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Metal-containing liquid crystals with potential application in optical storage devices

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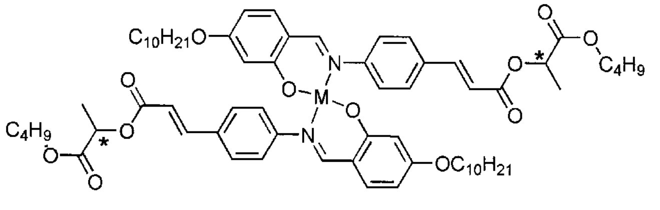
Three optically active oxovanadium(IV)-containing metallomesogens have been prepared and their mesomorphic properties investigated. It is found that enantiotropic chiral phases are stabilized when the molecular system promotes the anti-ferromagnetic coupling of individual molecules into associated pairs. The molecular optical rotation of the non-mesomorphic ligands is greatly enhanced on complexation to an oxovanadium(IV) metal centre to give the mesogenic complex. The mesophase alignment can be retained by cooling to room temperature and this may be utilized in the fabrication of a low cost, multi-session, 'write–read–erase' optical storage device with low power consumption.

1. Introduction

There has been considerable interest in metal-containing liquid crystals (metallomesogens) possessing a paramagnetic oxovanadium(IV) centre. The majority of these have been simple, symmetrical co-ordination complexes of either 1,3-diketone [1–3] or imine [4, 5] ligands. Surprisingly, there has been only one reported example of an oxovanadium(IV) complex (**1**) derived from a chiral ligand [5].



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The chiral imine ligand in **1** has the phase sequence Cr 52 S_C^* 92 S_A^* 113°C I. Complexation to an oxovanadium(IV) centre gives an expected increase in the melting and clearing temperatures although the phase sequence is unaffected: Cr 125 S_C^* 137 S_A^* 178°C I. The analogous copper(II) complex has the phase sequence: Cr 109 S_C^* 120 S_A^* 160°C I. The spontaneous polarization in the copper(II) and oxovanadium(IV) complexes was found to be similar, 23 and 20 nC cm^{-2}, respectively, and approximately half that of the parent ligand, 44 nC cm^{-2}. The reorientational viscosities and response times of the free ligand and the copper(II) complex were similar, while the oxovanadium(IV) complex showed a four-fold increase in viscosity and an approximately seven-fold increase in the response time when compared with the copper(II) complex. The decrease in spontaneous polarization in the complexes can be explained in terms of compensation between the two remote chiral centres; however, the anomalous viscosity and response time in the oxovanadium(IV) complex suggest that there is additional ordering in the liquid crystal phases relative to the copper(II) complex. This assumption is reinforced by the fact that the V=O stretching frequency in the chiral complex is observed at 976 cm^{-1}, indicating a degree of association between molecules. The V=O stretching frequency in a free, unassociated complex is typically 997 cm^{-1}.

While these results suggest that such materials are unsuitable for electro-optic fast switching devices, they may prove useful as optical storage media. This prompted us to investigate some new, chiral oxovanadium(IV) complexes based on novel 1,3-diketone ligands. In this paper we report the results of these studies and propose a possible application for the resulting materials.

2. Experimental procedure

The structures of all intermediates and final products were elucidated by standard analytical techniques. ^{1}H NMR spectra were recorded on a JEOL JNM-GX 270 FT NMR spectrometer, infrared spectra were recorded on a Perkin-Elmer 783 IR spectrometer as either KBr disks or liquid films, and mass spectra were recorded on a Finnigan Mat 1020 Automated GC/MS spectrometer. Elemental analyses were performed on a Carlo-Erba 1106 CHN analyser using cyclohexanone-2,4-dinitroph-

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enylhydrazone as the reference standard. Satisfactory analyses were achieved in all instances.

