

**SOLVENT-DEPENDENT ANALYSIS OF
ALKYLCYANOBIHENYLS AND DEVELOPMENT OF
LIQUID CRYSTAL-BASED SENSOR FOR THE DETECTION
OF HEAVY METAL IONS**

BY

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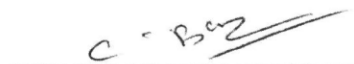


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[To my deceased sister Asmau Sani Dangombe]

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LIST OF ABBREVIATIONS

ICT	:	Intermolecular Charge Transfer
LC	:	Liquid crystals
nCB	:	4-Alkyl-cyano-4'-biphenyl
DMF	:	Dimethylformamide
HM	:	Heavy Metal
TCQDLC	:	Tricycloquinazoline-based discotic liquid crystals
LFSE	:	Linear Free Solvation and Energy
PBS	:	Phosphate buffered saline
MeDTC	:	N-methyl-N-dodecyldithiocarbamate
5CB	:	4-Pentyl-4'-cyanobiphenyl
SDS	:	Sodium Dodecyl Sulfonate
APTES	:	(3-Aminopropyl)triethoxysilane
CCD	:	Charged Coupled Device
THF	:	Tetrahydrofuran
DCM	:	Dichloromethane
PLL	:	Poly-L-lysine
TEM	:	Transmission Electron Microscopy

ABSTRACT

Full Name : Musa Sani Dangombe
Thesis Title : Solvent-Dependent Analysis of Alkylcyanobiphenyls and Development of Liquid Crystals-Based Sensors for Heavy Metal Ions Detection
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The 4'-alkyl-4-cyanobiphenyls (nCB) are an important class of liquid crystals, possessing hybrid liquid and solid-like properties. They are widely used for various applications. We developed a liquid crystal-based sensor owing to its highly responsive nature and capability to swiftly change orientation in response to any foreign impurity. In addition, six alkylcyanobiphenyl liquid crystal samples (5CB to 10CB) were examined using Raman, UV-visible and fluorescence spectroscopy in a total of twelve solvents of various polarities. For the Raman, distinctive bands contributed by the LC sample are from $\text{C}\equiv\text{N}$ stretch, $\text{C}-\text{C}$ aromatic ring breathing, $\text{C}-\text{C}$ biphenyl linking stretch, and $\text{C}-\text{H}$ in-plane deformation. These modes are found to be responsive to different solvent environments by shifting positions. While the absorption maximum shifts to a longer wavelength with an increase in solvent polarity, the fluorescence spectra do exhibit some pattern that points to an odd-even effect that leads to observed similarities in the solvent-dependent spectra of the odd-numbered 5CB and 7CB alongside the even-numbered 6CB and 8CB. The LC-based sensor showed good sensitivity in the detection of mercuric ions in solution indicated by the interaction of the metal ion and SDS at the LC/aqueous interface, which triggers the rearrangement of the LC and bright-to-dark transition of optical images.

ملخص الرسالة

الاسم الكامل: موسى ساني دانغومبي

عنوان الرسالة: تحليل يعتمد على المذيبات لألكيل سيانوب فينيل وتطوير أجهزة استشعار قائمة على البلورات السائلة

للكشف عن أيونات المعادن الثقيلة

التخصص: كيمياء

تاريخ الدرجة العلمية: ديسمبر 2023

alkyl-4-cyanobiphenyls (nCB)-4' هي فئة مهمة من البلورات السائلة ، تمتلك خصائص سائلة هجينة وشبيهة بالمواد الصلبة. تستخدم على نطاق واسع لمختلف التطبيقات. لقد طورنا مستشعرا قائما على الكريستال السائل نظرا لطبيعته عالية الاستجابة وقدرته على تغيير الاتجاه بسرعة استجابة لأي شوائب أجنبية. بالإضافة إلى ذلك ، تم فحص ست عينات بلورية سائلة من الألكيل سيانوبفينيل (CB5 إلى CB10) باستخدام مطيافية رامان والأشعة فوق البنفسجية المرئية والفلورية في ما مجموعه اثني عشر مذيبا من أقطاب مختلفة. بالنسبة للرامان ، فإن النطاقات المميزة التي ساهمت بها عينة LC هي من تمدد $C\equiv N$ ، وتنفس الحلقة العطرية C-C ، وامتداد ربط ثنائي الفينيل C-C ، وتشوه C-H في المستوى. تم العثور على هذه الأنماط لتكون استجابة لبيئات المذيبات المختلفة عن طريق تغيير الموضع. في حين أن الحد الأقصى للامتصاص يتحول إلى طول موجي أطول مع زيادة في قطبية المذيب ، فإن أطيف التآلق تظهر بعض الأنماط التي تشير إلى تأثير فردي زوجي يؤدي إلى أوجه تشابه ملحوظة في الأطيف المعتمدة على المذيب ل CB5 و CB7 ذات الأرقام الفردية جنبا إلى جنب مع CB6 و CB8 ذات الأرقام الزوجية. أظهر المستشعر القائم على LC حساسية جيدة في الكشف عن أيونات الزئبق في المحلول المشار إليه من خلال تفاعل أيون المعدن و SDS عند السطح البيني LC / المائي ، مما يؤدي إلى إعادة ترتيب LC والانتقال الساطع إلى الداكن للصور البصرية. |

CHAPTER

INTRODUCTION

1.1 Liquid Crystal Materials

A state of matter known as liquid crystals (LC) is in between that of an isotropic liquid and a crystalline solid.¹ They have many of the mechanical characteristics of liquids, such as great fluidity, the incapacity to withstand shear, and the propensity for droplets to form and agglomerate.²⁻⁴ They have characteristics with crystals in that they are anisotropic in terms of their optical, electrical, and magnetic characteristics.⁵⁻⁷ Lehmann was the first to propose the term "liquid crystal" to describe this condition of matter.⁸ The literature has also suggested and used words such as anisotropic or ordered liquids or fluids, paracrystals, mesomorphs or mesoforms, and mesomorphic states. Thermotropic liquid crystals are those that are created by melting crystalline solids.⁴ Certain colloidal solutions, such as tobacco mosaic virus aqueous solutions and certain polymers, also exhibit liquid crystalline behavior.⁹⁻¹¹ These kinds of liquid crystals are referred to as lyotropic, which are mostly controlled by the concentration of the molecules rather than temperature as in the thermotropic liquid crystals.^{4,9}

The liquid crystal molecules constitute well-known materials that are not only anisotropic in nature but also have high birefringence.¹² Having the characteristics essentially found in liquids as well as solid-state² makes them exhibit a high response to stimuli such as

temperature,¹³ applied magnetic and electric field,⁵ light,¹⁴ and interfacial interactions.¹⁵ With this exquisite combination of properties, and beyond their regular display applications, LC materials drew much attention over a range of applications, including liquid crystal lenses, smart windows, sensors, supercapacitors, drug delivery, and photovoltaic cells.^{7,16} Nematic liquid crystals, for instance, are crucial in terms of technology as a mesogenic unit for molecular engineering on account of their low transition temperatures and wide mesophases.²

1.2 Classification of Liquid Crystals

Generally, thermotropic liquid crystal materials exhibit various mesogens which include discotic, calamitic, polycatenary, bent-shaped, and polymeric mesogens. These compounds also contain core and terminal alkoxy or alkyl chains, one of which may be a polar moiety in some cases.¹⁷ The most well-known member of the LC series of calamitic compounds is 4-cyano-4'-alkyl biphenyl (nCB), where "n" is indicative of the quantity of carbon atoms constituted within the alkyl chain.³ At various phase transition temperatures, the nCB series showed the transition from other phases to the isotropic phase.¹⁸ These chemicals are well-suited as anisotropic solvents for polarization spectroscopy since they are known to create partially ordered structures.^{19,20}

1.2.1 Nematic And Cholesteric Liquid Crystals

The nematic phase of calamitics is the simplest liquid crystal phase. In this phase, the molecules maintain a preferred orientational direction as they diffuse throughout the sample. There exists no positional order. Figure 1.1 d shows the nematic phases occurring in different types of substances. The long-range

orientational order, or the tendency of the molecules long axes to align along a preferred direction, is a characteristic of the nematic phase. Throughout the medium, the locally preferred route may change, but it does not in the unstrained (equilibrium) natural state. The director field is easily deformed and alignable with the help of prepared surfaces, magnetic and electric fields, and other factors. Rarely does a nematic exhibit the idealized equilibrium structure upon optical observation. Nematics get their name from a few significant structural disturbances that show up as threads.^{21–23}

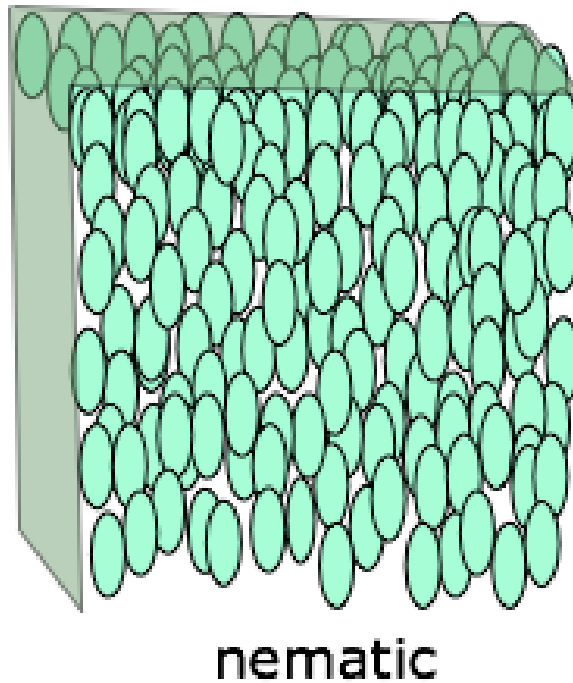
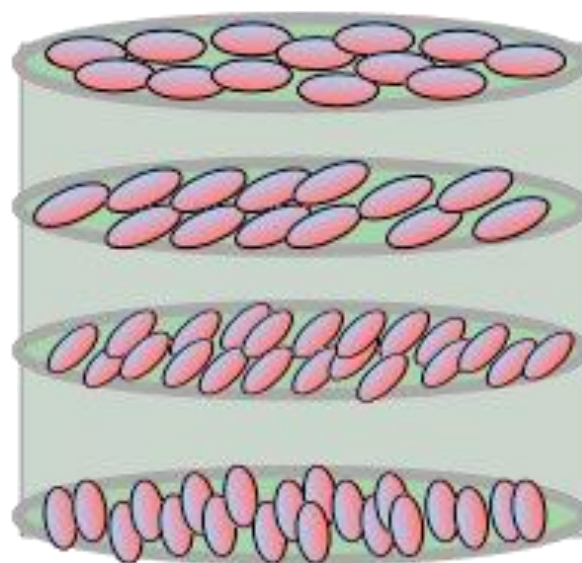


Figure 1.1 Molecules arrangement in a nematic phase (thread-like) aligned in the same direction and free to move around at random.

Similar to the nematic phase, the cholesteric phase lacks a long-range order in the locations of the molecular centers of mass while having a long-range orientational order (Figure 1.2). It is distinct from the nematic phase in that the director moves

in a regular manner throughout the medium. The configuration is exactly what would be obtained by twisting a nematic that was initially oriented along the y-axis about the x-axis. As one moves along the twist axis, the director and the Fresnel ellipsoid are seen to revolve. The long axes of the molecules tend to align in a number of equally spaced parallel planes rather than along a single favored direction in any plane perpendicular to the twist axis. The length of the twist axis, along which the director completes a full round, is what defines this cholesteric secondary structure. According to Robinson, a racemic blend of left- and right-handed forms shows a nematic structure.^{9,21-25}



**chiral
(cholesteric)**

Figure 1.2 The cholesteric phase of liquid crystal capable of existing in left- or right-handed forms that are incompatible with one another.

1.2.2 Smectic Liquid Crystals

A smectic system results from the loss of crystalline organization in two dimensions, giving rise to stacks of two-dimensional liquids as seen in Figure 1.3. The layered architectures of smectic liquid crystals can be determined by X-ray diffraction, which also provides a well-defined interlayer gap. In addition to the orientational ordering, the smectic molecules show various connections in their positions. The molecules can spin around one axis and move in two directions in the majority of smectics. The layers can slide over one another rather readily because the interlayer attractions are weaker than the lateral forces between the molecules. This results in a fluid property in the system that is more viscous than nematic. Stratification is a key characteristic of the smectic phase that sets it apart from the nematic. The molecules show certain connections and are layered. in their roles aside from the orientational placement. There are numerous classes of smectics that have been acknowledged.²²⁻²⁴

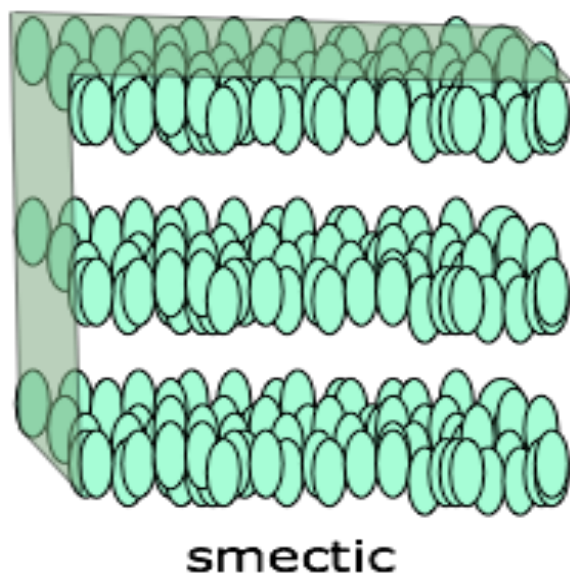


Figure 1.3 The smectic liquid crystals molecular axes layered in a soap-like phase, roughly perpendicular to the laminar planes.

1.3 Celebrity Molecules: Alkylcyanobiphenyl Liquid Crystals

The LC series of calamitic compounds that is most well-known is 4-cyano-4'-alkylbiphenyl (nCB). In order to create the nCB series, Gray *et al.* used three-step reactions: acylation of the 4-bromobiphenyl molecule in the first stage, reduction in the second step, and substitution of the cyano group for the bromide group in the last step. This led to a poor total yield.³ In a follow-up study, Gray and Mosley attempted to alter the synthesis parameters in order to obtain faster reaction times and larger yields of 4-cyano-4'-alkylbiphenyl.²⁶ But Dabrowski *et al.* suggested a straightforward technique to produce high yields of nCB molecules (Scheme 1.1). The biphenyl molecule was acylated in the first stage, and the 4-n-alkylbiphenyl was obtained in the second step by reducing the acylated group with hydrazine hydrate. Furthermore, they chose to iodinate the 4-n-alkylbiphenyl in the third step rather than bromate it since bromine is

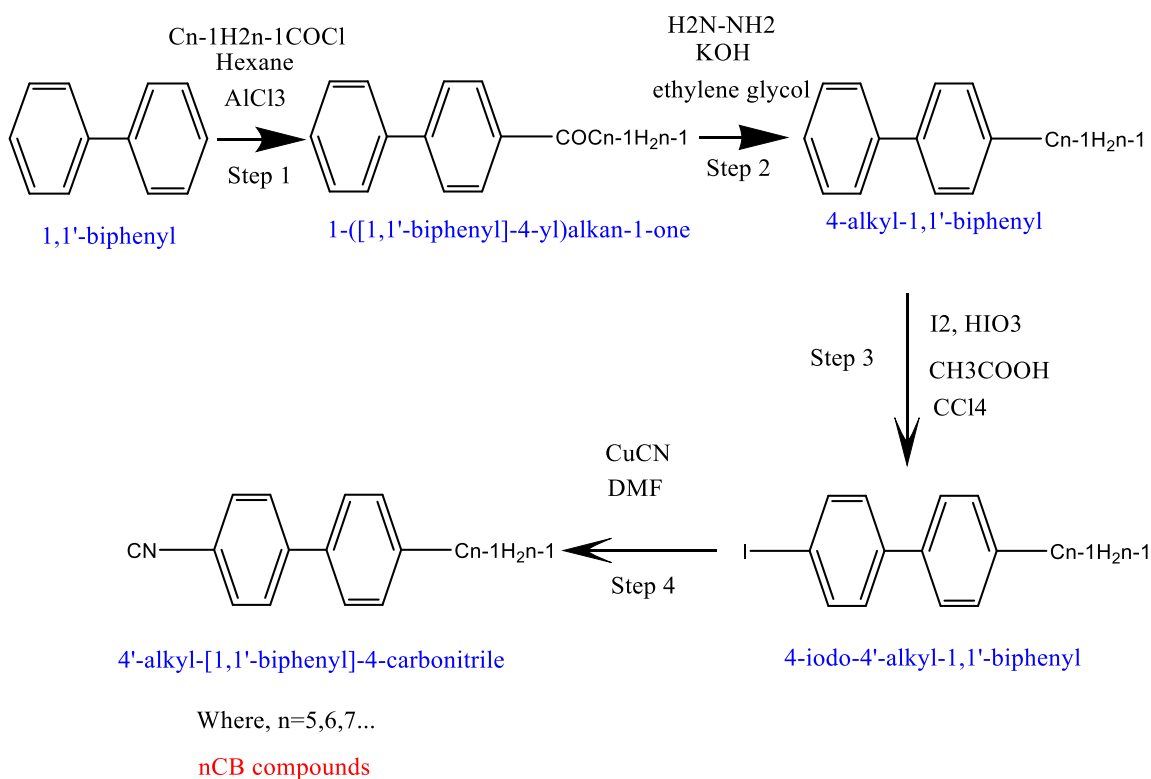
less reactive in the para-/4-position than iodine and the iodination reaction is a more selective process. Ultimately, by treating 4-iodo-4'-alkyl-1,1'-biphenyl with copper cyanide in dimethylformamide (DMF) solution, the cyano group replaced the iodo group, resulting in the predicted nCB molecules.²⁷ The nCB series, showed an odd-even trend of CN...CN and CN...phenyl interactions in all crystal structures. For higher homologs ($n < 7$), the odd-even effect in packing modes is recognized as a specific instance of CN...CN or CN...phenyl interactions.^{28–32} These materials are reported to exhibit transition temperatures as shown in Figure 1.4, from distinct phases of nematic or smectic to isotropic phase where they behave much like conventional liquids.^{22,26,33}

Table 1.1 Information on the alkylcyanobiphenyls crystal systems

nCB	Space group	Crystal system	Z	T/K	a/Å	b/Å	c/Å	$\beta/^\circ$
1CB ³⁴	P21/n	Monoclinic	8	296	15.71(8)	14.38(8)	9.61(6)	95.0(2)
2CB ³⁴	P21	Monoclinic	2	298	8.589(2)	5.864(1)	11.835(3)	92.41(1)
3CB ³⁵	P21/c	Monoclinic	4	298	6.259(3)	19.1216(9)	11.0473(5)	103.39(2)
4CB ³⁶	P21/c	Monoclinic	4	298	12.198(9)	9.204(8)	14.746(9)	123.4(3)
5CB ³⁷	P21/a	Monoclinic	4	253	8.249(2)	16.022(4)	10.935(3)	95.09(3)
6CB ²⁸	P1	Triclinic	4	200	12.427(4)	12.724(3)	10.857(2)	112.54(2)
7CB ²⁸	P1	Triclinic	4	240	11.438(2)	15.800(2)	9.674(2)	107.164(11)
8CB ³⁸	P21/n	Monoclinic	4	240	14.939(3)	6.078(4)	19.740(2)	102.345(12)
9CB ³⁹	P1	Triclinic	4	–	9.765(1)	11.460(2)	17.860(2)	80.870(1)
10CB ⁴⁰	P21/n	Monoclinic	4	–	15.813(1)	5.479(1)	23.179(2)	102.2(1)
11CB ⁴¹	P1	Triclinic	4	–	9.755(2)	11.322(1)	19.911(2)	94.41(2)

Interestingly, it is expected that these liquid crystal materials would interact differently through exposure to different molecular and environmental interactions which consequently affect their electronic properties.⁴² The impact of a molecule's surroundings on its photophysical properties is a topic of substantial current interest in

chemical physics. For instance, very thin films are made using solvents, but they are also generally viewed as being crucial to the organization of a variety of systems.⁴³ Moreover, the molecular ordering in each phase of these liquid crystal material is particularly sensitive to factors like temperature and the presence of undesirable foreign particles and impurities. As a result, such items can be classified as responsive materials. Not only the identity of impurities, but the shape, size, surface qualities, and other factors have a role in these LC orientational shifts.² Because the materials are optically anisotropic, they have received extensive research as potential point-of-care detection replacements for conventional analytical techniques.⁴⁴



Scheme 1.1 shows the synthetic pathway for molecules 4'-alkyl-[1,1'-biphenyl]-4-carbonitrile (nCB)

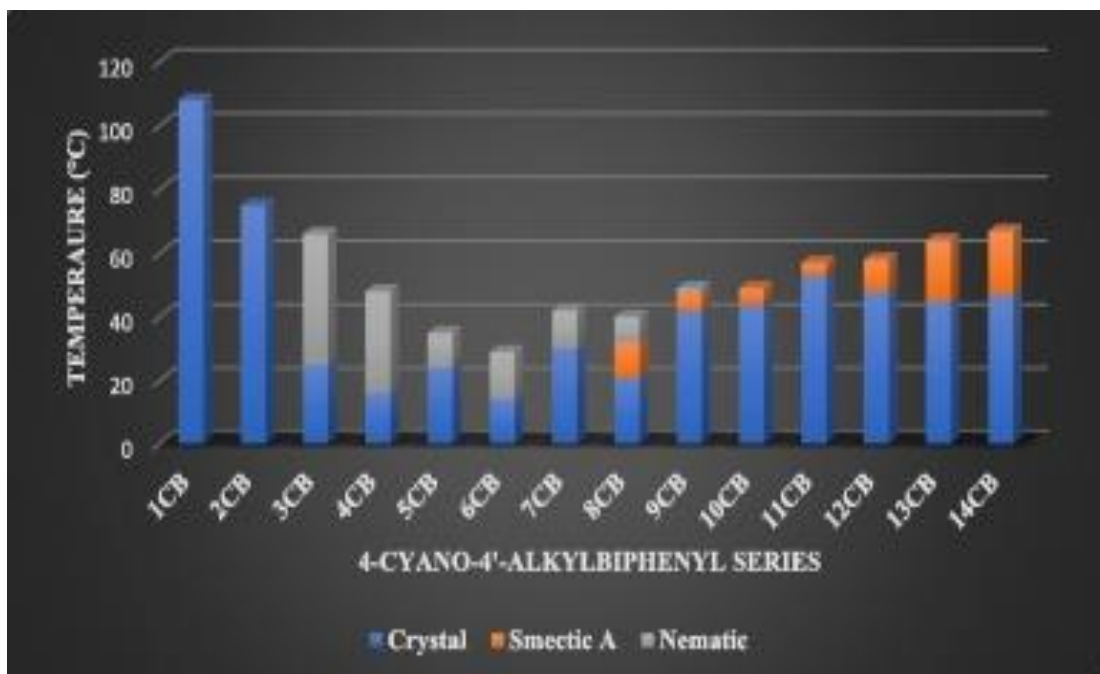


Figure 1.4 Transition temperatures for the 4-cyano-4'-alkylbiphenyl (nCB) series, in which 3–4CB molecules showed monotropic and 5–14CB molecules showed enantiotropic behavior.¹⁶

1.4 Applications of Alkylcyanobiphenyls

The applications of nCB LC-based sensors for heavy metal detection is an important area of interest, as illustrated in Figure 1.5.^{45–48} Globally, there is a lot of focus on the environmental issues brought on by rapid and extensive industrialization and urbanization.^{16,45,49} Environmental pollution linked to heavy metal (HM) ions is one of these issues and is getting worse in many nations.⁵⁰ Recent research has shown that pollutants of air such as smog or fine dust and ultrafine particles with high concentrations of HM ions from one country's industrial zones eventually cause environmental issues in the neighboring countries.⁵¹ Humans and other living things

require an ideal concentration of HM ions. However, when HM ions build up in the ecosystem and are absorbed in the body, they eventually have an impact on human health.⁵² Thus, the well-being of humans and the environment depends on the appropriate identification of these heavy metals. The majority of well-known techniques for heavy metal detection are laborious and costly. Therefore, the need for a straightforward, simple, and affordable method of detecting heavy metals with acceptable specificity and sensitivity may be fulfilled by LC-based sensors.^{16,45,53}

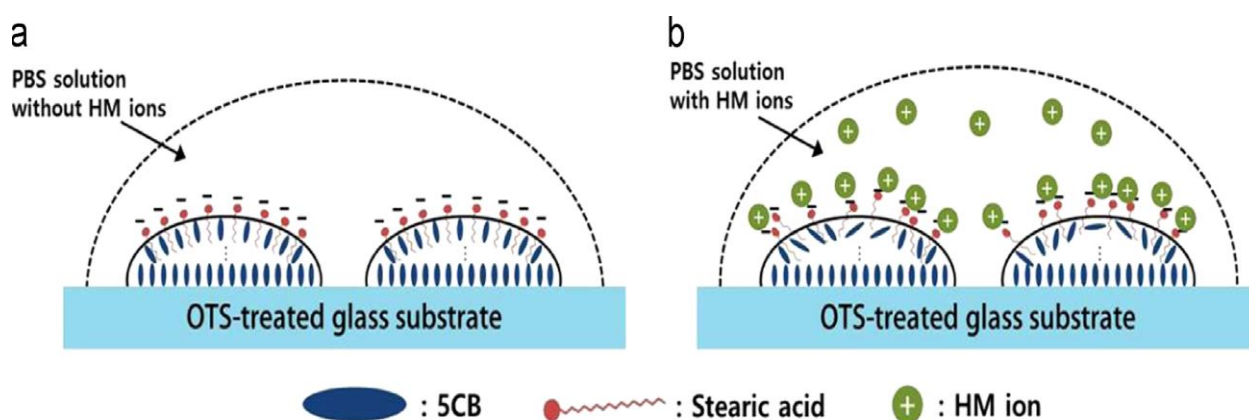


Figure 1.5 The orientation state of stearic acid-doped 5CB at the interface between aqueous solution and LC: (a) without heavy metal ions and (b) with heavy metal ions.⁵⁴

1.5 Influence of Solvents on the Behaviors of Alkylcyanobiphenyls in

Solution

The photophysical studies of this excellent class of compounds have received enormous attention owing to the aforementioned variety set of properties.^{6,55–60} Many reports have shown molecules' environment can exert a significant influence on the spectroscopic properties such as the vibrational modes (e.g. C≡N stretching mode)⁶¹, especially those which affect their electronic delocalization, light absorption, or scattering properties⁶².

