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Lamellar columnar mesomorphism in a series of oxovanadium(IV) complexes derived from N, N/-di-(4-n-alkoxysalicylidene)diaminobenzene

Chira R. Bhattacharjee [a,*], Gobinda Das [a], Paritosh Mondal [a], Subbarao Krishna Prasad [b], D. S. Shankar Rao [b]

[a] *Department of chemistry, Assam University, Silchar 788011, Assam, India*
[b] *Centre for Soft Matter Research, Jalahalli, Bangalore 560013, India*

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ABSTRACT

A series of new nondiscoid shaped square pyramidal oxovanadium(IV)-Schiff base complexes containing 4-substituted alkoxy chains on the aromatic rings, [VO(4-$C_nH_{2n+1}O$)$_2$salophen)] {n = 14, 16, 18; salophen = N, N/-phenylnebis(salicylideneiminato)} have been prepared and their mesogenic properties investigated. The ligands and the complexes were characterized by FT-IR, CHN, ^{1}H-NMR, UV–vis and FAB mass spectrometry. Presence of V=O stretching mode at ~980 cm^{-1} indicated absence of any intermolecular ···V=O····V=O··· interactions with no dependence on the chain length. Variable temperature magnetic susceptibility measurements of the complexes also suggested lack of such exchange interaction. Cyclic voltammetry showed a quasireversible one-electron response at 0.75 V for the VO(IV)–VO(V) redox couple. DSC coupled with polarized optical microscopy showed the ligands to be nonmesogenic but the complexes exhibited an unprecedented thermally stable columnar mesophase in the 136–154 °C. X-ray diffraction technique, confirmed that the structure of the mesophase is lamellar columnar in type (Col$_l$). DFT studies using DMol3 were carried out to obtain the optimized geometry of the complex.

Incorporating metal centers to create unique geometric structures has been widely exercised to generate metallomesogenic materials with novel physical properties during the past decade [1–5]. Numerous metallomesogenic structures exhibiting novel mesomorphic properties have continuously been reported and their physical properties studied [6–11]. Coordination compounds of redox active metals exhibit paramagnetism, and often undergo electronic excitations with visible light. Such properties can be exploited to produce novel conductors, magnetic materials, and display devices [12]. Unlike other first row transition metals, oxovanadium(IV) complexes owing to the weakened intermolecular …V=O........V=O… nonpolar interaction often frustrates exhibition of mesogenic properties [13–17]. Five coordinate vanadyl complexes are susceptible to intermolecular dative interactions through the VO^{2+} moiety which in square pyramidal vanadyl complexes form a linear chain-like (—V=O—V=O—)$_n$) structures generating a polar order along the column axis [12]. Such polar order is quite significant in the context of novel ferroelectric/piezoelectric and NLO materials [12]. Despite the inherent difficulties in synthesizing mesogenic vanadyl(IV) complexes, a number of vanadyl(IV) liquid crystalline complexes have been documented [11–30]. Rich but complex mesomorphism exhibited by the salicylaldimines and their metal complexes including vanadium has attracted considerable interests. The Schiff base complexes of vanadium(IV) that possess a calamitic (rod-like) mesogenic group to which terminal flexible alkyl or alkoxy chains are attached, results in mesogens which either exhibit nematic or smectic phases, have been rather extensively studied [20–30]. However, by coordinating non-discoid ligands, a molecular shape with a reduced length-to-breadth ratio is formed, mimicking disk-like metallomesogens [31]. Such structures will have a reduced tendency to form calamitic mesophases and favor formation of columnar mesophases [31].Complexes containing Schiff base ligands with long alkoxy chain at 5-position on aromatic rings have been reported to exhibit smectic A (SmA)or C (SmC) phase [17,32]. Four coordinated Ni(II), Cu(II)-salen complexes with 5-substituted long alkoxy chains forming a linear rod like (1-D) structure also show SmA mesophases [33–35]. In contrast, metallomesogens of Schiff bases with long alkoxy chain at 4-position have been sparsely investigated [14,15,19]. Abe et al. reported a series of vanadyl complexes, possessing an aliphatic (—CH$_2$)$_n$ rigid core showing an unusual rectangular (Col$_r$) columnar mesophase [15]. Complexes with shorter alkoxy substituent, [VO(4-$C_nH_{2n+1}O$)$_2$salen)]ClO$_4$ (n = 3, 8, 10) with (—CH$_2$)$_2$-rigid core lacked liquid crystalline behavior [14,15,19]. Metallomesogens exhibiting Col$_l$ mesophase are not ubiquitous [19,36]. Quite surprisingly, metallomesogen with 4-substituted Schiff base ligands with an aromatic rigid core are not known till date. Very recently we have reported synthesis of a series of novel fluorescent liquid crystalline Zn (II)-salophen complexes with methyl substituted phenylenediamine spacer [37]. Choice of metal ion, nature and position of the substituents on aromatic ring are known to greatly influence the