2.1. *(S)-(+)-4-[4-(2-Methylbutyl)phenyl]benzoic acid (***2***)*

A mixture of (*S*)-(+)-4-[4-(2-methylbutyl)phenyl]cyanobiphenyl (25·0 g, 0·1 mol), concentrated sulphuric acid (40 cm^3), concentrated nitric acid (5 cm^3), water (40 cm^3) and glacial acetic acid (400 cm^3) was stirred and heated under reflux (12 h). The hot, clear solution was poured over ice-water (1000 cm^3) with vigorous stirring, and the mixture was allowed to come to room temperature. The resulting white solid was collected by filtration and purified by recrystallisation from methanol. Yield = 24·9 g (92%); mesomorphism Cr 221 N* 246·8°C I. δ_H (270 MHz, $CDCl_3$, $Si(CH_3)_4$): 0·90 (3H, d, *J* 7·0, $*CHC\underline{H}_3$), 0·95 (3H, t, *J* 7·0, $CHC\underline{H}_3$), 1·25 (2H, m, $C\underline{H}_2CH_3$), 1·65 (1H, m, $CH_3CH_2\overset{*}{C}\underline{H}$), 2·40 (1H, ABX, *J* 13·5 (*gem*), 8·1 (*anti*), $*CHC\underline{H}_2Ar$), 2·65 (1H, ABX, *J* 13·5 (*gem*), 5·9 (*syn*), $*CHC\underline{H}_2Ar$), 7·25 (2H, AA′XX′, Ar–$\underline{H}$), 7·70 (4H, AA′XX′, Ar–$\underline{H}$), 8·05 (2H, AA′XX′, Ar–$\underline{H}$), 12·80 (1H, s, $COO\underline{H}$). ν_{max} (KBr)/cm^{-1}: 3000–2800 (CH str.), 2550 (br, OH), 1675 (br, C=O str.). *m*/*z*: 268 [M]$^+$, 211 (100%), 165, 152, 57. $[\alpha]^D = +8·2$ (25°C, *c* 0·02354 g cm^{-3} in $CHCl_3$).

2.2. *Ethyl (S)-(+)-4-[4-(2-methylbutyl)phenyl] benzoate (***3***)*

A mixture of **2** (2·7 g, 10 mmol), ethanol (0·5 g, 11 mmol), *N*,*N*-dicyclohexylcarbodiimide (DCC) (2·25 g, 11 mmol) and 4-pyrrolidinopyridine (0·15 g, 1 mmol) in dichloromethane (25 cm^3) was stirred at room temperature (24 h). The ester was purified by column chromatography (silica gel, 40–60 mm, dichloromethane) and isolated as a pale yellow liquid. Yield = 1·5 g (51%); m.p. = 22°C. δ_H (270 MHz, $CDCl_3$, $Si(CH_3)_4$): 0·88 (3H, d, *J* 7·0, $*CHC\underline{H}_3$), 0·93 (3H, t, *J* 7·0, $CHC\underline{H}_3$), 1·30 (2H, m, $C\underline{H}_2CH_3$), 1·40 (3H, t, $OCH_2CH\underline{H}_3$), 1·55 (1H, m, $CH_3CH_2\overset{*}{C}\underline{H}$), 2·41 (1H, ABX, *J* 13·5 (*gem*), 8·1 (*anti*), $*CHC\underline{H}_2Ar$), 2·68 (1H, ABX, *J* 13·5 (*gem*), 5·9 (*syn*), $*CHC\underline{H}_2Ar$), 4·39 (2H, q, *J* 7·0, $OC\underline{H}_2CH_3$), 7·24 (2H, AA′XX′, Ar–$\underline{H}$), 7·53 (2H, AA′XX′, Ar–$\underline{H}$), 7·64 (2H, AA′XX′, Ar–$\underline{H}$), 8·09 (2H, AA′XX′, Ar–$\underline{H}$). ν_{max} (KBr)/cm^{-1}: 3000–2800 (CH str.), 1715 (C=O str.). *m*/*z*: 296 [M]$^+$, 239 (100%), 211, 165. $[\alpha]^D = +4·6$ (25°C, *c* 0·04643 g cm^{-3} in $CHCl_3$).