On the potential energy surfaces themselves, these effects can include dynamic effects on the nuclear motions taking place on those surfaces⁶³. Raman spectroscopy of liquid crystals can yield information about intermolecular interactions in anisotropic phases⁶⁴. These interactions mainly include non-specific (dielectric enrichment) or specific interactions (e.g., hydrogen bonding, proton transfer, and intermolecular charge transfer (ICT)),^{65,66} whereas solvatochromism is phenomenal in providing insight into relationships between solute structures and the solvent environment.⁶⁷⁻⁶⁹ The solvatochromic behavior of liquid crystal molecules is influenced by the type and extent of interactions between the solute and solvent in the solution media. For instance, the optical properties of 5CB dimers and trimers were studied in order to evaluate the structural changes of the mesophase under the influence of various factors and external fields.⁶ Also, the molecular interactions of 2CB and 5CB in different solvents of varying polarities were studied in vibronic and vibrational spectra.⁶⁰ Moreover, the absorption and fluorescence of alkyl and alkoxy cyanobiphenyls in different solvents were reported.⁵⁹ In addition to the solvents effect on the UV-Vis spectral shifts of cyanobiphenyls, a different study examined the effect of the addition of oxygen atom nCB on the shifts.⁵⁵ In these studies, the absorption and fluorescence maxima of the LC molecules are found to experience red-shifts with an increase in the solvent polarity as a result of a consequent increase in the dipole moment of the excited state.^{55,59,60} The dielectric constants of nCB molecules were also found to be influenced by the solvent environment, as reported in dilute solvents of cyclohexane, hexane, benzene, and carbon tetrachloride, and evaluated the molecular dipole moments as the number of carbon atoms increases.⁷⁰

1.6 Objectives of the Study

The main research objective is to develop chip-based liquid crystal sensors using the exquisite 4'-alkyl-4-cyanobiphenyl for the detection of analytes in solution. The specific goals and benefits of this research work are stated as follows:

1. To develop a simple liquid crystal-based sensor using the 4'-pentyl-4-cyanobiphenyl (5CB) molecules study the effect of various organic media on the photophysical properties of the LC samples.
2. To detect reliably the presence of heavy metal ions in solution using the liquid crystal-based sensors.
3. To examine the solvent-dependent spectroscopic properties of the 4'-alkyl-4-cyanobiphenyl homologous series.

CHAPTER

LITERATURE REVIEW

2.1 Effects of Solvent on Spectroscopic Properties

Many reports in the literature have shown molecules environment can exert some substantial influence on the spectroscopic properties of vibrational bands such as C≡N stretch vibrational mode,⁶¹ especially those which affect their electronic delocalization, light absorption, or scattering.⁶² On the potential energy surfaces themselves, these effects can include dynamic effects on the nuclear motions taking place on those surfaces. Information regarding intermolecular interactions in anisotropic phases can be obtained from the Raman spectroscopy of liquid crystals.⁶⁴ These interactions can be non-specific such as dielectric enrichment or specific such as intermolecular charge transfer, proton transfer, and hydrogen bonding.^{65,66} However, Raman studies of the nCB series are largely unexplored. Only reports such as the Kang *et al.* studies of the temperature-dependent Raman spectroscopic study of the nematic liquid crystal 4-n-pentyl-4'-cyanobiphenyl, which showed the asymmetric bands in the C≡N stretching region were found to vary with changing temperature, are found in the literature.⁷¹ Another research conducted on a phthalocyanine compound that contains four alkoxysubstituents, having some Raman studies has yielded precise data on the arrangements of the molecules present in the liquid crystal phases. The study employed absorption, photoluminescence, and Raman scattering techniques, and the quantitative information about molecular alignment was extracted from analyzing polarized Raman

spectra of samples aligned in a homeotropic manner. The point dipole exciton theory⁷² and the coupled oscillator model⁷³ suggest that the fluorescence quantum yield in precisely stacked face-to-face aggregates is insignificant. Under irradiation, a monomeric emission can be seen, which implies that localized heating may cause the generation of disordered domains.⁷⁴ For absorption and fluorescence studies, many works can be found in the literature. For instance, a study by David *et al.*, four different forms of 4-cyanobiphenyl, 4-cyano-4-propyloxybiphenyl, 4-cyano-4'-octylbiphenyl, and 4-cyano-4-octyloxybiphenyl have had their absorption and fluorescence spectra examined in relation to solvent polarity and solute concentration. The authors concluded that the planar state polarized along the long axis of the molecule is the source of the fluorescence, which shifts to longer emission wavelength and loss of vibrational structure on increasing the polarity of the solvent environment. This red-shift is attributed to an orientation relaxation process of the solvent cage in the electric field of the excited molecule, where the dipole moment is larger than in the ground state.⁵⁹ In addition, solvent-dependent measurement of the dielectric constant of the alkylcyanobiphenyls (0CB–12CB) was carried out.⁷⁰ The influence of the number of carbon atoms on the molecular dipole moment was evaluated in different solvents; cyclohexane, hexane, carbon tetrachloride, and benzene. There were no significant changes in the dipole moment of the nCB observed in benzene and carbon tetrachloride while an obvious difference between the shorter alkyl chain and longer alkyl chain nCB is seen in hexane and cyclohexane.⁷⁰ Differently, Kukielski studied the FTIR, vibronic absorption, and emission spectra of 2CB and 5CB in nonpolar, moderately polar, and polar solvents. For these flexible molecules, a shift in the band position and changes in

shape have been seen in these two types of spectra as the solvent is varied. The cause of these findings was attributed to the influence of various contributions on the vibration and vibronic spectra as well as intra- and intermolecular interactions.^{60,75}

The solvatochromic behavior of liquid crystal molecules is prompted by the type and extent of interactions between the solutes and solvent in the solution media.^{76–78} The competition that exists between solute-solvent and solute-solute interactions affects the kind of solvatochromic behaviors the solute molecules exhibit. It is possible to gauge the solvent influence in solution using solvatochromic parameters or solvent polarity scales.⁷⁹ Organic solvents with various polarities cause solvent-sensitive molecules to modify their UV-Vis absorption or fluorescence emission band locations, intensities, and shapes.⁶⁹ Similarly, another work conducted systematic photophysical studies on Tricycloquinazoline-based discotic liquid crystals (TCQDLC) in different organic solvents and noticed a redshift in the emission spectra as the solvent polarity increased. Also, the observed photophysical properties suggest that various non-fluorescent DLC systems can be imaged with the help of the TCQDLC molecule.⁸⁰

Furthermore, the solvent effect on the absorption and fluorescence of other classes of liquid crystal molecules has been extensively reported.^{56,68,74,80–83} For example, a study on the spectral shift of the UV-Vis spectra alkoxycinnamic acid derivatives in different solvents having $\pi \rightarrow \pi^*$ transitions in the UV range, and $n \rightarrow \pi^*$ transitions in the visible range showed a decrease in the excited state energies and weak exciton coupling.⁵⁶ Also, liquid crystal molecules of benzoic acid derivatives, alkoxybenzoic acid⁸³ and alkyloxybenzoic acids^{68,82} existing as monomers and dimers were reported to be highly solvatochromic having larger excited state dipole moment than the ground

state dipole moment. Some other discotic liquid crystals were equally found to shift to longer wavelengths as the solvent polarity is tuned.^{74,80} Such studies facilitate the evaluation of Linear Free Solvation and Energy (LFSE) and solute-solvent interactions.^{68,74,82,83}

Furthermore, the results of the studied photo-acoustic spectra of alkylcyanobiphenyls for absorption and fluorescence were analyzed in a different study using the one-dimensional PA theory for condensed samples, leading to the conclusion that the nCB does not reveal features of twisted-excited state relaxation, but they relax to a more planar conformation in the first-excited-singlet state after photoexcitation.⁸⁴ The dielectric and thermodynamic properties of members of the nCB series appear to have higher dielectric permittivity as the alkyl chain becomes longer.^{85,86} Oladepo reported the temperature-dependent fluorescence and phase transition of 5CB and 6CB,³³ as were some other previous studies on phase transitions.^{32,57,58}

2.2 Liquid Crystal-Based Sensors

Considering the LC-based sensors, Oladepo has rationalized that they provide a quick, convenient, and affordable method of detecting heavy metals with reasonable sensitivity.⁴⁵ This is in agreement with the work of Han *et al.*, who found that when in contact with air, the droplet patterns had an optical appearance that resembled dark crossing textures, which matches the liquid crystal homeotropic orientation. The alkyl chain of the OTS-treated surface and the liquid crystal molecule steric contact produced this effect. Phosphate buffered saline (PBS) solution was added while the acid-doped LC patterns were still visible as black crossing patterns. The homeotropic anchoring of 5CB was assisted by the self-assemblies of the deprotonated stearic acid molecules at

the LC-aqueous interface. The bright optical images of the acid-doped LC droplet patterns treated with PBS solution having heavy metal ions revealed planar orientations of 5CB at the LC-aqueous interface.⁵⁴ In a similar vein, Singh *et al.* reported that recently synthesized amphiphilic potassium N-methyl-N-dodecylthiocarbamate (MeDTC), was doped with 4-cyano-4-pentyl biphenyl (5CB) LC, which aligns liquid crystal molecules at the interface with aqueous solution and functions as chelating ligands for mercury as seen in Figure 2.1. The picture of LC underwent a dark-to-bright transition when Hg^{2+} ions from an aqueous solution were introduced to this sensor device during incubation. The Hg^{2+} ions and the dithiocarbamate chelating group of MeDTC at the aqueous contact quickly and steadily formed a complex, which caused the LCs' orientation to be disturbed and produced a brilliant texture. The system can detect water Hg^{2+} ions down to 0.5M. Other metal ions, which are typical impurities in water and include Cu^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+} , Mg^{2+} , Ca^{2+} , and Na^{+} did not cause this sensor to respond.⁴⁶

Furthermore, fluorescence detection systems have seen significant success due to their excellent precision and high signal-to-noise ratio.⁸⁷ As reported by Du *et al.*, they studied novel fluorescence sensors for detecting Pb^{2+} ions in solution produced by liquid crystals doped with a luminogen that induces aggregation-induced emissions. The process is on account of the change in fluorescence intensities triggered by the rupture of an ordered LCs arrangement in the presence of Pb^{2+} , caused by DNAzyme and its catalytic cleavages. The low detection limit of the suggested fluorescence sensor is 0.65 nM, two orders of magnitude less than that of liquid crystal-based optical sensors that were previously described. The Pb^{2+} fluorescence sensor has a wide

detection range (from 20 nM to 100 M), and it precisely identifies Pb^{2+} ions from a variety of heavy metal ions, making it a very selective and sensitive, straightforward, inexpensive Pb^{2+} detection approach with potentials in chemical and biological applications.⁴⁷ Also, the fluorescent "Turn Off" phenomenon was successfully used by Jana *et al.* to efficiently detect the nitrite anion in an aqueous solution. Proper microscopic and spectroscopic investigations were done to learn more about the quenching mechanism. The linear detection range and limit of detection of the sensor were both excellent, measuring 2.3 M–7.7 mM and 7.9 nM, respectively.⁸⁸

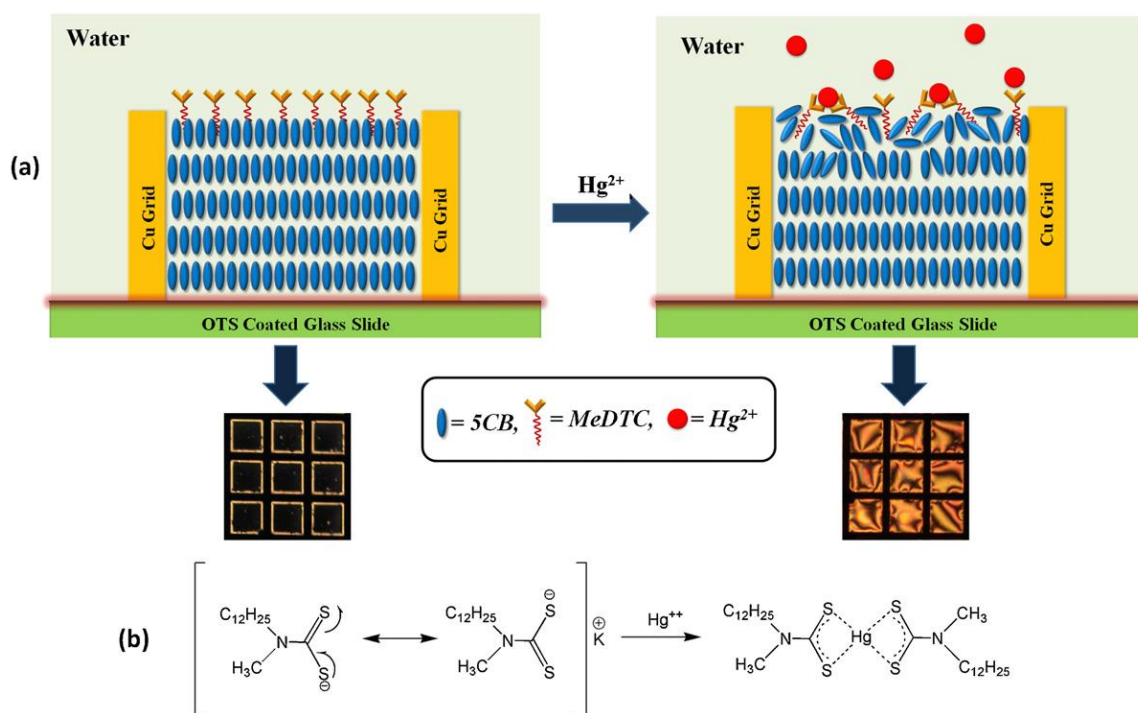


Figure 2.1 (a) Diagram showing the orientational changes of 5CB molecules doped with MeDTC at the interface (b) MeDTC and Hg-MeDTC resonance hybrid structures⁴⁶

Additionally, when 4-cyano-4'-pentylbiphenyl (5CB) was doped with tetradecyl 4-aminobenzoate (14CBA), cast on glass substrates, and submerged in aqueous solutions

devoid of nitrite, the LC orientation was planar and the LC images were bright, according to Ho *et al.*⁴⁹ Nitrite-induced reactions with alkyl anilines resulted in corresponding, positively charged diazonium ions, that aligned at the aqueous-LC interfaces causing homeotropic orientations of LC. The LC image underwent a bright-to-dark transition as a result. Different LC-based techniques for sensing have been developed for detecting parameters like enzymatic activity,^{44,87} biomolecular interactions,⁴⁴ and polymerization.⁸⁹ These techniques take advantage of the orientation behavior, anisotropic properties, and molecular sensitivity of these materials to convert nanoscopic chemical interaction into optical signals.⁴⁵

CHAPTER

MATERIALS AND METHOD

3.1 Materials

The 4'-alkyl-4-cyanobiphenyls (nCB) liquid crystals, with varied substituents from pentyl, hexyl, heptyl, octyl, nonyl, and decyl (Scheme 5.1) were purchased from Sarchem Laboratories Inc. (Atlantic Highlands, NJ) and were put to use without further purification. For the sensor development, slide glass was obtained from Blue Star, Mumbai, sodium dodecyl sulfonate (SDS) from Molecule-On (Auckland, New Zealand), and (3-aminopropyl)triethoxysilane APTES from Sigma Aldrich (St. Louis, MO). The solvents employed during the analysis were purchased as follows: N, N-dimethylformamide, 1-propanol, tetrahydrofuran, dichloromethane, and n-hexane from Sigma-Aldrich (St. Louis, MO); acetone from AppliChem ITW Reagents (Corso Milano, Italy); methanol, ethanol, acetonitrile, diethyl ether and 1,4-dioxane from Fisher Scientific (Loughborough, UK); while benzene was from Sisco Research Laboratories (New Mumbai, India). The parameters associated with the solvent's spectroscopic properties are presented in Table 3.1.

3.2 Preparation of APTES-Coated Glass Slide

Glass slides were first cleaned for two hours using concentrated sulfuric acid. After this, the slides were washed with distilled water, methanol, and ethanol, and then made to dry under nitrogen. After being thoroughly cleansed, the substrates are kept through

the night in an oven at 120⁰ C. The cleaned glass slides were submerged in an (3-aminopropyl)triethoxysilane APTES (0.12 mL)/n-heptane (50 mL) solution for thirty minutes to functionalize them with APTES. Then methylene chloride was used to rinse the substrates, and they were dried using a N₂ stream.

3.3 Preparation of Optical Cells

Nematic LC, 5CB was dissolved in ethanol after being doped with sodium dodecyl sulfate SDS (20% w/w). The isotropic point of this solution is reached by heating it to 36 °C. In accordance with standard procedure, TEM grids were put atop an APTES-coated glass slide, and 2μL of 5CB doped with SDS was dispensed onto the TEM grid.¹⁶

3.4 Examination of LC Textures

The optical textures of nematic 5CB were photographed using a polarized light microscope. The LC samples were positioned between two crossed polarizers on a spinning circular platform. Using an objective lens and crossed polarizer, all photos were acquired. A digital camera was used to take pictures of each LC cells optical appearance while it was connected to a compatible polarized light microscope. By analyzing textures using a grayscale of intensities and their luminosities, textures were quantified.

3.5 Raman Spectroscopy

solutions of the liquid crystal samples were made by dissolving the individual solute LCs in the various solvents to give a known concentration. The average concentration for all the solutions is 0.03M. The room temperature Raman spectra of the LC molecules in the different solvents were measured using a Lab Ram HR Evolution Raman spectrometer (Horiba Scientific, Kyoto, Japan) equipped with an internal He-Ne 17 mW laser at a 633 nm excitation wavelength, with the laser light focused using a 50x objective on an open vial that contained the LC solution. 25% power was used. Detection of the Raman scattering was via a charged coupled device (CCD) detector, with a spectral acquisition of 6 seconds over 6 accumulations. The solvent spectra were also acquired and compared with the pure LC sample spectrum in each case.

3.6 UV-Visible Absorbance Measurements

The ground state absorption of 4-cyano- 4' -alkyl biphenyls (nCB) extremely dilute solution of the liquid crystals was made from the pure samples and each of the solvents mentioned above at room temperature using a GENESYS 10S Thermo Scientific UV-Vis Spectrophotometer (Massachusetts, USA). The absorbance was measured using a micro quartz cuvette having a 10-mm path length (Cole-Parmer, Vernon Hills, IL, USA).

3.7 Fluorescence Measurement

The pure liquid crystals were dissolved in the different solvents to yield an average concentration of 0.03M solutions of the liquid crystal samples. An FLS920 fluorescence spectrophotometer (Edinburgh Instruments, Livingston, UK) was used to measure each fluorescence emission spectrum. The emission wavelength was fixed at 280 nm, and the excitation wavelength ranged from 300 to 600 nm. Fluorescence measurements of the solutions were performed using a sub-micro quartz cuvette with a 10-mm path length (Cole-Parmer, Vernon Hills, IL, USA). Throughout the measurements, the spectra were obtained at room temperature.

3.8 Data Analysis

The Raman spectra of all the solutions were processed using LabSpec 6. The spontaneous Raman spectra were analyzed as previously described⁹⁰. We used data normalization in our spectrum analysis to establish uniform intensity scales across the spectra for better comparisons. The spectral values were normalized by multiplying them by a scale factor. All the spectra were processed with OriginPro 2019 (Northampton, MA, USA)

Table 3.1 Some empirical parameters of the solvent employed in this work.^a

Solvent	Refractive Index	Dielectric Constant	Acceptor Number	Donor Number	Kamlet-Taft Dipolarity	Polarizability	Dipole moment
Acetone	1.3586	20.7	12.5	17	0.683	6.47	2.69
Acetonitrile	1.3441	36.6	18.9	14.1	0.713	4.44	3.44
Benzene	1.4957	2.28	8.2	0.1	0.588	10.44	0
Dichloromethane	1.4241	9.08	20.4	1	0.82	8.75	1.14
Diethyl ether	1.3524	4.34	3.9	19.2	0.273	8.98	1.15
1,4-Dioxane	1.4224	2.1	10.8	14.8	0.553	8.63	0.45
N, N-Dimethyl formamide (DMF)	1.4305	38.3	16	26.6	0.875	7.93	3.86
Ethanol	1.3614	24.3	37.9	19.1	0.54	5.13	1.66
Methanol	1.3284	32.6	41.5	19	0.586	3.21	2.87
N-Hexane	1.3749	2.02	0	0	0	11.63	0.08
1-Propanol	1.3856	20.1	33.7		0.52	6.96	3.09
Tetrahydrofuran (THF)	1.4072	7.52	8	20	0.576	7.97	1.75

^aDonor number^{91,92}, Acceptor number^{91,93}, Kamlet-Taft Dipolarity^{94,95}, Polarizability⁹⁶

CHAPTER

LIQUID CRYSTAL-BASED SENSOR

4.1 LC-Based Sensor Development

The use of 5CB to develop an LC-based sensor is an area that has been largely exploited.⁴⁵ Many of the work takes advantage of the high optical response of 5CB to any change in its surrounding environment, characteristic of the foreign material.^{15,46,54,97,98} For instance, electrostatic interactions between a positively charged poly-L-lysine (PLL) and a negatively charged phospholipid were the focus of Zhang *et al.* investigation of the orientation change of 5CB. Positively charged PLL were applied to the LC-aqueous solution interface to induce the orientation change of 5CB (from homeotropic to planar) at the interface, which was previously adorned with negatively charged phospholipids. They were able to create a trypsin detection system successfully owing to the electrostatic interaction and effects on the orientation state of the LC.⁹⁸ Sodium dodecyl sulfate (SDS) are example of traditional surfactant with a short alkyl chain length of 12 carbon atoms that Brake and his colleagues discovered to align the 5CB in a homeotropic orientation at the air-water/oil-water interfaces.⁹⁹ On this, we tried to observe at the aqueous-LC interface, the 5CB orientational response to SDS when a metal ion solution is introduced. TEM copper grids mounted on APTES-coated glass slides filled with 5CB doped SDS created a stable contact between the LC and the aqueous phase. The 5CB can arrange themselves in a well-defined orientation under specific conditions and when the conditions are slightly changed, they undergo an orientational transition such that when observed under a

polarized optical microscope (POM), the image appears dark or bright, depending on their orientation (Figure 4.1). The LC molecules may adopt a homeotropic alignment (perpendicular) or planar (or disordered) orientation with respect to the substrate, which is observed as a dark or bright image, respectively, under a polarized optical microscope (POM).