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* Corresponding author. Tel.: +91 03842 270848; fax: +91 03842 270342.
E-mail address: crbhattacharjee@rediffmail.com (C.R. Bhattacharjee).

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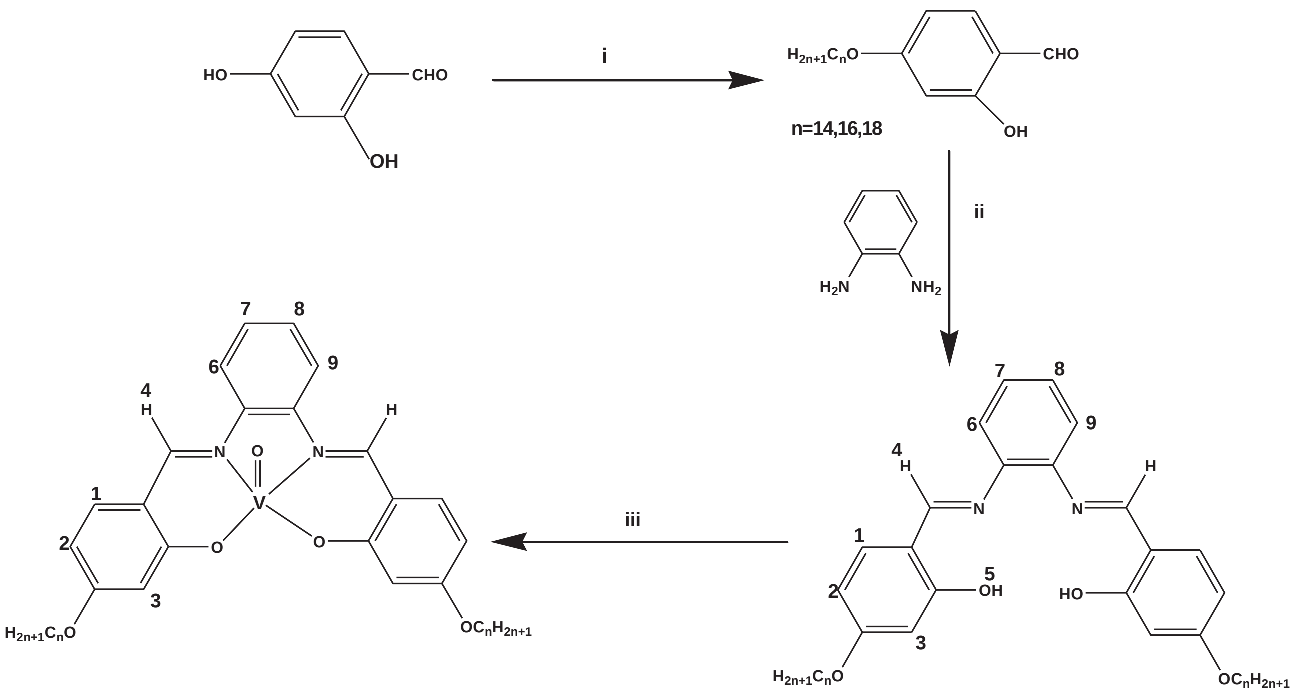

Scheme 1. (i) $C_nH_{2n+1}Br$, $KHCO_3$, KI, dry acetone, Δ, 40 h, and (ii) glacial AcOH, absolute EtOH Δ, 4 h (iii) $VOSO_4.5H_2O$, MeOH, TEA. Δ, 1 h.

mesogenic behavior [38]. Usually macrocyclic compounds possessing discoid molecular shape are known to stack and self assemble into columnar mesophase [39]. In the present study a series of new Schiff base [N_2O_2] donor with an aromatic rigid core and 4-substituted long alkoxy group at the side aromatic rings have been synthesized and its vanadyl(IV) complexes were accessed. Though the ligands are nonmesogenic, the complexes showed lamellar columnar mesophases (Col_l) hitherto unreported for such compounds with 4-substituted alkoxy group.

