

Ferroelectric and Mesomorphic Properties of Oxovanadium(IV) Complexes with Long Alkoxy Chains

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ABSTRACT

The chiral and racemic oxovanadium(IV) salen complexes, [VO(*X*)-(C16-salmen)] (*X* = *R*(**1**), *S*(**2**), and *rac*(**3**); C16-salmen = *N,N'*-monomethylenebis(5-hexadecyloxysalicylideneimine)) containing 5-substituted alkoxy chains on aromatic rings were synthesized, and their mesomorphic behaviors and ferroelectric properties were also investigated. All complexes exhibited both smectic A and chiral smectic C mesophases above 360 K, and they showed ferroelectric properties in the chiral smectic C mesophase.

Key words: Metallomesogen, Ferroelectricity, Liquid Crystal, Oxovanadium(IV) Complex

Metal-containing liquid crystals called metallomesogens exhibiting mesophase between the solid and the liquid states have been received attention as one of fascinating materials because it shows magnetic, electrical, optical, and electro-optical properties derived from the presence of metal ions within anisotropic phases [1-4]. Among them, ferroelectric metallomesogens are of current interest in the field of display devices owing to its switchable property and rapid electro-optic response on an electric field [5]. Generally, ferroelectric metallomesogens reveal very large permittivity and remain some residual electrical polarization after removing the field. The vast majority of ferroelectric metallomesogens are consisted of chiral smectic C (SmC*) order involving chiral molecules with strong dipole moments [6].

Oxovanadium(IV) (VO) salen complexes (salen = *N,N'*-ethylenebis(salicylideneimine) with long alkyl chain have been widely studied due to its unique square pyramidal structure and liquid crystalline phase resulted from the strong interaction of flexible alkyl chains. For instance, Swager *et al.* reported that the VO(salen) complexes with long alkyl chains at the 5-position on aromatic rings shows the liquid crystalline phase of smectic A (SmA) or C (SmC) phases [7]. Abe *et al.* also reported that the VO(salen) complexes containing 4-substituted alkoxy chains of aromatic rings exhibit the bilayer mesophase above at room temperature [8]. The

first ferroelectric VO metallomesogen based on chiral Schiff base was reported by Marcos and co-workers, and they have also expanded their research to chiral VO bis(salicylideneaniline) and chiral VO (β -diketonate) complexes showing both distinctive ferroelectricity and mesophase [9-11]. However, ferroelectric VO metallomesogens has not been reported for racemic form.

Keeping aforementioned research in mind, we herein report the synthesis of novel chiral and racemic ligands with long alkyl chains based on salen structure not only to impart different dipole moments but also to form a specific mesophase, and their VO complexes that would be expected to increase electric polarizability by an external electric field.

The (*X*)-C16-salmen ligand (*X* = *R*, *S* or *rac*) was synthesized by reaction of (*X*)-propane-1,2-diamine and 5-hexadecyloxy-2-hydroxybenzaldehyde under reflux in DMF [12-14]. The VO complexes [VO(*X*)-(C16-salmen)] (*X* = *R*(**1**), *S*(**2**), and *rac*(**3**)) **1-3** were also prepared by complexation between VOSO₄·*n*H₂O and (*X*)-C16-salmen ligand in MeOH to give green powder (Fig. 1) [15-16].

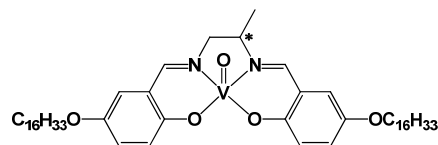


Fig. 1 Chemical structure of [VO(*X*)-(C16-salmen)] (*X* = *R*(**1**), *S*(**2**), *rac*(**3**); (i) DMF, (ii) VOSO₄·*n*H₂O, MeOH.

