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Controlling Intermolecular Associations with Molecular Superstructure: Polar Discotic Linear Chain Phases

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The design of new molecule-based materials which exhibit specific properties requires a careful balance of both intermolecular interactions and molecular superstructure. The generation of polar molecule-based materials is a particularly important objective since it is a necessary prerequisite for ferroelectricity^1 and second-order nonlinear optical susceptibility,^{2} properties of immense technological importance. However, it is generally difficult to generate thermodynamically stable polar assemblies due to the tendency of materials to avoid internal electric fields by adopting antiferroelectric structures. To overcome this obstacle and find an optimal balance of interactions which will generate an achiral ferroelectric liquid crystalline state,^{3,4} we have been interested in hexagonal columnar superstructures with axial polarity since the triangular symmetry of the lattice cannot accommodate bulk antiferroelectric order.^{5} We report herein a number of new hexagonal and rectangular columnar liquid crystalline phases (mesophases) with axial polarity resulting from head-to-tail alignment of vanadyl groups in linear chain structures, $(\text{- -V=O- -V=O- -})_n$. Further, we demonstrate the use of design principles whereby intermolecular associations may be controlled in a predictable fashion by designing correlated molecular superstructures.

A series of liquid crystalline vanadyl Schiff-base complexes **1**, **2**, and **3** (Scheme I) have been investigated which exhibit different degrees of intermolecular associations via dative bonding between vanadyl groups. The relative strength of dative bonding and subsequent strength of the linear chain structure $(\text{- -V=O- -V=O- -})_n$ may be determined qualitatively by analyzing the frequency of the V=O stretching mode, wherein stronger linear chains are observed at lower frequency.^{6} Consistent with our previous investigations on smectic liquid crystals,^{6} all of the materials are monomeric in their isotropic phases (V=O 992–994 cm^{-1}), **1b**, **2b**, and **3b** tend to exhibit the strongest linear chains (V=O 854–868 cm^{-1}), **1c**, **2c**, and **3c** display somewhat weaker linear chains (V=O 871–911 cm^{-1}), and **1a**, **2a**, and **3a** are monomeric (V=O 992 cm^{-1}). The electronic transitions of **1**, **2**, and **3** are insensitive to the nature of the mesophase; however, in monomeric form these complexes are green with broad metal-centered transitions at 401–404 nm, and in linear chain structures they are orange with transitions at 347–355 nm.

The complexes in Scheme I were also chosen to produce columnar mesophases.^{7} A hexagonal organization of columns (D_h) implies that the molecules are perpendicular to and project a time-averaged circular shape along the column axis. In rectangular (D_r) or oblique (D_{ob}) columnar mesophases, the molecules project an elliptical shape and are generally tilted with respect to the column's normal. Complexes with general structures **1** and **2** do not have the disc-like shape generally required for a columnar liquid crystal, and hence columnar phases of these molecules exhibit the correlated structures shown in Scheme I.^{8} The complexes in series **3**, with twice the number of side chains, approximate a disc-like shape in monomeric form, and hence columnar phases of these compounds have less correlation.

With the exception of **2c**, all of the complexes display enantiotropic mesophases as shown in Table I. The phase assignments were made through a combination of X-ray diffraction (XRD),^{9} optical textures, and miscibility studies.^{7} Phases labeled as disordered (D_{rd}, D_{hd}, D_{hd1}, etc.) exhibited XRD patterns with broad amorphous halos at wide angles, indicating liquid-like order of the mesogens along the column axis, and phases labeled as ordered (D_{ro}, D_{ho}) displayed wide-angle peaks consistent with a more regular period along the column axis.