2.3. *1-(S)-(+)-4-[4-(2-Methylbutyl)biphenyl-4′-yl] undecan-1,3-dione (***4***)*

A solution of decan-2-one (0·8 g, 5 mmol) in dry 1,2-dimethoxyethane (25 cm^3) was added cautiously with stirring at room temperature to sodium hydride (60% in mineral oil, 0·4 g, 10 mmol) which had been prewashed with *n*-hexane. A solution of **3** (1·4 g, 5 mmol) in dry 1,2-dimethoxyethane (25 cm^3) was added slowly and the mixture was heated under reflux (6 h). After cooling to room temperature, a small amount of water was carefully added to the suspension and the mixture was acidified to pH 2 using 20% aqueous hydrochloric acid. The separated organic layer was washed with water (2 × 50 cm^3), the solvent removed *in vacuo* and the product recrystallised from ethanol to give white crystals. Yield = 1·2 g (59%); mp = 86°C. δ_H (270 MHz, $CDCl_3$, $Si(CH_3)_4$): 0·85 (9H, d, *J* 7·0, $C\underline{H}_3CH_2*CHC\underline{H}_3$ and $CH_2C\underline{H}_3$), 1·00–1·45 (14H, m, $CH_3C\underline{H}_2*CHCH_3$ and $(C\underline{H})_6CH_3$), 1·60 (1H, m, $CH_3CH_2*C\underline{H}$), 2·35 (2H, t, *J* 7·0, $COC\underline{H}_2$), 2·33 (1H, ABX, *J* 13·5 (*gem*), 8·1 (*anti*), $*CHC\underline{H}_2Ar$), 2·60 (1H, ABX, *J* 13·5 (*gem*), 5·9 (*syn*), $*CHC\underline{H}_2Ar$), 6·10 (1H, s, $C\underline{H}$=enol), 7·15 (2H, AA′XX′, Ar–$\underline{H}$), 7·45 (2H, AA′XX′, Ar–$\underline{H}$), 7·60 (2H, AA′XX′, Ar–$\underline{H}$), 7·85 (1H, s, $O\underline{H}$ enol). ν_{max} (KBr)/cm^{-1}: 3000–2800 (CH str.), 1600 (br, C=O str.). *m*/*z*: 406 [M]$^+$, 349, 308, 251 (100%), 165. $[\alpha]^D = +8·0$ (25°C, *c* 0·01489 g cm^{-3} in $CHCl_3$). Analysis for $C_{28}H_{38}O_2$ requires (found): C 82·60 (82·71), H 9·20 (9·41)%.

