Study of Molecular Interaction and Electro-Optical Properties of Liquid Crystal Molecules using Density Functional Theory

Summary

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Submitted by

Mirtunjai Mishra

(Enrollment No. 1687/19)

Co-supervisor
Dr. Devendra Singh

Supervisor
Prof. (Dr.) Devesh Kumar

DEPARTMENT OF PHYSICS
SCHOOL OF PHYSICAL & DECISION SCIENCE
BABASAHEB BHIMRAO AMBEDKAR UNIVERSITY
(A CENTRAL UNIVERSITY) (NAAC: A++ ACCREDITED)
RAEBARELI ROAD, LUCKNOW-226025, U.P. (INDIA)

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Chapter 1: Introduction and aim of research work

The states of matter are mainly classified into solid, liquid, and gas. Different properties are exhibited by these states of matter. Solids have a definite shape, liquids can flow, and gases do not have fixed shape or volume. The concept of liquid crystal lies between a crystalline solid and an isotropic liquid as shown in figure 1. The Liquid crystal (LC) phase represents a different state of matter characterized by the molecule's mobility and order.

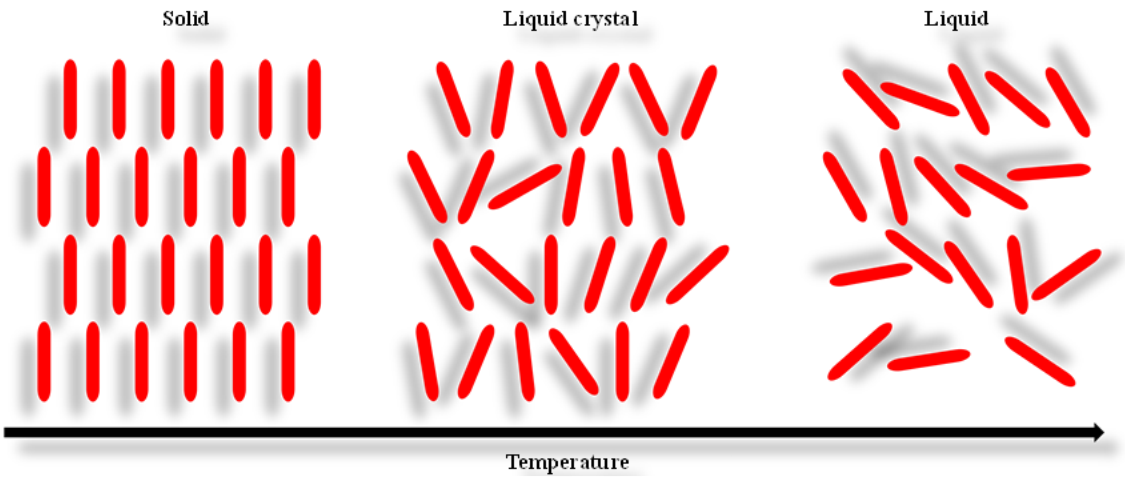


Figure 1: Molecular orientation of molecules with temperature in different states.

All the particles in the crystalline state possess an orientational and three-dimensional positional order. Liquid crystal phases possess both orientational order and, in some cases, positional order in one or two dimensions. The molecules' behavior is responsible for the different types of intermolecular interaction acting between the sides, planes, and ends of a molecule pair. LC phases are formed by anisotropic molecules, having one molecular axis very different from the other two. The rod-like molecule is the most common type of LC molecular shape. The nematic phase exhibits long-range orientational order but no positional order of the molecule. The external electric field's impact on liquid crystal can be studied by Vuk's theory and analyze the molecule's polarizability.

In liquid crystals, the molecular polarizability and its anisotropy are important inherent molecular properties because the intermolecular interaction energies depend on them. LC materials may consist of polar and non-polar molecules that depend upon LC's physical structure. The LC molecules can possess permanent dipole along the long

molecular axis, enhancing the LC's dielectric anisotropy. The dipole moment parallels the long molecular axis, then $\Delta\varepsilon>0$, and the molecules tend to orient along the electric field direction because LC possesses more significant dielectric anisotropy along the molecular axis (x-axis). The orientational order of the LC molecule does not change in the applied external electric field. The applied external electric field to the LC molecule causes the reorientation of the director angle. The LC molecule responds to the applied external electric field E collectively, causing the director angle to fluctuate.

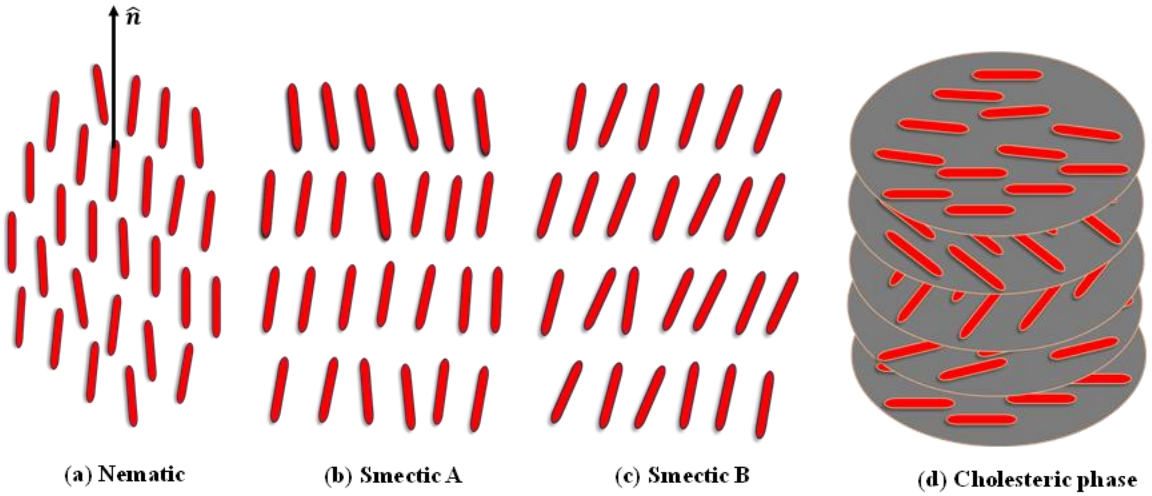


Figure 2: The structure of (a) Nematic phase (b) Smectic A (c) Smectic B and (d) Cholesteric phase.

The calamitic thermotropic liquid crystals are classified into nematic and smectic liquid crystals as shown in Figure 2. The subsequent class is discotic nematic and columnar. By the influence of solvents, the liquid crystals are named Lyotropic liquid crystals. The role of a surfactant is very crucial in this case. The liquid crystals in the nematic phase do not change their propagation direction while going through the sample. But positional order is absent. If we take the case of isotropic liquid–nematic transition, the translational symmetry is maintained while the rotational symmetry is lost.