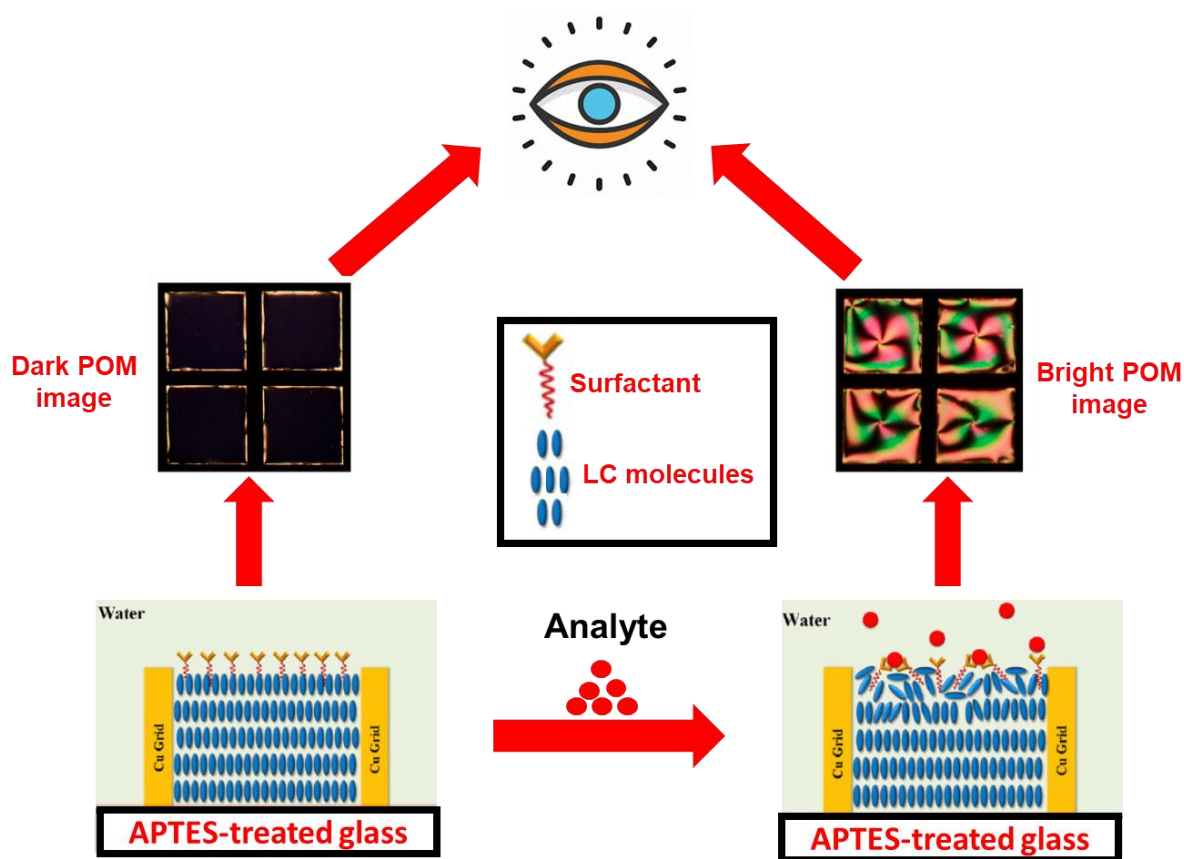


Figure 4.1 The orientational alignment of LC molecules doped with surfactant in the presence (right), in the planar orientation, bright picture, and in the absence (left), of the analyte (dark image). It is also possible to have opposite transitions, such as a bright image when the analyte is absent and a dark image when the analyte is present.

4.2 Detection of Mercury Ions in Solution

In this study, the texture of the 5CB-doped SDS as observed in Figure 4.2 (a) showed a bright image when seen between crossed polarizers before the addition of an aqueous solution. The bright appearance of the LC denotes an inclined anchoring of the LCs at the air-LC interfaces, indicating that the APTES-coated glass slide anchors the LC at the interface in an inclined or planar orientation. To the grid with 5CB-doped SDS dissolved heptane on the APTES-coated slide, a 2 μ L of 0.08M of the mercuric solution was added as seen in Figure 4.2 (b) showed a distinct transition from bright to dark image which suggested a change in orientation from inclined to homeotropic arrangement. Previous studies reported the appearance of dark textures when the 5CB is homeotropically aligned using a longer alkyl chain anchor molecule such as OTS which then switches to a bright image when the analyte is added.^{46,97} We ascribed such observed difference to the alkyl chain length of the anchor molecules in which APTES employed during our studies, having a relatively shorter alkyl chain when compared to the OTS. The shorter alkyl chain of the APTES resulted in the planar orientation of the 5CB molecules and a consequent bright texture when observed under a cross polarizer. The observation of bright-to-dark transition was previously reported by Ho *et al.* when detecting the presence of nitrites in solution using a liquid crystal-based sensing technique which indicates a transition from a planar to a homeotropic arrangement.¹⁰⁰ As a control experiment, we examined the texture of the grid by removing SDS in one case and by replacing the mercuric solution with water in the other case, as can be seen in Figure (c) and (d). The result showed a flat bright image in all cases which makes possible the inference that bright to dark transition is a consequence of

the interaction between the mercuric ion and the head of the SDS molecule that triggers the rearrangement.

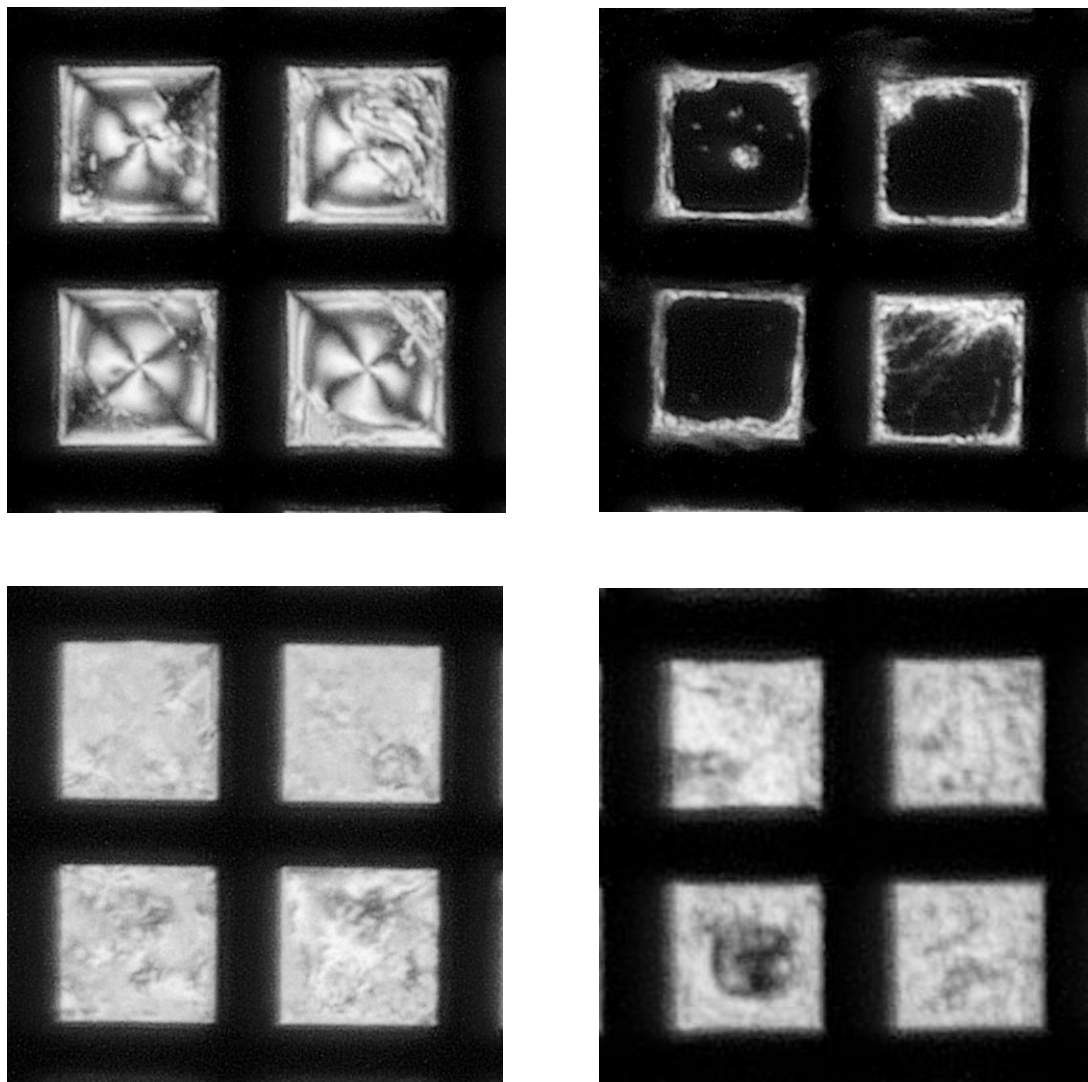


Figure 4.2 POM of 5CB-doped SDS grid patterns in heptane (a) without Hg^{2+} (b) with Hg^{2+} (c) without SDS (d) with water

4.3 Detection of Cerium Ions in Solution

In order to test for the detection of cerium ions in solution, Figure 4.4 (a) shows the 5CB-doped SDS in heptane before the addition of the metal ions. As seen, a bright image

denoting a planar or tilted alignment of the LC molecules is observed. However, the addition of 3 μ L of cerium ion solution to the TEM grid (Figure 4.4 (b)) having 5CB-doped SDS shows there was no distinct change in the optical image which suggested no apparent interaction between the metal ion and SDS that can cause a planar-homeotropic realignment of the LC as in the case mercury. Such observations are indicative of the potential selectivity of the sensor towards the detection of mercuric ions in solutions.

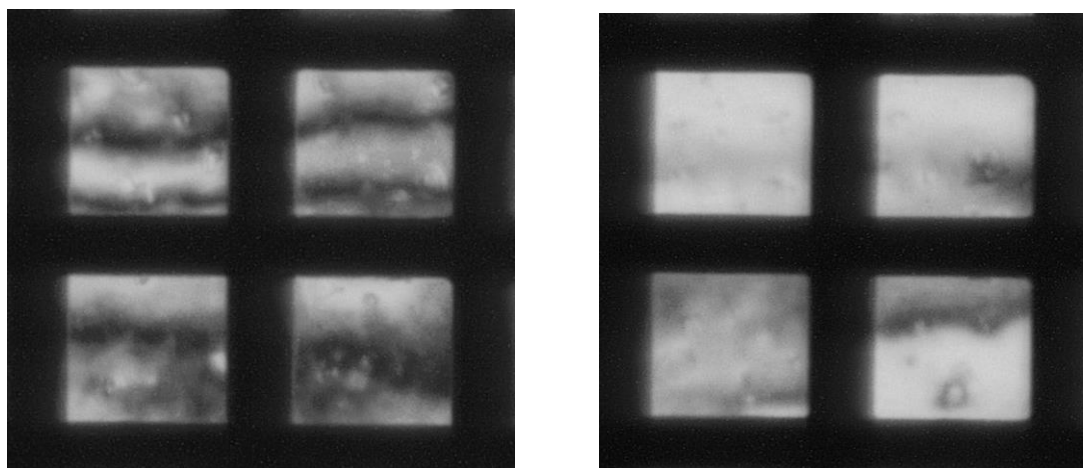


Figure 4.3 POM of 5CB-doped SDS grid patterns in heptane (a) without Ce^{2+} (b) with Ce^{2+}

4.4 Effect of Solvents on the Liquid Crystal Arrangements

In order to observe the effect of the solvent medium on the sensing process, the solvent is changed from nonpolar heptane to highly polar ethanol while keeping all other conditions the same as in the previous case. The slightly bright image seen in Figure 4.5 (a) before the addition of mercury, and the dark image (Figure 4.5 (b)) after the addition of mercury is consistent with the transition from tilted to a homeotropic arrangement of the LC molecules as triggered by mercury/SDS interactions. Under the same condition, the LC system shows no sensitivity to cerium ions in solution Figure 4.5 (c) and (d), just as in heptane. Solvent environments are known to cause an effect on the sensing behavior of heavy metal ion

sensors.^{101–103} For example, a mixed solvent ratio system was used in the detection of copper and uranium dioxide ions in water/DMSO.¹⁰¹ Not only does the change in the solvent ratio cause a change in color but also in the selectivity and sensitivity of the heavy metal ions detection.¹⁰¹ Potential interactions between the metal ions and solvent environment can increase or decrease the sensitivity of the system.^{102,103} In our own case, it is justifiable to infer that no obvious effect of the solvent medium is observed on the solvent response to the metal ions.

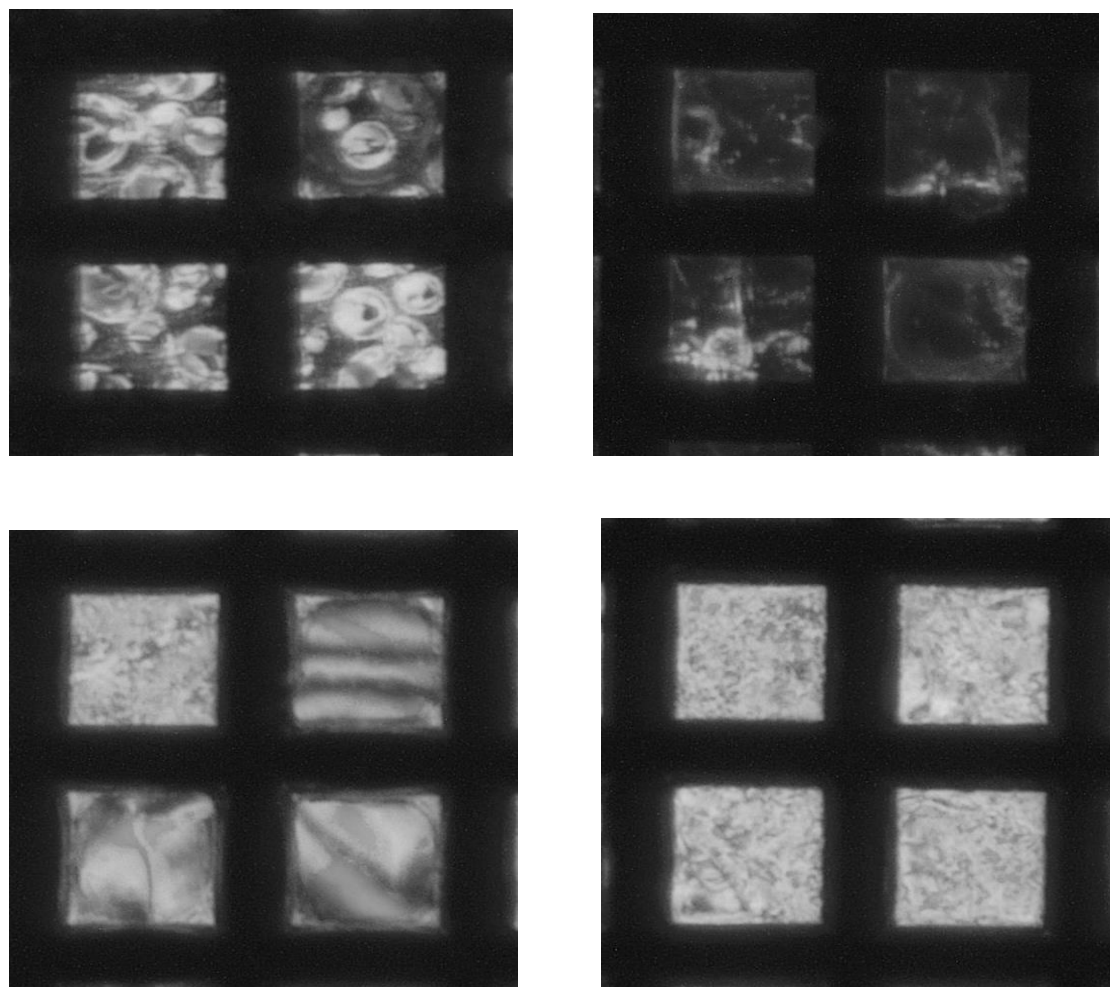


Figure 4.4 POM of 5CB-doped SDS grid patterns in ethanol (a) without Hg^{2+} (b) with Hg^{2+} (c) without Ce^{2+} (d) with Ce^{2+}

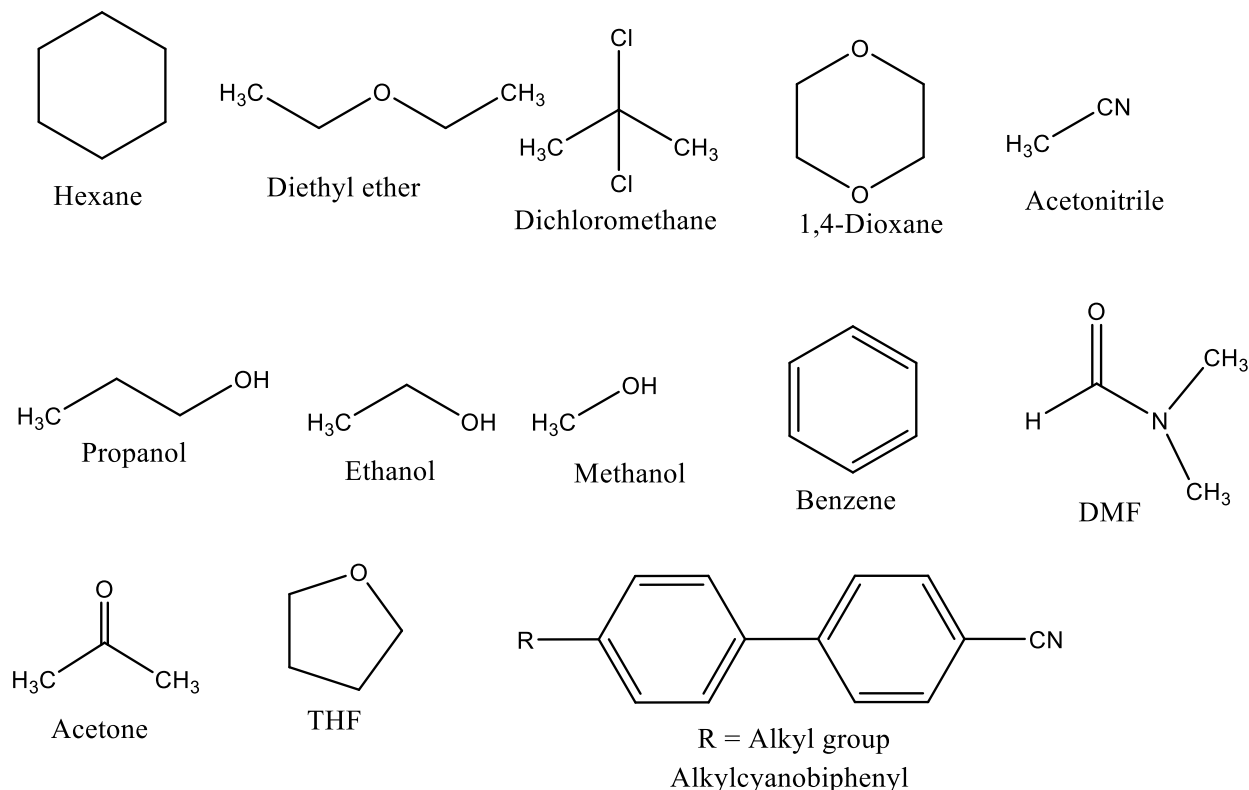
CHAPTER

SOLVENT-DEPENDENT RAMAN

5.1 Spontaneous Raman of Alkylcyanobiphenyl series

Figure 5.1 presents the Raman spectra of the pure LC molecules under study here, which exhibit several vibrational modes as shown. Assuming a C_{2v} point group, the bands related to the ring's vibrational modes in the LC molecules can be separated into four symmetry species. The in-plane A_1 ring modes appear in the range $3073\text{-}3079\text{ cm}^{-1}$, $1607\text{-}1609\text{ cm}^{-1}$, $1522\text{-}1527\text{ cm}^{-1}$, $1239\text{-}1247\text{ cm}^{-1}$, $1179\text{-}1186\text{ cm}^{-1}$, $1114\text{-}1125\text{ cm}^{-1}$, $1020\text{-}1023\text{ cm}^{-1}$.¹⁰⁴ The out-of-plane A_2 mode appears within $776\text{-}781\text{ cm}^{-1}$.¹⁰⁵⁻¹⁰⁷ Other significant peaks in the range of $1282\text{-}1287\text{ cm}^{-1}$ and $636\text{-}629\text{ cm}^{-1}$ can be assigned to the in-plane B_2 mode, while out-of-plane B_1 mode appears within $823\text{-}835\text{ cm}^{-1}$ and $805\text{-}815\text{ cm}^{-1}$. In addition, some bands contributed by the substituents fall within $2222\text{-}2230\text{ cm}^{-1}$ and are assigned to $\nu(C\equiv N)$, $479\text{-}484\text{ cm}^{-1}$ band has been assigned to $\delta_{as}(CN)$, $405\text{-}411\text{ cm}^{-1}$ assigned to $\gamma_s(CN)$, $2862\text{-}2897\text{ cm}^{-1}$ assigned to $\gamma_s(CH_2)$ and $2882\text{-}2970\text{ cm}^{-1}$ band was assigned to $\gamma_{as}(CH_2)$. The assignment of these vibrational modes is consistent with the report of Kang *et al.* on the study of temperature-dependent Raman scattering of 5CB, which found the $\nu(C\equiv N)$ stretching band to split within the temperature range of -10 and $20\text{ }^{\circ}\text{C}$, implying the presence of solid crystalline polymorphism.⁷¹ The Raman spectra of the alkylcyanobiphenyl LC molecules in acetone, acetonitrile, benzene, DCM, dioxane, DMF, diethyl ether, ethanol, hexane, methanol, propanol, and THF as presented in Scheme 5.1 were obtained in order to examine their sensitivity to the solvent environment. Throughout

this paper, the solvent properties, which include polarizability, acceptor and donor number, and polarity will be used as necessary to explain the differences in the observed Raman shifts with changes in the solvent environment.



Scheme 5.1 The structure of the solvents and the LC molecules used in the study

Generally, the spectral patterns are similar for each LC sample in all the solvents investigated in this study. In all the spectra of the samples in the various solvents, the focus of this study is on four distinctive Raman bands of the LC molecules, which were observed within the range $2222\text{--}2229\text{ cm}^{-1}$, ascribed to $\text{C}\equiv\text{N}$ stretch; $1596\text{--}1611\text{ cm}^{-1}$ ascribed to $\text{C}\text{--}\text{C}$ aromatic ring stretch; $1274\text{--}1289\text{ cm}^{-1}$ from the $\text{C}\text{--}\text{C}$ stretching of the biphenyl link; and $1169\text{--}1185\text{ cm}^{-1}$ for the $\text{C}\text{--}\text{H}$ in-plane deformation. We focus on these four bands because they have appreciable intensities that can be more accurately compared with the pure

sample spectra, as most of the other bands are virtually invisible when dissolved in the solvents.