Accordingly, we describe herein the synthesis, structures and mesogenic properties of some nondiscoid Schiff base-oxovanadium (IV) complexes with different 4-substituted long alkoxy group.

Synthesis of the compounds (n-opd and VO-nopd) could be achieved through a facile and straightforward procedure [40]. The synthetic strategy for the ligands [(L = N,N/-bis(4-(4/-n-alkoxy)-salicylidene)1,2phenylenediamine), hereafter abbreviated as n-opd, where n indicates the number of carbon atoms in alkyl chains, n = 14, 16, 18 and opd = 1,2phenylenediamine] and the mononuclear oxovanadium(IV) complexes (VO-nopd) are presented in Scheme 1.

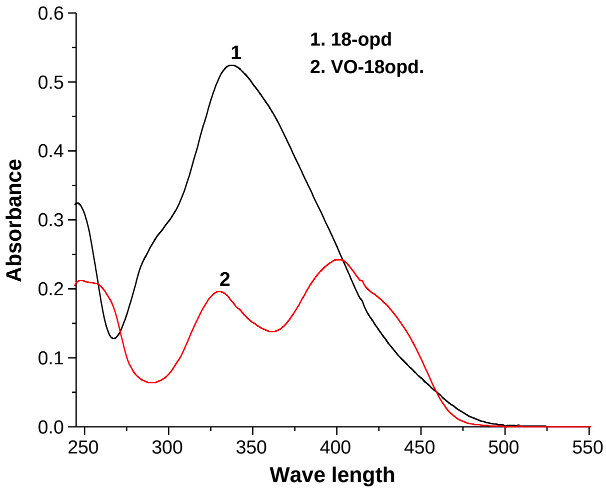

Fig. 1. UV–visible spectra of 18-opd and VO-18opd.

The mononuclear oxovanadium(IV) complexes, VO-nopd (n = 14,16,18), were prepared by the reaction of appropriate ligand with vanadyl sulfate in hot ethanol (1:1 molar ratio) and recrystallized from methanol/CH_2Cl_2; the complexes were isolated as greenish solids in good yields.

The characterizations of the compounds were made by elemental analyses, FT-IR, UV–vis, ^{1}H-NMR, and mass spectrometry [40]. The analytical data of the compounds are in good agreement with the proposed formulae of the compounds. The shift of νCN vibrational stretching frequency at ca.1625 cm^{-1} to lower wave number ($\Delta\nu \sim 30$ cm^{-1}) and absence of νOH mode and phenolate oxygen upon chelation, clearly suggested the coordination of azomethine N and phenolate oxygen to the metal. The νC=N stretching frequency is rather independent of the length of alkoxy side chain in both ligands and their complexes. The vanadyl (V=O) stretching at ca.980 cm^{-1} is suggestive of the absence of any intermolecular (…V=O…V=O…) interaction indicating the monomeric nature of the complexes. The presence of linear chain interactions usually cause νV=O to shift to lower wave number (ca.870 cm^{-1}) [14,15]. The IR data also revealed V=O stretching frequency to be insensitive to the length of the alkoxy side chain. ^{1}H NMR spectra of ligands showed a signal at $\delta = 13.4$–13.8 ppm, corresponding to the OH-proton. The imine proton appeared at 8.5 ppm. The FAB-mass spectra of the vanadyl(IV) complexes are concordant with their formula weights. The electronic absorption spectrum (Fig. 1) of ligand 18-opd showed a strong band at ~337 nm, ($\varepsilon = 5400$ l mol^{-1} cm^{-1}) attributed to π–π* transition localized on the aromatic rings. Upon complexation with VO(IV), this

Table 1
The UV–visible absorption data of n-opd and VO-nopd.

