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Low absorption liquid crystals for mid-wave infrared applications

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Abstract: A partially fluorinated terphenyl liquid crystal with low absorption in both mid-wave infrared (MWIR) and near IR regions is developed and its properties evaluated. This compound exhibits a nematic phase (although only about 2 °C), reasonably high birefringence ($\Delta n \sim 0.2$), low visco-elastic coefficient, and modest dielectric anisotropy ($\Delta \epsilon = -2.7$). This compound serves as an important first example for future development of low-loss MWIR liquid crystals and devices.

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1. Introduction

Linearly conjugated liquid crystals (LCs) exhibit a relatively high birefringence in the infrared (IR) region [1,2] and thus have been used in the 8-12 μm range as dynamic scene projectors for infrared seekers [3], and at $\lambda = 10.6 \mu\text{m}$ and $1.55 \mu\text{m}$ for laser beam steering [4] and infrared light shutter [5], and photonic crystal fiber [6]. A major concern for IR applications using LCs is the inherent absorption loss due to the existence of molecular vibration bands. Even in off-resonance regions, the baseline absorption coefficient may reach as high as $\alpha \sim 10 \text{ cm}^{-1}$ [7], but if the LC layer is thin ($\sim 5 \mu\text{m}$), then the absorption loss may be negligible. However, to achieve a sufficient phase change a minimum cell gap is required and as the cell gap increases, so the absorption loss increases exponentially. In the vicinity of resonance wavelengths where α is about 10^4 cm^{-1} , the 5- μm LC layer is now essentially opaque.

In the mid-wave infrared (MWIR) region (3-5 μm), several molecular vibration bands exist, such as CH, CH₂, CH₃, CN, and NCS stretching. The CH, CH₂, and CH₃ absorption bands overlap closely and are centered at $\sim 3.4 \mu\text{m}$ with a bandwidth from 3.2 to 3.7 μm . On the other hand, the strong cyano (CN) absorption peak occurs at $\sim 4.48 \mu\text{m}$ and isothiocyanato (NCS) polar group has a broad and strong absorption in the 4.5-5.2 μm spectral regions.

The molecular vibration frequency (ω) depends on the spring constant (κ) and reduced mass (μ) of the diatomic group as:

$$\omega = \sqrt{\kappa / \mu}. \quad (1)$$

As the reduced mass increases, the vibration frequency decreases, i.e., the absorption band shifts toward a longer wavelength [8]. To prove this concept, a perdeuterated ($\sim 95\%$ ^2H) 5CB (4'-pentylbiphenyl-4-carbonitrile) compound, designated as D5CB was developed [9,10]. The carbon-deuteron (CD) absorption peak shifted from 3.5 μm to 4.6 μm . In both the near IR (0.75-3 μm) and long wavelength IR (8-12 μm) regions, D5CB has a much cleaner absorption spectrum and lower absorption coefficient than 5CB in the off-resonance region while other physical properties, such as phase transition temperatures and birefringence remain more or less unchanged. To ensure a low absorption in the desired MWIR window, we need to shift the absorption band further out to longer wavelength IR region. To do so, we need to replace hydrogen with a still heavier atom, such as fluorine.

Fluorinated liquid crystals have often been used in active matrix liquid crystal displays, and their properties have been reviewed elsewhere [11,12]. In these compounds the fluoro substitutions are installed mainly in the phenyl ring in order to create dielectric anisotropy ($\Delta\epsilon$), while keeping the alkyl chain untouched. As a result, the strong CH absorption bands still exist, although they are not important for display applications. Very little research has been done to tailor fluorinated liquid crystals for reduction of MWIR absorption as the molecular design strategies for these two applications (visible wavelength displays and IR phase modulators) are quite different. For MWIR applications of a liquid crystal material, besides a wide nematic temperature range, high birefringence (Δn), low viscosity, and a modest $\Delta\epsilon$, low absorption in MWIR is required, which would result in a different molecular structure and in turn affect the physical properties. Therefore, a good balance between physical properties and MWIR loss should be considered.

In this paper, we outline our molecular design strategy and demonstrate a first partially fluorinated LC compound to clean up the MWIR absorption bands, while exhibiting a nematic phase (although only about 2°C), high birefringence ($\Delta n \sim 0.2$), a low visco-elastic coefficient, and a modest dielectric anisotropy ($\Delta\epsilon = -2.7$).

Table 1. Chemical Structures and Properties of Compounds Studied, where Cr Stands for Crystalline, N for Nematic, and I for Isotropic Phase

Compound #.	Chemical Structure	Abbreviation	PTT (°C)	ΔH (cal/mol)
1		1CB	Cr109N(45)I ^a	5400
2		5CB	Cr24N35.3I	4100
3		FB	Cr88I	2198 ^b
4		F7CB	Cr120.4I	10719
5		FT	Cr85.8N87.6I	4921

^a() indicates a monotropic phase.