The monomeric complex **1a** exhibits a single D_{hd} phase, whereas the linear chain derivatives **1b** and **1c** display a number of additional unusual hexagonal phases (D_{hd1}, D_{hd2}, D_{hd3}, and D_{ho1}). **1a** displays a D_{hd} XRD pattern (a = 44.7 Å) consisting of only a strong (100) peak indicating a fairly disordered phase. However, the mesophases of **1b** and **1c** display a number of stronger and higher order diffraction peaks.^{9} These polymeric phases still exhibit liquid-like order within the columns, and the higher order XRD peaks index to a 2D hexagonal lattice, indicating a more regular organization of the columns.^{10} The antiparallel correlation in **1c**'s superstructure positions the geminal methyls in the clefs presented by nearest-neighbor complexes. This lock-and-key organization restricts the mobility of **1c**'s mesophases and results in a much larger isotropic transition enthalpy than is observed for **1b**. The higher correlation in **1c**'s phases produces larger intercolumnar spacings which range from 46.8 Å in the D_{hd1} to 49.0 Å in the D_{hd3}, whereas those of **1b** range from 44.6 Å in the D_{hd1} to 45.8 Å in the D_{ho1}. The V=O stretching bands of both **1b** and **1c** shift with cooling by 4 and 17 cm^{-1}, respectively, to lower energy, indicating a strengthening of the linear chain. The larger range of the V=O stretching band of **1c** is also a consequence of the steric demands of geminal methyls since torsional motions between mesogens generate steric repulsions.

2a exhibits a single D_{hd} mesophase (a = 46.5 Å), whereas the linear chain analog **2b** displays a D_{hd} phase (a = 43.2 Å) at high temperature, followed by rectangular disordered and crystal (D_{rd} and K) phases at lower tempertures. The similarities of these lattice constants with those of **1a** and **1b** are consistent with the correlated superstructures shown in Scheme I.^{8} **2c** does not display a stable mesophase since the superstructure shown in Scheme I directs the geminal methyls toward the aromatic rings and thereby introduces steric repulsions which reduce dipolar and dative interactions. In the case of **2b**, the D_{hd}-to-D_{rd} transition is accompanied by an abrupt shift of the V=O band from 855 to 861 cm^{-1} and a large decrease in birefringence. This weakening of the linear chain and the change in birefringence in **2b**'s D_{rd}-($P21/a$) phase indicates a substantial tilting of the mesogenic cores which reduces the interaction between the apical oxos and neighboring vanadium centers.

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(1) (a) Goodby, J. W.; Blinc, R.; Clark, N. A.; Lagerwall, S. T.; Osipov, M. A.; Pikin, S. A.; Sakurai, T.; Yoshino, K.; Zeks, B. *Ferroelectric Liquid Crystals: Principles, Properties, and Applications*; Gordon and Breach Science Publishers: Amsterdam, The Netherlands, 1991.

(2) *Materials for Nonlinear Optics: Chemical Perspectives*: Marder, S. R., Sohn, J. E., Stucky, G. D., Eds.; ACS Symposium Series 455; American Chemical Society: Washington, DC, 1991.

(3) Ferroelectricity has been studied extensively in chiral liquid crystals (ref 1). However, the achiral liquid crystals there has been only one report of ferroelectricity (ref 4).

(4) Tournilhac, F.; Bilnov, L. M.; Simon, J.; Yablonsky, S. V. *Nature* **1992**, *359*, 621.

(5) Xu, B.; Swager, T. M. *J. Am. Chem. Soc.* **1993**, *115*, 1159.

(6) Serrette, A.; Carroll, P. J.; Swager, T. M. *J. Am. Chem. Soc.* **1992**, *114*, 1887.

(7) (a) Destrade, C.; Foucher, P.; Gasparoux, H.; Nguyen, H. T.; Levelut, A. M.; Malthete, J. *Mol. Cryst. Liq. Cryst.* **1984**, *106*, 121. (b) Billard, J. *Liquid Crystals of One- and Two-Dimensional Order*; Springer Series in Chemical Physics; Springer: Berlin, 1980, p 383. (c) Chandrasekhar, S.; Ranganath, G. S. *Rep. Prog. Phys.* **1990**, *53*, 57 and references therein.

(8) For a previous demonstration of this concept, see: Lai, C. K.; Serrette, A.; Swager, T. M. *J. Am. Chem. Soc.* **1992**, *114*, 7948–7949.

(9) XRD data are given in the supplementary material.

(10) Similar XRD patterns have been reported for other metallomesogens: Ohta, K.; Hasebe, H.; Moriya, M.; Fujimoto, T.; Yamamoto, I. *Mol. Cryst. Liq. Cryst.* **1991**, *208*, 43.