Compound	λ_{max}(nm)	
	π → π*	MLCT
18-opd	337	
VO-18opd	329	400
16-opd	331	
VO-16opd	328	398
14-opd	331	
VO-14opd	328	398

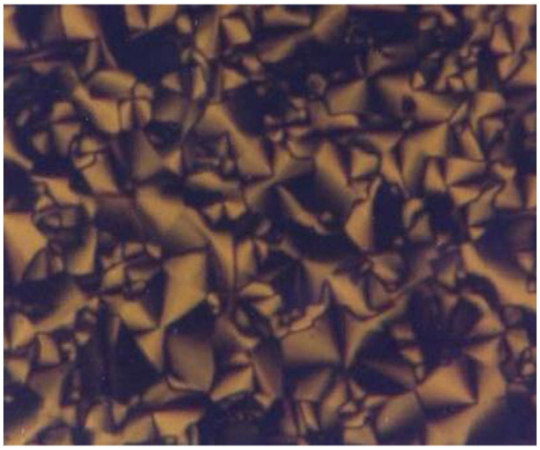

Fig. 2. Optical micrographs of the VO-18op.

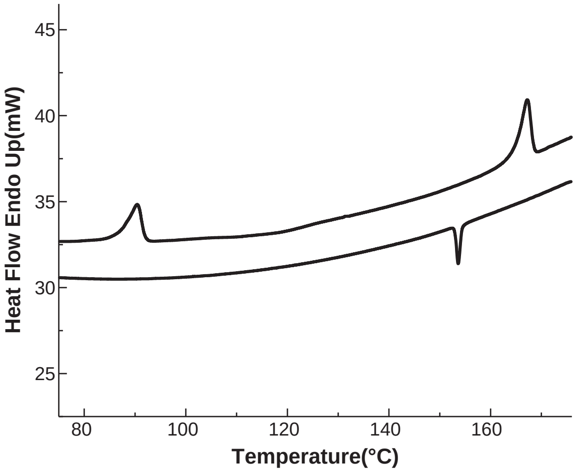

Fig. 3. DSC thermogram of the VO-18opd.

band is blue shifted to a lower wave length at ~328 nm. In addition, the vanadyl complex also showed a strong band at ~400 nm, ($\varepsilon = 2400\ \mathrm{l\ mol^{-1}\ cm^{-1}}$) due to MLCT transition. A similar observation (Table 1) was noted for 16-opd and 14-opd and their complexes.

The ligands lack mesogenicity, while their vanadyl complexes exhibited monotropic mesmorphism in the temperature range 136–150 °C. Mesomorphism induced by the vanadyl ion is quite unique as in many cases the mesophase of organic ligands are destroyed or destabilized upon complexation. A classical fan like texture of a typical columnar mesophase (Fig. 2) appeared at 150 °C upon cooling from the isotropic melt that remained stable down to room temperature. Noteworthy here is to mention that most vanadyl-mesogens show either rectangular or hexagonal mesomorphism [12–14,20,23,27]. DSC thermograms (Fig. 3) of the complexes exhibited three transitions (Table 2) in heating and one in cooling cycle. The phase transition for the complex VO-18opd at 154 °C ($\Delta H = 3.2\ \mathrm{kJ\ mol^{-1}}$) is due to I-Col.

Table 2
DSC data of the VO-nopd complexes.

Compounds	T (°C)	Transition	ΔH ($\mathrm{kJ\ mol^{-1}}$)
VO-18-opd	96.9	Cr–Cr_1	61.7
	115.6	Cr_1–Cr_2	11.2
	167.9	Cr_2–I	16.0
	154.0	I–Col_l	3.3
VO-16-opd	84.3	Cr–Cr_1	17.2
	118.4	Cr_1–Cr_2	10.7
	170.9	Cr_2–I	12.2
	146.3	I–Col_l	2.5
VO-14-opd	88.4	Cr–Cr_1	13.7
	123.1	Cr_1–Cr_2	6.0
	176.7	Cr_2–I	14.6
	136.5	I–Col_l	2.0