The liquid crystals in the smectic phase are obtained when the crystalline order is absent in two dimensions. By this, we get a stack of two-dimensional liquid. These have well-defined structures with well-defined interlayer spacing. In smectics, the positional and orientational ordering remains intact. This helps in translation in two directions and rotation in one direction. The strength of interlayer attractions was weak in comparison to lateral forces, so the layers of the molecules can slide over one another. This enhances the fluidity of smectics over the nematics as smectics have higher viscosity. Another key feature of the smectic phase is it has periodicity along one direction. One can find a large number of

smectic phases as no point group is forbidden. From layer formation, one smectic phase is different from the other one another. SmecticA phase is considered to be the simplest phase in which the average molecular axis is perpendicular to the smectic layers. There is a random arrangement of different layers of the smectic phase, and they are capable of translating and rotating along their axes. One can observe optical patterns arising due to the distortion caused by the flexibility of layers. To get a phase having a bit lower symmetry, the temperature must be decreased up to a certain level. These phases produce a crystalline structure when the long axes of the molecule are orthogonal to the plane of the layers. One of the exceptions is the smectic D phase, which is a cubic phase but does not contain layers. Some smectic phases possess 2D characters like smectic B, smectic I, and smectic F. The higher-order smectic phase possesses 3D character smectic L and smectic J.

Discotic liquid crystals (DLCs) represent a fascinating subset of liquid crystalline materials distinguished by their unique structural and functional properties. These materials are composed of disk-shaped molecules, typically featuring a rigid aromatic core surrounded by flexible aliphatic side chains. This molecular design facilitates the formation of columnar phases (shown in Figure 3) where the discs stack over one another, leading to a variety of mesophases depending on the thermal and environmental conditions. This progress underscores a growing interest and research focus on the unique properties and potential applications of discotic LCs, contributing to the extensive diversity within the field of liquid crystalline materials.

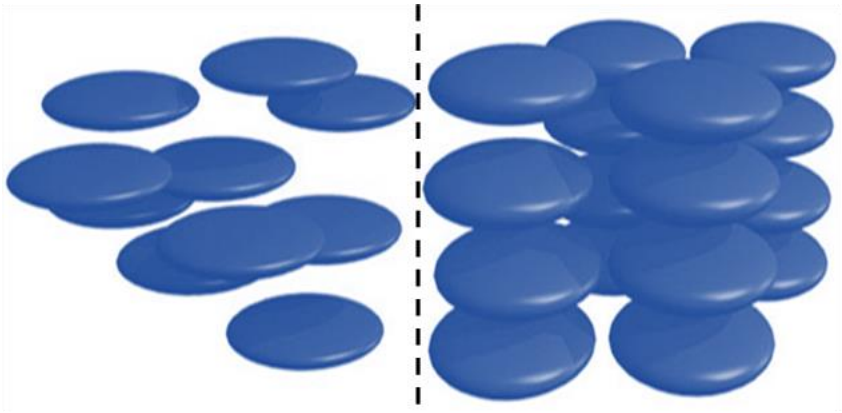


Figure 3: Schematic diagram of (a) Discotic Nematic and (b) Discotic Columnar.

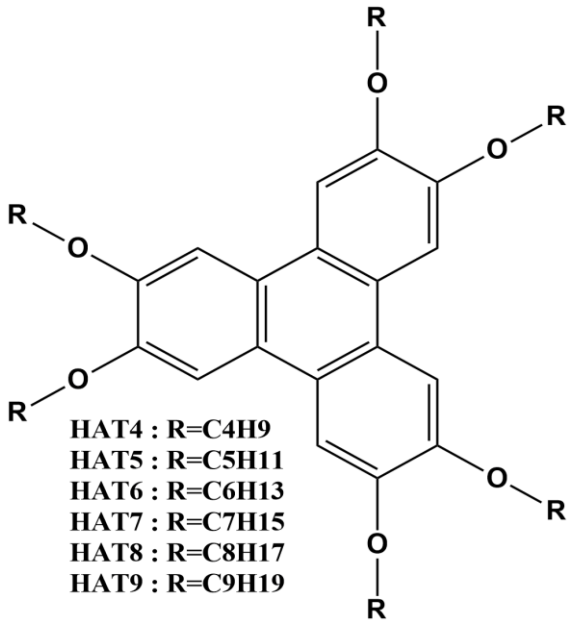


Figure 4: Typical DLC molecules.

A common discotic liquid crystal molecule, depicted in Figure 4, is usually classified into one of two primary structural types: columnar or nematic. Within the columnar phase, the disk-shaped molecules are stacked in a non-periodic manner, creating columnar structures that behave like liquids. These columns are then arranged into a two-dimensional lattice. The arrangement of these columns can manifest in several forms, such as hexagonal, rectangular, and oblique patterns.

Thermotropic liquid crystalline phases are also displayed by specific polymers. These polymers are composed of fundamental monomer units that are mesogens of lower molecular weight, which can be either rod-like or disc-like molecules. The mesogenic units in these polymers are either incorporated directly into the main chain of the polymer or attached as side groups, as depicted in Figure 5. The particular type of mesophase that forms is greatly dependent on the structure of the polymer backbone, the type of mesogenic unit, and the spacers utilized.

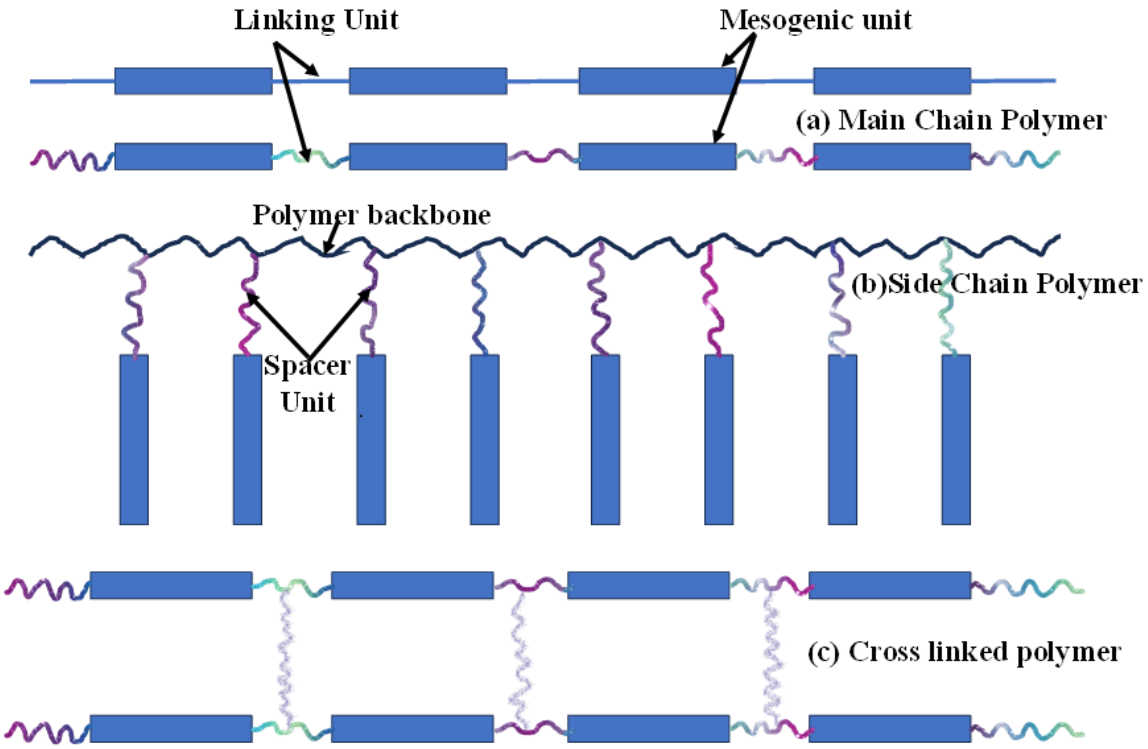


Figure 5: Schematic diagram of (a) Main chain polymer (b) Side chain polymer and (c) Cross-linked polymer.

