

Optical and Thermal studies on binary Liquid Crystal Mixture

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Abstract

The novel binary liquid crystal mixture is designed and synthesized from 4-methoxycinnamic acid (MCA) and 4-ethoxycinnamic acid (ECA). Quantum chemical (DFT) calculation for MCA+ECA geometry is optimized by DFT/B3LYP with 6-311G (d, p) basis set and its results are in good agreement with experimental data. Fourier-transform infrared spectroscopic (FT-IR) study confirms the presence of intermolecular hydrogen bond in the liquid crystal mixture. The paramorphic changes in nematic phase and thermo-optic properties of binary liquid crystal mixture is analyzed using polarizing optical microscope (POM) and differential scanning calorimetry (DSC) techniques. A noteworthy observation in the present liquid crystal mixture possesses smectic A phase along with nematic phases. Intermolecular hydrogen bond interaction and its stabilization energy of present mixture is studied by natural bond orbital (NBO) analysis. Due to the $n \rightarrow \pi^*$ transition, the present liquid crystal mixture induces smectic A phase. The molecular properties of present binary liquid crystal mixture is analyzed by HOMO-LUMO and experimental UV-Visible studies. Thermal spanwidth, stability factor and quantum chemical properties of the liquid crystal mixture are calculated. Molecular electrostatic potential, Mulliken atomic charge distribution of the optimized MCA+ECA geometry is also reported.

Keywords: Binary liquid crystal mixture; POM; smectic A; DFT method; HOMO-LUMO analysis.

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1. INTRODUCTION

Nematic liquid crystal (NLC) mixtures are the promising material in the field of liquid crystal science and technology due to its tunable structural properties. [1-3] This eutectic liquid crystal (LC) mixture is very important for technological device applications. [4-6] Thermo-optical properties of various liquid crystals (LCs) can be improved by mixing of different mesogens. Although, binary liquid crystal mixtures are essential due to its superior physico-chemical properties. [7]

Generally, NLCs are easily reacting with the external field such as magnetic and electric field [8] which is more significant for optical applications [9-10]. Due to intermolecular hydrogen bonding interaction between mesogenic-mesogenic compounds, it yields new type of hydrogen bonded liquid crystal (HBLC) complex mixture. Hydrogen bonds silently tuning the proton donor and acceptor which shows better liquid crystalline nature. [11] Density functional theory (DFT) is a well-known theoretical technique to validate the experimental data such as electronic transition, intermolecular interaction and band gap energy calculation. [12] Very few reports [13-14] are available to explain the HBLC system in experimental and theoretical (DFT) method.

The present study deals with the mixtures of nematogenic 4-methoxycinnamic acid (MCA) and 4-ethoxycinnamic acid (ECA). alkyloxy cinnamic acid is a novel LC material to study the

mesogenic behavior of mixtures due to its unique mesomorphic nature and stability. [15] This study aimed to improve binary liquid crystal mixtures through H-bonding in experimental as well as theoretical (DFT) point of view.

2. Experimental details

4-Ethoxycinnamic acid (ECA), 4-Methoxycinnamic acid (MCA) and solvents such as Dimethylformamide (DMF) were purchased from TCI, Tokyo, Japan. Synthetic procedure of binary liquid crystal mixture is reported. [15] The optimized geometry of ECA+MCA liquid crystal mixture is illustrated in Fig. 1. H-bond in the ECA+MCA liquid crystal mixture is confirmed by FT-IR (ABB BOMEM, Canada) technique. Textural analysis of the present liquid crystal mixture is observed by POM (BX53M, Olympus, Japan) which is interconnected with temperature controller (MicroOptik). The UV-Visible absorption spectrum of ECA+MCA liquid crystal mixture is studied by UV-VIS spectrophotometer (UV-1800 series, Shimadzu, Japan). The Thermal studies of ECA+MCA liquid crystal mixture are carried out using Differential Scanning Calorimeter (DSC-60Plus) Shimadzu, Japan.