^bEnthalpy of sublimation

2. Molecular design strategy

Substitution of all the CH bonds in the alkyl chain and phenyl rings with CF might appear to be a straightforward approach to suppress MWIR absorption. However, these completely fluorinated compounds themselves exhibit some undesirable properties, such as high melting temperature (T_m), large heat fusion enthalpy (ΔH), and no liquid crystalline phase (or, at least, a propensity to form smectic phases). In order for a compound to exhibit a nematic phase, the compound ought to have certain flexibility and aspect ratio. Based on the IR absorption spectra, the CH bonds in a phenyl ring have a much weaker and narrower absorption than those found for CH bonds in flexible alkyl chains. To further validate this concept, Compounds 1, 2, 3 and 4 (listed in Table 1) were prepared, dissolved in CCl_4 at a concentration of $\sim 5 \times 10^{-5}$ mol/ml and then filled in a NaCl IR cell with cell gap (0.5 mm). The measurement of MWIR transmission spectra were carried out on a Perkin Elmer Spectrum One FT-IR Spectrometer. The transmission spectra of the compounds were normalized to that of CCl_4 . As illustrated in Fig. 1, both 1CB (4'-methylbiphenyl-4-carbonitrile) and 5CB exhibit a much broader and stronger absorption near $\lambda = 3.4 \mu\text{m}$ than FB (#3, 4,4'-difluorobiphenyl) does. The reference compound FB has no alkyl chain, but has two phenyl rings. It does not have mesogenic phase. This comparison is to confirm that indeed the CH bonds in the alkyl chain make a stronger absorption near $\lambda = 3.4 \mu\text{m}$ than the CH bonds in the phenyl rings. The 5CB has a longer alkyl chain with more CH bonds in $-\text{CH}_2-$ and $-\text{CH}_3$ structures. Therefore, its absorption near $3.4 \mu\text{m}$ is much stronger. The absorption from $\text{C}\equiv\text{N}$ ($4.48 \mu\text{m}$) in 1CB and 5CB is almost the same because of similar concentration.

Next, we synthesized a compound (#4, F7CB) with all the hydrogen atoms in the alkyl chain of 7CB (4'-heptylbiphenyl-4-carbonitrile) replaced with fluorine. As expected, and like 5CB and 1CB, the F7CB has a strong absorption peak at $4.48 \mu\text{m}$ due to $\text{C}\equiv\text{N}$ stretching, but its absorption at $\sim 3.4 \mu\text{m}$ is significantly reduced since all the C-H bonds in the alkyl chain have been replaced by C-F bonds. It is known that $-\text{CF}_2-$ and $-\text{CF}_3$ have a broad and strong absorption in $7.1\text{--}9.5 \mu\text{m}$ [13], while the relatively weak absorption at $\sim 4.25 \mu\text{m}$ is an overtone of the strong C-F vibration centered near $8.5 \mu\text{m}$. This overtone can be further reduced by decreasing the number of CF groups, i.e., employing a shorter fluorinated alkyl chain. The residual absorption of C-H bonds in the phenyl rings, as in F7CB, is much more tolerable. The phase transition properties and ΔH of F7CB were measured using Differential Scanning Calorimetry (DSC, TA Instruments Q2000). With a long perfluorinated alkyl chain, F7CB does not exhibit any mesogenic phase. Rather, its melting point is $\sim 120^\circ\text{C}$ (c.f. 30°C for 7CB) and its ΔH is increased dramatically so that its solubility in an LC host is limited to $<5 \text{ wt}\%$.

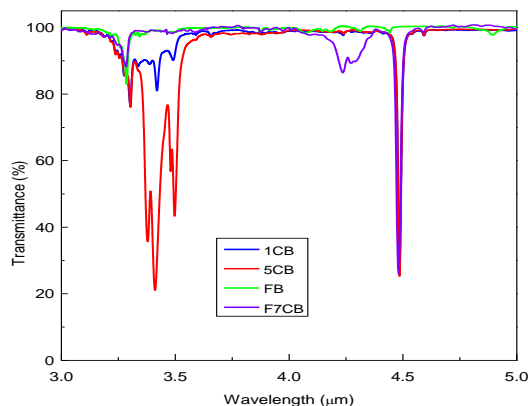


Fig. 1. Measured transmission spectra of 5CB (Red), 1CB (Blue), FB (Green) and F7CB (Violet).