Liquid-crystalline properties for **1-3** were confirmed firstly by the measurement of powder X-ray diffraction (PXRD) at 298 and 413 K, respectively. As shown in Fig. 2, the PXRD pattern for **1** reveals the mesophase state at 413 K. In the wide-angle region a diffuse and broad scattering halo is indicative of the liquid-like order of the aliphatic chains leading to the fluid-like nature of the phase. In the small-angle region (1, 2, 3) the PXRD pattern shows three reflections in a ratio of 1:1/2:1/3, which could be indexed as the (001), (002) and (003) reflections of a lamellar phase with a periodicity $d = 36.2 \text{ \AA}$ ($2\theta = 2.44^\circ$). On the other hand, there are some of sharp peaks in the wide-angle region at 298 K, indicating that **1** is in the crystal state at room

temperature. A rod-like geometry is proposed for the molecular structure for the compounds **1-3** by computer simulation. The interlayer spacing of 36.2 Å is considerably less than the molecule's length (49.8 Å) calculated. This is indicated that the smectic layers are tilted or highly interdigitated. In the small-angle region (4, 5, 6) the PXRD pattern also shows three reflections in a ratio of 1:1/2:1/3, which could be indexed as the (001), (002) and (003) reflections of a lamellar phase with aperiodicity $d = 32.2 \text{ \AA}$ ($2\theta = 2.74^\circ$) [17].

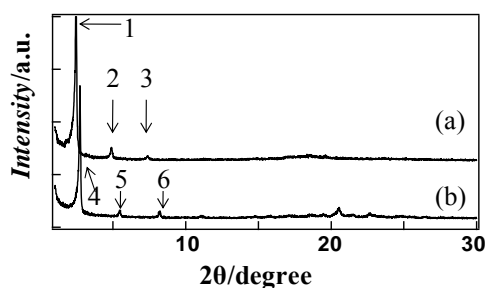


Fig. 2 PXRD patterns for **1** at 413 K (a) and 298 K (b).

To gain more insight into the liquid crystalline property, the polarized optical microscopy (POM) texture of **1** was observed at 373 K and 417 K, respectively. At 373 K, it shows a typical fingerprint-like texture (Fig. 3(a)) which is consistent with SmC* mesophase, whereas a typical fan-shape was observed at 417 K (Fig. 3(b)) corresponding to SmA mesophase.

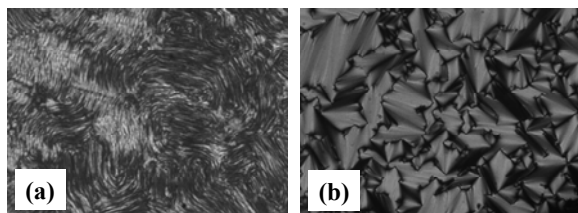


Fig. 3 POM images of **1** at 406 K (a) and 416 K (b).

In general, the fingerprint-like texture can be observed in SmC* or Crystal E phases, and circular dichroism (CD) spectra were measured for the compounds **1**, **2** and **3** (Fig. S3). The samples for CD spectra were prepared by cooling until room temperature after melting. The fingerprint-like texture was kept even at room temperature. The CD spectra for **1** and **2** in the texture phase are active symmetrically, but that of **3** is very weak. Therefore, it was assigned that the phase was SmC* mesophase by PXRD patterns and viscosity.

We also investigated the phase transition for **1** by using differential scanning calorimetry (DSC), and summarized in Table 1. At first, two crystal to crystal transitions were observed at 326.9 K ($\text{Cr}_1 \rightarrow \text{Cr}_2$) and 340 K ($\text{Cr}_2 \rightarrow \text{Cr}_4$) in the virgin sample. Further heating, crystal phases Cr_{3v} and Cr_4 transform to the liquid crystal (LC) phases at 354.1 K and 362.9 K, respectively. LC

phase transforms to isotropic liquid (IL) phase at 417.8 K. On cooling, the clear peaks were not observed. In additional heating, four peaks were observed, i.e. $\text{Cr}_1 \rightarrow \text{Cr}_2$ at 326.9 K, $\text{Cr}_2 \rightarrow \text{Cr}_4$ at 340 K, $\text{Cr}_4 \rightarrow \text{LC}$ at 362.9 K and $\text{LC} \rightarrow \text{IL}$ at 417.8 K. The clear phase transition was not observed in DSC, but the phase transition from fan-shape texture (SmA) to the fingerprint-like texture (SmC*) was revealed at 408 K in POM observation. The liquid properties (PXRD, POM and DSC) for **2** and **3** were also similar to those for **1** (Fig. S1, Fig. S2 and Table S1).