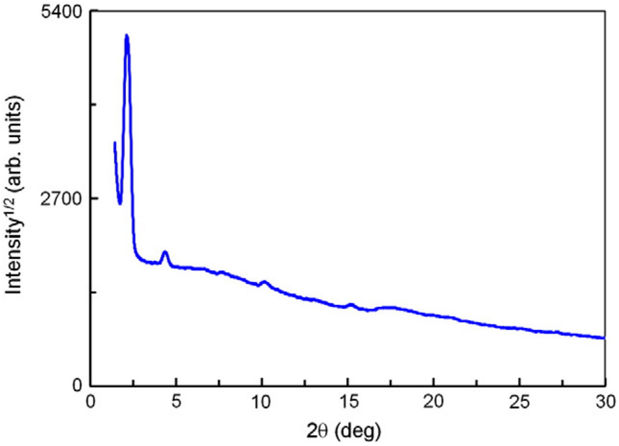

Fig. 4. X-ray difractogram of VO-18opd.

To confirm the structure of the mesophase, powder XRD measurements were carried out using an image plate detector (Mac Science DIP1030, Japan) equipped with double mirror focusing optics, and the sample contained in a Lindmann capillary tube. The XRD pattern (Fig. 4) for VO-18opd carried out at 130 °C showed overall four sharp reflections, and a diffuse peak in the wide angle region. The d-spacings corresponding to these reflections are given in Table 3. The broad and diffuse scattering peaking at 4.98 Å (h_{ch}) corresponds to the short range order of the molten chains. The four sharp reflections can be indexed in two ways. Considering the first reflection to have a *hkl* value of (100), the other three reflections, can be indexed as (010), (500) and (700), with lattice dimensions of a = 41.05 Å and b = 20.23 Å of a rectangular lattice. The *l* value being zero for all the reflections suggests the fluid nature of the structure in one direction. The need for the second possibility arises owing to the fact that the spacing of the second reflection is nearly half of that of the first one, a feature characteristic of lamellar structures. In fact, the spacings of the four reflections turn out to be in the ratio of 1:2.03:4.8:7, supporting such a conjecture with a layer thickness of ~41 Å. It may be noted that the molecular length for the extended molecule as computed from DFT studies is 42.1 Å. This value is comparable to the longer dimension for the rectangular lattice as well as the interlayer spacing for the columnar structure. Owing to the fact that only a few sharp reflections are seen, we cannot assert either of the structures. However, noting that the intensity of even the second reflection is very weak, we tend to believe the layered order and keeping in view of the shape of the molecule propose a lamellar columnar structure [19,41,42]. In such a scenario, the half-disk shaped molecules pack themselves into a layer, but order in a face-to-face

Table 3
XRD data of VO-18opd (s: sharp peak, d: diffuse peak).

Observed spacing (Å)	Rectangular lattice calculated spacing (Å)	Rectangular lattice Miller indices (*h k l*)	Lamellar structure Miller indices (*h k l*)
41.02^s	41.05	(100)	(100)
20.23^s	20.23	(010)	(200)
8.66^s	8.21	(500)	(500)
5.83^s	5.86	(700)	(700)
4.98^d		Lattice constant (Å) a = 41.05 b = 20.23	Layer spacing (Å) a = 41.02