Therefore, a practical solution is to substitute only the CH bonds in the alkyl chain while keeping the core structure unaltered. Moreover, the fluorinated alkyl chain should not be too long, otherwise, the LC phase would be suppressed and the C-F vibrational overtone grows. Meanwhile, two or three phenyl rings are needed to ensure a high birefringence. To realize a useful electro-optic effect, the compounds should be polar with a modest $\Delta\epsilon$, either positive or negative. To replace CN, we could choose $-F$, $-CF_3$, or $-OCF_3$ as polar groups. Based on these guidelines, we synthesized a new fluorinated terphenyl compound (#5, abbreviated as FT) and evaluated its properties.

3. Results

As shown in Fig. 2, the absorption of FT at $\sim 3.4\mu\text{m}$ is significantly reduced, compared to that of 5CB. Only small absorption exists due to the residual CH bonds in the phenyl rings. The fairly weak absorption at $\sim 4\mu\text{m}$ is the overtone of C-F stretching vibration. Overall, from $3\mu\text{m}$

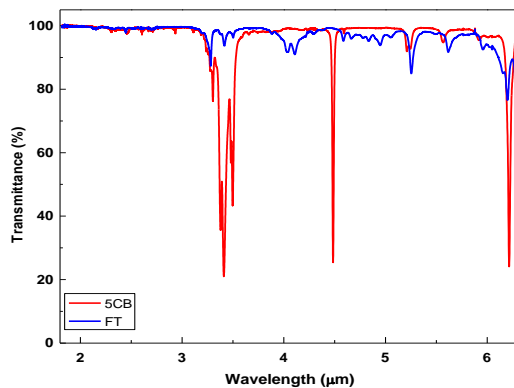


Fig. 2. Measured transmission spectra of 5CB (red line) and FT (blue line) in MWIR region.

to $5\mu\text{m}$, the absorption is quite clean. Note that the absorption peak due to the C-O single bond stretching vibration is shifted to the wavelength longer than $7.5\mu\text{m}$ [13], which is out of MWIR window. For MWIR application, the absorption of glass substrates and indium-tin-oxide (ITO) electrodes is another big concern. Germanium is a good substrate candidate due to its low loss and high electrical conductivity [14,15]. The LC alignment layer (polyimide or SiO_x) is usually very thin ($\sim 80\text{ nm}$) which will not cause much absorption.

We also compared the absorption spectrum of FT with 5CB in the $0.6\text{-}3.2\mu\text{m}$ range. Since the absorption is relatively small in this spectral region, a 2-mm-thick quartz cell was used

and the concentrations for both compounds were increased to 5×10^{-4} mol/ml in CCl_4 . A Cary UV/Vis/NIR spectrophotometer was employed to record the near IR transmission spectra. In Fig. 3, the blue and red lines represent the transmission spectra for FT and 5CB, respectively. The overall outcome is that some overtone absorption bands appear in this region, but FT exhibits a much higher transmittance than 5CB. In the spectral range of 2.2-3.0 μm , where the absorption is due to the combination of C-H stretching, FT shows much weaker absorption than 5CB does. In addition, the $\lambda \sim 1.7$ μm band resulting from the second harmonic of the 3.4- μm CH band becomes narrower for FT.

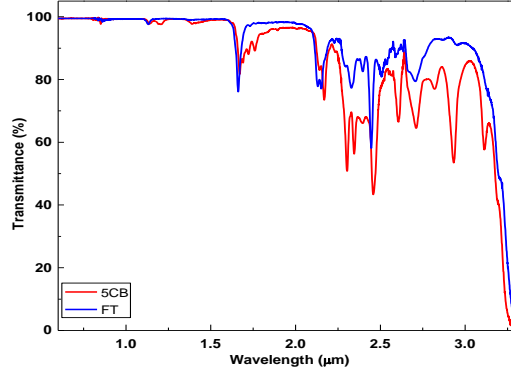


Fig. 3. Measured transmission spectra of 5CB (red line) and FT (blue line) in near IR region.

For MWIR applications, in addition to low absorption we also require the compound to have a nematic phase, high birefringence, low viscosity, and a large dipole moment. Therefore, we also characterized the physical properties of FT. From DSC measurements, FT exhibits a narrow ($\sim 2^\circ\text{C}$) but enantiotropic nematic phase from 85.8°C to 87.6°C . To measure the physical properties, we doped FT into a commercial negative LC host, MLC-6882 (Merck) at 10 wt% and 15 wt% ratios. The Δn of the mixture was measured through phase retardation of a LC cell sandwiched between two crossed polarizers. Vertical aligned (VA) cells with a cell gap $d \sim 9$ μm were prepared. The LC mixtures before and after doping were filled into these cells at $\sim 50^\circ\text{C}$. The cell was mounted in a Linkam LTS 350 Large Area Heating/Freezing Stage controlled by a Linkam TMS94 Temperature Programmer. A 1 kHz square-wave AC signal was applied to the LC cell. A linearly polarized He-Ne laser ($\lambda = 632.8$ nm) was used as probing light source. The light transmittance was measured by a photodiode detector (New Focus Model 2031) and recorded digitally by a LabVIEW data acquisition system (DAQ, PCI 6110). The VT curves and then the phase retardation (δ) of the VA cells were then measured by the LabVIEW system. The LC birefringence at wavelength λ and temperature was obtained from the phase retardation using the following equation [16]:

$$\delta = 2\pi d \Delta n / \lambda, \quad (2)$$

where d is the cell gap. For the LC host cell with $d = 9.29$ μm and $\delta = 2.77\pi$, we obtained $\Delta n = 0.094$ from Eq. (2). Similarly, for the 10 wt% and 15 wt% doped samples, we obtained $\Delta n = 0.105$ and 0.111 , respectively. The birefringence of FT was extrapolated by weight ratio to be $\Delta n \sim 0.205$ ($\lambda = 632.8$ nm). According to the birefringence dispersion of liquid crystals [2], Δn decreases with wavelength and gradually saturates in the near IR region. In the MWIR region, the Δn is $\sim 10\%$ lower than that at $\lambda = 633$ nm, i.e., $\Delta n \sim 0.18$. High Δn enables a thin cell gap to be used for achieving a certain phase change, say 2π , which in turn helps to reduce response time and absorption loss. For example, at the edge of C-H absorption band, say $\lambda = 3.5$ μm , the estimated transmission of 5CB with 2π phase retardation is only 6.2%, but it is increased to 93% for the FT LC with the same phase retardation.

The $\Delta \epsilon$ was determined through the capacitance measurements of parallel- and perpendicular-aligned LC cells [16]. An HP-4274 multi-frequency LCR meter was employed

for the capacitance measurements. MLC-6882 has a modest dielectric anisotropy $\Delta\epsilon = -2.56$ and a fairly low rotational viscosity ($\gamma_1 \sim 70$ mPa·s) at room temperature (24°C). The extrapolated dielectric anisotropy of FT is $\Delta\epsilon = -2.71$.

By measuring the free relaxation (decay) time for a controlled phase change, visco-elastic coefficient (γ_1/K_{33}) was obtained according to following equations [17]:

$$\delta(t) = \delta_0 \exp(-2t / \tau_0), \quad (3)$$

$$\tau_0 = \gamma_1 d^2 / (K_{33} \pi^2), \quad (4)$$

where δ_0 is the total phase change, γ_1 is rotational viscosity, and K_{33} is the bend elastic constant. We measured the decay time constant τ_0 and calculated the γ_1/K_{33} of MLC-6682 and the 10 wt% and 15 wt% doped mixtures. Our results show that the τ_0 of the two doped samples decreases from 59.0 ms to 58.2 ms and 55.3 ms, and accordingly the calculated γ_1/K_{33} was slightly reduced from 6.75 ms/ μm^2 to 6.56 and 6.41 ms/ μm^2 , respectively. Although γ_1/K_{33} cannot be linearly extrapolated, the relative low γ_1/K_{33} of the doped mixtures indicates that FT has a somewhat lower γ_1/K_{33} than MLC-6682. Such a low viscosity originates from the $-\text{OCF}_3$ group [11,18–21].

The nematic range of our fluorinated terphenyl is only 2°C. This sample serves as an important first example for proving our design concepts, but its nematic range is too narrow for practical applications. To widen the nematic range, several compounds have to be developed for formulating eutectic mixtures. As illustrated in Fig. 4, the general molecular structure shows some compounds which not only satisfy the low-loss criterion but also have potential for wider temperature range. However, the phase transition temperatures of a compound are difficult to predict before it is synthesized.

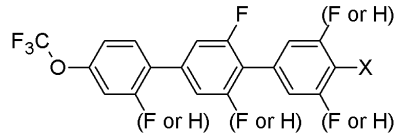


Fig. 4. Proposed compound structure with potentially wider nematic range ($X = \text{F}$ or OCF_3).

3. Conclusion

We have demonstrated a fluorinated terphenyl liquid crystal with low absorption in both MWIR and near IR regions. Although this LC compound has a negative $\Delta\epsilon$ and narrow nematic phase range, it possesses some attractive properties, such as low absorption loss in MWIR, high birefringence, moderate $\Delta\epsilon$, and low visco-elastic coefficient. With additional molecular design and synthesis, e.g., substituting fluoro groups in different positions of the phenyl rings or employing $-\text{OCF}_3$ at one phenyl ring terminal as a polar group [11,18,19], a positive $\Delta\epsilon$ and potentially wider nematic range could result. In order to further widen the nematic range for room temperature operation, forming eutectic mixtures is a common practice. To achieve this objective, we have proposed some modified molecular structures. The FT compound reported here serves as an important first example for future development of low-loss MWIR liquid crystals, which would extend the application of LCs to MWIR for both amplitude and phase modulations.

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