Table 1 Phase transition temperatures and enthalpy changes of **1**.

Complex	Phase	T / K	$\Delta H / \text{kJmol}^{-1}$	Phase
1	Cr_1	326.9	17.4	Cr_2
	Cr_2	340	2.33	Cr_4
	Cr_4	362.9	69.4	LC
	LC	417.8	27.0	IL
	Cr_{3v}	354.1	20.7	

Phase nomenclature: Cr = crystal, LC = liquid crystal, IL = isotropic liquid, v = virgin state

The temperature-dependent dielectric constants in the frequency range of 100 Hz and 1 kHz for **1** were measured by the inductance capacitance and resistance (LCR) meter on heating mode (Fig. 4). The frequency sweeps were carried out isothermally. As the frequency of 100 Hz was used, the dielectric value (ϵ_r) was almost constant from 300 K to 357 K, and one peak was observed at 373 K. Further heating, an abrupt elevation of dielectric value was observed, which is consistent with the phase transition temperature from mesophase to liquid. However, upon 1 kHz frequency, the variation of ϵ_r value is quite small because the dipole cannot give response to electric field due to the fast frequency. From these results, it was found that the dipole is possible to respond easily to electric field at the liquid crystal phase.

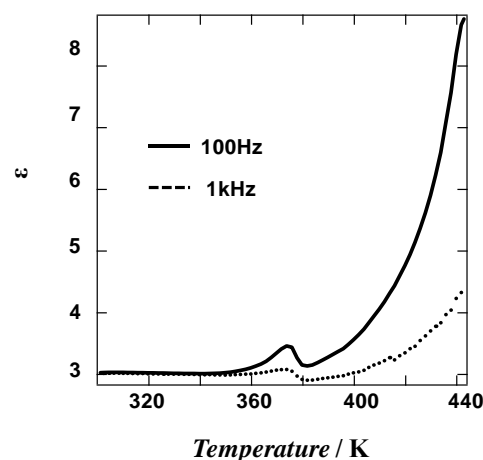


Fig. 4 Temperature-dependent dielectric constant of **1**.

To study further the influence of the phase transition on the ferroelectric property both in the solid state at 298 K and in the mesophase at 383 K, we also investigated the hysteresis loop characteristic of ferroelectric materials by using (TF Analyzer1000) in the form of P - E curve, where P is polarization and E is electric field (Fig. 5). The ferroelectric hysteresis loop of **1** in the mesophase (383 K) displays a strong frequency relaxation at $\sim 253 \text{ kVcm}^{-1}$, and the remnant polarization is 128 nC cm^{-2} , which is identical to a typical ferroelectric feature [18]. However, the crystal phase of **1** at 298 K does not show ferroelectric behavior. The resulting P - E curves suggesting that the ferroelectricity of **1** is ascribed to mesophase. Similar ferroelectric behaviors were also observed in **2** and **3** (Figs. S4 and S5). It is thought that the ferroelectricity was observed even for a racemic form because of pyramidal structure of VO complex.

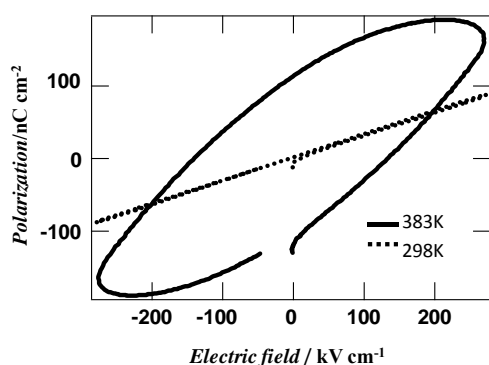


Fig. 5 Hysteresis loop of electric polarization for **1** at 383 K and 298 K.

In summary, we have succeeded in synthesizing novel multifunctional VO salmmsen complexes with long alkoxy chains exhibiting mesomorphic properties and ferroelectric behavior. The chiral and racemic [VO(X)-C16-salmmsen] compounds ($X = R, S$ and rac) showed SmC* and SmA phases in the temperature range of 362.9–408 K and 408–417.8 K, respectively. More interestingly, the compounds show a typical ferroelectric feature in SmC* mesophase even for a racemic compound.