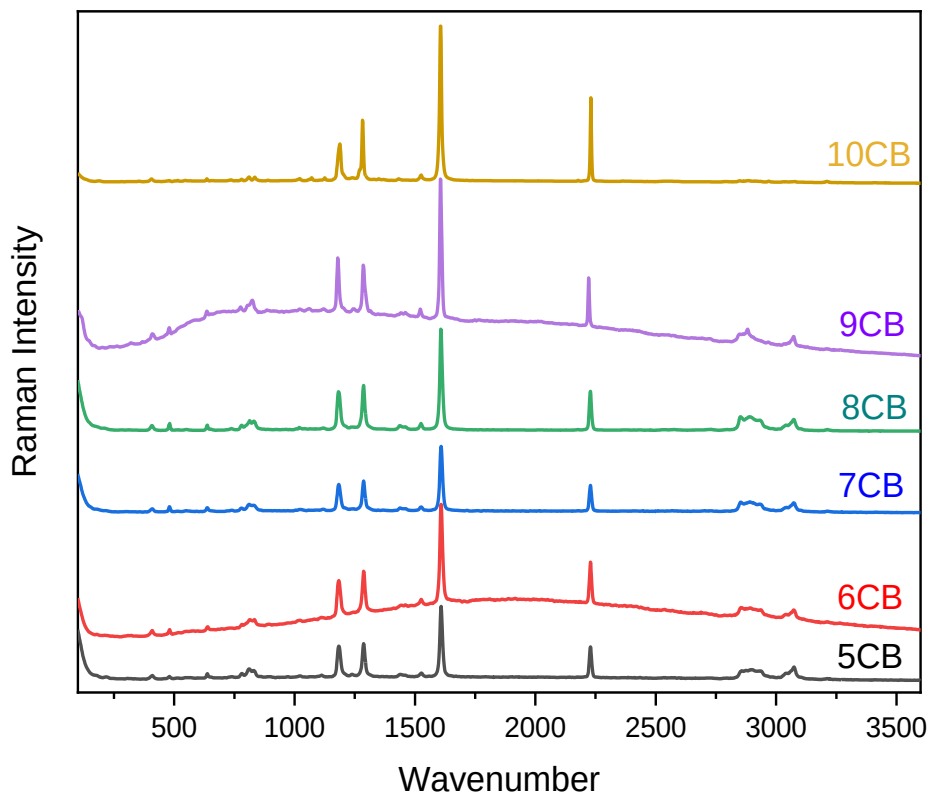


Figure 5.1 Raman spectra of pure LC samples

5.2 Alkylcyanobiphenyl in Polar Protic Solvents

Wavenumber shifts are observed in the solvent-dependent Raman spectra of the LC molecules thereby providing vital information regarding the nature of solute-solvent interactions in this family of molecules. Raman spectra of the LC samples examined in methanol are presented in Figure 5.2. As seen in the figure, only four distinct bands are contributed by the solute LC molecules. Based on the spectral patterns of all the samples,

and the assignment preciously given above, the peaks around 2220, 1600, 1280, and 1180 cm^{-1} are ascribed to $\text{C}\equiv\text{N}$ stretching mode, C–C aromatic ring breathing, C–C biphenyl linking stretch, and C–H in-plane deformation, respectively. In 5CB, the cyano group is well solvated, thus $\text{C}\equiv\text{N}$ stretching mode that is originally at 2229cm^{-1} in the pure sample shifted to a lower wavenumber of 2220cm^{-1} as a result of interaction between the electrons of the $\text{C}\equiv\text{N}$ bond and the hydrogen of methanol (HOCH_3).¹⁰⁸ Furthermore, the electron density of the biphenyl makes it capable of interacting with HOCH_3 molecules, thus the 5CB ring breathing positioned at 1609 cm^{-1} in the pure sample is shifted to 1598 cm^{-1} .^{109–111} Similarly, the peak ascribed to the C–C biphenyl link stretching mode is red-shifted from 1287 cm^{-1} for the pure 5CB to 1277 cm^{-1} when dissolved in methanol. The C–H in-plane deformation of 5CB originally at 1184 cm^{-1} is red-shifted to 1171 cm^{-1} as induced by the surrounding methanol molecules. The spectrum of 6CB in methanol is also shown in Figure 5.2, whereby in comparison to the pure 6CB spectrum shown in Figure 5.1, the cyano stretching mode remains unshifted at 2229 cm^{-1} as in the pure sample, so this band does not appear to be affected by the solvent molecules. Similarly, other Raman bands from 6CB in methanol comprising 1608, 1288, and 1182 cm^{-1} assigned to C–C aromatic ring breathing, C–C biphenyl link stretch, and C–H in-plane deformation, respectively, are not significantly affected by the solvent environment. On the other hand, the Raman spectra of 7CB are significantly affected by the methanol solvent. For example, the pure 7CB peak at 2229 cm^{-1} ascribed to $\text{C}\equiv\text{N}$ stretching mode is shifted to 2221 cm^{-1} in methanol, while the C–C aromatic ring breathing mode around 1609 cm^{-1} is shifted to 1599 cm^{-1} in methanol.^{31,108} Moreover, the C–C biphenyl link stretch is shifted from 1287 cm^{-1} in pure 7CB to 1278 cm^{-1} in methanol. The C–H in-plane deformation originally around 1184 cm^{-1}

¹ is also shifted to 1172 cm⁻¹ in methanol. In the case of 8CB, 9CB, and 10CB, which have longer alkyl chains, the C≡N stretching band around 2229 cm⁻¹ is shifted to 2220, 2221, and 2222 cm⁻¹, respectively, in methanol. Also, the ring breathing mode around 1609 cm⁻¹ in these three LC molecules was shifted to 1599 cm⁻¹ in methanol. For the C–C biphenyl link stretching band, there is a shift in the wavenumber from 1287 to 1279 cm⁻¹ for 8CB, 1285 to 1279 cm⁻¹ for 9CB, and 1282 to 1278 cm⁻¹ for 10CB. Similarly, the C–H in-plane deformation shifted from 1182 to 1172 cm⁻¹ for 8CB, 1179 to 1174 cm⁻¹ for 9CB, and 1189 to 1173 cm⁻¹ for 10CB.

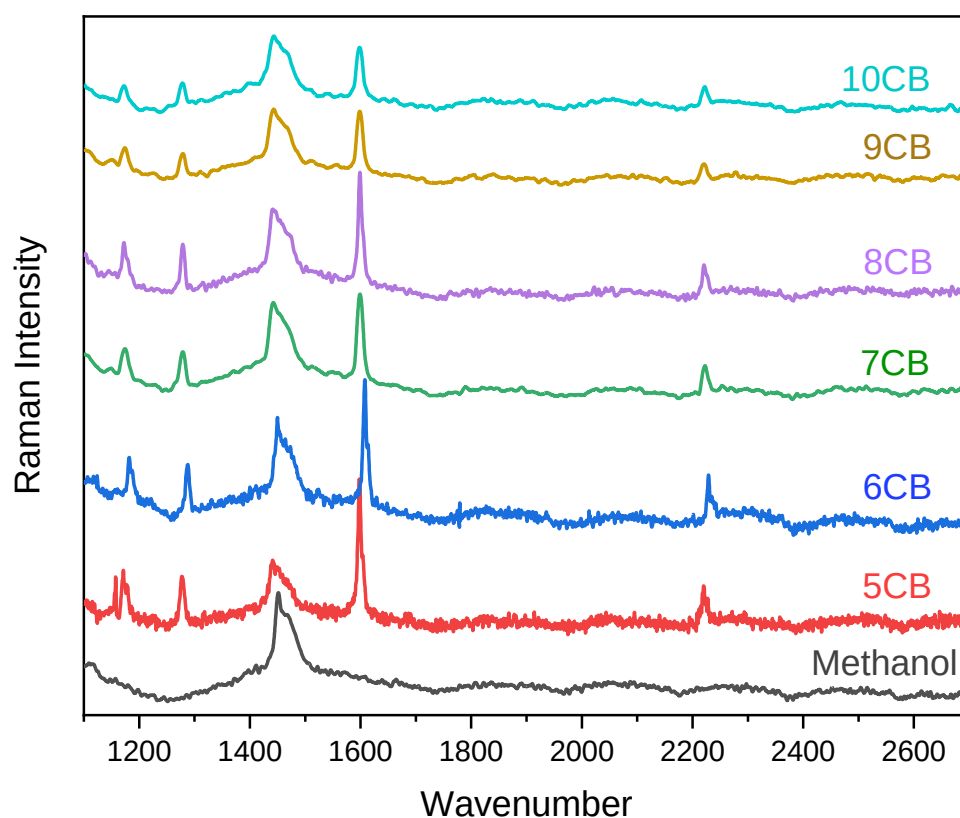


Figure 5.2 Raman spectra of LC samples in methanol. The spectrum of the solvent is also shown for reference.

According to the theories developed by Schweizer and Chandler, the intermolecular repulsive forces against the stretching vibrator of the solute molecule produce a blue-shift, and the attractive forces produce a red one.¹¹² The observed red-shift in 5CB and 7CB could thus be a result of the participation of the cyano group in a significant attractive interaction with the methanol molecules via hydrogen bonding. Zakerhamidi and Shahrabi characterized some cyanobiphenyls in order to obtain their solvatochromic polarity parameters. Their findings concluded that cyanobiphenyls have higher values of hydrogen bond acceptor and dipolarity/polarizability, which suggest that there is a strong interaction between the cyanobiphenyls and polar groups, as well as hydrogen bond donors.⁸¹ The interaction of the cyano group with the methanol solvent molecules is between the electron-rich triple bond of the $C\equiv N$ group and the hydrogen of the hydroxyl group present in methanol. Such interaction stabilizes the vibrational mode involved as reported in the study of solvation of *p*-aminobenzonitrile in water and methanol, performed experimentally and via DFT calculations.¹⁰⁸ The authors interpreted the observed low-frequency shift in the structure as the result of weakening of the $C\equiv N$ bond by the dipole in the CH_3OH molecule, which seems to be hydrogen-bonded perpendicularly to the $C\equiv N$ triple bond (π -type hydrogen bond).¹⁰⁸ The observed similarity in shift patterns in 5CB and 7CB can be explained by the findings of Kobayashi *et al.* on the odd-even effect on the molecular alignment of the alkylcyanobiphenyls using a resonance Raman probe.³¹ The result indicated the better orientation of the odd-numbered alkyl groups with the rigid core compared with those of the even-number.³¹ This could explain why there was no shift observed in 6CB, while 5CB and 7CB show similar shift patterns. The alkyl chain of 6CB is relatively shorter and has a tilted alignment with the rigid core, which induces some

repulsive interactions with solvent molecules. The repulsion causes destabilization of the stretching modes that nullifies the effect of interaction with the methanol molecules.^{29,112}

In the case of 8CB, 9CB, and 10CB, where the alkyl chain is long enough, the stabilization of the vibrational modes to a similar extent is observed across all the solvents used in this study, regardless of polarity and other properties of the solvents. An explanation for this could be linked to dimers or multimers formed in solution and the folding back effect.^{113,114}

The nCB molecules of $n \geq 8$ have been reported to substantially form anti-parallel dimers in an isotropic solution.^{114,115} The dimerization of these molecules is established by examining the Kirkwood factor (g_k) via dielectric relaxation and subsequently confirmed by a downward shift in the IR band. Although lower members of the nCB saw the existence of this phenomenon, the dimerization constant is very significant for the longer chain nCB molecules. Consequently, the stabilization of these dimers is facilitated by the available hydrogen bond interaction between the cyano group of the longer chain nCB and the solvent environment thereby resulting in red-shift. Additionally, owing to the longer terminal alkyl chain of these molecules, the folding back effect could play a key role in the stabilization of the stretching modes. The folding back effect could be observed in molecules having phenyl rings at the end of a longer alkyl chain, which yields a g1g3g4 conformer that folds the alkyl chain back towards the phenyl rings, thereby providing an electron-rich π cloud to interact with the alkyl chain through attractive dispersion forces that are rather stronger than between two alkyl chains.^{113,116} Bright *et al.* presented the influence of alkyl chain length on di-n-alkylpolyfluorenes (pentyl to decyl) in a dilute solution. As reported, the folding back enhances the available van der Waal force, which stabilizes the steric repulsion.¹¹⁷ Essentially, when the alkyl chain folds, it comes in close

proximity with the aromatic core of the molecule, providing additional intramolecular interaction that gives importance to the alkyl chain in the intermolecular interaction. Hence the behavior of 8CB, 9CB, and 10CB is very similar in all the solvents studied in this work. However, as the alkyl chain becomes longer, the observed shifts show that the odd-even effect is not significant, given the similar shifts in the longer 8CB, 9CB, and 10CB with no regard to the effect.

The biphenyl aromatic rings are rich in electrons and are polarizable, which makes them capable of acting as hydrogen bond acceptors. As Levitt and Perutz have rationalized, the aromatic ring centers are good hydrogen bond acceptors with about half the strength of the normal hydrogen bond.¹¹¹ Also, Zhao *et al.* studied the effect of hydrogen bonds on aromatic rings as acceptors using Raman and IR spectroscopy. They found the IR spectra show large red-shifts of the symmetric OH-stretching transitions of the H₂O-complexes and CH₃OH-complexes, together with large intensity enhancement.¹⁰⁹ Matisz *et al.* also performed a computational study of the methanol-benzene cluster and found a very stable cluster characterized by a hydrogen-bonded CH₃OH chain interacting with benzene via π – HO and O–HC (benzene) hydrogen bonds.¹¹⁰ In this case, the aromatic C–C modes engage in a hydrogen bond interaction with the protic hydrogen of methanol, which consequently stabilizes the ring modes and induces the observed red-shifts. In addition, the aromatic rings are capable of acting as hydrogen bond donors with the OH of methanol, which results in significant stabilization of the C–H deformation mode to lower wavenumber.

As can be seen in Figure 5.3 and Figure 5.4, the position of the Raman bands of the LC molecule is very similar in both ethanol and propanol. In each case, the vibrational bands

of 5CB are shifted to a lower wavenumber. For instance, the cyano stretching mode is shifted from 2229 cm^{-1} in the pure sample to 2220 and 2219 cm^{-1} in ethanol and propanol, respectively, as a result of hydrogen-bonding with solvent molecules, while the C–C aromatic ring breathing, C–C biphenyl link stretch, and C–C in-plane deformation are shifted from 1609 , 1287 , and 1184 cm^{-1} in pure samples to 1598 , 1277 , and 1171 cm^{-1} , respectively, in both solvents. For 6CB and 7CB, peak positions are not affected in ethanol and propanol. The cyano stretching mode appears at 2229 cm^{-1} , the same position at which the mode is observed in both pure samples. Likewise, other vibrational modes of the 6CB and 7CB are not shifted, the bands appear at 1608 , 1287 , and 1180 cm^{-1} for the C–C aromatic ring breathing, C–C biphenyl linking stretch, and C–C in-plane deformation, respectively. The 6CB and 7CB have intermediate alkyl chain lengths, and the solvent molecules are slightly bulkier than methanol, therefore the stabilizing effect of hydrogen-bonding established between the stretching modes and solvent molecules is countered by steric repulsion with the alkyl chains,¹¹⁸ and so the modes are not shifted in ethanol and propanol. As mentioned above, the vibrational modes of 8CB, 9CB, and 10CB experienced shifts to the same band positions in all solvents, including ethanol and propanol. In these solvents, the cyano mode is shifted from 2229 , 2222 , and 2230 cm^{-1} for the pure samples to around 2220 , 2221 , and 2222 cm^{-1} for 8CB, 9CB, and 10CB, respectively. This is also in line with the anti-parallel dimerization and folding back effect of these LC molecules in solution.

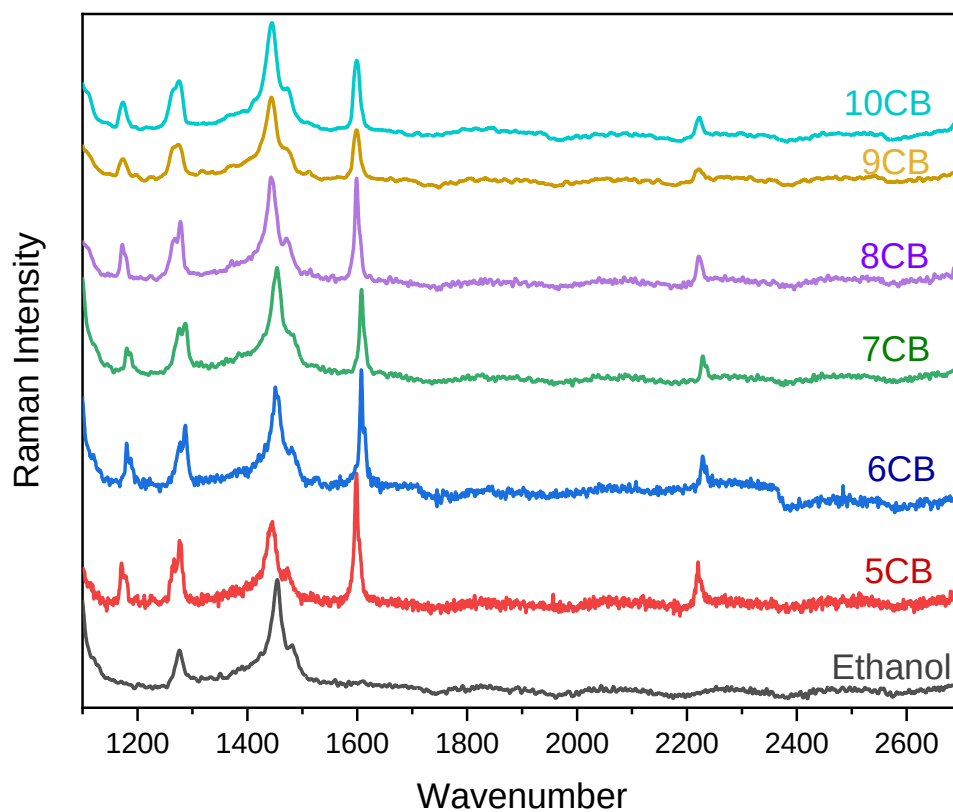


Figure 5.3 Raman spectra of LC samples in ethanol. The Raman spectrum of the solvent, ethanol, is also shown for reference.

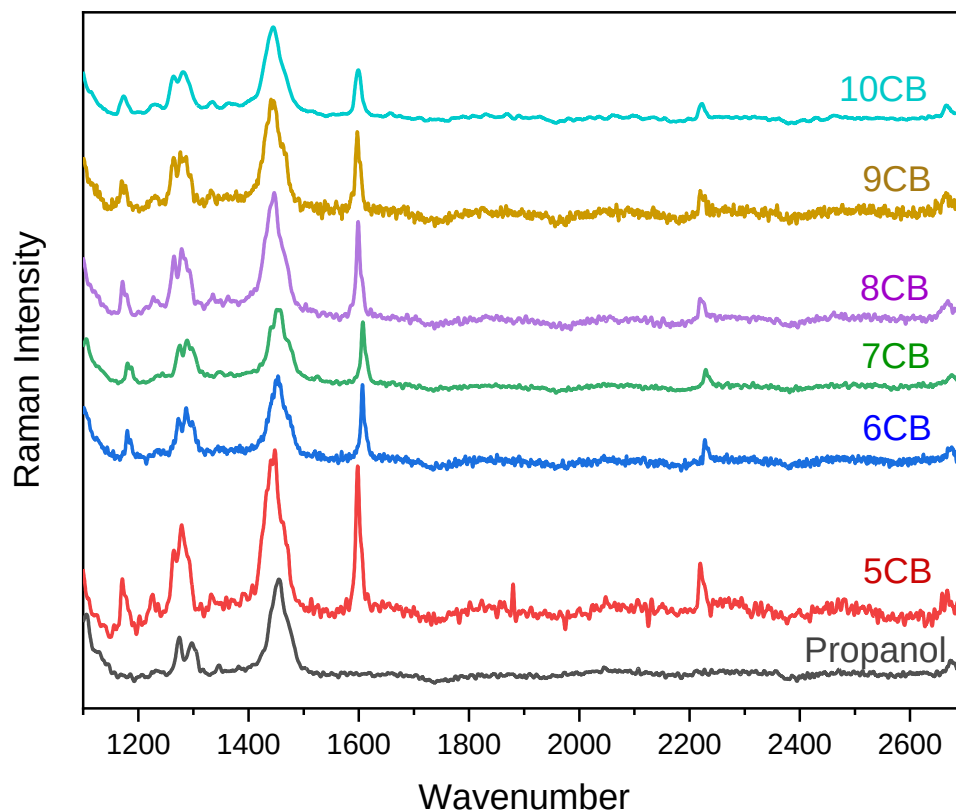


Figure 5.4 Raman spectra of LC samples in propanol. The Raman spectrum of the solvent, propanol, is also shown for reference.

5.3 Alkylcyanobiphenyl in Polar Aprotic Solvents

The solvent-dependent Raman spectra of the six alkylcyanobiphenyls were also studied in polar aprotic solvents that comprise DMF, acetonitrile, acetone, DCM, and dioxane. From Figure 5.5, the cyano stretching mode in DMF for 5CB at 2228 cm^{-1} , and 7CB at 2226 cm^{-1} , is not significantly affected when compared with the pure sample peak (2229 cm^{-1} for both) despite having a large Kamlet-Taft dipolarity constant. However, for 6CB the cyano stretching mode is largely red-shifted in DMF to 2216 cm^{-1} compared to 2229 cm^{-1} in the

pure 6CB. Moreover, a similar shift to lower wavenumber is observed in 8CB, 9CB, and 10CB from 2229, 2222, and 2230 cm^{-1} in the pure samples to 2218, 2217, and 2218 cm^{-1} , respectively. In the same vein, the C–C ring breathing and C–C biphenyl link stretch for 5CB and 7CB respectively occurs at 1606 and 1287 cm^{-1} for both solutes. The DMF solvent environment did not considerably shift the peak positions of 1609 and 1287 cm^{-1} seen in the pure samples. For 6CB modes, the aromatic ring stretch and biphenyl link stretch are shifted to 1596 and 1277 cm^{-1} , respectively. For 8CB, 9CB, and 10CB, the two stretching bands are shifted to 1597, 1598, and 1598 cm^{-1} for ring breathing, and 1279, 1279, and 1280 cm^{-1} for C–C biphenyl link stretch, respectively. Also, DMF caused no effect on the peak position of the C–H in-plane deformation of 5CB, observed at 1185 cm^{-1} . Similarly, this deformation appears at 1182 cm^{-1} for 7CB, showing no apparent shift compared to the original position of the band in the pure sample. For 6CB, the C–H in-plane deformation band is significantly shifted to 1173 cm^{-1} . As well, the band is shifted to 1174, 1175, and 1175 cm^{-1} for 8CB, 9CB, and 10CB, respectively.

Observations made in DMF show that the interactions of 5CB and 7CB in DMF are rather not strong such that short-range repulsive forces and long-range attractive forces cancel out. The observed wavenumber shift for 5CB, 6CB, and 7CB in DMF is the direct opposite of what we see in methanol. This can be explained by the odd-even effect in the alkylcyanobiphenyls. As reported by Kobayashi *et al.*, the odd-numbered nCB have better orientation and alignment with the rigid core ³¹. The cyano group is capable of forming dipole-dipole interaction with the CHO group in DMF. However, because DMF has a high donor and acceptor number, the orientation of these molecules results in some short-range repulsive forces that are fairly substantial to nullify the long-range attractive forces.

Therefore, the stabilization effect afforded by the interaction between the $\text{C}\equiv\text{N}$ of 5CB and 7CB with CHO of DMF is nullified by the repulsive interaction with the molecules, whereas in 6CB, the orientation poses no significant repulsion with DMF, thus the mode is stabilized, and shifted to 2216 cm^{-1} . Similarly, this repulsion leads to the nullification of the effect made by dipole-dipole and dipole-induced dipole interactions between the biphenyl stretching modes of 5CB and 7CB and CHO of DMF. Conversely in 6CB, the magnitude of the long-range attractive interaction outweighs the short-range repulsion such that the modes are shifted to a lower wavenumber. For the 8CB, 9CB, and 10CB, the molecules appear to show some folding back effect and good dimerization in DMF, in addition to the dipole-dipole interaction with the solvent.

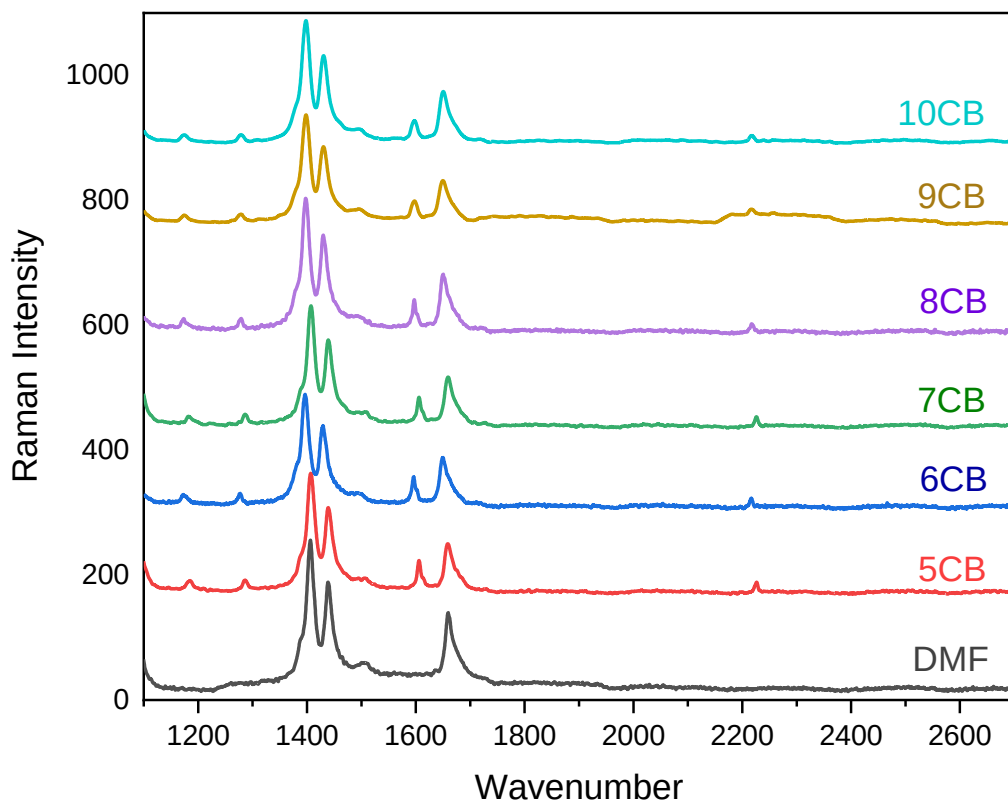


Figure 5.5 Raman spectra of LC samples in DMF. The Raman spectrum of DMF is also shown for reference.