Research work aims to study the molecular interaction and electro-optical properties of LCs of different structures with the help of interactions with other molecules. The interactions in liquid crystalline molecules with the different molecules are to be done by DFT methodology of the specific basis set because the interaction studies are targeted to get some insight towards the design of a stable cluster for desirable properties of the devices. To enhance the potential applications of the LCs, the fine-tuning of electro-optic parameters for selective applications in optoelectronic devices is crucial. Here, we have chosen discotic liquid crystals to explore their use in optical devices based on the literature review. Besides, chemical sensing properties of LC molecules have been studied to help detect environmental gas pollutants by understanding the parameters governing their interaction with analytes, which may ultimately aid in selectively eliminating them and improving the ambiance of living space.

Chapter 2: Computational methodology

The main methods used in the present thesis are discussed below:

Density functional theory (DFT)

DFT is a quantum mechanical approach used to investigate the electronic structure (mainly the ground state) of many body systems, in particular atoms, molecules, and the

condensed phases. Using this theory, the properties of many-electron systems can be determined by using functional, i.e. functions of function, which in this case is the spatially dependent electron density. Hence the name DFT comes from the use of functional electron density which is a function of position. DFT is among the most popular and versatile methods available in condensed matter physics, computational chemistry, and computational physics. The geometry optimization of liquid crystal molecules was done by different functional B3LYP/M06-2X/CAM-B3LYP with 6-31G, 6-311G, 6-31G(d,p), and 6-311G(d,p) basis sets.

Chapter 3: Theoretical Prediction (DFT) and experimental observation of electronic and electro-optical properties of HATn (n=5,6,7,8) molecules for optoelectronic applications

In this chapter, a comprehensive theoretical investigation was done to explore a series of discotic liquid crystal molecules based on a triphenylene core (shown in figure 6), labeled as HATn (n = 5, 6, 7, 8), utilizing Density Functional Theory (DFT) calculations at the B3LYP/6-31G**, CAM-B3LYP/6-31G**, and M06-2X/6-31G** level of basis.

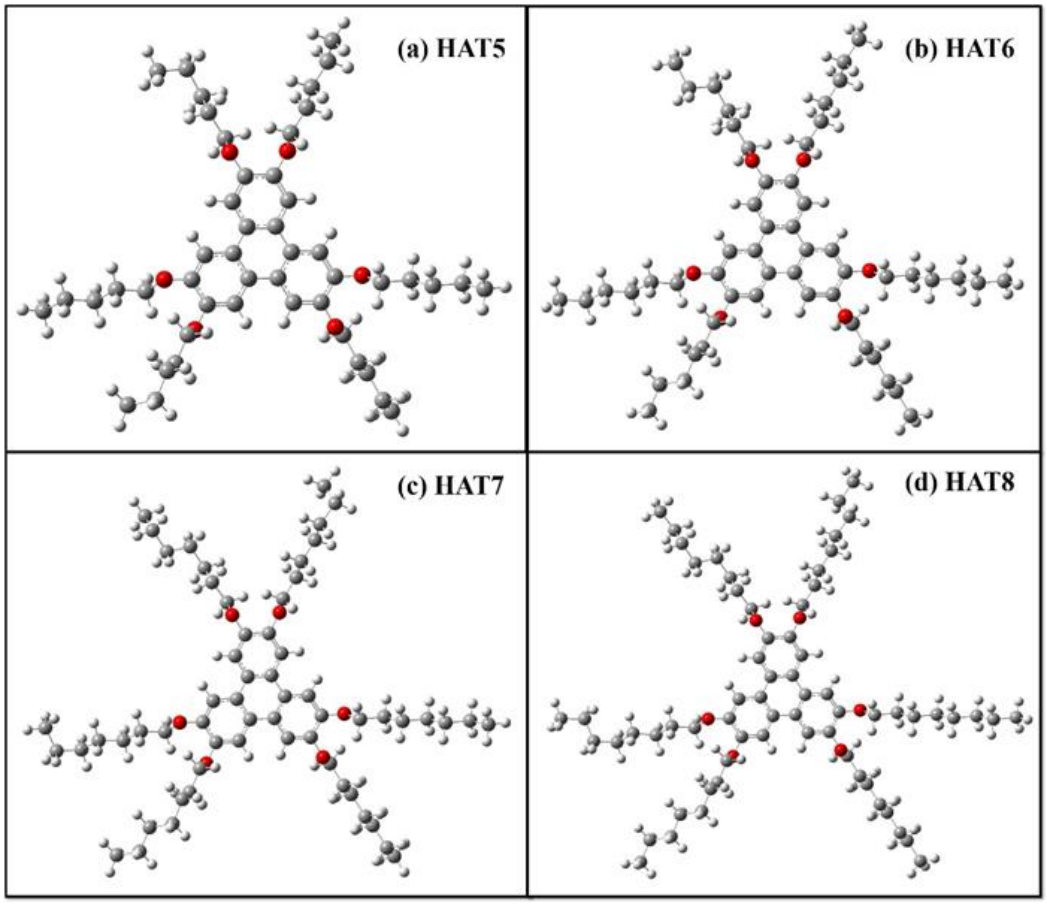


Figure 6: Optimized structural geometries of the (a) HAT5, (b) HAT6, (c) HAT7, (d) HAT8 DLCs.

Our study encompassed a wide range of electronic, electro-optical, and non-linear optical properties that were rigorously compared with experimental findings, leading to valuable insights. Our simulations unveiled a consistent trend: an inverse relationship between the length 'n' of the peripheral alkyl chain and their properties such as ionization potential, electron affinity, electronegativity, chemical potential, and electrophilicity index. The mentioned monotonic changes with the elongation of the alkyl chain influence the molecular architecture.