0002-7863/93/1515-8879$04.00/0

Scheme I

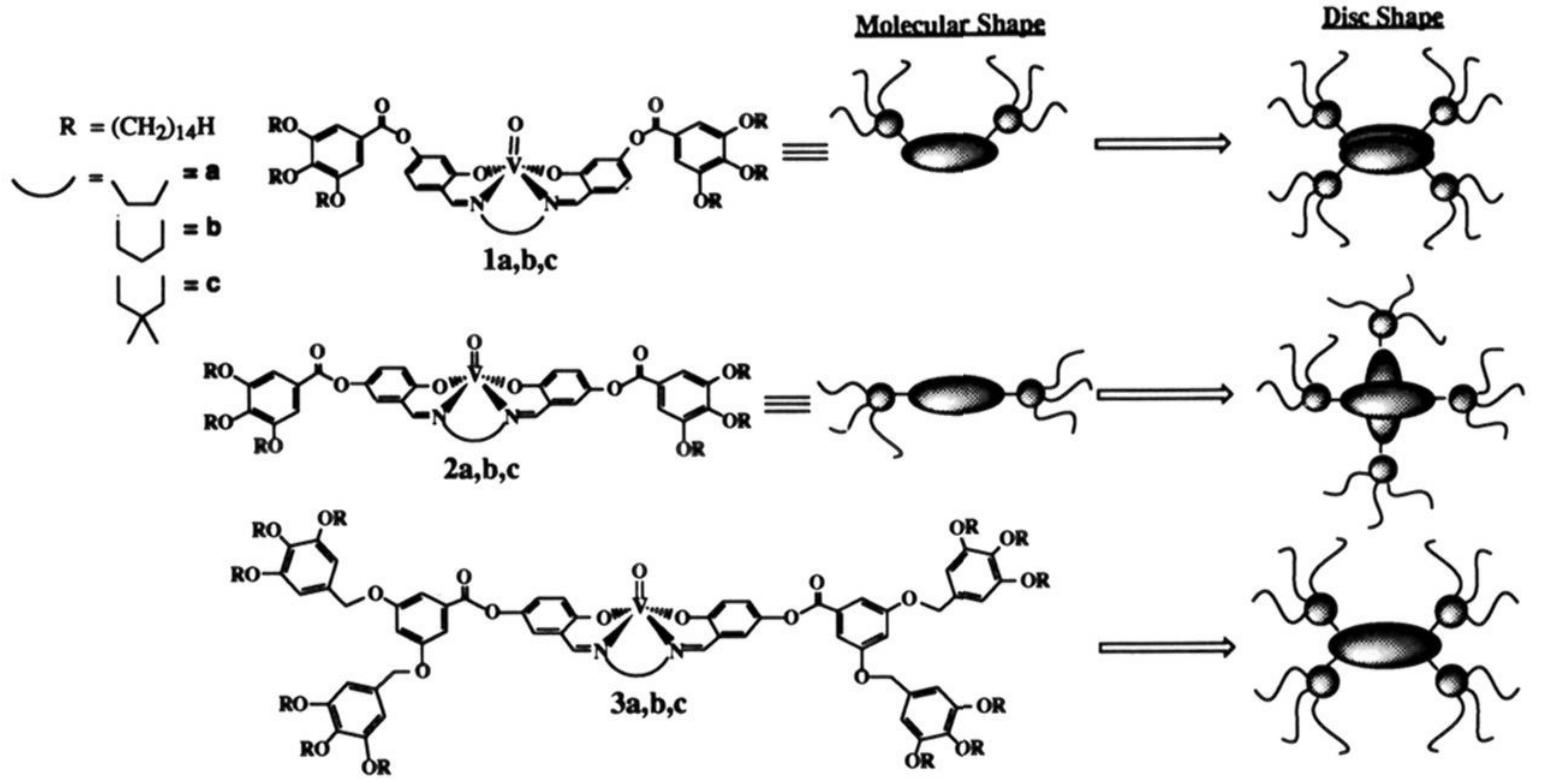

Table I. Phase Assignments, Transition Temperatures (°C, above arrow), and Transition Enthalpies (kcal mol, below arrows, in parentheses) for All Compounds Described (The range of the V═O stretching band frequency (cm^{-1}) is given below the phase designation.)