Figure 5.6 shows the spectra of the LC samples in acetonitrile. As seen in this figure, there is an intense peak around 2253 cm^{-1} contributed by cyano groups of the solvent molecules⁶¹. Nonetheless, a weak shoulder on the left side of the peak, which appears only in LC-containing solutions is ascribed to the cyano mode of the LC samples. In the spectra, the position of the cyano stretching of 5CB and 7CB is not shifted in acetonitrile, which appears at 2229 cm^{-1} . However, the cyano stretching mode is shifted to 2220 cm^{-1} in 6CB. Similarly, the band is shifted to 2220 cm^{-1} in 8CB and 10CB, and 2219 cm^{-1} in 9CB. The

aromatic ring breathing mode also shows no shift for 5CB and 7CB by appearing at 1608 cm^{-1} , while it is shifted to 1599 cm^{-1} for 6CB. In the case of 8CB, 9CB, and 10CB, the ring breathing experienced a similar shift to around 1599 cm^{-1} . For C–C biphenyl link stretch and C–H in-plane deformation, the peak positions do not shift considerably in acetonitrile, being at 1289, 1181 cm^{-1} for 5CB and 1288, 1183 cm^{-1} for 7CB, respectively. With regard to 6CB, the C–C and C–H modes are shifted to 1278 and 1172 cm^{-1} , accordingly. In the case of 8CB, 9CB, and 10CB, the ring breathing band appears around 1279 cm^{-1} in these three samples, whereas C–H in-plane deformation is deflected to around 1174 cm^{-1} . The pattern of the Raman shifts observed in acetonitrile is very similar to those observed in DMF. Acetonitrile and DMF have comparable Kamlet-Taft dipolarity constants (0.71 and 0.87) and acceptor number (18.9 and 16), as such the existence of dipole-dipole interaction between the cyano group of nCB and the cyano group of acetonitrile is viable. Such dipole-dipole interaction between benzonitrile and acetonitrile has been previously reported ¹¹⁹, where the $\text{C}\equiv\text{N}$ of the benzonitrile and acetonitrile align antiparallel to each other, with interactions involving the π -electrons, which consequently leads to a shift to lower wavenumber. However, in the case of 5CB and 7CB, they have odd-numbered alkyl chains which make the molecules have orientations that cause a slight destabilization of the dipole-dipole interaction via dipolar repulsion; thus, the band shows no shift in the wavenumber positions. In the case of 6CB, the dipolar repulsion is minimized as a result of the orientational alignment between the flexible even-numbered chain and the rigid core within the molecules, which consequently shifted the stretching modes to lower wavenumber. Likewise, the repulsion between the vibrational modes in 8CB, 9CB, and 10CB is not significant, thus the stabilization of the modes as aided by the dimerization

and folding back effect makes the bands appear at lower wavenumber of 2220, 1599, 1279, and 1174 cm^{-1} for cyano stretch, ring breathing, C–C biphenyl linking stretching and C–H in-plane deformation, respectively.

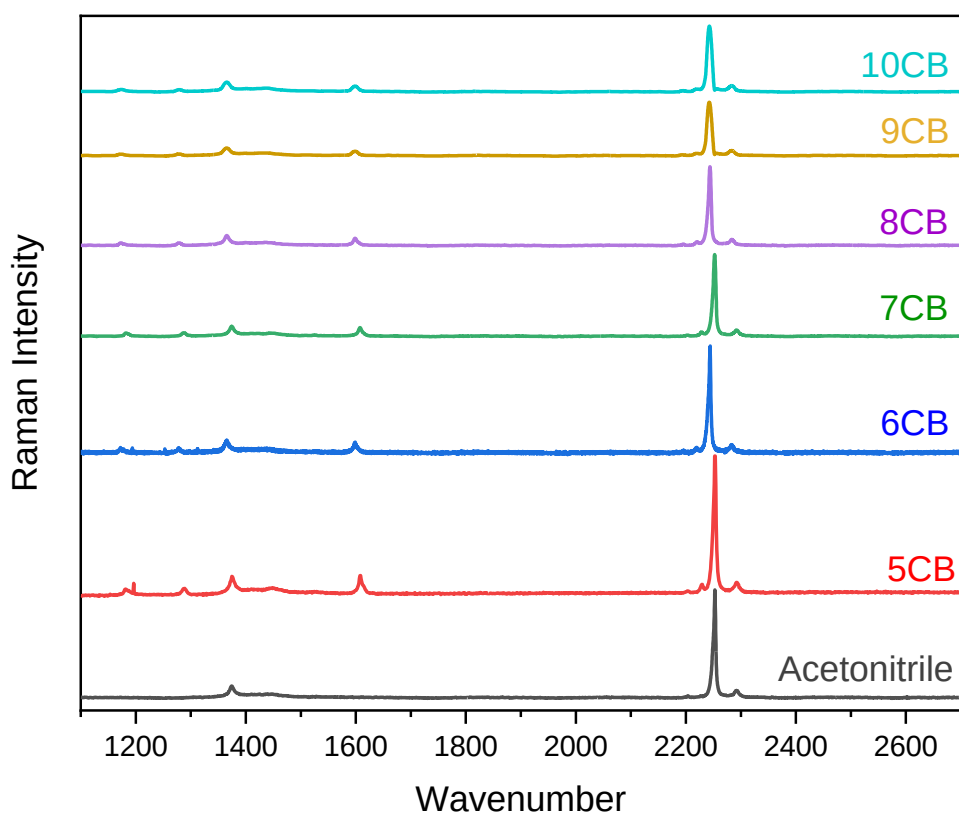


Figure 5.6 Raman spectra of LC samples in acetonitrile. The Raman spectrum acetonitrile is shown for reference.

Furthermore, Figure 5.7 shows the Raman spectra of the LC molecules in DCM. Baseline correction was conducted for the spectra of the samples in DCM, on account of its high volatility. As seen, DCM does not substantially induce a shift in the vibrational stretching band of $\text{C}\equiv\text{N}$ for 5CB and 6CB, being at 2230 and 2228 cm^{-1} , respectively, from 2229 cm^{-1}

¹ in pure samples. However, this band is significantly shifted to 2219 cm⁻¹ in 7CB. Likewise, the other solutes of 8CB, 9CB, and 10CB observed a shift in the band to 2221, 2220, and 2219 cm⁻¹ from the original 2229, 2222, and 2230 cm⁻¹, respectively. The C–C aromatic ring breathing is also unshifted in 5CB and 6CB; the band position being at 1608 cm⁻¹ for both samples in DCM. With regard to 7CB, 8CB, 9CB, and 10CB, the C–C aromatic ring breathing and biphenyl link stretch bands are shifted to lower wavenumber: ring breathing is shifted to around 1598, 1599, 1598, and 1599 cm⁻¹, respectively, while the biphenyl link stretch shifted to 1280, 1278, 1277, and 1278 cm⁻¹, respectively, in these molecules. For the C–H in-plane deformation, the band is not significantly shifted in 5CB being at 1185 cm⁻¹ but red-shifted to 1180 cm⁻¹ in 6CB. For 7CB, 8CB, 9CB, and 10CB, the deformation is shifted to 1179, 1172, 1174, and 1174 cm⁻¹, respectively. DCM has a high dipolarity/polarizability of about 0.82 that favors the interaction of the cyano stretching mode in LC molecules via dipole-dipole interaction with the hydrogens of DCM molecules. However, the comparatively shorter alkyl chains in 5CB and 6CB induce some short-range repulsion which consequently nullifies the stabilization effect on the cyano group by its interaction with the H of DCM molecules. Also, these repulsive forces affect other dipole-dipole and dipole-induced dipole interactions between the solvent and other distinctive modes of ring breathing, biphenyl link stretch, and C–H in-plane deformation, thus resulting in no net effect on these vibrational modes. However, when the alkyl chain gets longer, 7CB, 8CB, 9CB, and 10CB, the dimerization and folding back effect favor the interaction of the cyano stretching modes with DCM molecules, and the stretching mode is therefore stabilized.

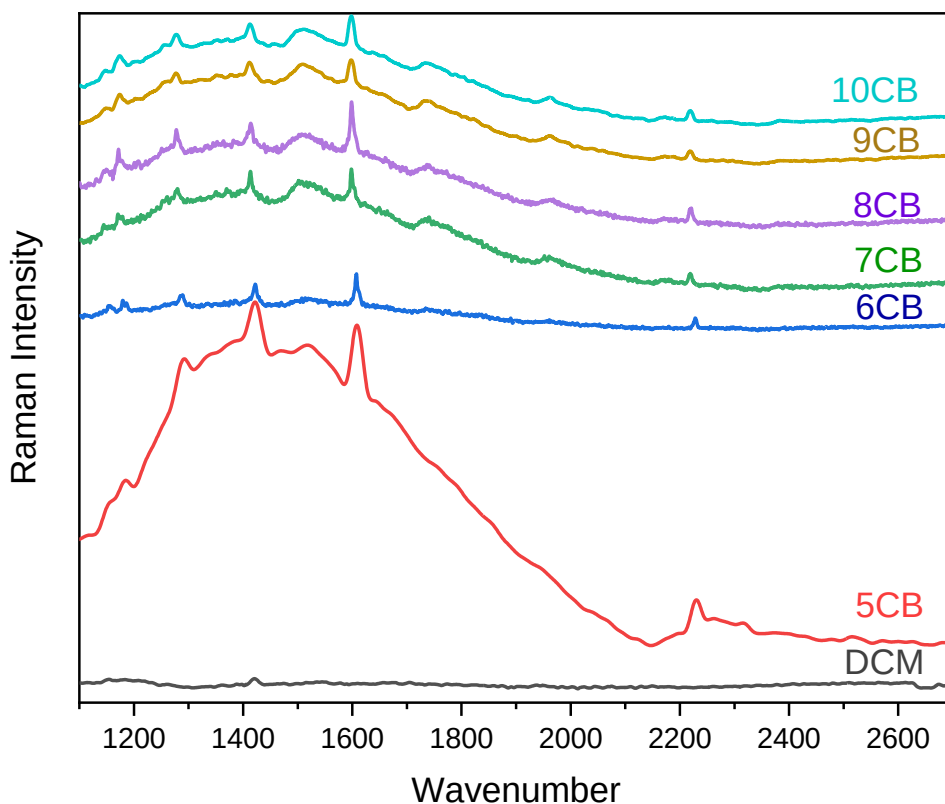


Figure 5.7 Raman spectra of LC samples in dichloromethane. The spectrum of the solvent is placed at the bottom of the figure for reference.

The spectra of the LC samples in acetone are presented in Figure 5.8. As shown in this figure, the cyano stretching modes of 5CB and 6CB, having shorter alkyl chain lengths, are not considerably shifted in acetone, appearing at 2228 cm^{-1} . This is indicative of the comparable influence of the attractive forces and repulsive forces between the dipolar $\text{C}\equiv\text{N}$ of the LC molecules and dipolar $\text{C}=\text{O}$ of the solvent. Moreover, other vibrational modes of the 5CB and 6CB molecules, the C–C ring breathing, C–C biphenyl link stretch, and C–H in-plane deformation, did not experience considerable shifts in the acetone solvent

environment, appearing at 1607, 1289, and 1183 cm^{-1} for 5CB, and 1607, 1287, and 1183 cm^{-1} for 6CB, respectively. With regards to 7CB, the $\text{C}\equiv\text{N}$ stretching mode is shifted to 2220 cm^{-1} , while in 8CB, 9CB, and 10CB the band appears at 2219 cm^{-1} . In addition, the ring breathing and biphenyl link stretch of 7CB, 8CB, 9CB, and 10CB experienced a shift to around 1599 and 1278 cm^{-1} , respectively. The C–H in-plane deformation is also shifted to a lower wavenumber, appearing at 1172 cm^{-1} for 7CB, 1173 cm^{-1} for 8CB, 1174 for 9CB, and 1175 cm^{-1} for 10CB. In line with the higher Kamlet-Taft dipolarity and donor number (0.68 and 17, respectively) of acetone, and available dipoles to engage in dipole-dipole interaction with the cyano group via the $\text{C}=\text{O}$, the $\text{C}\equiv\text{N}$ stretching could be stabilized by acetone. Such interactions have been reported between acetone and benzonitrile ¹²⁰, where the authors posited an antiparallel configuration between the dipoles, such that the π -bonds interact, consequently weakening the $\text{C}\equiv\text{N}$ bond and lowers the energy of the mode. However, the comparably shorter alkyl chain length of 5CB and 6CB causes some repulsion that cancels out the stabilization effect. In the case of 7CB, 8CB, 9CB, and 10CB, such repulsion is minimized by the folding back effect of the alkyl chain.

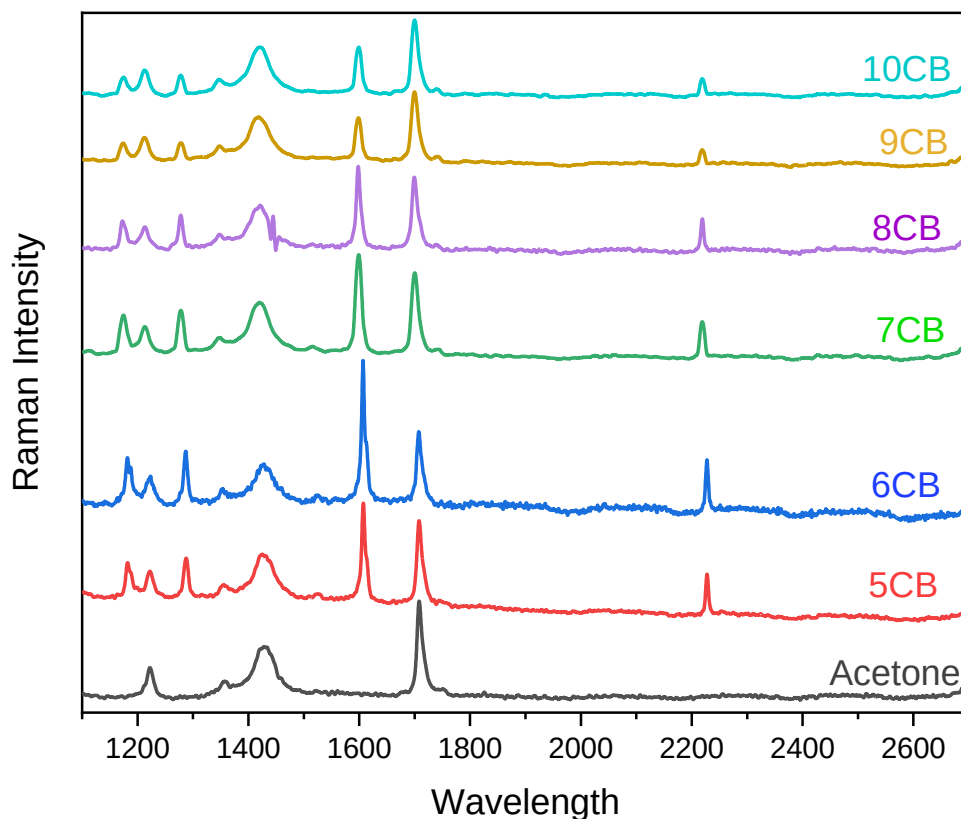


Figure 5.8 Raman spectra of LC samples in acetone. The Raman spectrum of acetone is also shown for reference.

Furthermore, as can be seen in Figure 5.9, the cyano stretching band of 5CB appears around 2228cm^{-1} when dissolved in dioxane. Also, the position of other modes in 5CB is not shifted in the dioxane solvent environment, appearing at 1609 , 1288 , and 1285 cm^{-1} for C–C aromatic stretch, C–C biphenyl link stretch, and C–H in-plane deformation, respectively. In the case of 6CB, 7CB, 8CB, 9CB, and 10CB, all the characteristic vibrational modes are shifted to a lower wavenumber. Where the C≡N stretching band, C–C aromatic stretch, C–C biphenyl link stretch, and C–H in-plane deformation are shifted to around 2219 , 1599 ,

1280, and 1174 cm^{-1} , respectively. Dioxane has a high polarizability value of 8.63 owing to the two oxygen atom centers at positions 1 and 4. The C–O bonds have appreciable dipole moment capable of dipole-dipole interaction with the cyano group. As observed, stabilization from the dipole-dipole interaction in 5CB is neutralized by short-range repulsion from the alkyl chain, thereby showing no shift in band positions. However, for 6CB the dioxane molecule does not affect much the alignment of the molecule such that the interacting dipolar $\text{C}\equiv\text{N}$ and C–O are not disrupted by the chain. Consequently, the modes are stabilized and shifted to a lower wavenumber. A similar explanation holds for 7CB, 8CB, 9CB, and 10CB, where the dimerization and folding back effect result in lesser repulsion of the solvent molecules around the solutes.

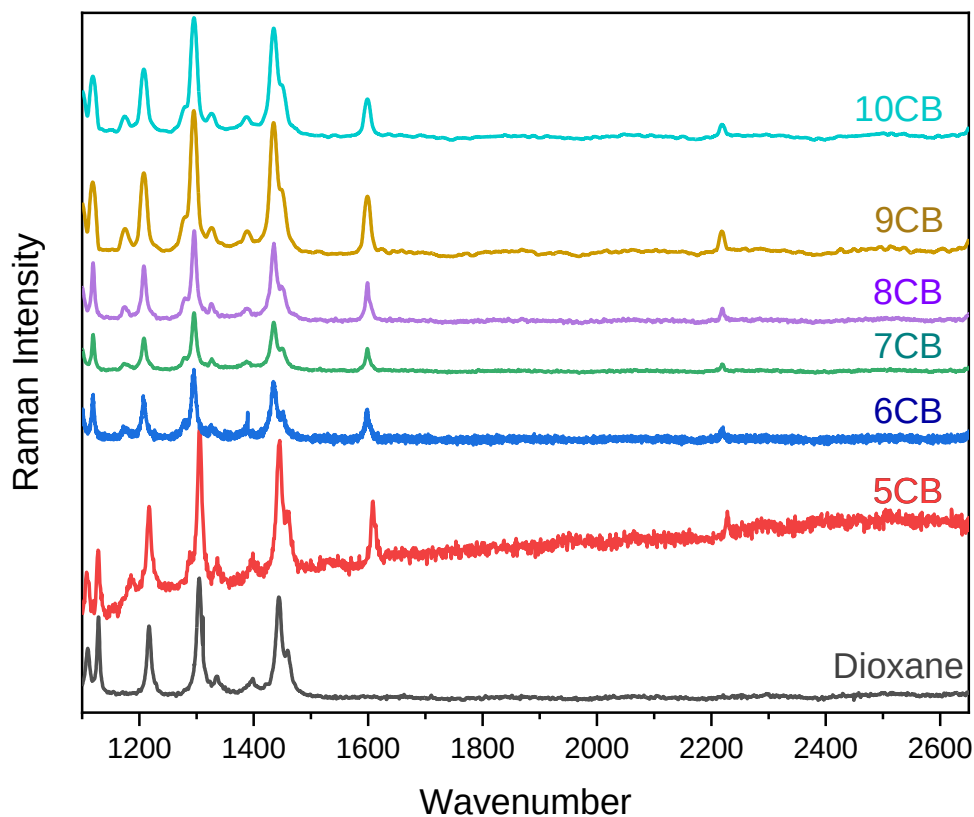


Figure 5.9 Raman spectra of LC samples in dioxane. The Raman spectrum of dioxane is also shown for reference.

5.4 Alkylcyanobiphenyl in Nonpolar Solvents

The Raman shifts of the alkylcyanobiphenyls are studied in some nonpolar solvents that comprise benzene, THF, diethyl ether, and hexane. As shown in Figure 5.10, the positions of the vibrational modes of 5CB are not significantly shifted when dissolved in benzene, with distinctive peaks appearing at 2229 cm^{-1} for $\text{C}\equiv\text{N}$ stretch, 1610 cm^{-1} for ring breathing, and 1288 cm^{-1} for biphenyl link stretch, while only C–H in-plane deformation is slightly shifted to 1179 cm^{-1} . For the other solutes, the peaks are substantially shifted in benzene. For example, the $\text{C}\equiv\text{N}$ stretching mode of 6CB, 7CB, 8CB, 9CB, and 10CB is shifted to

around 2220 cm^{-1} . As for the ring breathing and biphenyl link stretching modes, the bands shifted to 1279 cm^{-1} for 6CB, 8CB, and 10CB, and 1277 cm^{-1} for 7CB and 9CB, while the C–H in-plane deformation band shifted to 1169 cm^{-1} in these samples. As reported by Praveen and Ojha when they studied the molecular interactions and chain length effect on the photosensitivity of 6CB and 7CB, an increase in alkyl chain length leads to more planar structure. The more planar structure favors π – π stacking of the molecular dimers.⁵⁸ Thus, the observed red-shifts in benzene could be a result of the more planar orientation of the rigid core that leads to better π – π stacking. This explains why the vibrational modes of 5CB with a shorter alkyl chain were not significantly affected in benzene, but did in others. Their rigid core is relatively planar, and the longer alkyl chain does not considerably cause the repulsion to destabilize the π – π stacking interaction between the longer nCB molecules and benzene solvent.

Similarly, in THF the position of the $\text{C}\equiv\text{N}$ stretching mode is not considerably shifted for 5CB, 6CB, and 7CB, being at 2228 , 2227 , and 2227 cm^{-1} , respectively (Figure 5.11). Similarly, the ring breathing, biphenyl link stretch, and C–H in-plane deformation of these samples are not shifted, appearing around 1607 , 1287 , and 1182 cm^{-1} , respectively. For 8CB, 9CB, and 10CB, the $\text{C}\equiv\text{N}$ stretching band shifted to 2218 cm^{-1} , whereas the ring breathing, biphenyl linking stretch, and C–H in-plane deformation shifted to 1598 , 1277 , and 1173 cm^{-1} , respectively. In order to explain the observed Raman shifts of samples in THF, a reference could be made to the behavior of monomer and dimer models of cyanobiphenyl in THF and cyclohexane as reported by Hayashi and Ichimura on studying a dimer model (1,3-di([4'-cyano-4-biphenoxy]propoxy)benzene) that displayed excimer fluorescence in less polar cyclohexane, whereas the fluorescence spectrum was almost

identical to that of a monomer model (4'-cyano-4-propoxybiphenyl) in THF. They ascribed this behaviour to the solvation by THF, which results in the separation of the two fluorophores to hinder intramolecular excimer formation ¹²¹. As observed here, the vibrational modes of 5CB, 6CB, and 7CB are not considerably shifted in THF, which could be linked to the solvation and screening of molecules to engage in intramolecular interaction. Therefore, the dipole-dipole interaction between these molecules and the C–O of THF alone is not strong enough to induce any considerable shift. However, for the molecules with longer alkyl chain lengths: 8CB, 9CB, and 10CB, the dimerization and folding back effect, in addition to the dipole-dipole interaction with THF, results in the shifts to lower wavenumbers.

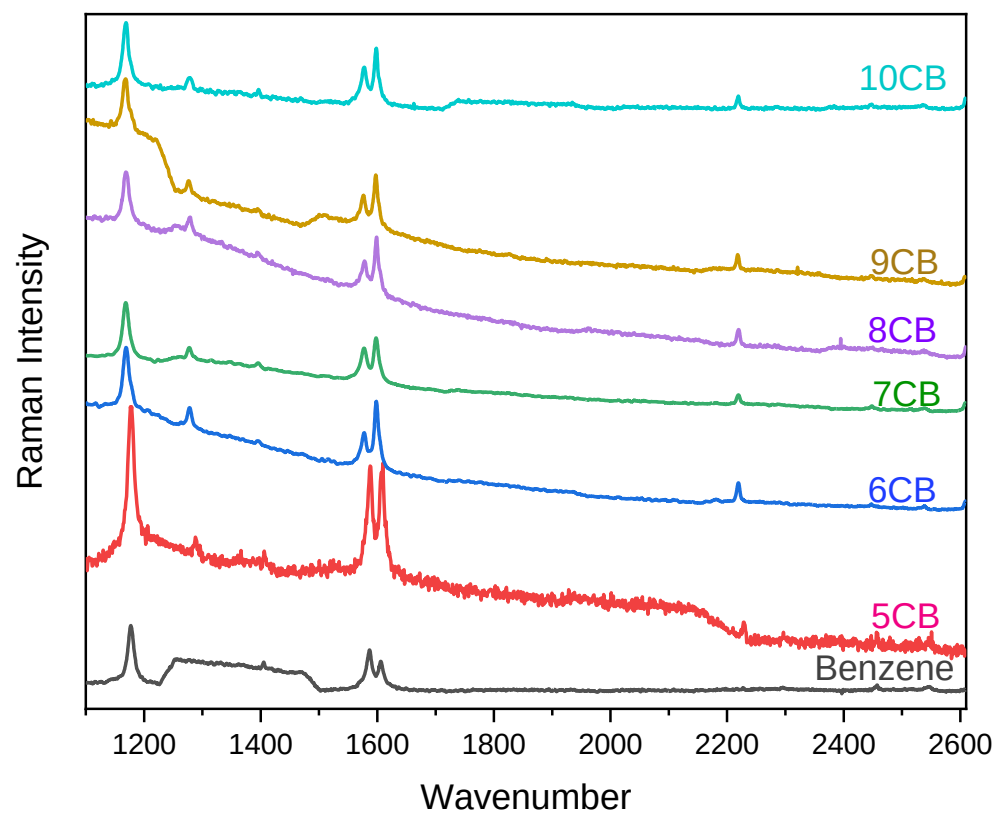


Figure 5.10 Raman spectra of LC samples in benzene. The Raman spectrum of benzene is also shown for reference.