2.1. Computational details

The electronic structure of ECA+MCA liquid crystal mixture were optimized by the density functional theory (DFT) methods by the Gaussian 09 software package [16] using B3LYP/ 6-311++G(d,

p) basis set. [17-20] The natural bonding orbital (NBO) study [21] executed by NBO 3.1 program (Gaussian 09 package). Frontier molecular orbital was studied by Gauss View 5.0 software. [22] The ESP study and Mulliken analysis were obtained from the optimized geometry of liquid crystal mixture.

The HOMO energy, LUMO energy, electro negativity (χ), chemical potential (μ), global hardness (η), global softness (S) and global electrophilicity index (ω) of individual compound and ECA+MCA liquid crystal mixture calculated from reported formula [23] is given in Table 1. The hydrogen bond length/angle of ECA+MCA liquid crystal mixture is given in Table 2.

3. Results and discussion

3.1. FT-IR studies

FT-IR spectrum clarifies the intermolecular hydrogen bond interaction between different mesogens or organic compounds. FT-IR spectrum of ECA+MCA liquid crystal mixture is shown in Fig. 2. The carbonyl stretching ($C=O$) of monomeric LCs was detailed. [24]

It is reported [7, 15] that in the MCA+nOBA HBLC complex shows stretching of $C=O$ group and $O-H$ group at 1685cm^{-1} and 2926cm^{-1} respectively. The ECA+MCA liquid crystal mixture reveals stretching of carbonyl group at 1670cm^{-1} . The presence of H-bond in the present liquid crystal mixture is validated and hydroxyl group ($O-H$) stretching is observed at 2978cm^{-1} .