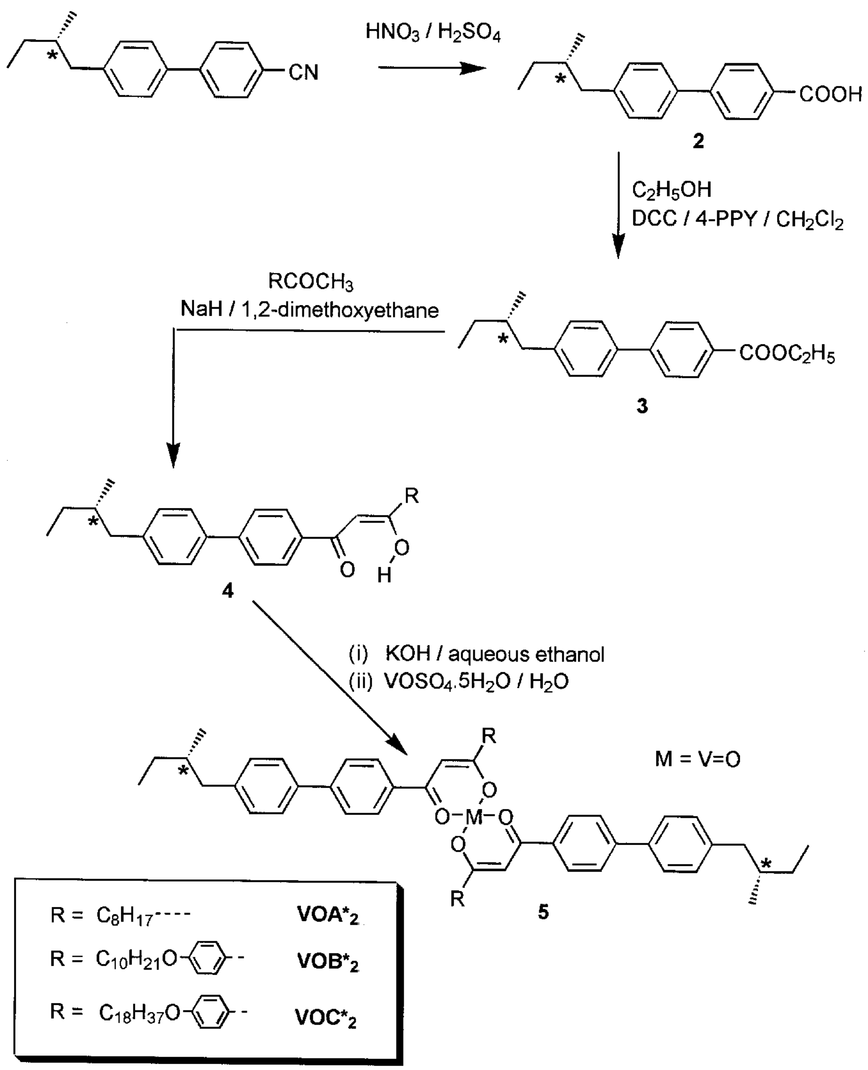
2.4. *Bis{1-(S)-(+)-4-[4-(2-Methylbutyl)biphenyl-4′-yl]undecan-1,3-dionato}oxovanadium (IV) (***5/VOA$_2^*$***)*

A solution of potassium hydroxide (0·1 g, 2 mmol) in ethanol (25 cm^3) was added to a stirred warm solution of **4** (0·4 g, 1 mmol) in ethanol (25 cm^3). An ice-cooled solution of oxovanadium(IV) sulfate pentahydrate (0·3 g, 1 mmol) in water (25 cm^3) was added with continued stirring and the final mixture stirred at room temperature (2 h). The resulting green precipitate was collected by filtration and washed with water and ethanol. The product was purified by repeated recrystallisations from acetone until constant, sharp transition temperatures were achieved. Yield = 0·30 g (71%). ν_{max} (KBr)/cm^{-1}: 3000–2800 (CH str.), 1550 (br, C=O) str), 995 (V=O str). Analysis for $C_{56}H_{76}O_5V$ requires (found): C 76·64 (76·60), H 8·28 (8·49) %. $[\alpha]^D = +5·0$ (25°C, *c* 0·00475 g cm^{-3} in $CHCl_3$).

The other complexes were prepared using the same procedure. Satisfactory analyses were achieved in each case: **VOB$_2^*$** C 77·08 (77·32), H 8·17 (8·11); **VOC$_2^*$** C 78·81 (78·77), H 9·45 (9·29).

3. Thermal and optical properties

The three examples reported in this paper are the first oxovanadium(IV) complexes of 1,3-diketone ligands to show calamitic mesomorphic behaviour. Phase identification was achieved by polarized light microscopy using a Zeiss Universal microscope equipped with a Mettler FP82 HT furnace and a Mettler FP90 temperature processor. Transition temperatures were confirmed, and transition enthalpies determined, by differential scanning calorimetry using a Perkin Elmer



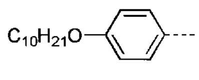
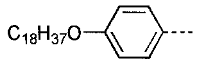
Scheme. Synthesis of the chiral 1,3-diketone ligands and oxovanadium(IV) complexes.