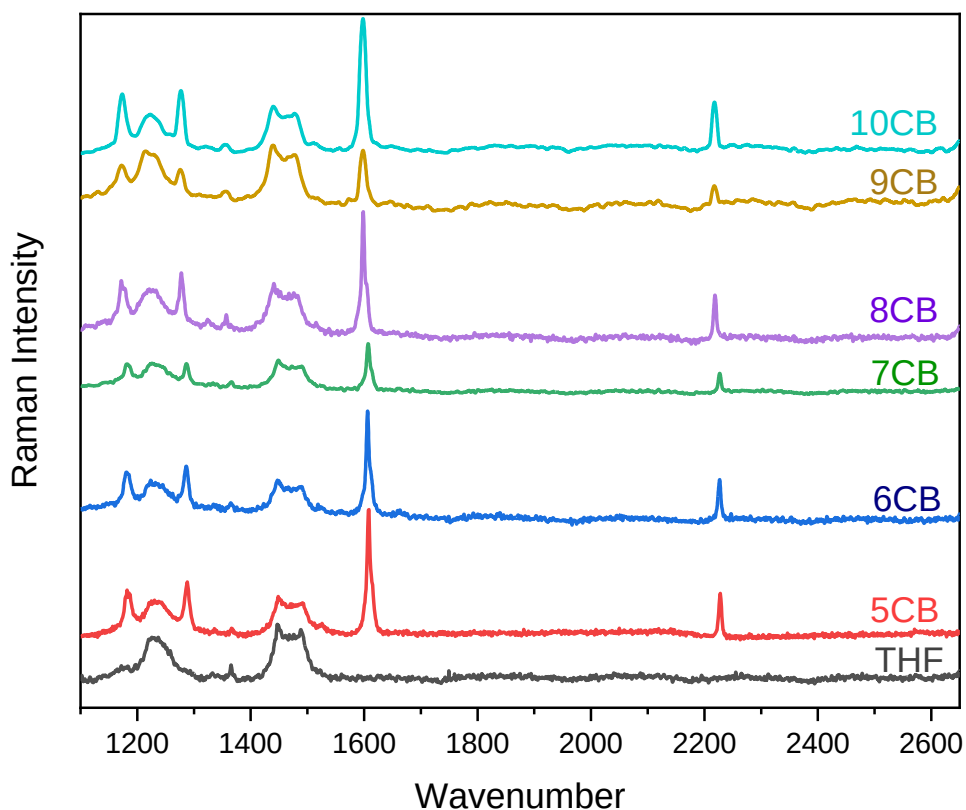


Figure 5.11 Raman spectra of LC samples in THF. The Raman spectrum of THF is also shown for reference.

The six nCB molecules were also studied in diethyl ether as presented in Figure 5.12. It can be observed that diethyl ether caused no significant shift on the $\text{C}\equiv\text{N}$ stretching mode of 5CB and 6CB, being at 2230 and 2229 cm^{-1} , respectively. In the same way, the $\text{C}-\text{C}$ aromatic ring stretch of 5CB and 6CB appears at 1610 and 1608 cm^{-1} respectively. For the biphenyl link stretch and $\text{C}-\text{H}$ in-plane deformation, the bands appear at 1288 and 1182 cm^{-1} in both samples, respectively. For 7CB, the $\text{C}\equiv\text{N}$ stretch is significantly shifted to 2221 cm^{-1} . This is similar to what is observed for 8CB, 9CB, and 10CB, appearing around 2220 cm^{-1} . The ring breathing, biphenyl link stretch, and $\text{C}-\text{H}$ in-plane deformation appear

around 1600, 1279, and 1173 cm^{-1} , respectively, for these samples. As with the proposition in DCM, the observations made for 5CB and 6CB in diethyl ether suggest a balance between the competing attractive and repulsive solute-solvent interaction such that the cohesive intermolecular interaction, which attracts molecules together is countered by the repulsive interactions that prevent the molecules from being engaged. Thus, the stretching modes in these two solutes are not considerably shifted. Although diethyl ether has a small Kamlet-Taft dipolarity constant of 0.27, the observed shifts in 7CB, 8CB, 9CB, and 10CB indicate low repulsion from the alkyl chain of the molecules and the influence of the dipole-dipole interaction between the $\text{C}\equiv\text{N}$ stretching mode of 7CB, 8CB, 9CB, and 10CB and the C–O bond of diethyl ether results in the stabilization of the mode and consequent shift to lower wavenumber.

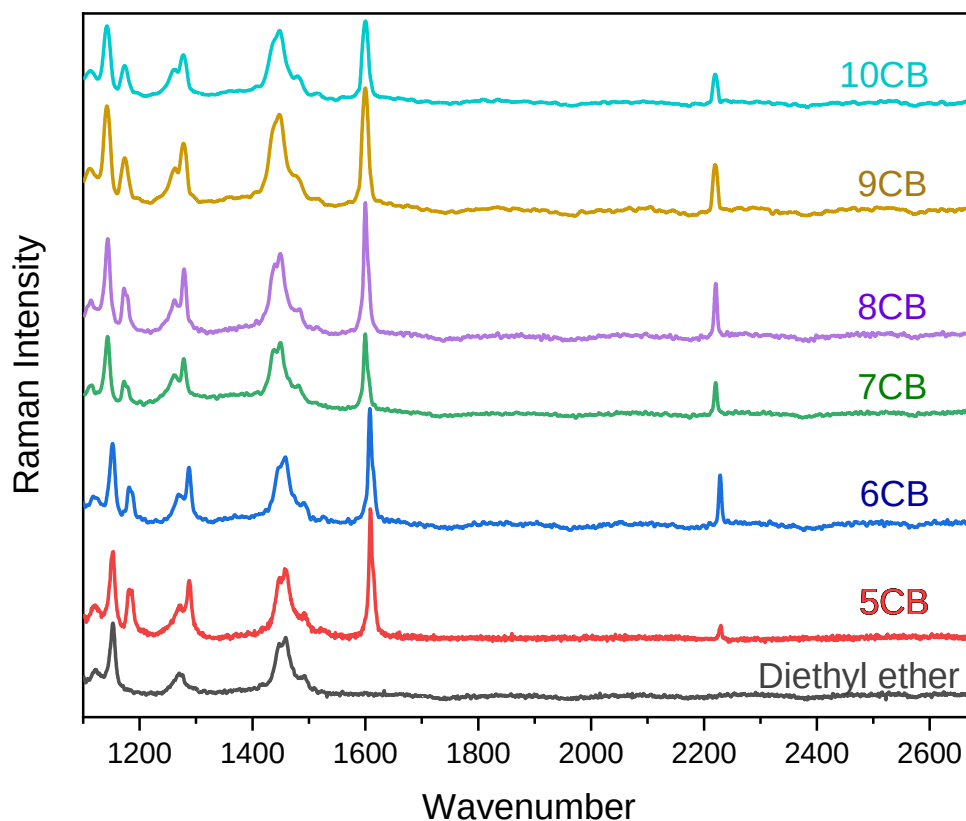


Figure 5.12 Raman spectra of the six LC samples in diethyl ether. The Raman spectrum of diethyl ether is also shown for reference.

On the extreme, the solvent environment of hexane has 0 solvent acceptor and donor number. As shown in Figure 5.13, it is interesting to note that the $\text{C}\equiv\text{N}$ stretching modes of 5CB experienced a blue-shift to 2233 cm^{-1} when dissolved in hexane. While C-H in-plane deformation is slightly shifted to lower wavenumber at 1179 cm^{-1} , the C-C ring breathing and C-C biphenyl link stretch are not considerably shifted, observed at 1611 and 1289 cm^{-1} , respectively. In the case of 6CB, 7CB, 8CB, 9CB, and 10CB, the $\text{C}\equiv\text{N}$ stretching band and ring breathing appear around 2222 and 1600 cm^{-1} , respectively, whereas the biphenyl link stretch and C-H in-plane deformation are observed around 1279 ,

and 1172 cm^{-1} , respectively. The low electrophilic and nucleophilic character of hexane predicts that it will not participate in any substantial solute-solvent donor and acceptor interaction. Therefore, the solute-solvent interaction will mainly be dispersive interactions. Of particular interest is that the $\text{C}\equiv\text{N}$ mode of 5CB was observed to shift considerably to a higher wavenumber, which justifies our earlier suggestion of short-range repulsion as a result of the shorter alkyl chain of the 5CB molecules. In this case, the solute-solvent interactions are not significant, while the effect of the repulsions, aided by the alkyl chain of 5CB, between the cyano group and the solvent bath, has superseded the attractive dispersion interaction. Consequently, the energy of the cyano stretching mode is increased and shifted to a higher wavenumber. A similar phenomenon was reported in the study of solvent-induced nitrile shift for benzonitrile in hexane¹²⁰. The investigators correlated the induced shifts with the solvent acceptor number, having the $\text{C}\equiv\text{N}$ stretching at 2233 cm^{-1} , being the highest wavenumber observed in benzonitrile solution, while other solvents such as acetone, DCM, and ethanol caused a shift to a lower wavenumber. This was ascribed to an increase in dipolar interactions between $\text{C}\equiv\text{N}$ groups in the various media. For the case of other nCB samples that experienced some red-shifts in hexane, it is in agreement with the proposition of increased dimerization and intramolecular dispersive interactions with the alkyl chains. This argument could be substantiated by the report of Hayashi and Ichimura on the existence of cyanobiphenyls as dimers in cyclohexane but not in THF, as discussed earlier.¹²¹

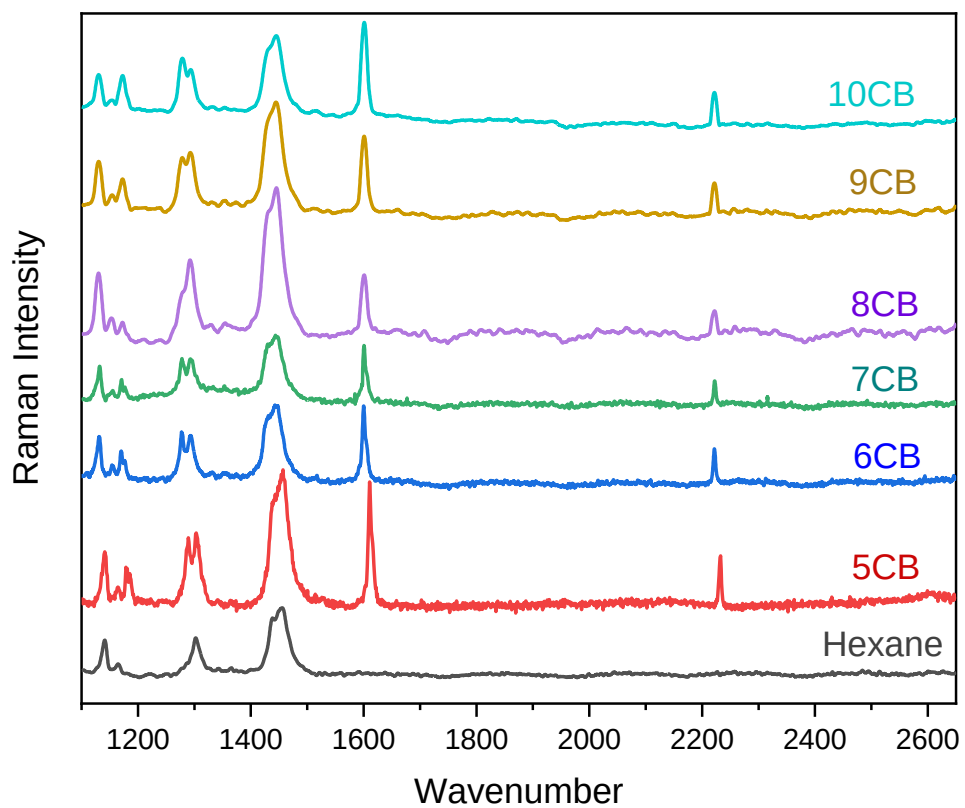


Figure 5.13 Raman spectra of LC samples in hexane. The Raman spectrum of hexane is also shown for reference.

CHAPTER

SOLVATOCHROMIC EFFECT

6.1 Solvatochromism of Pentylcyanobiphenyl (5CB)

Absorption and fluorescence spectra of some alkylcyanobiphenyls (nCB) comprising pentyl, hexyl, heptyl, octyl, nonyl, and decyl substituents were investigated in nonpolar, polar aprotic, and polar protic solvents of different polarities. Scheme 5.1 shows the nCB liquid crystals with their unique structural features that give them the ability to exist in the hybrid liquid-crystal state. The peculiarity of these classes of molecules incurred many research works on their various optical properties.⁵⁵⁻⁵⁸ Figure 6.1 shows UV-Vis spectra of 5CB in various solvents. As observed, the 5CB molecules have an absorption maximum of around 280 nm of the UV region, with bathochromic shifts on moving from nonpolar to most polar solvents. There is no absorption band in the visible region for all the nCB molecules. The intensity of the absorbance obviously decreased in the most polar solvents – DMF, propanol, ethanol, and methanol. Moreover, there is a change in the shape of the 5CB in DMF. Other solvents that cause a change in the shape of 5CB are THF and benzene. However, there is no absorbance observed in acetone and DCM. More significantly, the fluorescence spectrum is more sensitive to changes in the solvent environment as seen in Figure 6.2 for the fluorescence spectra of 5CB than the absorption spectra. In the fluorescence spectra, a clear bathochromic shift on moving from nonpolar solvents to polar solvents is observed. An obvious change in shape is observed in hexane which is broadly

wider than in other solvents. The intensity is most enhanced in DCM, while acetone and THF exhibit a very low-intensity fluorescence.

For the absorption spectra, the band in the UV region is a result of HOMO – LUMO $\pi-\pi^*$ transitions of the phenyl rings.^{55,56,70,82} The absorption maximum wavelength of the 5CB in the less polar hexane is seen at 275 nm which shifts to 284 nm in the most polar DMF, giving a difference of 9 nm as given in Table 6.1. This observed shift can be ascribed mainly to the better stabilization of the π^* orbital more than the π orbital as the solvent polarity is increased as reported previously.^{56,60,68,80} Benzene, DMF, and THF caused a larger red-shift in the absorption band by inducing the π -electrons in the 5CB molecules. In addition, the fluorescence spectrum of 5CB shows some fine structure in hexane and diethyl ether which disappears as the polarity of the solvents increases, and the fluorescence maximum shifts to a longer wavelength. In the nonpolar hexane and diethyl ether, the change in the band shape is a result of the contributions from $\pi-\pi^*$ and $n-\pi^*$ electronic transitions to the absorption spectrum. This is similar to the findings of David *et al.* on the studies of some cyanobiphenyl derivatives, in which there was a disappearance of fine vibrational structures as the solvent polarity was increased. The authors proposed that the vibrational modes carried the geometry from the nonplanar ground state to the planar excited state having a higher dipole moment, which is very sensitive to the solvent environment for the emission of the fluorescence.⁵⁹ Likewise, Kukielski had previously studied the absorption and fluorescence of 2CB and 5CB in three different solvents. For the absorption spectrum, having maxima around 280 nm characteristic of $\pi-\pi^*$, in which a shift to a longer wavelength is observed with an increase in the solvent polarity, there is no change in the shape whereas the fluorescence spectrum shows a stronger red-shift as the

polarity of solvent increases and slight changes in the band shape. The author argued that solute-solvent interactions cause some changes in the molecular geometry of the solute by twisting the dihedral angle between two subunits as solvent polarity varies, which consequently shifts the band to longer wavelengths.^{60,75} Also, Yu *et al.* concluded that the luminescence spectra of 5CB are affected by the molecular geometry and intramolecular charge transfer when they study the photoluminescence of 5CB in liquid crystal and solid crystal states.¹²² Moreover, Sidir *et al.* presented the solvatochromism of three different benzoic acid liquid crystals in a series of organic solvents by evaluating the absorption and fluorescence spectra of the LC molecules. The molecules have an absorption band range within 224-278 nm, ascribed to $\pi-\pi^*$ of alkoxy-phenyl-carboxylic interactions. The investigators account for the shift in the fluorescence wavelength of the molecules as being connected to a locally excited state and intramolecular charged transfer.⁶⁸ Accordingly, the shift in the absorption and fluorescence spectrum in this study is a result of the intramolecular electron transfer and molecular geometric changes as the solvent environment is varied.

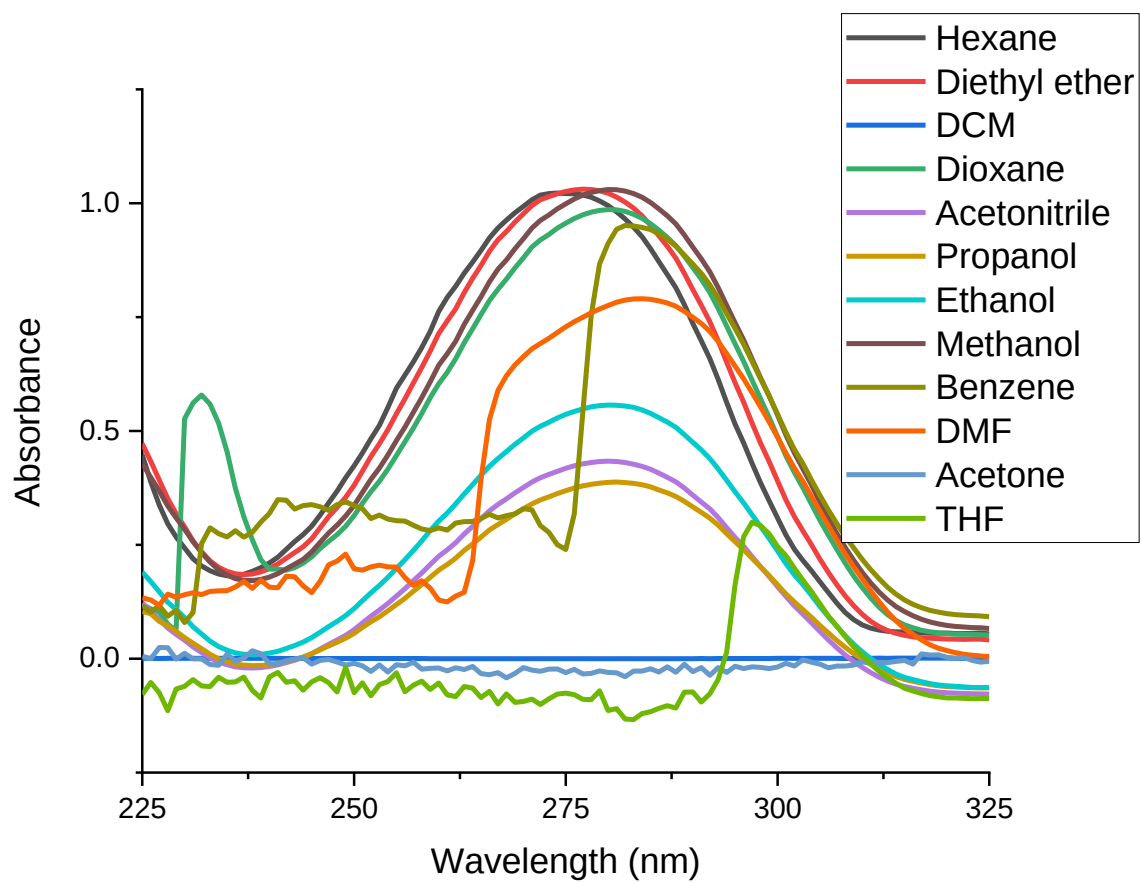


Figure 6.1 Absorption spectra of 5CB in various solvents

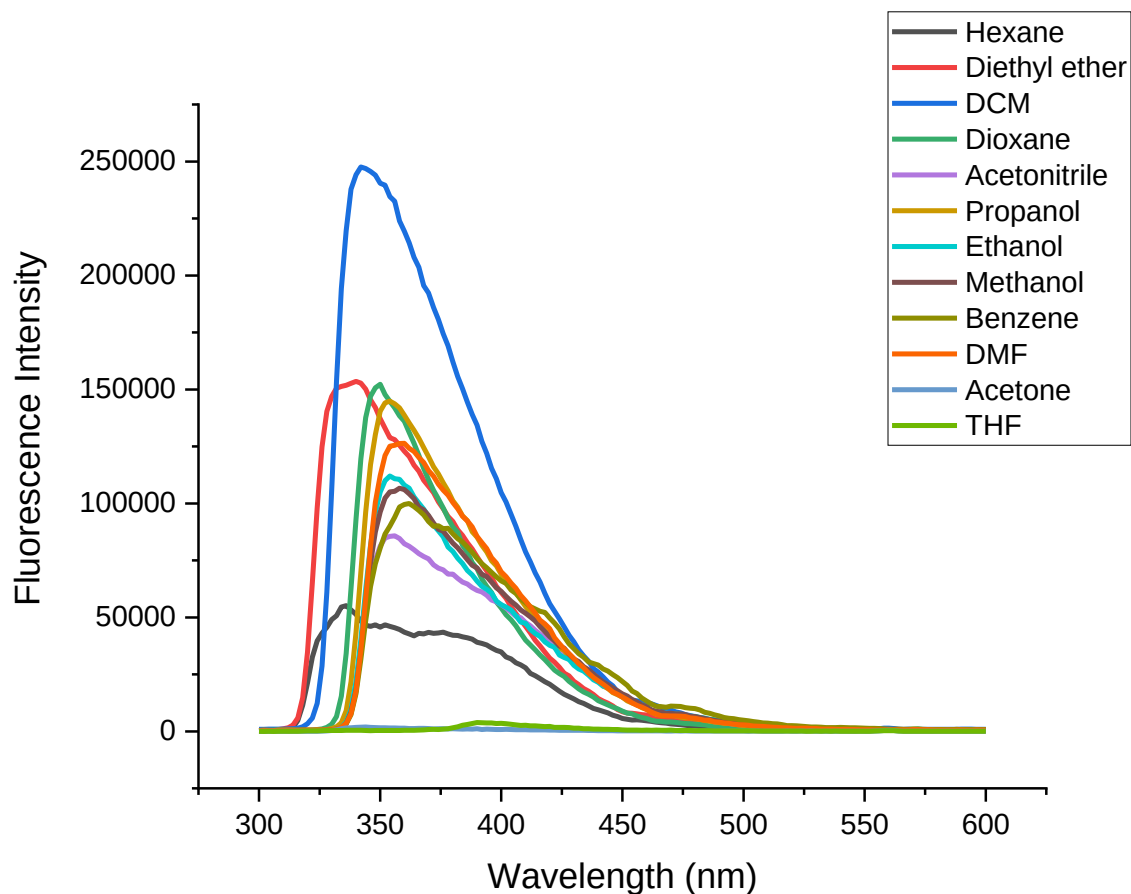


Figure 6.2 Fluorescence spectra of 5CB in various solvents

In another solvent-dependent study on the absorption spectral shifts of cyanobiphenyl molecules reported by Praveen showed that the spectra of the LC molecules undergo a red-shift in the absorption maximum wavelength due to lower energy required for the charge carriers to cross the band gap.⁵⁵ This finding is similar to the result reported by the same author on the spectral shifts of thermotropic LC materials of varying chain lengths in different solvents. The spectra of the molecules indicated an $n-\pi^*$ transition within the visible region and $\pi-\pi^*$ transitions in the UV range. A low exciton coupling of chromophores is shown by a red-shift of the absorption wavelength and a decrease in excited energies. This results from an increase in the dipole moment upon electron

excitation, a shift in the distribution of charges inside the band, and consequently an increase in electron delocalization and enhanced electrostatic interaction.⁵⁶ Thus, the solvation of the 5CB solutes by solvent molecules enhances the electron transitions and decreases the band gap energy as the polarity of the solvent is increased. Furthermore, the 5CB sample displayed low absorbance and fluorescence intensity in acetone and THF solvents. Initially, there was an observed disappearance of the liquid crystalline properties of 5CB was observed when dissolved in acetone and likewise, THF, just as previously reported for 6CB in acetone.³³ Such disruptions might contribute to the poor optical properties within the given concentration. Additionally, Rathad *et al.* reported a study on columnar liquid crystals which showed a low fluorescence and absorbance intensity in highly polar DMF and DMSO but higher intensity in moderately polar THF. They ascribed this observation to the compatibility of the sample with the moderately polar nature of the solvent.¹²³ In this case, we suppose the compatibility of the 5CB with acetone and THF, given their moderate polarity, affects the intramolecular charge transfer mechanism in the LC sample which consequently lowers the optical response.