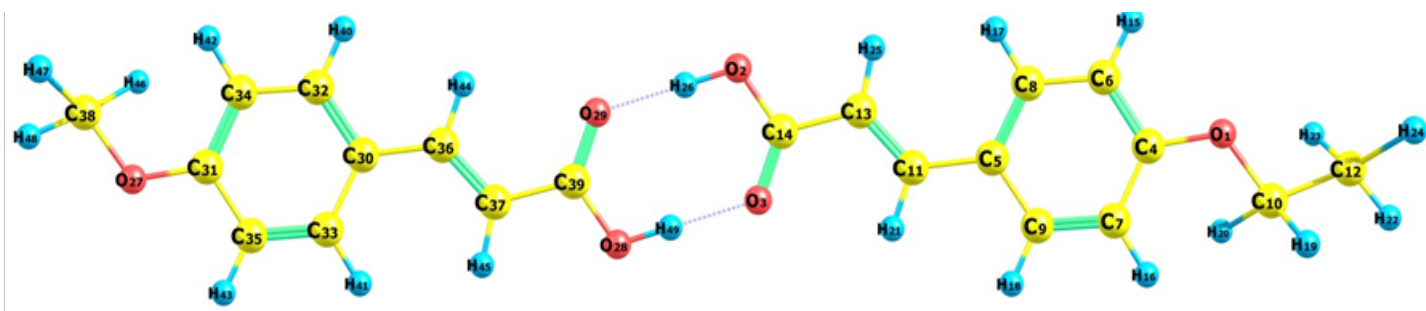


Fig.1

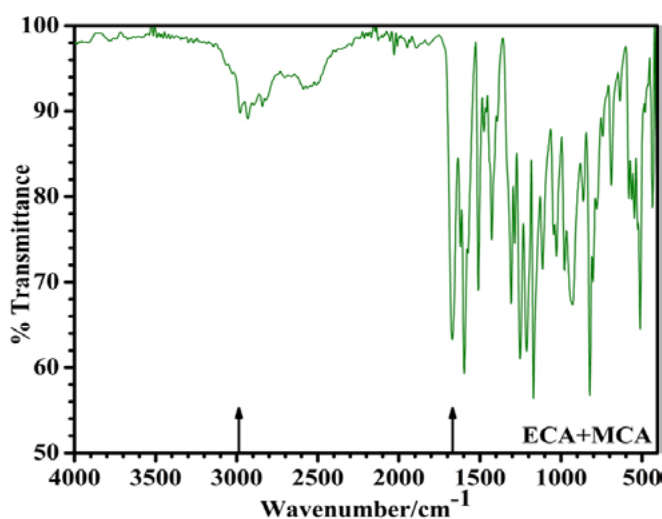


Fig.2

3.2. POM studies

The morphological LC textures of ECA+MCA liquid crystal mixture is identified by POM. Due to the change in optical properties of ECA+MCA liquid crystal mixture it shows paramorphic phase change in nematic phase (Fig.3). Microscopic LC phases of textures are shown in Fig.4. From Fig. 4, Nematic (brushes texture), batonnets texture of Smectic A ($Sm A$) is observed at 187.1°C , 154.6°C during cooling process. The observed textures of ECA+MCA liquid crystal mixture is good agreement with reported LC phase. [25, 26]

3.3. DSC studies

The DSC studies mainly deals with the enthalpy changes for mesophase transitions in both heating and cooling process. Fig. 5 shows the DSC thermogram of ECA+MCA liquid crystal mixture. The DSC thermogram of ECA+MCA liquid crystal mixture evidently revealed two phase transitions, smectic A–nematic and nematic–isotropic during cooling and heating process. Phase transition of ECA+MCA liquid crystal mixture studied by POM is confirmed by DSC technique (Table 3). The thermal span width of nematic and induced $Sm A$ phase of ECA+MCA is shown in 3D pie chart (Fig.6). The higher thermal span width of nematic phase is 32.5. Thermal stability factor of ECA+MCA liquid crystal mixture is shown 3D pie chart (Fig.7). The higher thermal stability factor for nematic

phase is 5552.

3.4.UV-Visible studies

UV-Visible absorption spectrum deals with the electron transitions from the ground state to the excited state. UV-Visible absorption spectrum of ECA+MCA liquid crystal mixture is shown in Fig.8. The strong absorption peak at 364nm is created by the $n-\pi^*$ transition. Another important point is that $\pi-\pi^*$ transition is resulting the wide absorption peak at 436nm. The lengthened of mesogenic aromatic compound significance the $\pi-\pi^*$ transition at the lower absorption wavelength. The band gap energy of ECA+MCA liquid crystal mixture is calculated

using the relation ^[14] and is found to be 3.4065eV which is more suitable for opto-electronic devices.

3.5.Density functional theory (DFT) studies

3.5.1.NBO studies

NBO study is a significant method to stabilize proton donor and acceptor of complex system and confirms the intermolecular hydrogen bond interaction between different compounds. ^[27, 28] The charge transfer interactions between bonding (π) and anti-bonding (π^*) orbitals is substantial for intramolecular charge transfer which gives stabilization of the complex system. The