1a	D_{hd}	$\xleftrightarrow[(5.3)]{150.1}$	I						
	992		992						
1b	D_{ho1}	$\xleftrightarrow[(4.4)]{119.5}$	D_{hd3}	$\xleftrightarrow[(2.5)]{156.1}$	D_{hd2}	$\xleftrightarrow[(4.4)]{168.4}$	D_{hd1}	$\xleftrightarrow[(0.76)]{175.0}$	I
	861-862		862-863		863		863-865		994
1c	K	$\xleftrightarrow[(11.9)]{27.7}$	D_{hd3}	$\xleftrightarrow[(3.4)]{66.6}$	D_{hd2}	$\xleftrightarrow[(4.0)]{91.1}$	D_{hd1}	$\xleftrightarrow[(11.6)]{146.8}$	I
	871		871-873		873-883		883-888		992
2a	D_{hd}	$\xleftrightarrow[(0.71)]{155.8}$	I						
	992		992						
2b	K	$\xleftrightarrow[(20.7)]{62.1}$	D_{rd1}	$\xleftrightarrow[(2.2)]{107.4}$	D_{hd}	$\xleftrightarrow[(1.0)]{169.7}$	I		
	861^{a}		858-861^{a}		855-861		994		
2c	K	$\xrightarrow[(18.3)]{78.3}$	M^{b}	$\xrightarrow[(8.1)]{114.8}$	I				
	865		865-875		992				
3a	D_{ro}	$\xleftrightarrow[(4.4)]{119.5}$	D_{rd}	$\xleftrightarrow[(2.5)]{156.1}$	I				
	992		992		992				
3b	D_{ho}	$\xleftrightarrow[(20.8)]{36.4}$	D_{hd}	$\xleftrightarrow[(2.6)]{97.5}$	D_{rd}	$\xleftrightarrow[(2.5)]{151.4}$	I		
	864-868		868-854		854-856		994		
3c	D_{hd}	$\xleftrightarrow[(13.9)]{55.3}$	D_{rd}	$\xleftrightarrow[(8.7)]{107.8}$	I				
	911^{a}		904-889		992				

[a] The stretching band changes very abruptly at the phase transition.
[b] Transient mesophase observed only on first heating.

The greater side-chain density in **3a**, **3b**, and **3c** destabilizes the hexagonal structure, and all three compounds exhibit D_{rd} phases at higher temperatures. **3c** has a weakened linear chain and a lower clearing point than **3a** and **3b**, which is consistent with steric interactions between the randomly oriented geminal dimethyl groups and neighboring mesogens. Interestingly, both **3b** and **3c** exhibit an unusual inverted phase behavior[11] with the more ordered D_{rd} phase at higher temperatures, followed by a less ordered D_{hd} phase at lower temperatures. The intercolumnar spacing of **3b**'s D_{hd} phase is 51.0 Å, which is very similar to those of **1c**, suggesting that the steric locking in **1c**'s mesophases produces similar spatial requirements. In contrast to what was observed for **2b**, the linear chains of **3b** and **3c** are stronger in the D_{rd} phases than in the D_{hd} phases. The origin of this unexpected result is unclear; however, these D_{rd} phases have *C*2/*m* symmetry and exhibit similar birefringence to that of the D_{hd} phases, suggesting that the D_{rd} phase is only slightly tilted.

In summary, we have demonstrated that liquid crystalline superstructures can be designed which selectively control the degree of intermolecular associations. In general, intermolecular dative interactions and the resulting polar order produce a richer liquid crystalline behavior.[12] Linear chain D_{hd} phases were observed which gave XRD profiles typical of monomeric liquid crystals. The linear chains in these phases are partly melted and/or weak and thereby allow some transverse mobility of the mesogens and less ordered columns. Linear chain structures can also produce highly organized columnar structures in which the mesogens are held in tight registry. We find that depending on their nature, rectangular phases can weaken or strengthen the dative bonding between vanadyl groups relative to a hexagonal organization.

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Supplementary Material Available: Plots of V═O stretching frequency as a function of temperature, XRD data, and infrared data for V═^{18}O-labeled compounds (9 pages). Ordering information is given on any current masthead page.

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(11) For other examples of inverted behavior in discotics, see: Destrade, C.; Gasparoux, H.; Babeau, A.; Nguyen, H. T. *Mol. Cryst. Liq. Cryst.* **1981**, *67*, 37.

(12) Monomeric discotics with dipoles normal to the mesogens plane have been previously found to exhibit antiparallel dipolar organization. Piechocki, C.; Boulou, J.-C.; Simon, J. *Mol. Cryst. Liq. Cryst.* **1987**, *149*, 115.