Table 6.1 Absorption and fluorescence maximum wavelength of the LC samples in various solvents

	Solvents	5CB		6CB		7CB		8CB		9CB		10CB	
		λ_{abs}	λ_{fl}	λ_{abs}	λ_{fl}	λ_{abs}	λ_{fl}	λ_{abs}	λ_{fl}	λ_{abs}	λ_{fl}	λ_{abs}	λ_{fl}
1	Hexane	275	336	275	340	275	336	275	334	275	356	275	354
2	Diethyl ether	277	340	277	378	277	344	277	362	277	366	277	362
3	Dichloromethane		342		360		340		366		376		374
4	Dioxane	280	350	280	350	280	348	281	366	281	368	280	364
5	Acetonitrile	280	354	280	362	280	354	280	360	280	382	280	378
6	Propanol	281	354	281	356	281	354	281	372	281	376	282	374
7	Ethanol	280	354	280	354	280	352	280	356	280	378	280	378
8	Methanol	281	358	280	360	280	354	280	356	281	380	281	376
9	Benzene	282	360	283	352	282	348	282	352	282	368	282	364
10	DMF	284	360	284	360	285	356	285	354	286	388	282	382
11	Acetone		344		384		366		378		380		380
12	THF	297	392	297	392	297	388	297	388	297	390	297	390

6.2 Solvatochromism of Hexylcyanobiphenyl (6CB)

The absorption and fluorescence spectra of 6CB are presented in Figure 6.3 and 6.4. The absorption maximum spectra of 6CB is similar to 5CB, having the wavelength of maximum absorption shifts to longer wavelengths with an increase in polarity of the solvents from hexane to DMF, with slight changes in intensity. A marginal shift is observed from 280 nm to 281 nm in methanol for 5CB and 6CB, respectively. Also, the band shape has slight changes in DMF, benzene, and THF. However, the fluorescence spectra of 6CB (Figure 6.4) showed a structured band in nonpolar hexane and diethyl ether at longer wavelengths while in the polar protic solvents – methanol, ethanol, and propanol the peak is seen at shorter wavelengths. These evident fine structures of the 6CB in nonpolar solvents with a

more intense part appearing at a longer wavelength, agree with the electron transition of the vibrational energy level from the excited state as reported.⁶⁰ The absorption wavelength maximum of 6CB (Figure 6.3) has a difference of 9 nm from the most nonpolar hexane to the most polar DMF, whereas the difference is 22 nm for the fluorescence spectra. Moreover, the spectrum of 6CB in hexane is not as broad as is for 5CB in hexane, and a marginal blue shift is observed from the nonpolar diethyl ether to the protic solvents (methanol, ethanol, and propanol). This can be connected to the tilted alignment of the alkyl chain of 6CB with the rigid core, as opposed to parallel alignment in 5CB as previously reported.^{29,31} This makes the dipole moment in the ground state of the 6CB in the protic solvents comparably higher than in the excited state, and a consequent increase in the energy gap between these states results in the blue-shift. A similar result was obtained by Satapathy *et al.* in the studies of some bent-core liquid crystal molecules that showed a blue-shift in the fluorescence spectrum as the polarity of the solvents used increased from hexane to methanol. They ascribed this to structural changes in the molecules from the ground state to the excited that is influenced by the solvent polarity.¹²⁴ In the same way, Sidir and Sidir found a more red-shift in hexane and diethyl ether than in protic solvents (methanol, ethanol, and propanol) when they studied the solvatochromism of some alkoxy benzoic acids. This observation was linked to intramolecular charge transfer that favored dimerization of C=O ... H-O by hydrogen-bonding of the benzoic acids in the nonpolar solvents.⁸³ Therefore the observed blue-shift in protic solvents relative to the nonpolar solvent may be a result of solute-solvent interactions capable of affecting the intramolecular charge transfer and molecular geometry that possessed higher dipole

moments in the excited state in nonpolar solvents. Such inference is corroborated by the findings of the previous solvent-dependent studies on liquid crystals.^{83,124}

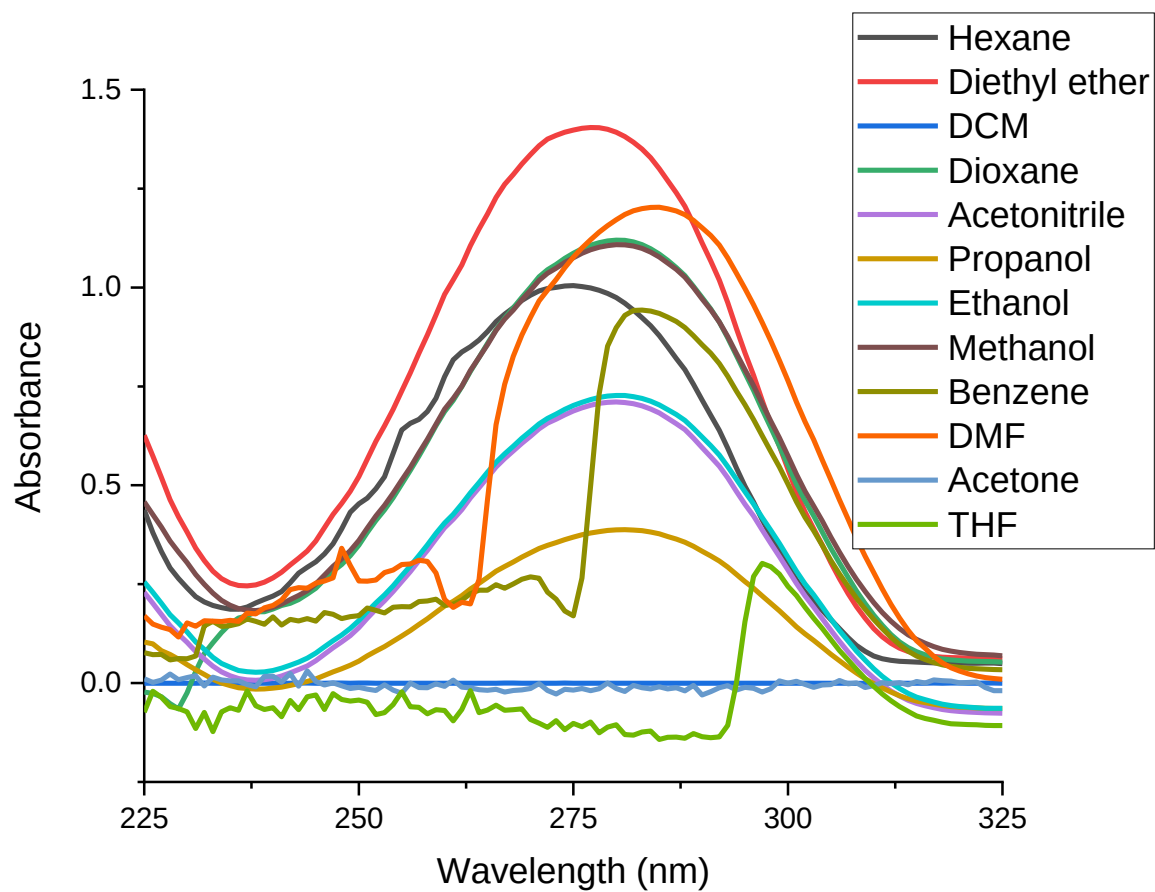


Figure 6.3 Absorption spectra of 6CB in various solvents

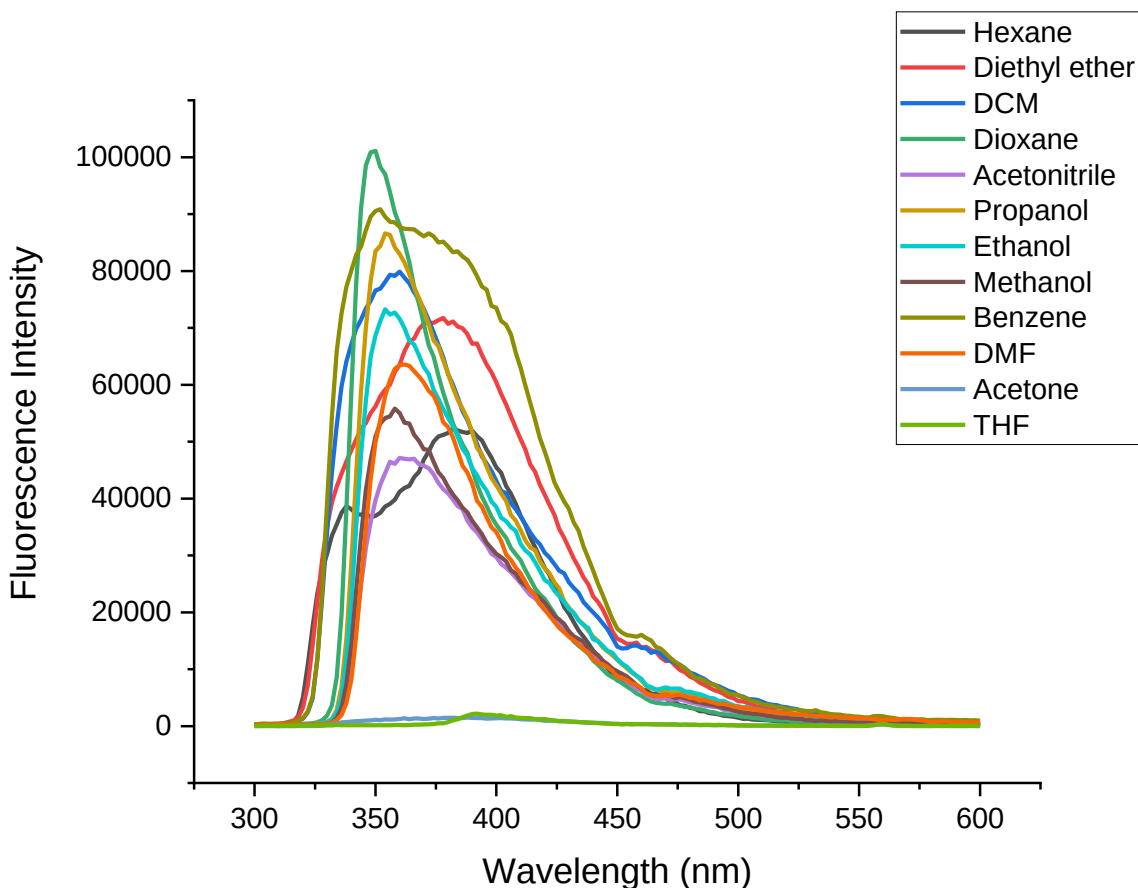


Figure 6.4 Fluorescence spectra of 6CB in various solvents

6.3 Solvatochromism of Heptylcyanobiphenyl (7CB)

From Figure 6.5, the absorption band of 7CB can be seen as having undergone a bathochromic shift moving from nonpolar to most polar solvents just as 5CB, with subtle changes in intensity. Also, the fluorescence maximum wavelength of 7CB (in Figure 6.6) is very similar to that observed in 5CB (Figure 6.2), refer to Table 6.1 for comparison. The most significant difference is seen in benzene with a blue-shift from 360 nm in 5CB to 348 nm in 7CB. Also, a slight blue-shift is observed in methanol and DMF, where the maximum fluorescence bands for 5CB are 358 nm and 360 nm which shifted to 354 nm and 356 nm

in 7CB, respectively. Such similarities can be linked to the observed and reported odd-even effect in the alkylcyanobiphenyl compounds.^{30,31,58,125} For example, Kobayashi *et al.* reported the odd-even effect of the series using a resonance Raman probe method and concluded that the odd-numbered nCB members tend to have a parallel long axis and a rigid core which gives them higher molecular anisotropy that results in larger order parameters.³¹ In addition, molecular dynamic simulations have been carried out on the odd-even effect of the nCB series and found the number of carbon atoms in the alkyl chain has an effect on the corresponding energy of the molecule in relation to odd and even-numbered substituents.^{29,30} In a different study of the experimental observations of alkyl benzenes, Toledano *et al.* report suggested higher aromatic character of odd-numbered than those with even numbers, and also of similar magnitude.¹²⁶ In agreement with these studies, the shift in fluorescence maximum wavelength observed in 5CB and 7CB to virtually the same position in most solvents indicates a similar solute-solvent interaction in the respective solutions, such that the conformation of the 5CB and 7CB molecules makes the substituent alkyl chains interact similarly with the biphenyl core which makes the energy band gap for the electronic structures similar. However, the blue-shift observed in benzene can be ascribed to the nature of the π - π stacking of the 7CB biphenyl and benzene molecules. Malecki and Nowak reported a peculiar structural existence of 7CB in benzene solution, which indicates a stronger self-association of dimers and multimers of 7CB in benzene.¹²⁷ This is especially true given the π - π interaction of benzene and the excited state of 7CB multimers causes the electronic structure of the 7CB to have a larger excited state dipole moment in the ground state than is for 5CB, and thus a less polar excited state that results in an increase in the energy band gap leading to the blue-shift of 7CB in benzene compared

to 5CB. This observation is consistent with previously reported solvent-dependent studies of liquid crystals.^{55,68,83,124} While we observe a blue-shift in fluorescence maxima in the 7CB benzene spectrum compared to 5CB, despite being similarly affected by changes in solvent polarity in the same way, it is especially important to underscore the observed intense fluorescence emission in benzene. As seen in Figure 6.6, the fluorescence spectra of 7CB have excellent fluorescence quantum yield that led to more intense emission which makes them suitable in fluorescence enhancement of other materials.⁸⁰

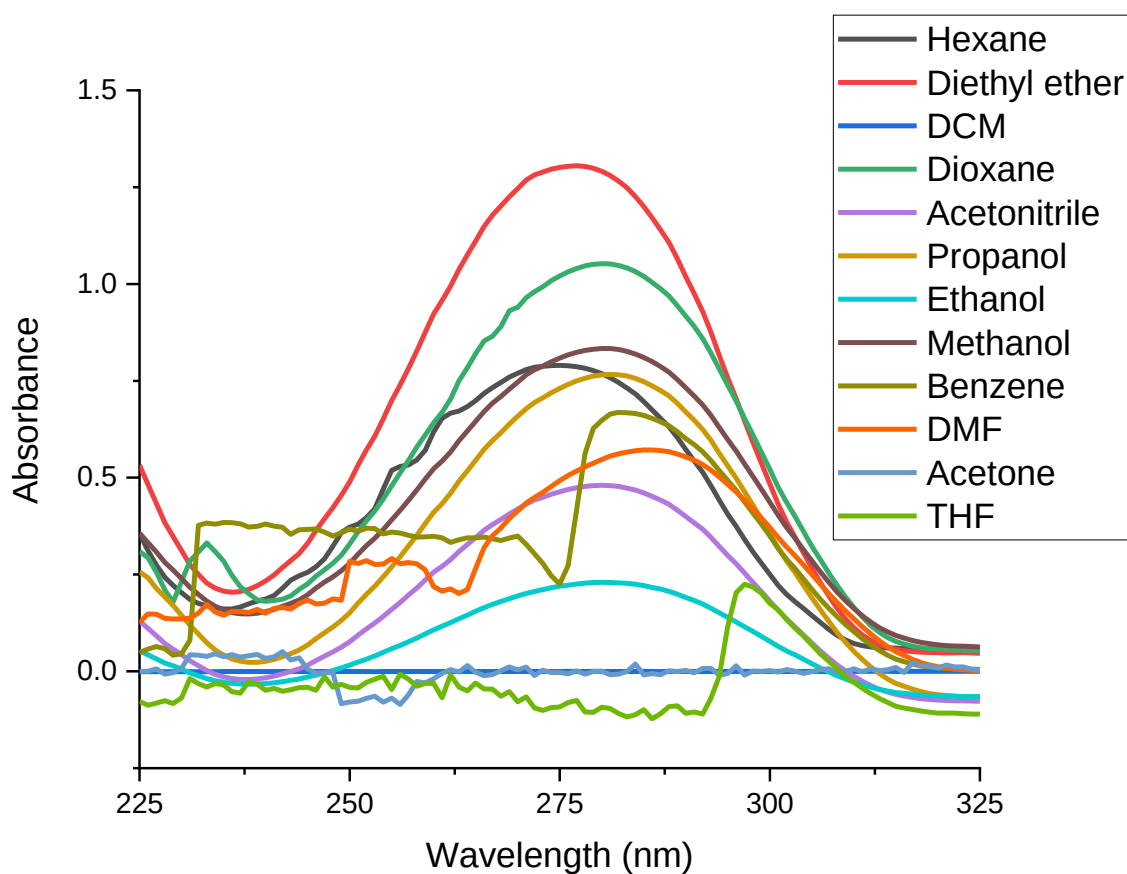


Figure 6.5 Absorption spectra of 7CB in various solvents

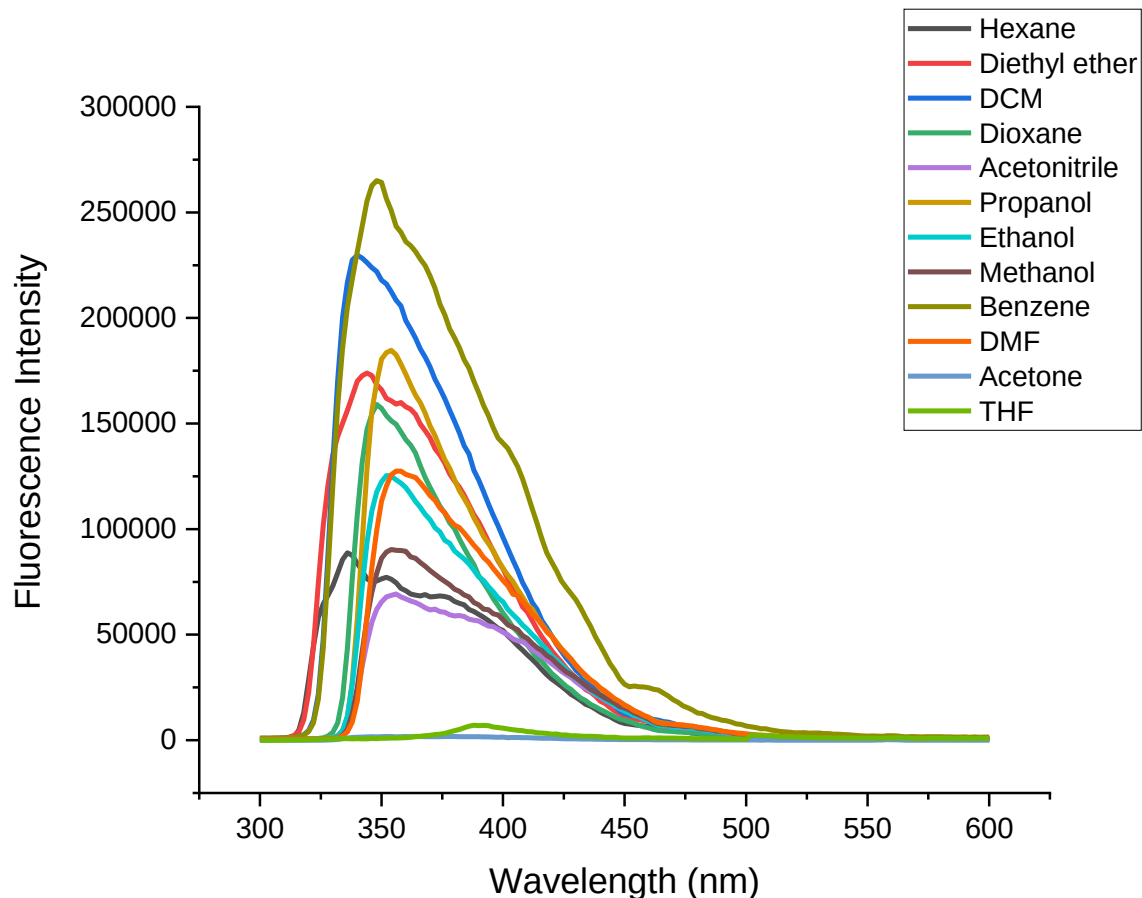


Figure 6.6 Fluorescence spectra of 7CB in various solvents

6.4 Solvatochromism of Octylcyanobiphenyl (8CB)

The absorption and fluorescence spectra of 8CB in the solvents are shown in Figure 6.7 and 6.8. The figure 6.7 shows similar absorption bands like the previous 5CB, 6CB, and 7CB, which shift to longer wavelength solvent polarity changes from hexane to DMF, with subtle changes in intensity and band broadening. However, regarding the fluorescence spectra (Figure 6.8), the maximum fluorescence wavelength shifts as the polarity of the solvent is varied in a similar way as 6CB. The positions of the fluorescence maxima of

8CB in the solvents are affected in the same manner as 6CB), with only significant differences in diethyl ether and dioxane which shifted from 378 and 350 nm to 362 and 366 nm in 6CB and 8CB, respectively. Such observation substantiates the significance of the odd-even effect in the alkylcyanobiphenyl molecules studied.^{28-31,126} The even-numbered alkyl chains of the 6CB and 8CB exhibit a geometrical conformation that provides a molecular anisotropic field slightly out-of-plane with the rigid core.^{30,31} The slight difference in the maximum fluorescence wavelength position in diethyl ether, owing to its lower dipole moment, indicates that the dipole moment of the 8CB is not significantly increased when it is taken to the excited state given the relatively longer alkyl chain of the solute. However, the transition of the molecules from the ground to the first excited state in dioxane causes an increase in the dipole moment and a relaxation by the solvent molecules that shifts the fluorescence emission to a longer wavelength. The apparent appearance of fine structures in the spectrum of 8CB in benzene and hexane could be linked to the de-excitation of molecules from the planar Frank-Condon excited state to the nonplanar ground state with the retention of the vibrational structures.⁵⁹ These structures disappear as the polarity of the solvents is increased because the electronic structure of the excited solute, having a longer alkyl chain, relaxes to the equilibrium excited state by the orientation relaxation process of the solvent cage which causes the loss of the vibrational structures.^{59,60,75}

