 ($R_{int}=0.0733$)
Final *R* indices	$R1=0.0693$, $wR2=0.1377$

Table 4 Bond lengths [Å] and angles [°] for bis[1-(2′-hydroxyphenyl)-3-(4′-octyloxyphenyl)propane-1,3-dionato]oxovanadium

V–O(9)	1.605(2)	V–O(2)	1.971(2)
V–O(3)	1.972(2)	V–O(6)	1.976(2)
V–O(7)	1.978(5)	V–O(10)	2.418(3)
O(1)–C(1)	1.360(4)	O(2)–C(7)	1.306(3)
O(3)–C(9)	1.295(3)	O(3)–C(13)	1.360(3)
O(4)–C(16)	1.438(3)	O(5)–C(24)	1.364(4)
C(1)–C(2)	1.395(4)	C(1)–C(6)	1.413(4)
C(2)–C(3)	1.372(4)	C(3)–C(4)	1.384(5)
C(4)–C(5)	1.383(4)	C(5)–C(6)	1.422(4)
C(6)–C(7)	1.484(4)	C(7)–C(8)	1.394(4)
O(2)–V–O(2)	101.16(10)	O(9)–V–O(3)	100.94(10)
O(2)–V–O(3)	88.84(8)	O(9)–V–O(6)	100.65(10)
O(2)–V–O(6)	158.20(9)	O(3)–V–O(6)	86.94(8)
O(9)–V–O(7)	100.78(10)	O(2)–V–O(7)	87.10(8)
O(3)–V–O(7)	158.28(9)	O(6)–V–O(7)	88.87(8)
O(9)–V–O(10)	179.39(9)	O(2)–V–O(10)	79.39(8)
O(3)–V–O(10)	79.32(8)	O(6)–V–O(10)	78.81(2)
O(7)–V–O(10)	78.96(8)	C(7)–O(2)–V	129.8(2)
C(9)–O(3)–V	128.6(2)	C(13)–O(4)–C(16)	118.4(2)
C(30)–O(6)–V	129.9(2)	C(32)–O(7)–V	129.2(2)
O(1)–C(1)–C(2)	116.3(23)	O(1)–C(1)–C(6)	123.4(3)
C(2)–C(1)–C(6)	120.2(3)	C(3)–C(2)–C(1)	120.5(3)
C(2)–C(3)–C(4)	120.4(3)	C(5)–C(4)–C(3)	120.0(3)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y$, $-z+1$.

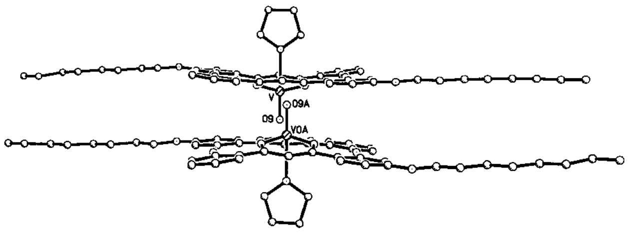

Fig. 5 An example of crystal packing viewed approximately down the *a*-axis.

calculated *ca.* 4.0 and 7.0 Å. Unfortunately, the attempt to grow a single crystal for compound **2** was not successful.

Summary

A new type of monovanadyl complex was prepared and their mesomorphic properties reported. The formation of columnar hexagonal phases and polymeric linear chains were also found to be dependent on sidechain density, *i.e.* the numbers of alkoxy sidechains, around the mesogenic core. EPR studies and single crystal X-ray analyses confirmed the structure of the monovanadyl complexes prepared. Possible physical properties of these polar materials are under study.

Experimental procedures

^{1}H and ^{13}C NMR spectra were measured on a Bruker DRS-200. Infrared spectra were recorded on a Bio-Rad FTS-155 using polystyrene as a standard. The DSC thermographs were performed on a Perkin-Elmer DSC-7 and optical polarized microscopy was observed under Nikkon MICROPHOT-FXA with a Mettler FP90/FP82HT hot stage system. Elemental analysis for carbon, hydrogen, and nitrogen were conducted on a Heraeus CHN-O-Rapid elemental analyzer, and the results are listed in Table 5. The compounds of 1-(2′-hydroxyphenyl)-3-(3′,4′,5′-trialkoxyphenyl)propane-1,3-diones were prepared according to a previous paper.[4a]

1-(2′-Hydroxyphenyl)-3-[3′,4′,5′-tris(hexyloxy)phenyl]propane-1,3-diones

Yield 80%, light yellow solids. ^{1}H NMR (ppm, $CDCl_3$): 0.87 (t, –CH_3, 9H), 1.27–1.78 (m, –CH_2, 24H), 4.04 (t, –OCH_2, 6H), 6.68 (s, –CHCO, 1H), 6.88–7.82 (m, Ph, 6H), 12.02 (s, –OH, 1H), 15.92 (s, HO–CH=C, 1H). ^{13}C NMR ($CDCl_3$): 14.69, 14.74, 23.30, 23.35, 26.38, 26.45, 30.02, 30.79, 32.26, 32.41, 70.18, 74.35, 92.50, 106.50, 119.48, 119.71, 128.98, 129.07, 136.32, 143.21, 153.93, 163.03, 178.67, 195.65.

Bis{1-(2′-hydroxyphenyl)-3-[3′,4′,5′-tris(dodecyloxy)phenyl]-propane-1,3-dionato}oxovanadium (2; *n* = 12)

1-(2′-Hydroxyphenyl)-3-[3′,4′,5′-tris(dodecyloxy)phenyl]propane-1,3-dione (0.30 g, 0.38 mmol) dissolved in 2.0 ml of CH_2Cl_2 was added to a hot CH_3OH (10 ml) solution of vanadyl sulfate hydrate (0.06 g, 0.38 mmol) dissolved in a minimum amount of water. A KOH pellet (0.02 g, 0.38 mol) was added to the reaction mixture, and the solution was refluxed for 2 h. The yellow solution was concentrated to give brownish solids. The light orange solids were obtained after recrystallization from CH_2–Cl_2–CH_3OH. Yield 60%. Elemental analysis: calcd. for $C_{90}H_{142}O_{13}V$: C, 72.89; H, 9.65%; found C, 73.34; H, 9.89%. IR (thin film): 2923.3, 2854.5, 1623.3, 1539.5, 1488.1, 1389.4, 1323.5, 1192.3, 1120.9, 899.1, 786.8, 723.5, 575.3 cm^{-1}.

Table 5 Elemental analysis[a] of compounds **1** and **2**

Compds.	*n*	C (%)	H (%)
2	5	68.28 (67.84)	7.99 (7.78)
	6	69.01 (69.15)	8.25 (8.26)
	7	70.67 (70.22)	8.90 (8.68)
	8	71.01 (71.26)	9.22 (9.05)
	10	73.34 (72.89)	9.89 (9.65)
	12	74.87 (74.19)	10.34 (10.13)
	14	75.98 (75.25)	10.85 (10.52)
1	8	69.23 (68.90)	7.01 (6.79)
	16	73.16 (72.56)	8.79 (8.45)

[a] Calculated values in parenthesis.

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