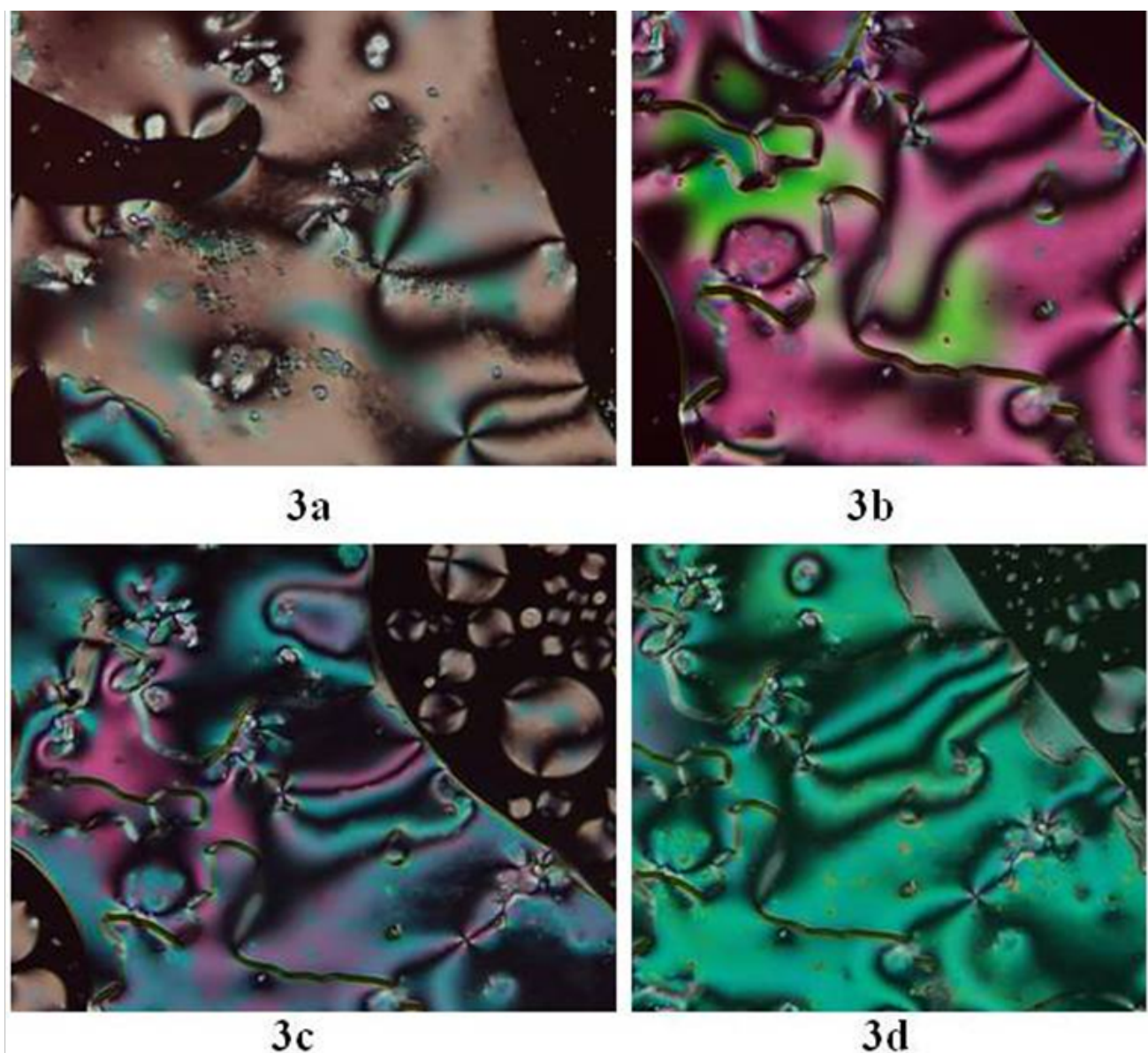


Fig.3

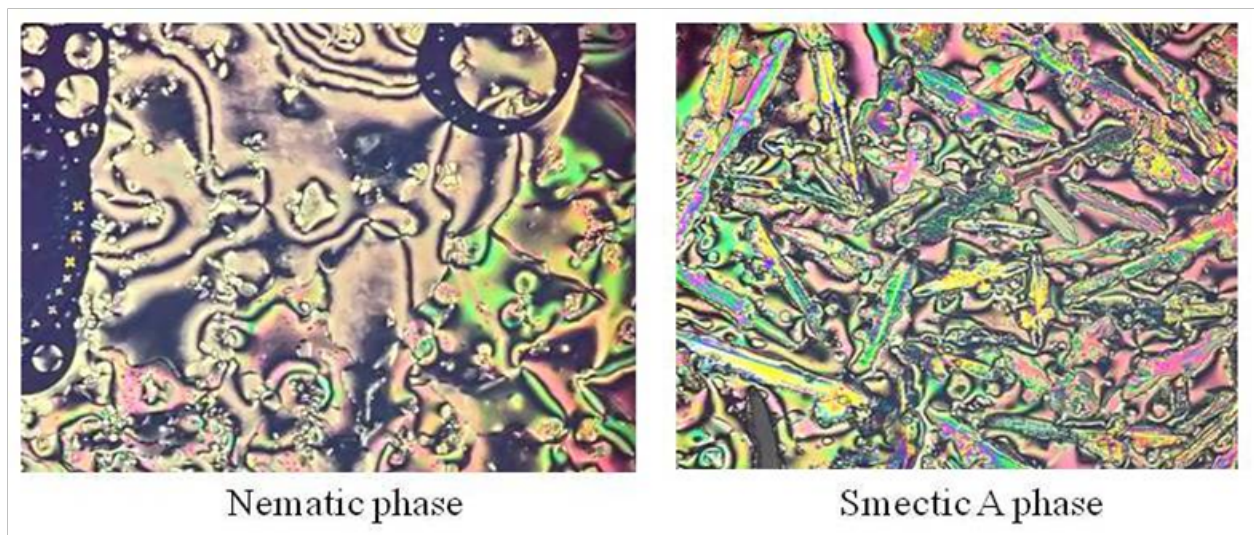


Fig.4

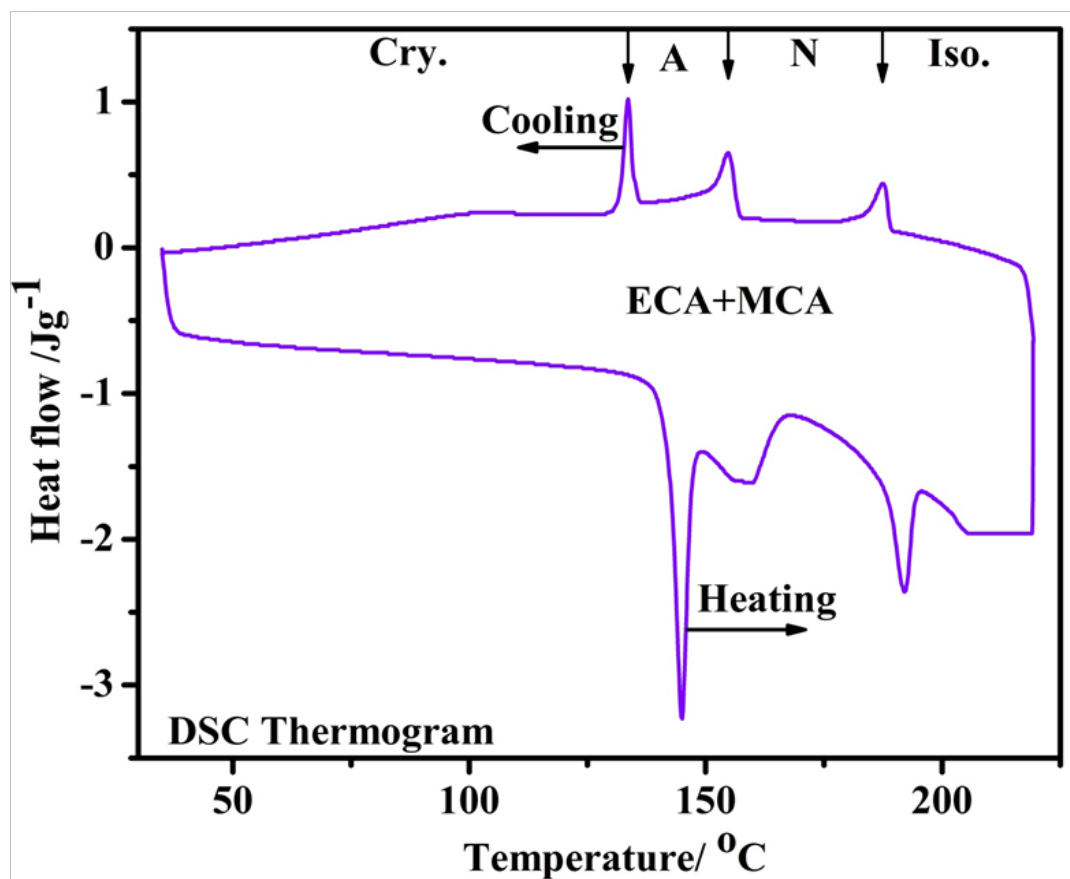


Fig.5

ECA+MCA liquid crystal mixture shows [lone pair LP(1) (O3) $\rightarrow \pi^*$ (O28-H49) and LP(1) (O29) $\rightarrow \pi^*$ (O2-H26)] the interaction between the ECA and MCA which results in the molecular stability. The other interaction with stabilization energy of ECA+MCA liquid crystal mixture is given in Table 4. The intermolecular interaction of lone pair LP (2) (O3) $\rightarrow \pi^*$ (O28-H49) and LP(2)(O29) $\rightarrow \pi^*$ (O2-H26) confirms the hydrogen bond interaction.

The lone pair of oxygen atoms determines polarity of molecule with the maximum electron density.

3.5.2. HOMO-LUMO studies

The HOMO-LUMO study explains a electron charge transition from the ground to excited state for complex system [29,30]. The HOMO-LUMO energy diagram of ECA+MCA is shown in Fig. 9. The HOMO-LUMO energy gap of ECA+MCA liquid crystal mixture is 4.2488eV which is compared with experimental data and shows good agreement. Due to the π - π^* transition, the present liquid crystal mixture shows lower absorption in UV-Visible absorption spectrum. This HOMO-LUMO energy gap indicates high stability.