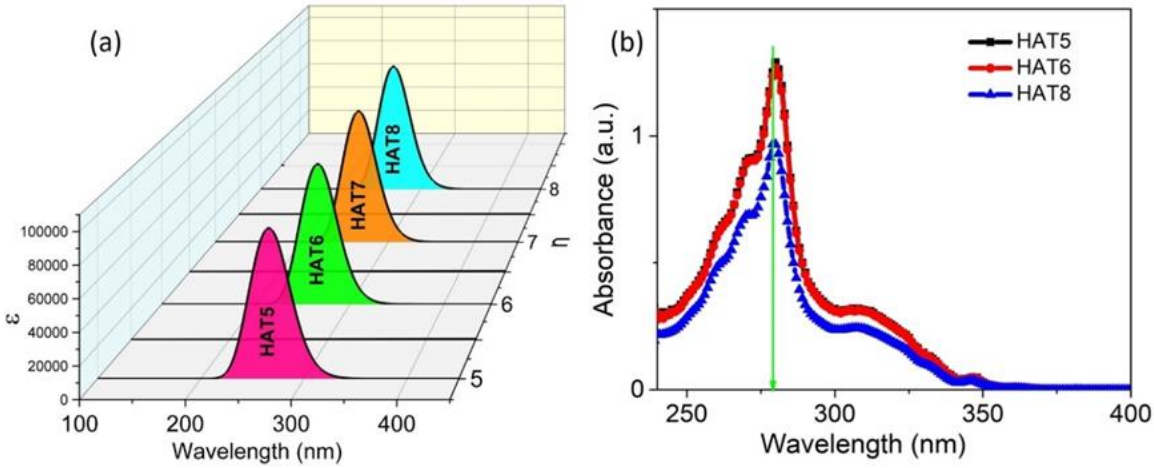


Figure 7: UV-visible absorption curves for HATn(n = 5-8) DLC (a) simulation, (b) experimental.

Thermodynamic parameters were computed and revealed that thermal energy, specific heat at constant volume, and entropy increase as the alkyl chain length (i.e., n = 5, 6, 7, and 8) increases. Additionally, the UV-vis absorption spectra of HATn yielded a maximum absorbance (λ_{max}) at approximately 266nm, corresponding to π-π* transitions in the C=C bonds of the triphenylene core. However, it was noted that the experimental absorption was centered on 280nm as shown in Figure 7.

Table 1: The isotropic polarizability (α), anisotropy polarizability (Δα), first-order hyperpolarizability (β), and dielectric constant of HATn (n=5-8) DLCs.

Molecules	Functional /basis set	Isotropic polarizability (α) (a.u.^{3})	Anisotropy polarizability Δα (a.u.^{3})	First-order hyperpolarizability β (a.u.^{5})
HAT5	B3LYP/6-31G**	602.81	339.3673	37.5143

	CAM-B3LYP/6-31G**	576.38	312.8600	7.5335
	M06-2X/6-31G**	586.65	338.43	28.94
HAT6	B3LYP/6-31G**	673.55	365.6495	20.7025
	CAM-B3LYP/6-31G**	644.82	336.1850	9.3325
	M06-2X/6-31G**	657.58	369.43	57.2744
HAT7	B3LYP/6-31G**	741.58	385.8103	28.8810
	CAM-B3LYP/6-31G**	710.93	354.0937	16.6879
	M06-2X/6-31G**	725.85	391.5639	103.6380
HAT8	B3LYP/6-31G**	811.61	410.8752	37.5143
	CAM-B3LYP/6-31G**	778.79	377.0492	18.7386
	M06-2X/6-31G**	793.92	427.1933	83.7912

The polarizability, dielectric constant, and density of state for HATn of homologs have also been theoretically computed as given in table 1 and compared with those of the available experimental values. Further, the change in these properties has also been correlated with that of the molecular ordering and charge transport properties, in understanding the structure-property relationship. The reported study could be used as the potential applications in optoelectronics devices and organic electronics that employ triphenylene core-based discotic liquid crystals.

Chapter 4: Enhancement of electro-optical and non-linear optical parameters of halogenated hexahexyloxy triphenylene (HAT6) molecule: A computational approach

In the present chapter, the different geometries of pure HAT6 and halogenated HAT6 molecules were optimized with B3LYP and 6-311G basis set. After geometry optimization, the planarity of the ring group was confirmed. It was found that the molecular

polarizability of the HAT6 molecule enhanced by the halogenation with single and double atoms of Cl and Br in structures as shown in Figure 8.

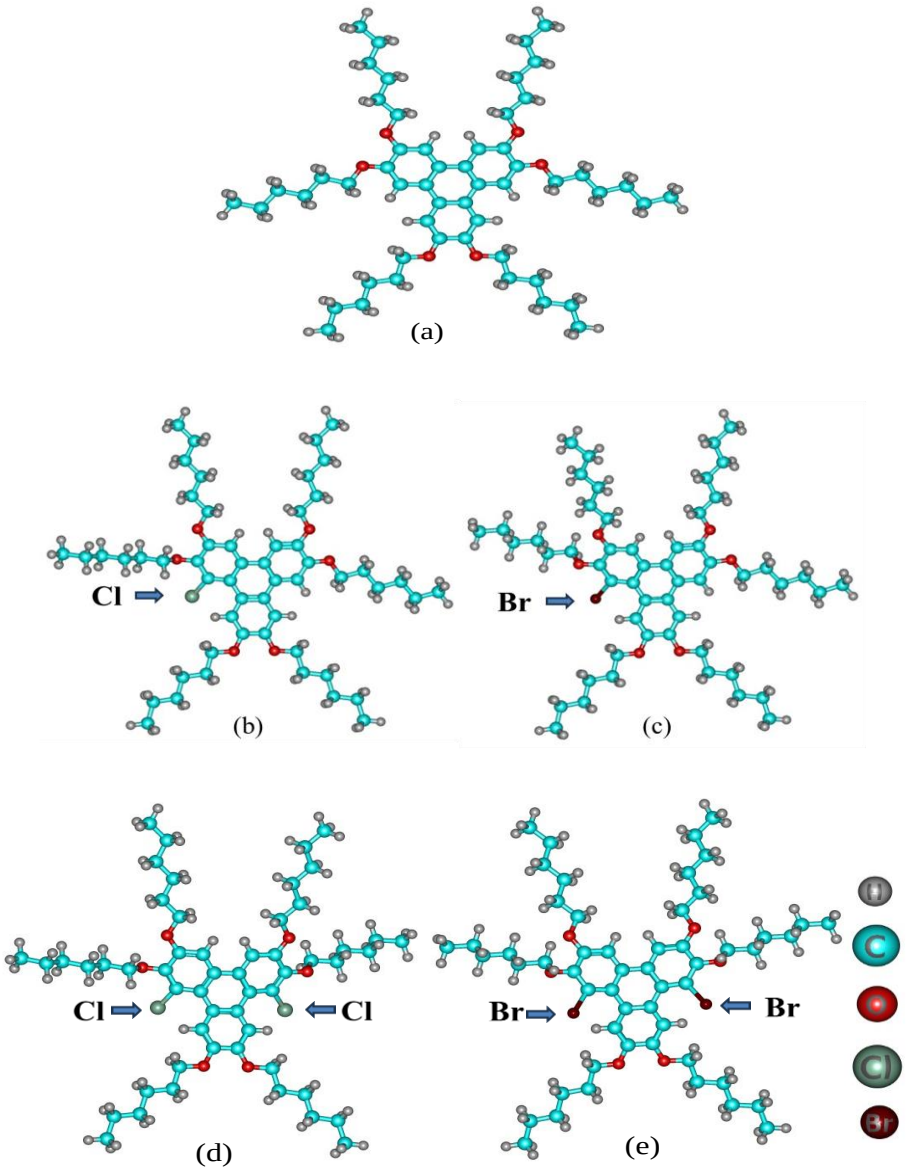


Figure 8: Optimized geometries of HAT6, chlorinated, and brominated HAT6 molecules.