DSC7-PC calorimeter. Indium metal was used as the reference standard. In each case the recorded transition temperatures were consistent with those from the optical studies.

The ligands themselves were found to be non-mesomorphic, displaying simple melting behaviour. The melting points and molecular optical rotations $[M]_D$ at 20°C are summarized in table 1.

The three complexes were each found to exhibit liquid crystalline behaviour as shown in table 2. Interestingly, the complex of ligand **A*** which possesses a simple *n*-octyl substituent, $\mathbf{VOA}^*_2$, shows the most promising phase behaviour, exhibiting an enantiotropic chiral nematic (N*) phase over a 6°C temperature range. Microscopy revealed the phase to possess a left handed helical twist sense as it gave *dextro* rotation of plane polarized light. Complexes $\mathbf{VOB}^*_2$ and $\mathbf{VOC}^*_2$, which are derived from ligands **B*** and **C*** respectively, showed monotropic smectic C* (S^*_C) phases over short temperature ranges. On cooling each of the complexes from the mesophase, distinct crystallization was not observed

Table 1. Melting points and molecular optical rotations of the chiral 1,3-diketone ligands **4**—see scheme.

R	Ligand	M.p./°C	$[M]_D$/°
C_8H_{17}---	**A***	86	+32·5
	**B***	138	+30·6
	**C***	124	+29·4

and in fact the texture of the mesophase was retained at room temperature in a highly viscous, glass-like state. The texture was found to remain indefinitely in annealed samples which were stored at room temperature. Here we have examples where liquid crystalline materials may be produced from non-mesomorphic precursor ligands by complexation to a transition metal centre. The bent geometry of the ligands, constrained by intramolecular hydrogen bonding, is not conducive to mesophase formation, having an unfavourable length to width ratio. Chelation of two ligands to the metal centre produces a significant increase in this ratio and therefore increases the structural anisotropy in the complex. The flexibility of the *n*-octyl chains allows them to pack close to the long axis of the molecule (*c*. 25° from the hard rod axis), while in the 4-alkoxyphenyl systems, the additional aryl ring forces the hydrocarbon chains to lie well off-axis (*c*. 60° from the hard rod axis) and so the complexes become less linear. Consequently, **VOA$_2^*$** shows an enantiotropic chiral nematic phase while **VOB$_2^*$** and **VOC$_2^*$** show only monotropic phases.

In the 4-alkoxyphenyl substituted complexes, the recorded effective paramagnetic moment (μ_{eff}) was found to be close to the spin-only value of 1·73 μ_B which is characteristic of monomeric complexes, free from intermolecular O … V interactions. Isothermal (21°C) magnetic moments were determined using a Johnson-Matthey susceptibility balance of the Gouy type calibrating against an analytical sample of mercury(II) cobalt(II) thiocyanate [$HgCo(NCS)_4$], $\chi_g(20°C) = 20·64 \times 10^{-8}\ m^3\ kg^{-1}$. Errors for the mesomorphic complexes were calculated to be ±0·09 μ_B, taking into account the large contributions from the diamagnetic ligands. Further evidence for the monomeric nature of the complexes was obtained from the V=O stretching frequency in the infra-red spectrum. Polymeric interactions have been observed in other oxovanadium(IV) complexes, but show a reduced V=O stretching frequency of 850–800 cm^{-1}. Furthermore, the infra-red spectra of samples of **VOA$_2^*$** which had been annealed by slow cooling from the mesophase showed no shift in the V=O stretching frequency ($\nu_{obs} = 995\ cm^{-1}$). This suggests that intermolecular V=O interactions are not important in the stabilization of calamitic mesophases, although they may become significant in the stacking of columnar mesophases. While the value of 1·61 ± 0·09 μ_B for **VOA$_2^*$** cannot be unequivocally identified as being significantly low, due to the errors calculated for the measurements, it is interesting to speculate that, if genuine, it may well represent evidence for some antiferromagnetic coupling, as observed in some structurally related oxovanadium(IV) complexes [6]. Complexes **VOB$_2^*$** and **VOC$_2^*$** gave effective paramagnetic moments of 1·81 ± 0·09 and 1·77 ± 0·09 μ_B, respectively, somewhat higher than that observed for **VOA$_2^*$**. Further studies are planned to investigate this effect in greater detail.