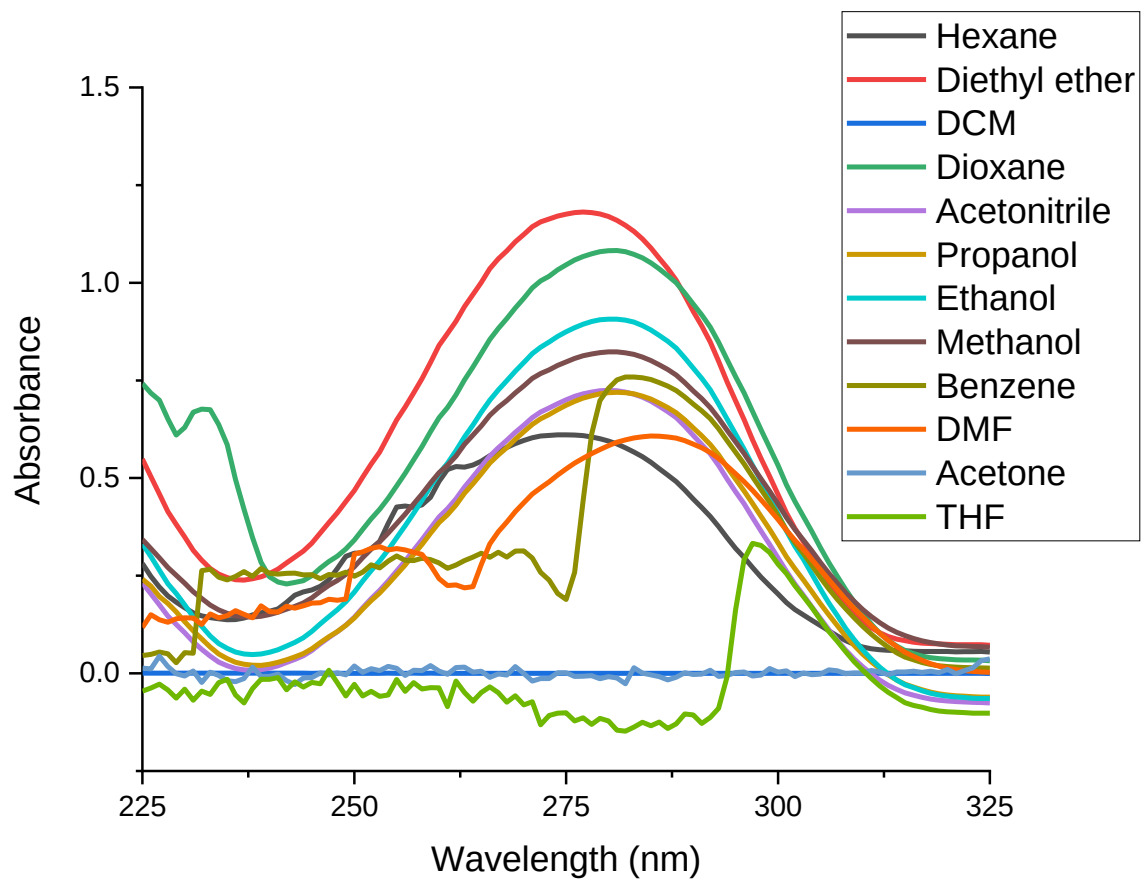


Figure 6.7 Absorption spectra of 8CB in various solvents

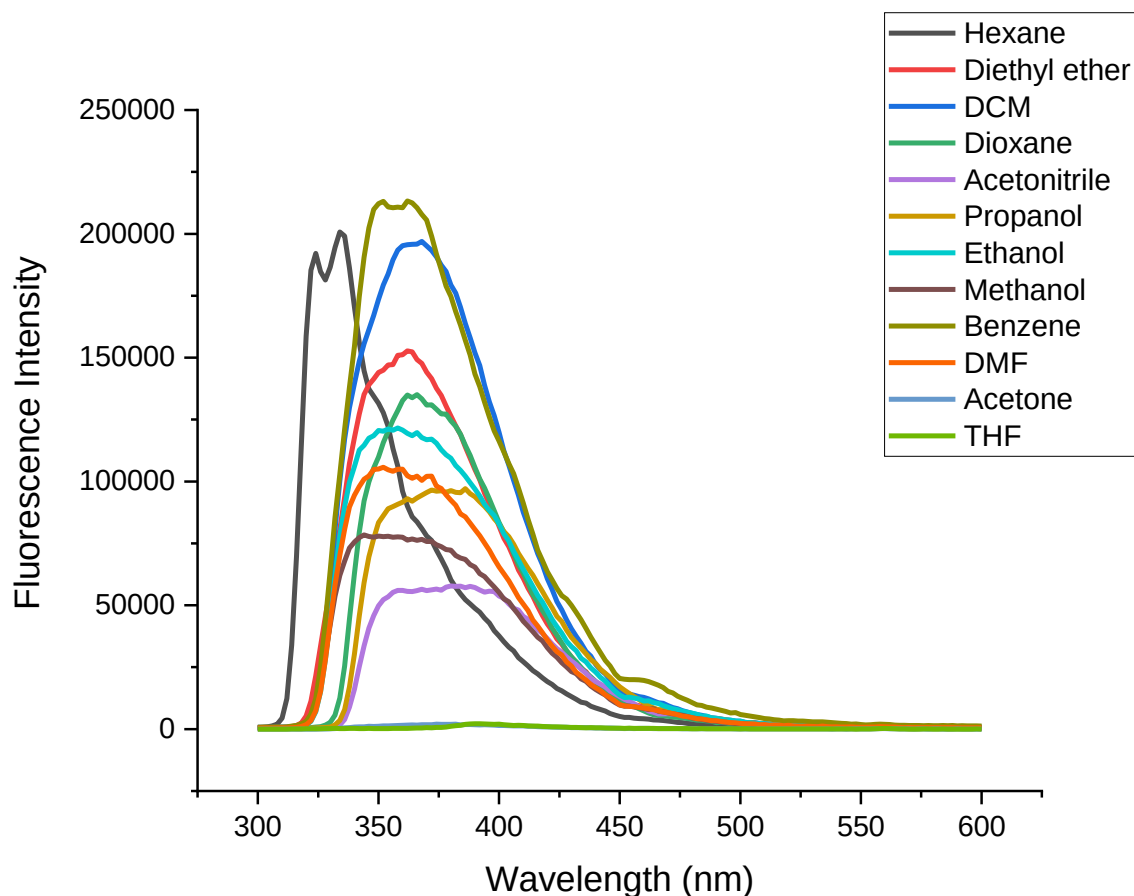


Figure 6.8 Fluorescence spectra of 8CB in various solvents

6.5 Solvatochromism of Nonyl and Decylcyanobiphenyl (9CB and 10CB)

As can be seen in Figure 6.9 and Figure 6.11, the absorption bands of 9CB and 10CB follow the trend in the previous samples observing a bathochromic shift of the $\pi-\pi^*$ transition from hexane to DMF. However, there is an obvious hypochromic shift for these samples with the longest alkyl chain. Praveen and Ojha reported such observation in their studies of the spectral shifts in thermotropic liquid crystals of *p-n*-alkoxy cinnamic of

varying chain lengths. The authors observed a slight blue shift and decrease in intensities of the absorption spectra on going from four alkyl chains to six and subsequently to eight alkyl chains, which was initially increased (hyperchromic effect) and a red-shift after increasing from two to four alkyl chains. The investigators argued that increasing chain length reduces the flexibility and oscillator strength of the chromophores. However, the hyperchromic effect was ascribed to the reduction of packing density when molecules get slightly elongated.⁵⁶ For this study, these conclusions are consistent with the observed increase in the absorption intensity going from 5CB to 6CB; and decrease in intensity going from 8CB to 9CB, and a slight red-shift in the absorption maxima, which suggests a weak exciton coupling of the chromophores.^{55,56}

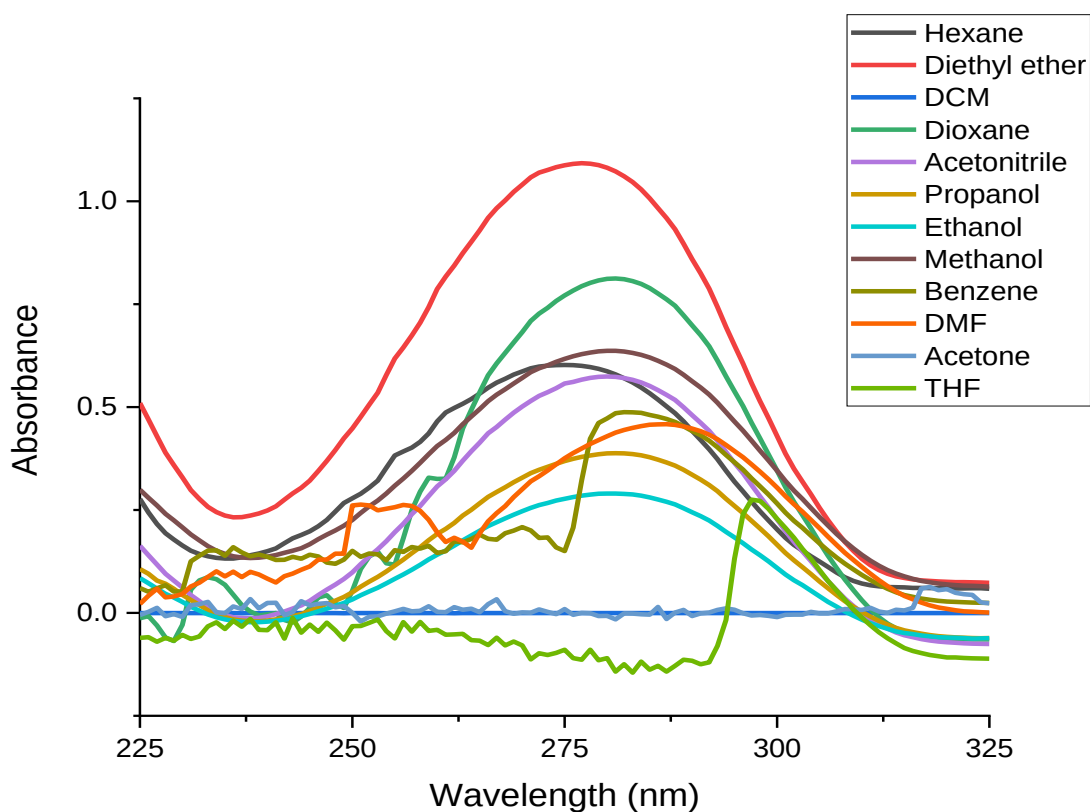


Figure 6.9 Absorption spectra of 9CB in various solvents

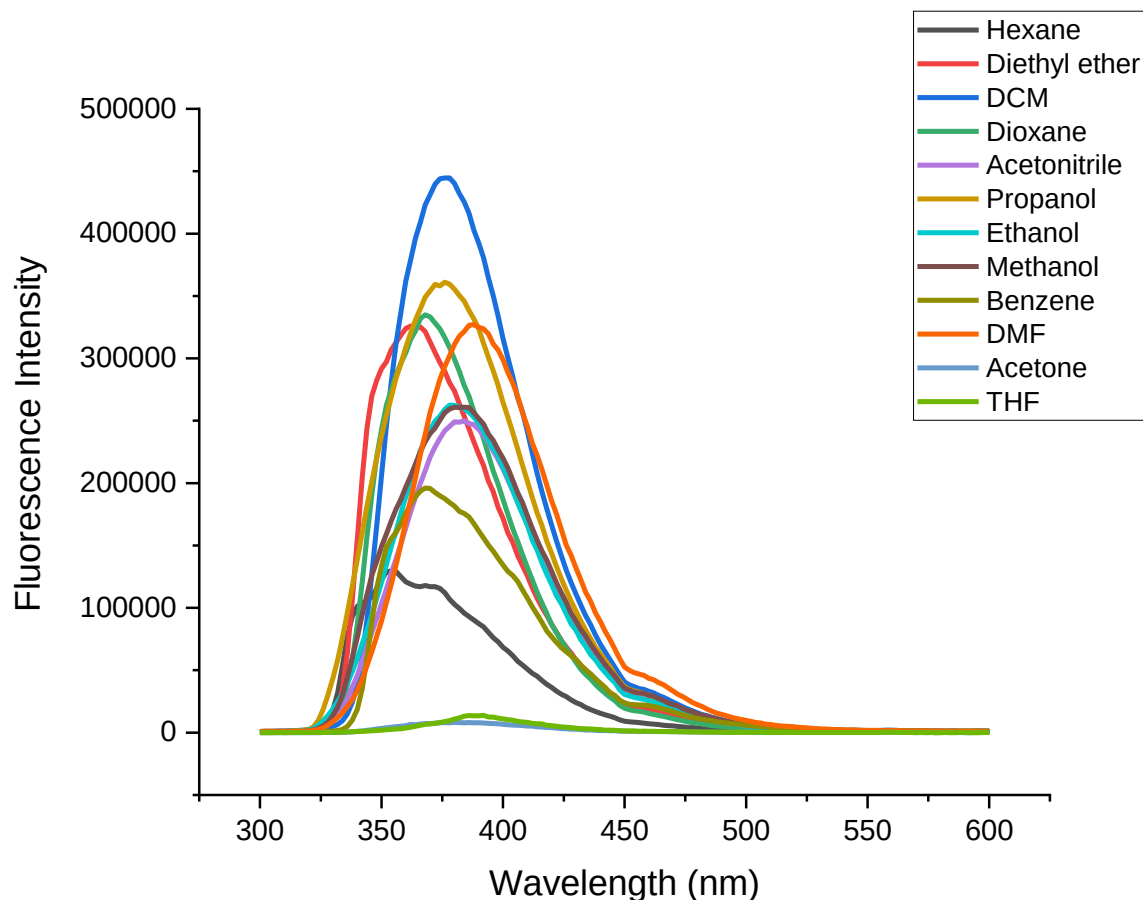


Figure 6.10 Fluorescence spectra of 9CB in various solvents

The fluorescence bands in the spectra of 9CB and 10CB (Figure 6.10 and 6.12) appear at longer wavelengths relative to the previous samples such that the band in hexane mostly found around 336 nm shifts to around 355 nm for 9CB and 10CB, shifting progressively to a longer wavelength as the solvent polarity is increased. The red-shift in the fluorescence for the 9CB and 10CB is a result of longer alkyl chain-induced associative effect having stronger dispersion forces that consequently decrease the energy gap for the electron transition, thus the observed shifts to longer wavelengths.^{29,59,60,70} Gueu *et al.* further suggested the existence of a folding back effect in the higher members of the

alkylcyanobiphenyls series that leads to increased interaction between the flexible alkyl chains and the biphenyl core.⁷⁰ Therefore the red-shift in fluorescence maximum wavelength of 9CB and 10CB suggests a folding back effect that leads to an increase in the excited dipole moment and a decrease in energy gap. Of particular interest, the observed fluorescence trend in these molecules do not show the influence of the odd-even effect in these longer alkyl chain-containing molecules. This finding is corroborated by previous reports of an increase in conformational flexibility occurring due to the presence of the longer alkyl chain at the molecular end of 9CB and 10CB molecules and thus the odd-even effect in the higher members of the series is either diminished or completely vanished.^{32,128,129}

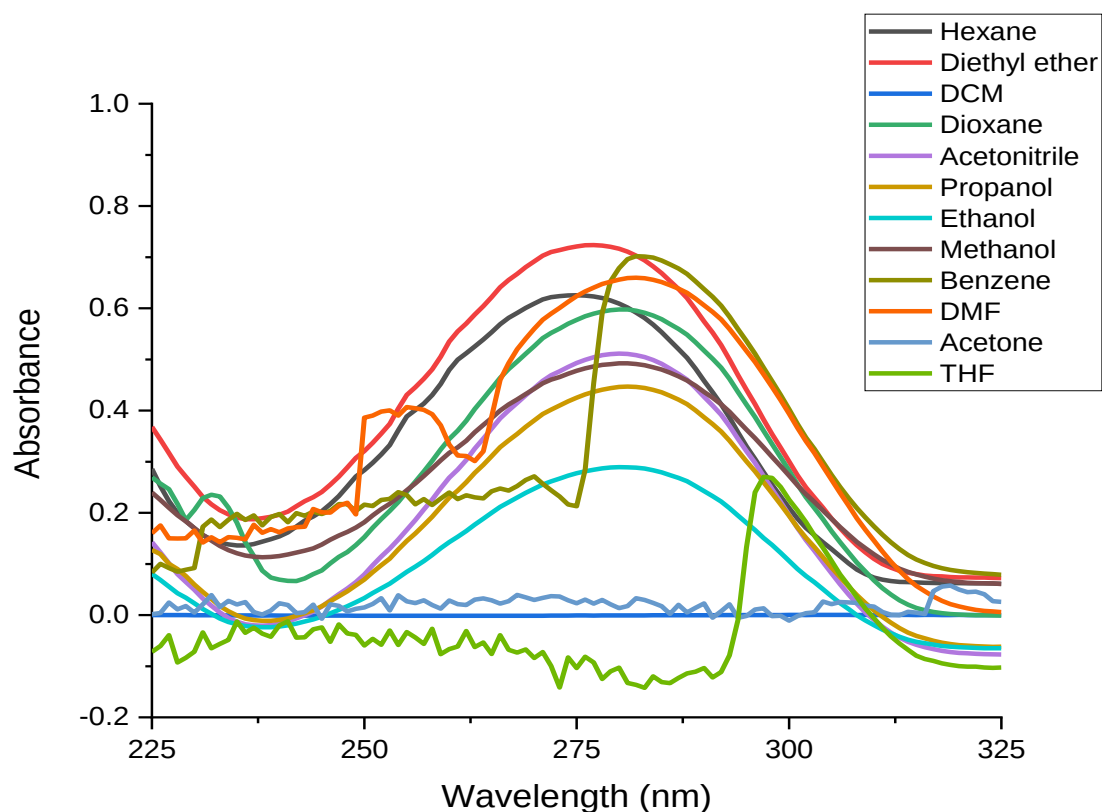


Figure 6.11 Absorption spectra of 10CB in various solvents

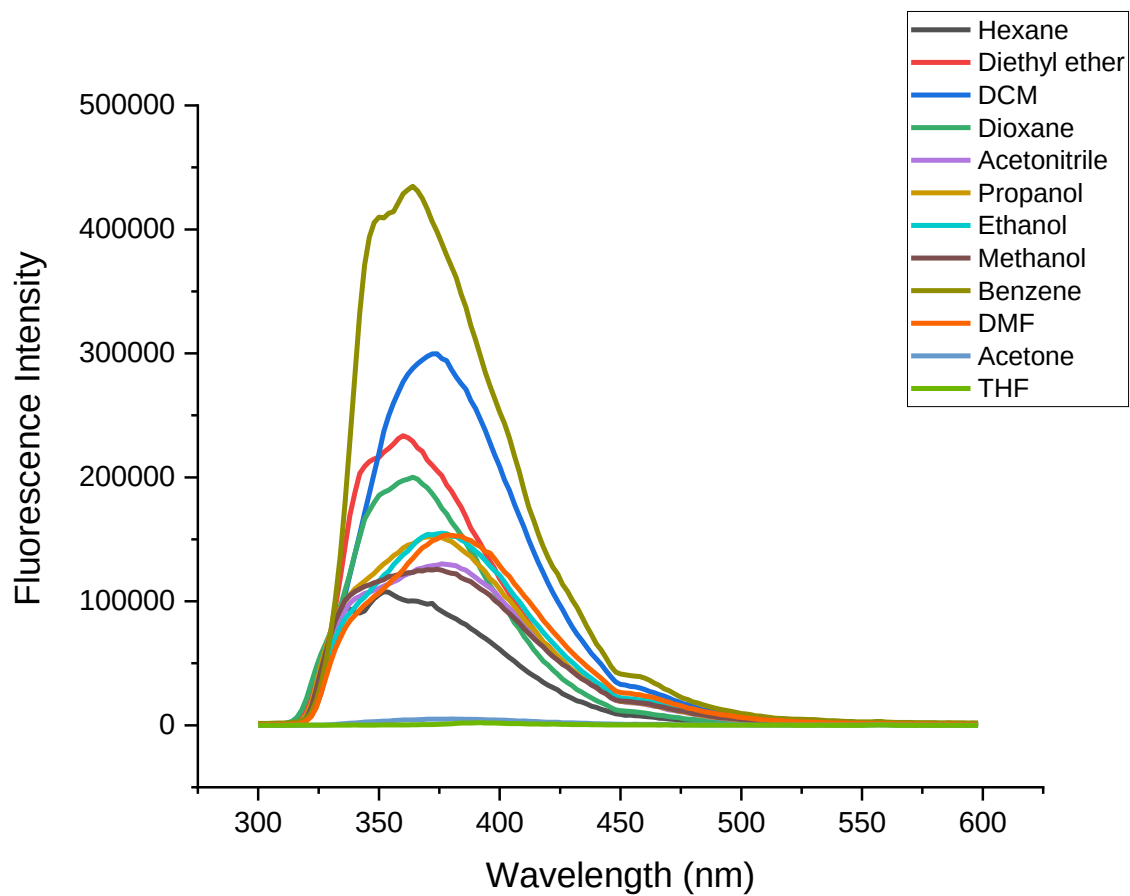


Figure 6.12 Fluorescence spectra of 10CB in various solvents

CHAPTER

CONCLUSION

7.1 Conclusion

An attempt to develop an optical-based liquid crystal sensor for detecting heavy metal ions in solution on an APTES-coated slide has been made using 5CB and SDS to anchor the rearrangement at the LC/aqueous interface. There was an observed response when mercury solutions were added indicated by a transition from bright to dark image obtained using POM. The addition of the mercuric ion results in an interaction with SDS that consequently induces the rearrangement at the LC/aqueous interface. However, in the used condition, there was no clear response of the sensor to cerium metal ions which indicated no interaction with SDS molecules at the interface. The sensing technique exhibits good sensitivity to the mercuric ions in solution.

In addition, the Raman spectra of six alkylcyanobiphenyl liquid crystal samples 5CB to 10CB in twelve solvents of varying polarity. The Raman bands of the LC molecules, which include C $\equiv$ N stretch, C–C aromatic ring breathing, C–C biphenyl link stretch, and C–H in-plane deformation show shifts due to changes in the solvent environment. Blue-shift was only observed in the spectrum of 5CB in hexane solvents for C $\equiv$ N stretching, which was ascribed to lesser interaction with the hexane molecules and induced repulsion by the alkyl chain of the 5CB in solution. Other LC molecules exhibited red-shifts across the various solvents. The observed Raman shifts showed no fixed consistency with polarity as the solvent is varied, but the shifts better correlate with the Kamlet-Taft dipolarity, acceptor

number, donor number, and polarizability of the solvents. It was observed that only the protic solvents (methanol, ethanol, and propanol) having the highest acceptor number, caused a red-shift to the cyano mode of 5CB. These solvents displayed hydrogen bond stabilization of the vibrational stretching modes. The Raman bands observed for samples with longer alkyl chains: 8CB, 9CB, and 10CB, were essentially around the same position in all the solvents used in this work. Such observations are linked to increased dimerization constant with chain length and folding back effect.

Furthermore, the solvent effect on the absorption and fluorescence of the members of the alkylcyanobiphenyl liquid crystal molecules was examined and evaluated. The maximum absorption wavelength of the six nCB molecules is similar with a subtle difference in fluorescence, which shifts to a longer wavelength as the polarity of the solvent environment is increased. However, the fluorescence spectra show some pattern as the solvent polarity is varied which is suggestive of an odd-even effect having similar wavelength maxima for the odd-numbered 5CB and 7CB and for even-numbered 6CB and 8CB. The fluorescence maximum wavelength of 5CB and 7CB red-shifted progressively as the polarity of the solvent was increased whereas in 6CB and 8CB diethyl ether was found to largely red-shift the band more than DMF, which is ascribed to the tilted alignment of the even-numbered nature of the molecules. Conversely, such an odd-even effect was not observed for the longer members – 9CB and 10CB – having appeared at longer wavelengths and were found to have strong associative interactions between the flexible alkyl chain and the rigid core as rationalized by some previous studies.

7.2 Future Prospect

As we aim to achieve the fabrication of a very reliable and sensitive heavy metal ion detection sensor, a proposal to obtain specific recognition molecules of individual metal ions is already in place. Slide glass functionalization molecules, OTS and/or DMOAP, are also on the waitlist in order to achieve efficient anchoring of the LC molecules. Upon arrival of these materials, this work will advance to test selectivity, sensitivity, and limits of detection. Ultimately, the fabrication of the chip-based LC sensor can be brought to life. Additionally, we look forward to conducting computational DFT studies of the alkylcyanobiphenyl series solvatochromism.

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Academic Background : MS Chemistry, BS Chemistry (First Class).

Professional Experience

- **Research and Teaching Assistant - King Fahd University of Petroleum and Minerals Sep 2021 – Present**
Operate numerous spectroscopic instruments
Instruct freshmen on basic chemistry practical
- **Assistant Technologist - Federal University Oye-Ekiti Dec 2020 - July 2021**
Charged with the responsibility of samples preparation for teaching labs
Maintained teaching instruments and provided technical assistance
- **Graduate Assistant - Kano University of Science and Technology Wudil Sep 2019 - Aug 2020**
Instructed level freshmen and sophomore's practical session
Assisted in teaching freshmen physical chemistry
Took part in the grading of courses

Leadership Experience

- **Member KFUPM Young Leaders Advisory Board Jan 2023 – Present**
Supervised the delivery of executed projects
Developed various proposals for extracurricular activities
- **Caretaker Chairman - Bayero University Association of Physical Science Students 2018**
Developed student impactful initiatives
Organized Social Events and Free and Fair Elections

Achievements & Awards

- Michael Collins Memorial Prize for Best Graduating Student in Chemistry - Registrar's Office, Bayero University Kano - 2019
- Student of the Year Award - National Association of Physical Science Students, Kano Chapter - 2019
- Bayero University Scholarship for Best Level 300 Student 2018
- Bayero University Scholarship for Best Level 200 Student 2017

Professional Membership

- | | |
|---|----------------------------------|
| • American Chemical Society | December 2022 - Present |
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| • Institute of Chartered Chemists of Nigeria | September October 2021 - Present |

Publications

Musa S. Dangombe and Sulayman A. Oladepo. Investigation of Solvent-Solvent Interactions of 4'-alkyl-4-cyanobiphenyls using Raman spectroscopy. Prepared manuscript

Musa S. Dangombe and Sulayman A. Oladepo. The Effect of Solvents on the Absorption and Fluorescence of 4'-alkyl-4-cyanobiphenyls Liquid Crystal Molecules. Prepared manuscript

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