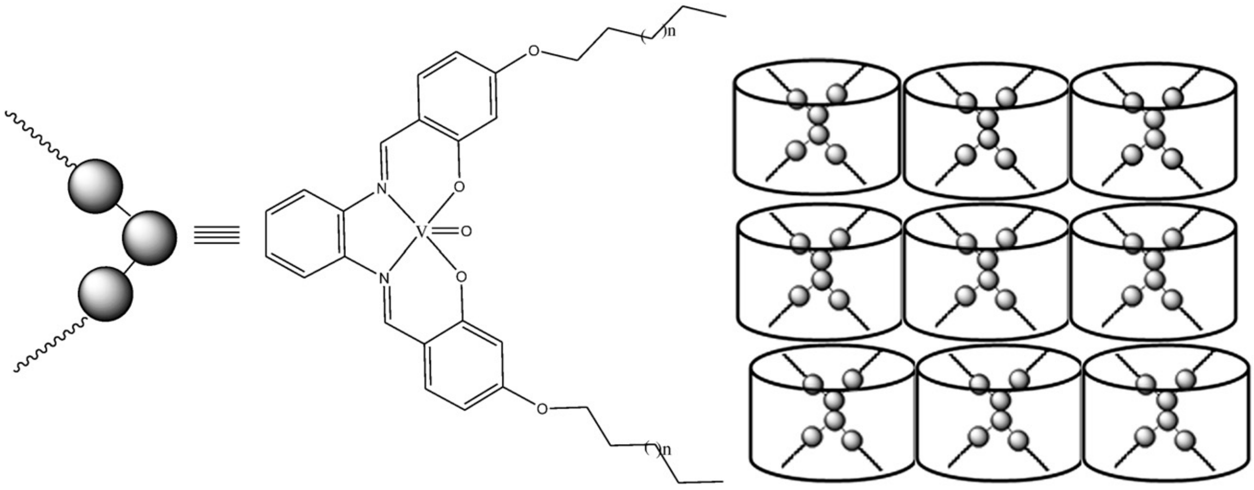

Fig. 5. Antiparallel arrangement of molecules in the lamellar columnar mesophase.

antiparallel dimeric fashion (Fig. 5) within the layer resembling a columnar structure.

The variable temperature magnetic susceptibility measurements were carried out for a representative complex, VO-18-opd (Fig. 6). The compound follows the Curie–Weiss law. Absence of any maximum in χ_M vs T indicated nonexistence of strong exchange interactions between the spin centers. The strength of the efficient superexchange path is presumably hindered by the coordinating ability of metal ions. The vanadium complexes can thus be considered as magnetically isolated spin centers.

The redox natures of the complexes were probed by cyclic voltammetry in acetonitrile solution in the potential range −1.2 to 1.2 V versus SCE electrode. The voltammogram (Fig. 7) displayed a quasireversible (peak-to-peak separation >100 mV) one-electron response at 0.75 V ($Ep^c = 0.64$ V, $Ep^a = 0.86$ V, $\Delta Ep = 0.22$ V) assigned to the VO(V)/VO(IV) couple. On scanning to negative potential (0.0 to −1.2 V), no response is observed implying redox innocent characteristics of the ligand, supported also by the free ligand cyclic voltammetry.

As efforts to obtain a single crystal of the complexes failed, the density functional theory (DFT) calculation is performed to investigate the electronic structure of the V(IV) complex ,VO-18-opd (Fig. 8). Full geometry optimization of the complex without symmetry constraint has been carried out with DMol3 program package [43] using the Kohn–Sham Theory [43,44]. We used the generalized gradient approximation (GGA) in our calculations. At the GGA level, we have chosen the BLYP functional which incorporates Becke's exchange and the Lee–Yang–Parr correlation [43–45]. The length and bent angle of the molecule are found to be ~42 Å and 92.8°, respectively, from DFT calculation. Some of the selective geometric parameters of the optimized VO(IV) complex, evaluated by DFT calculation at BLYP/DNP level are shown in (Table 4). From DFT study, it has been found that the complex has average V—O and V—N bond lengths of 2.0 and 2.1 Å, respectively, which matched well with the other related vanadium salen complexes [14,15]. The bond angles 92.8° and 76.7° for O—V—O and N—V—N, respectively, suggest a distorted square pyramidal geometry around the vanadyl centre. The 3D isosurface plots of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the complex are shown in Figs. 9 and 10 respectively. The HOMO and LUMO energies of the

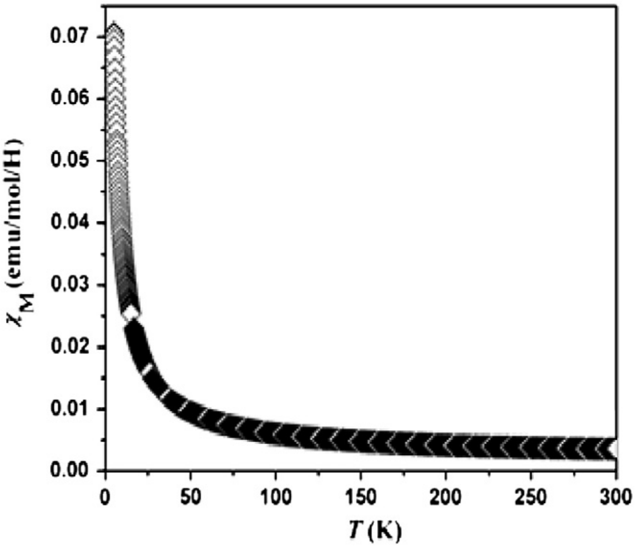

Fig. 6. Variation of magnetic susceptibility of (VO-18opd) with temperature.