A reduction in the energy band gap of the frontier molecular orbital is also observed. The maximum absorption of halogenated HAT6 is located in the UV region, and different halogen atoms (Cl, Br) show a very small impact on the absorption spectra. Based on the obtained results, the halogenated HAT6 is a potential candidate for nonlinear optical applications including a doubly chlorinated HAT6 shows greater potential for nonlinear optical performance among all four configurations of optimized HAT6 molecules. The nonlinear activity of HAT6 has also been enhanced by its interaction with halogens leading

to fine-tuning of nonlinearity which may be useful in harmonic generation, electro-optic, and biological processes. The electro-optical properties of the considered molecule can be customized by employing various basis sets and amplifying the impact of halogenation. Owing to the influence of halogenation, thermodynamic properties such as entropy and specific heat exhibit a consistent increase (as shown in Figure 9), thereby rendering these halogenated discotic molecules notably more stable than pure discotic materials.

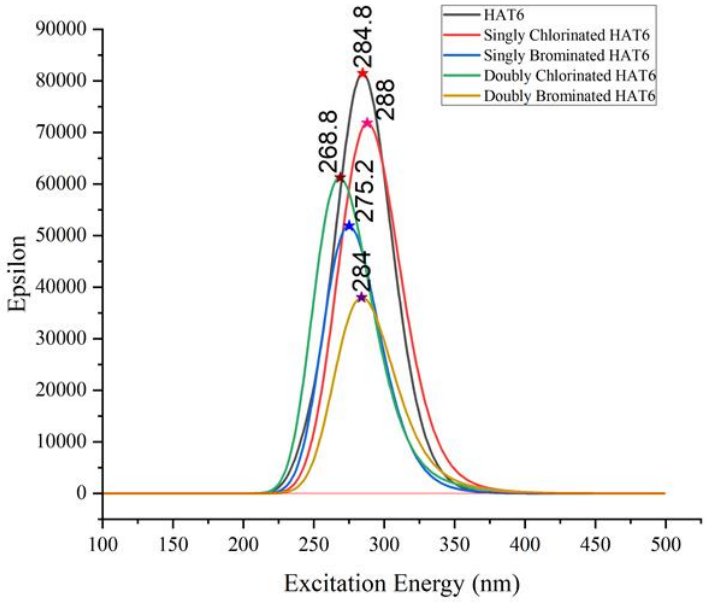


Figure 9: UV-vis spectra of HAT6, chlorinated, and Brominated HAT6 molecules.

Chapter 5: DFT study of difluoro & trifluoro bi-cyclohexane based dimer for application in electronic and optical devices

Here, we have studied the interaction of 4-(2,2,-difluorocyclopropyl)-4′-propyl-1,1′-bi(cyclohexane) and 4-propyl-4′-(1,2,2,-trifluorocyclopropyl)-1,1′-bi(cyclohexane) molecules in stacked parallel, stacked anti-parallel, in-plane parallel, and in-plane anti-parallel configurations. Schematic stacking and in-plane interactions are shown in Figure 10.

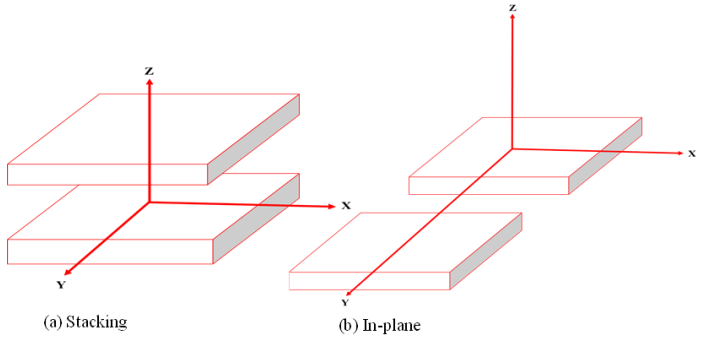


Figure 10: Schematic diagram of stacking and in-plane interactions conformation.

Based on different types of configurations, we have investigated the effect on properties like non-linear optical parameters, chemical reactivity parameters, FMO, etc. FMO analysis may be used to predict accurately chemical reactivity and charge transfer properties of considered molecules. The major contribution to the stability of the stacked and in-plane obtained is due to the induced dipole-induced dipole-type interactions (shown in Figure 11 and Figure 12).