Table 2 also contains the molecular optical rotations, determined at 20°C for chloroform solutions of the complexes. It was expected that, upon complexation, the optical rotatory power would be either up to twice that of the ligand or that it would decrease due to compensation between the two chiral centres. This was found to be the case for the octyl substituted complex, **VOA$_2^*$**, which showed a 1·3 times enhancement in $[M]_D$ over **A***. However, in the two 4-alkoxyphenyl derivatives, there is a greater increase in the magnitude of the optical rotatory power. For the complex **VOB$_2^*$** the enhancement of $[M]_D$ is 5·1 times and for **VOC$_2^*$** it is 3·6 times that of the respective ligands. The cause of this enhancement has not yet been identified, but studies are continuing to investigate the effect in both isotropic solution and in the liquid crystalline phase. It is interesting to note that the sign of optical rotation in the alkoxyphenyl substituted materials is reversed on complexation while in the alkyl substituted material the sign remains unchanged. This difference in the interaction with plane polarized light of the two types of molecule is reflected in the different helicities observed in the respective liquid crystalline phases.

4. Device properties

In the case of complex **VOA$_2^*$**, the enhancement of mesogenicity and optical rotatory power, together with the enantiotropic nature of the chiral nematic phase on complexation, led us to investigate the material in display device applications. Metallomesogens have yet to find an area of application, primarily due to their generally high transition temperatures, questionable thermal and photochemical stabilities and low stability in applied electric fields over prolonged periods. Therefore, we have used **VOA$_2^*$** as the optical component in an optical storage device where switching can be achieved using an electric field pulse and where the material need only be heated into the phase momentarily and then cooled rapidly. In the absence of an electric field at 114°C, the material appears highly iridescent in the device cell. This is a consequence of the helical pitch in the chiral nematic phase which causes selective reflection at visible wavelengths. On cooling, a glass-like phase was formed which was highly viscous yet retained the optical texture of the chiral nematic phase. When the cell was reheated and an electric field of 15 V μm^{-1} was applied momentarily to the 0·25 cm^2 electrode area, the molecules reoriented in that area to give a colourless region which remained on cooling to room temperature. The contrast between the highly coloured non-addressed region of the cell and the colourless addressed area is excellent and remains indefinitely. The process can be reversed by reheating

Table 2. Transition temperatures, effective paramagnetic moments, V=O infra-red stretching frequencies and molecular optical rotations of the chiral complexes **5**—see scheme.

Complex	Transition temperatures/°C [Transition enthalpies]/kJ mol^{-1}	$\mu_{\mathrm{eff}}/\mu_{\mathrm{B}}$ ($\pm$0·09)	ν_{vo}/cm^{-1}	$[M]_{\mathrm{D}}$/°
VOA$_2^*$	Cr 109 N* 115·0 I [51·9] [0·5]	1·61	995	+43·9
VOB$_2^*$	Cr 209 (S_C^* 171·8) I [62·0] [−0·5]	1·81	995	−155·5
VOC$_2^*$	Cr 178 (S_C^* 145·4) I [56·7] [−0·3]	1·77	995	−107·3