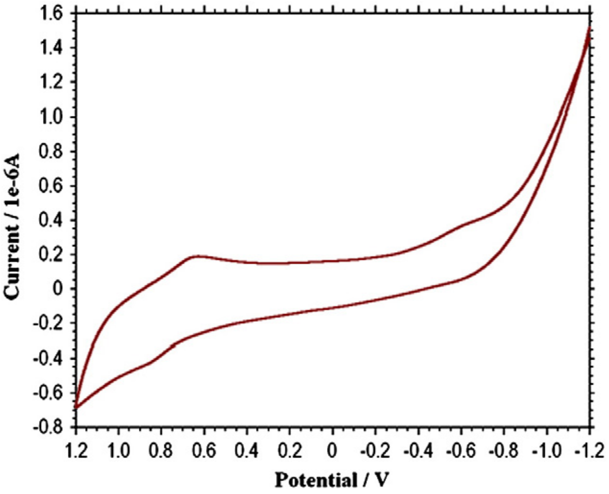

Fig. 7. Cyclic voltamogram of VO-18opd.

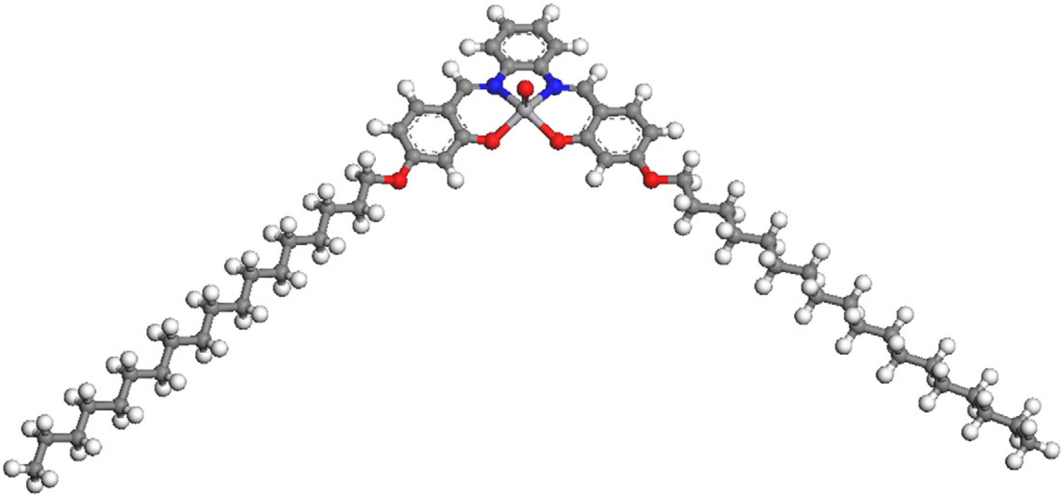

Fig. 8. DFT structure of VO-18opd.

Table 4
Selected bond length and bond angles of VO-18opd, from DFT study.

Structure parameter[a]	Distance/angles
V—N	2.1
V—O	2.0
V=O	1.8
N—V—O	84.0
O—V—O	92.8
N—V—N	76.7

[a] Bond lengths are reported in Å and bond angles in degrees.

complex are calculated to be −5.4 eV and −3.5 eV, respectively, ΔE = 1.9 eV. The LUMO is a n* MO localized on the salophen ligand and the HOMO is mainly a 3d orbital of the V metal center.