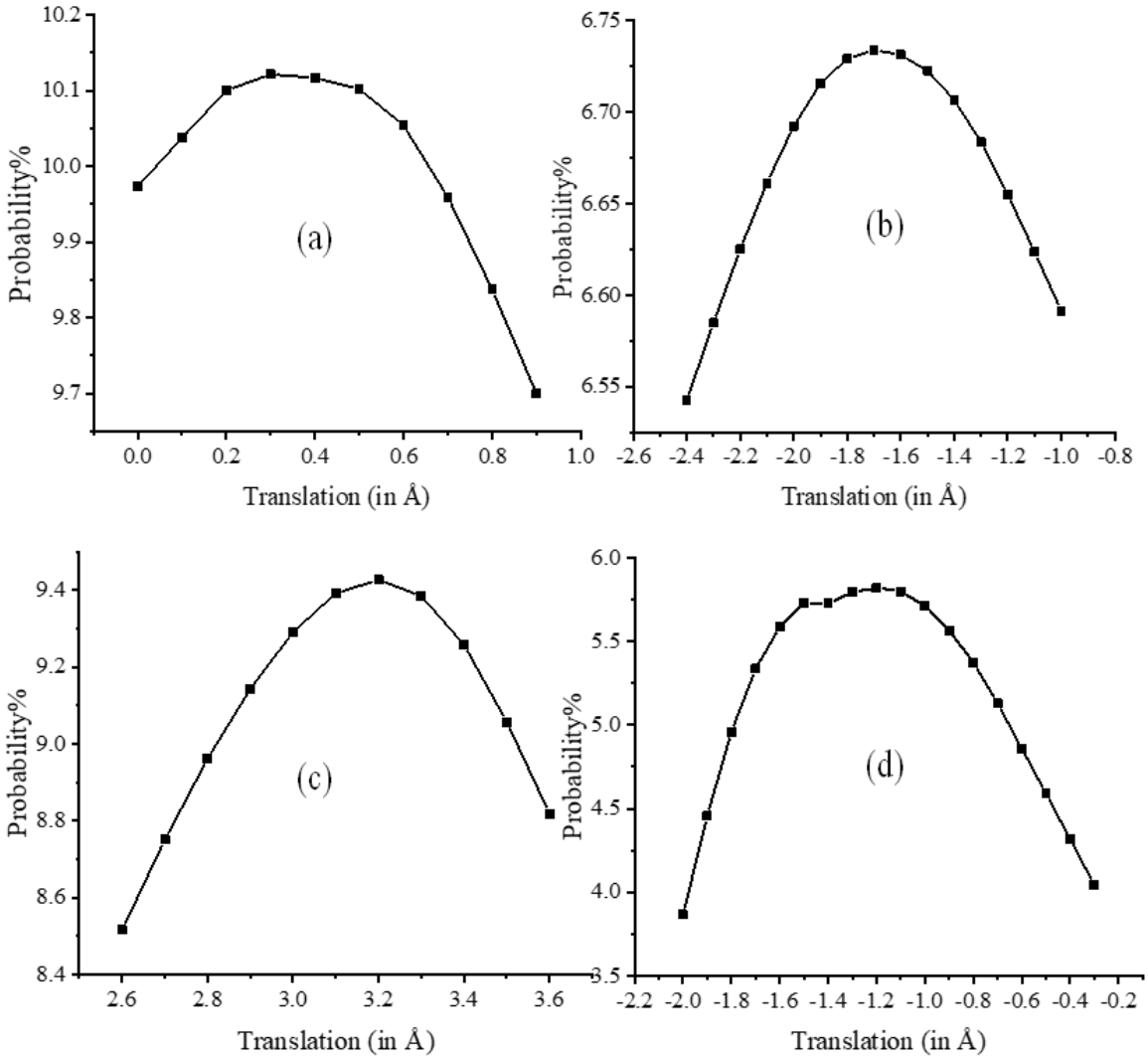


Figure 11: Variation of probability with the translation of dimer 4-(2,2,-Difluorocyclopropyl)-4′-propyl-1,1′-bi(cyclohexane) molecules (a) Stacking parallel configuration (b) Stacking anti-parallel configuration (c) In-plane parallel and (d) In-plane anti-parallel configuration.

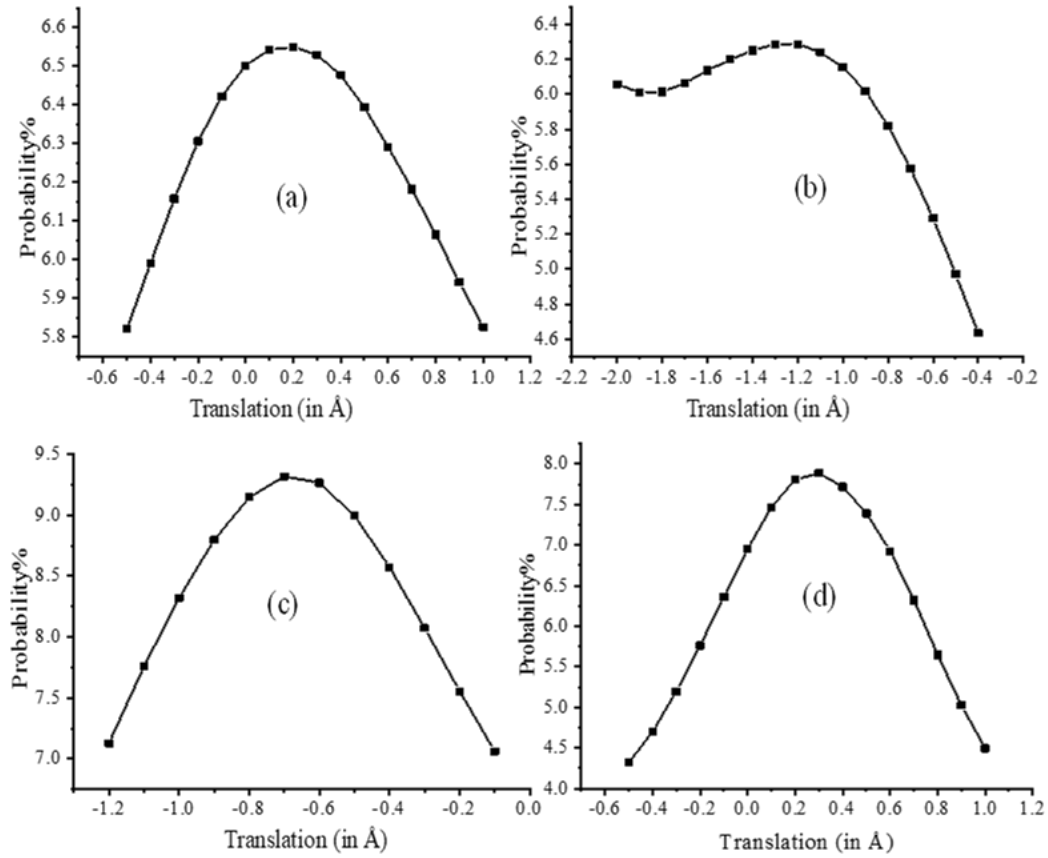


Figure 12: Variation of probability with the translation of dimer 4-propyl-4′-(1,2,2,-trifluorocyclopropyl)-1,1′-bi(cyclohexane) molecules (a) Stacking parallel configuration (b) Stacking anti-parallel configuration (c) In-plane parallel and (d) In-plane anti-parallel configuration.

Our results support the smectic behavior as presented in the literature for specific configurations. The findings derived from Density Functional Theory (DFT) with B3LYP/6-311G(d,p) analyses reveal that considered molecules exhibit superior nonlinear optical properties compared to urea, as evidenced by increased values of mean polarizability (α) and hyperpolarizability (β).

Table 2: Chemical reactivity parameters of dimer 4-(2,2,-Difluorocyclopropyl)-4′-propyl-1,1′-bi(cyclohexane) molecules.

Chemical reactivity parameters	In-plane anti-parallel configuration	In-plane parallel configuration	Stacking anti-parallel configuration	Stacking parallel configuration
E_{HOMO} (in eV)	-7.62145	-7.62689	-7.55993	-7.45131
E_{LUMO} (in eV)	0.47130	0.55756	0.39130	0.25660
χ (in eV)	3.57507	3.53467	3.58431	3.59736

μ (in eV)	-3.57507	-3.53467	-3.58431	-3.59736
η (in eV)	4.04637	4.09223	3.97561	3.85396
S (in eV^{-1})	0.12357	0.12218	0.12577	0.12974
E_g (in eV)	8.09275	8.18445	7.95123	7.70792
ω (in eV)	1.57933	1.52654	1.61576	1.67892
ΔN_{max}	0.88353	0.86375	0.90157	0.93342

Table 3: Chemical reactivity parameters of dimer 4-propyl-4′-(1,2,2,-trifluorocyclopropyl)-1,1′-bi(cyclohexane) molecules.

Chemical reactivity parameters	**In-plane anti-parallel configuration**	**In-plane parallel configuration**	**Stacking anti-parallel configuration**	**Stacking parallel configuration**
E_{HOMO} (in eV)	-7.58307	-7.59504	-7.70910	-7.58279
E_{LUMO} (in eV)	0.42014	0.61824	0.16735	0.16898
χ (in eV)	3.58146	3.48840	3.77088	3.70691
μ (in eV)	-3.58146	-3.48840	-3.77088	-3.70691
η (in eV)	4.00160	4.10664	3.93823	3.87589
S (in eV^{-1})	0.12495	0.12175	0.12696	0.12900
E_g (in eV)	8.00321	8.21329	7.87645	7.75178
ω (in eV)	1.60271	1.48162	1.80532	1.77264
ΔN_{max}	0.89501	0.84945	0.95751	0.95640

The variations in the HOMO-LUMO energy gaps (as shown in tables 2 &3) of these molecules contribute to different charge transfer characteristics, further underscoring their potential applications. Consequently, the molecules may be identified as excellent candidates for developing various opto-electronic applications, including photovoltaic cells, organic light-emitting diodes (OLEDs), field-effect transistors (FETs), all-optical switches, bistable devices, and metamaterials, according to the obtained results.