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- [13] Synthesis of (*rac*)-C16-salmmsen: a mixture of 5-hexadecyloxyaldehyde (1.01 g, 2.79 mmol) and (*rac*)-1, 2-diaminopropane (0.11 g, 1.42 mmol) in EtOH (50 mL) was heated at 60 °C for 2 hours. The solvent was distilled under reduced pressure and purified by column chromatography (SiO₂, hexane:ethyl acetate=3:1), yielding an orange powder. Yield: 0.83 g (39 %). ¹H-NMR: (500 MHz, CDCl₃): δ=8.21 (s, 1H, CH=N-), 8.17 (s, 1H, CH=N-), 6.83-6.77 (m, 4H, CH=CH), 6.65 (s, 2H, CH=C-), 3.79 (t, 4H, O-CH₂), 3.66-3.59 (m, 2H, CH₂-C-), 1.66 (sext, 4H, -CH₂-), 1.33-1.32 (m, 1H, CH-N), 1.23-1.16 (m, 55H, -CH₂-CH₃-), 0.81 (t, 6H, CH₃-).
- [14] Synthesis of (*R* or *S*)-C16-salmmsen: (*R*) and (*S*)-C16-salmmsen were prepared following to [13] from (*R* or *S*)-1,2-diaminopropane. Yield: 50 % for (*R*)-C16-salmmsen and 47 % for (*S*)-C16-salmmsen. ¹H-NMR((*R*)-C16-salmmsen): (500 MHz, CDCl₃): δ=8.21 (s, 1H, CH=N-), 8.18 (s, 1H, CH=N-), 6.88-6.80 (m, 4H, CH=CH), 6.65 (s, 2H, CH=C-), 3.80 (t, 4H, O-CH₂), 3.66-3.58 (m, 2H, CH₂-C-), 1.68 (sext, 4H, -CH₂-), 1.33-1.32 (m, 1H, CH-N), 1.25-1.16 (m, 55H, -CH₂-CH₃-), 0.81 (t, 6H, CH₃-). ¹H-NMR((*S*)-C16-salmmsen): (500 MHz, CDCl₃): δ=8.22 (s, 1H, CH=N-), 8.18 (s, 1H, CH=N-), 6.83-6.80 (m, 4H, CH=CH), 6.66 (s, 2H, CH=C-), 3.80 (t, 4H, O-CH₂), 3.66-3.58 (m, 2H, CH₂-C-), 1.67 (sext, 4H, -CH₂-), 1.34-1.32 (m, 1H, CH-N), 1.25-1.16 (m, 55H, -CH₂-CH₃-), 0.82 (t, 6H, CH₃-).
- [15] Synthesis of [VO(*rac*)-C16-salmmsen]: a mixture of (*rac*)-C16-salmmsen (0.37 g, 0.49 mmol), VO(SO₄)_nH₂O (0.13 g, 0.79 mmol) and pyridine (1.5 mL) in MeOH (250 mL) was heated at 60 °C for 3 hours. The solvent was distilled under reduced pressure and purified by column chromatography (SiO₂, CHCl₃) to give green powder. Yield: 0.12 g (30 %). Anal. Calcd. for C₄₉H₈₀N₂O₅V: C, 71.07; H, 9.74; N, 3.38. Found: C, 70.85; H, 9.91; N, 3.41.

- [16] Synthesis of [VO(*R or S*)-C16-salmen]: [VO(*R or S*)-C16-salmen] were synthesized following to [15] from (*R or S*)-C16-salmen. Yield: 70 % for [VO(*R*)-C16-salmen], Anal: Calcd. for $C_{49}H_{80}N_2O_5V$: C, 71.07; H, 9.74; N, 3.38. Found: C, 70.87; H, 9.85; N, 3.43, and Yield: 74 % for [VO(*S*)-C16-salmen], Anal: Calcd. for $C_{49}H_{80}N_2O_5V$: C, 71.07; H, 9.74; N, 3.38. Found: C, 70.90; H, 9.82; N, 3.41.
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