In summary, a series of new nondiscoid mononuclear oxovanadium(IV) complexes of tetradentate [N_2O_2] donor Schiff base with 4-alkoxy substituent on the aromatic ring have been successfully synthesized. The complexes exhibited unprecedented lamellar columnar mesophase in the temperature range 136–154 °C. Quite notable is the trend of progressive hike in isotropisation temperature and a steady decrease in the mesophase appearance as a function of decreasing carbon chain length of alkoxy substituent. The cyclic voltammetry of a representative complex VO-18-opd displayed a quasireversible (peak-to-peak separation >100 mV) one-electron response at 0.75 V for the VO(V)/VO(IV) redox couple. Based on DFT, spectral and magnetic studies, a square pyramidal five-coordinate structure has been proposed. The synthetic strategy adopted herein can be effectively employed to access newer mesogenic vanadyl complexes.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.01.041.

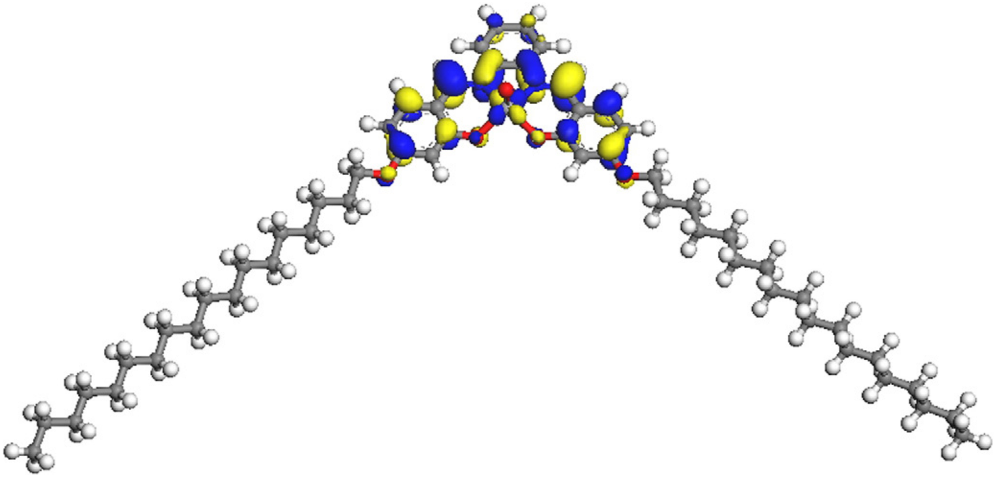

Fig. 9. LUMO energy diagram of VO-18opd.

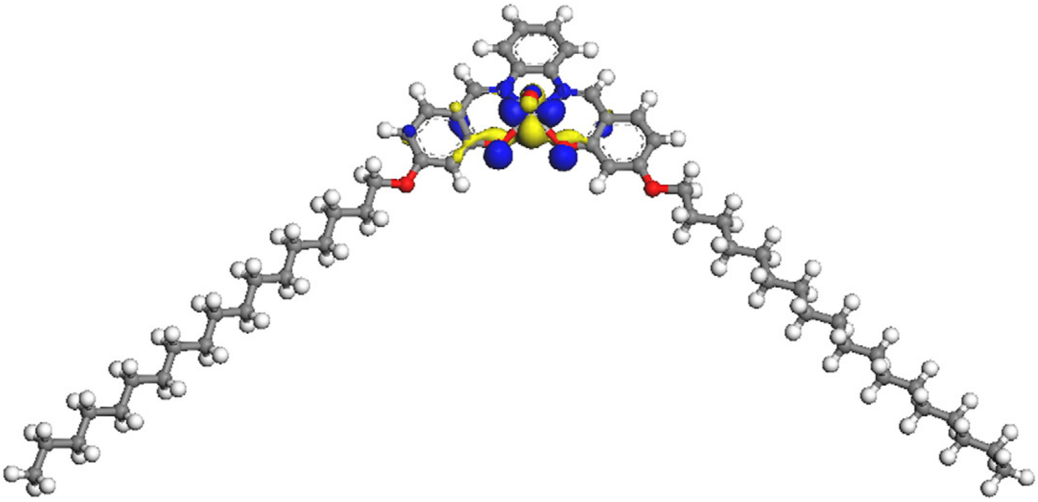

Fig. 10. HOMO energy diagram of VO-18opd.

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