Chapter 6: Interaction of environmental pollutants with HAT6 molecule: A DFT study for chemical sensing

In this chapter, we have studied theoretical investigations of the interaction energies, density of states (DOS), and electronic properties of the HAT6 DLC molecule

with various gases were conducted using Density Functional Theory (DFT) methods, specifically the B3LYP and M06-2X functionals with a 6-311G(d,p) basis set.

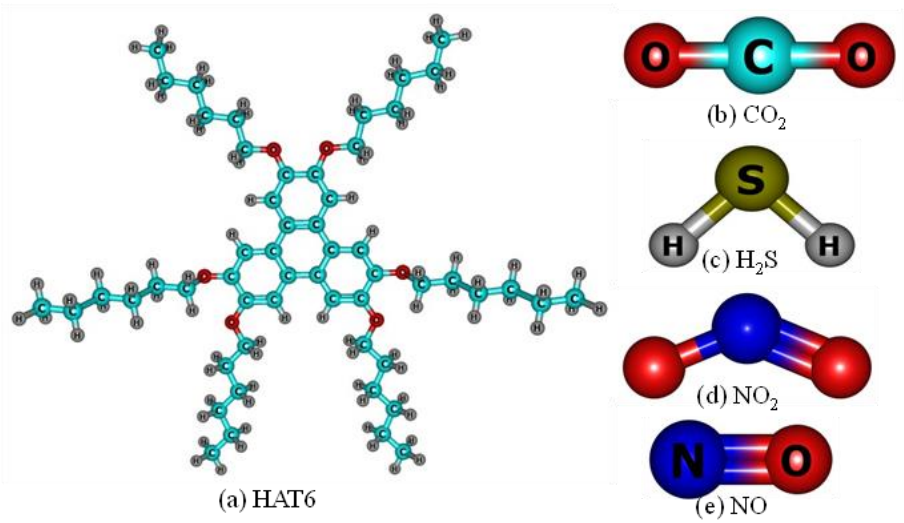
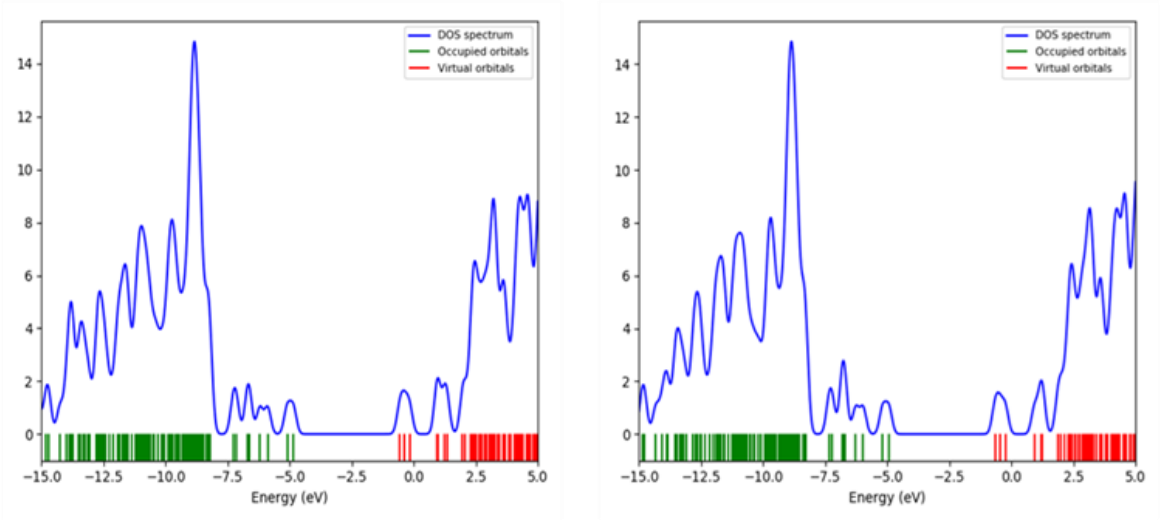


Figure 13: Optimized structures of (a) HAT6, (b) CO_2, (c) H_2S, (d) NO_2, and (e) NO molecules.

The study focused on understanding the effects of CO_2, H_2S, NO_2, and NO gases on the HAT6 DLC molecule's interaction, electronic, DOS, and structural properties as shown in Figure 13.



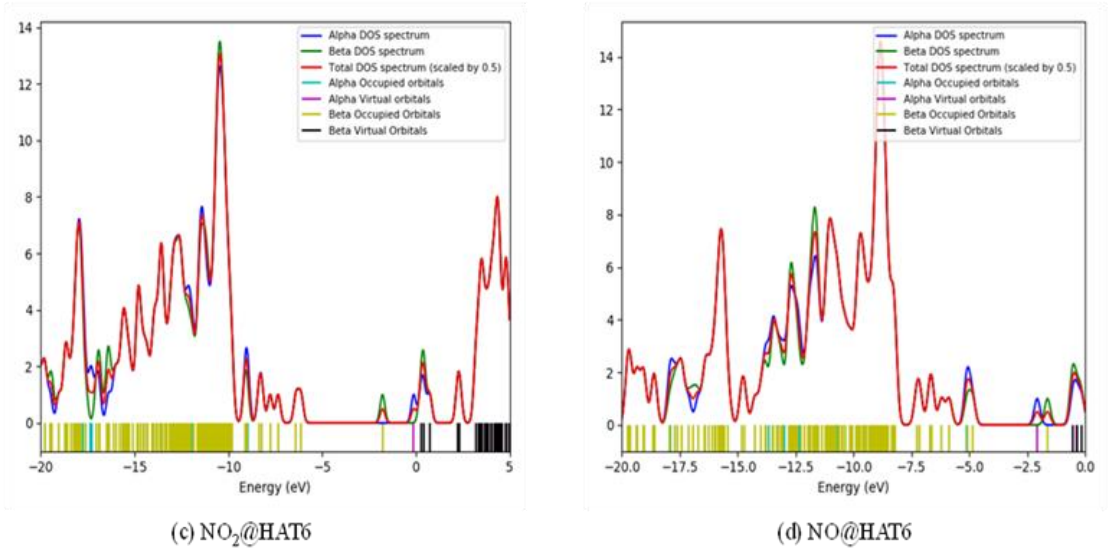


Figure 14: DOS plot of (a) CO_2, (b) H_2S, (c) NO_2, and NO molecules at B3LYP/6-311G (d,p) method.

In the calculation of RDG, NCI, electronic, and DOS parameters, significant changes were observed indicating alterations in the chemical properties due to these interactions. Notably, H_2S demonstrated a pronounced influence on the electron density on the molecule's surface compared to the other gases (shown in figure14). Based on these findings, HAT6 DLC can act as a potential candidate for development as a chemical sensor for H_2S gas.