the sample into the chiral nematic phase in the absence of an applied field, to regenerate the helical structure, and then cooling into the glassy state. The performance of a non-optimized prototype device has been determined. Switching is slow due to the high viscosity of the phase (typically in the order of 500 ms) but this is not important in optical storage device applications where video frame rates are not required. The contrast ratio was determined for three device configurations using a diode laser (1 mW, 670 nm) and a photodetector mounted on an optical track, together with a sample stage and polarizer holders. The photodetector was connected to a Wavetek 9020 20 MHz Dual-Trace Delay-Timebase oscilloscope. The contrast ratio determined using the cell alone, with no polarizing filters was 3:1 between the helical area and the addressed area. This is in sharp contrast to a colourless, purely organic system where there is zero contrast without the use of crossed polarizers, and reflects the dichroic nature of the metal-containing liquid crystalline materials. In our cell configuration, light is transmitted more efficiently through the helical region than the addressed area, resulting in a white character on a coloured background (see the figure). Addition of a single polarizer results in a four-fold enhancement of the contrast ratio to 12:1. Surprisingly, only a small enhancement is achieved by the use of crossed polarizers, giving a contrast ratio of 14:1. While these values are comparable with other systems involving metal complexes [7, 8] and are not yet of a high enough value for them to be considered in practical devices, it should be stressed that this is a completely unoptimized system and efforts are currently been made to optimize alignment, switching performance and contrast ratio.

Therefore, we have the basis of a very simple and recyclable 'write–read–erase' optical display. While the colour of the non-addressed area is due to the helicity of the chiral nematic phase, the colourless switched areas are due to the electrical unwinding of the helix. Light is guided through the switched region of the cell which is not transparent, rather translucent (see the figure). This is because the complexes possess a negative dielectric anisotropy [9] which forces the molecules to align in the cell with their long axes perpendicular to the applied electric field and consequently perpendicular to the optic axis. The negative dielectric anisotropy is due to the strong dipole moment associated with the axial V=O bond which lies perpendicular to the chelation plane and therefore perpendicular to the ligands. It should be noted that while the contrast between the two areas is excellent relative to organic liquid crystals without crossed polarizers, improvements can be made by subtle changes to the molecular design. We are now attempting to design new molecules with strong dipole moments parallel to the molecular long axis which will perhaps yield materials of positive dielectric anisotropy and therefore enable us to construct devices capable of displaying negative images. The major advantages of this new type of metallomesogen optical storage device are that the materials are inexpensive to prepare and the high contrast is achieved without the need for two expensive polarizers.

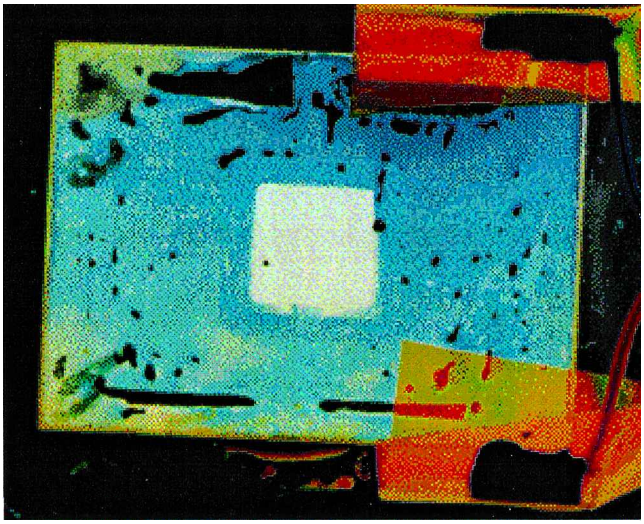


Figure. A prototype optical storage device filled with **VOA$_2^*$**, addressed in the central electrode area.

5. Conclusions

We have demonstrated that the choice of organic chelating ligand is important in the stabilization of chiral mesophases. We propose that if the molecular system allows pair-wise molecular interactions, rather than long-range supramolecular association, enantiotropic phases are stabilised. The mesophases do not undergo true crystallization but form glass-like states at room temperature in which the mesophase alignment is retained. We have gone on to demonstrate how this may be utilized in the fabrication of low cost optical storage devices which can give excellent contrast ratios with the need for only one or even no expensive polarizing filter. In our present case, the display consists of white characters written on a green–blue iridescent background.

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