Chapter 7: Conclusion and Future Prospects

Researchers are currently investigating the aggregation of liquid crystal molecules with nanoparticles to develop materials with potential future applications. Computer simulations have been instrumental in analyzing the behavior of various phases of liquid crystals through realistic models. Looking towards the future of optical electronics, the field of active optics, that involves the active control of the wavefront of light, needs to be explored. Liquid crystals play a crucial role in adaptive optics by correcting wavefront aberrations. In optical space modulators, smectic materials are preferred due to their ability to stabilize temperature variations. The advancement of future technologies such as the image processors and the development of electronic paper hinge on the innovation of new liquid crystal materials.

In the biological domain, the fabrication of artificial membranes could be improved by employing discotic liquid crystals. Additionally, the lyotropic liquid crystalline structure inherent in biological systems warrants further investigation for its potential applications

in future technologies. Liquid crystal technology has evolved to develop the enhancing optical computing, offering significant advantages in device performance and cost reduction. Mesogens, with their highly ordered structures, are utilized in applications such as smart surfaces and microlens arrays. Combination of liquid crystals with graphene and reduced graphene oxide have shown chemical stability and are promising for large-scale production of transparent conductive electrodes. However, gold nanoparticles do not disperse well in liquid crystals, which poses challenges for further research in this area. One notable property of liquid crystals is charge transfer; thus, ion-based liquid crystals with π-electron conjugation are deemed the materials of the future. The guest-host aggregation in liquid crystal-based display devices is already implemented in automotive dashboards. Moreover, donor-acceptor complexes like tetrathiafulvalene represent the next generation of organic conductors.

Sensitive and selective detection has always been a crucial criterion in design of a good sensor. The severity of adverse health effects associated with certain gaseous environmental pollutants have motivated various research groups to develop detection technologies that measure adverse level of pollutants and are also immune to potential interfering compounds. The LC molecules have been observed to exhibit analyte-induced ordering transition and shown promise to operate at room temperature. In the development of LC-based sensors, it is crucial to study the intricate balance of intermolecular forces within liquid crystals, as well as the diverse interactions of the LC phase with analytes.

The integration of the Monte Carlo method with semi-empirical quantum approaches offers a robust framework for advancing the study of liquid crystals. Using above approach, researchers have calculated the high magnetic susceptibility of mesogens that holds significant promise for future investigations. Noteworthy endorsements from institutions such as IBM Research Laboratory underscore the potential of liquid crystals in technological innovations. Ferroelectric liquid crystals, with their adjustable polarity under electric fields, present a compelling alternative to inorganic crystals for various applications. Additionally, the combination of liquid crystals with silicon VLSI technology is pivotal in advancing thin-film technologies. The use of photochromic chiral liquid crystals in a sensing device exemplifies the potential for innovation in light modulation based on exposure parameters. While emerging technologies may supersede current liquid crystal displays, the foundational knowledge acquired through research on liquid crystals

will continue to inform and enhance our understanding of material self-assembly and its applications in future technologies.

A comprehensive theoretical investigation, employing Density Functional Theory (DFT) with B3LYP/6-31G**, CAM-B3LYP/6-31G**, and M06-2X/6-31G** basis sets, has provided a deep insight into the electronic, electro-optical, and non-linear optical properties of a series of discotic liquid crystal molecules based on a triphenylene core, designated as HATn (n = 5, 6, 7, 8). The analysis is highlighted a consistent inverse relationship between the length of the peripheral alkyl chain ('n') and key molecular properties including ionization potential, electron affinity, electronegativity, chemical potential, and electrophilicity index. This monotonic variation as the alkyl chain elongates significantly influences the molecular architecture and subsequently the functional characteristics of the materials.

The revealing an increase with the extension of the alkyl chain length, thermodynamic parameters such as thermal energy, specific heat at constant volume, and entropy were also calculated. Furthermore, UV-vis absorption spectra analysis of HATn showed maximum absorbance at approximately 266 nm, indicative of π-π^* transitions within the triphenylene core, albeit with a notable deviation from the experimental peak at 280 nm. Theoretical evaluations of polarizability, dielectric constant, and density of states of the considered molecules were systematically compared with experimental data, providing a correlation with molecular ordering and charge transport properties. This detailed theoretical exploration has not only aligned well with experimental observations but also enriches the understanding of the structure-property relationships in these materials. The findings underscore the potential of employing HATn (n=5,6,7,8) based discotic liquid crystals in advanced applications within optoelectronics and organic electronics, where the unique properties of the triphenylene core can be effectively harnessed. This study paved the way for further research into the optimization and practical implementation of these materials in next-generation technological applications culminating into LC based light modulators having high refresh rates enabling image de-blur in replaying a fast movie.

The enhancement of electro-optical and non-linear optical parameters of the halogenated hexahexyloxytriphenylene (HAT6) molecule has meticulously optimized the geometries of pure and halogenated HAT6 molecules using the B3LYP/6-311G basis set, confirming the planarity of the ring structures post-optimization. Halogenation of HAT6 with chlorine and bromine atoms significantly enhanced its molecular polarizability and altered the

electronic properties, notably reducing the energy band gap of the frontier molecular orbitals. The absorption maxima of these halogenated derivatives were predominantly located in the UV region, with minimal spectral shifts induced by different halogens. Among the variants studied, the doubly chlorinated HAT6 molecule exhibited superior potential for nonlinear optical applications due to its enhanced nonlinear optical activity, which is pivotal for uses in harmonic generation, electro-optic modulation, and possibly biological interactions. Additionally, halogenation was found to increase thermodynamic stability, as evidenced by higher entropy and specific heat values, making these halogenated HAT6 derivatives notably more stable and potentially more functional than their unmodified counterparts. This investigation highlighted the tunability of electro-optical properties through halogenation and suggested significant implications for the development of advanced discotic materials for nonlinear optical applications, that may pave the path for research towards a wide range of photonic and electronic applications.

The impact of various interactions on the electronic and electro-optical properties of long chain molecules have primarily divided into three categories: stacking, in-plane, and terminal interactions. Among these, stacking interactions are the most influential, playing a crucial role in stabilizing molecular complexes. In-plane interactions, while less significant in magnitude, are pivotal in defining the mesogenic properties of the molecules. The studies help in study of intermolecular interactions that lead us to cluster analysis of a small group of molecules with custom made properties leading to development of organic nanomaterials. However, such studies require high computational facilities for studying various conformations.

The influence of various gases CO_2, H_2S, NO_2, and NO on the HAT6 discotic liquid crystal (DLC) molecule. Significantly examined the electronic properties, global reactivity, molecular electrostatic potential (MESP), and structural characteristics of the HAT6 molecule. Among the gases tested, H_2S was found to have the most substantial impact on the properties of HAT6, affecting it more profoundly compared to CO_2, NO_2, and NO. This suggests a unique sensitivity of HAT6 to H_2S, highlighting potential areas for further research in gas sensing and molecular interaction studies. The chemical and shape selectivity of analytes may further be explored in detail to lead us to advanced applications in selective pollutant removal or pollutant de-toxification or neutralization. AI/ML algorithms may help in efficient studies of sensing bigger analytes including biomolecules.