The chemical hardness and softness of a LC molecule is important parameter to study the chemical stability LC moiety. [31,32] The electronegativity and the hardness are precise to explain chemical behavior and aromaticity of synthesized compounds. [33] The computed physic-chemical properties of ECA+MCA liquid crystal mixture is given in Table 1.

3.5.3. ESP studies

ESP is one of important DFT method to confirm the intermolecular hydrogen bonding between different

moiety which is also used to determine electrophilic and nucleophilic nature of complex system. [34, 35] Based on the color determination of ESP [36] the optimized ECA+MCA liquid crystal mixture shows hydrogen bond formed between O29...H26 and O3...H49 of ECA and MCA mesogen.

The ECA+MCA liquid crystal mixture shows rich negative potential surface on oxygen atoms and positive potential surface spreads on hydrogen atoms of optimized ECA+MCA liquid crystal mixture. The ESP of ECA + MCA liquid crystals mixture is shown in Fig.10 in the transparent view.

3.5.4. Mulliken charge distribution

Mulliken charge distribution analysis is an another important method to explain atomic charges through the theoretical method. [37] The Mulliken charge of ECA+MCA liquid crystal mixture is performed by DFT method of B3LYP level of 6-311G(d,p) basis set and shown in Fig. 11. The total atomic charge values of present LC mixture are studied by Mulliken Charge distribution analysis.

The mulliken atomic charge of present LC mixture shows that the H26 (0.170634e), H49 (0.160420e) and C14 (0.400511e), C39 (0.389764e) atoms has larger positive atomic charges than the other hydrogen atoms. O1 (-0.364185e), O2 (-0.399258e), O3 (-0.270242e), O27 (-0.370757e), O28 (-0.382258e) and O29 (-0.278791e) atoms are most negative atomic charges.

This is due to the presence of intermolecular hydrogen bonding in O2-H26...O29 and O28-H49...O3 of ECA and MCA mesogen. This result shows is good agreement with the molecular electrostatic potential analysis.

ESP and Mulliken charge distribution study is used to forecasting the active reactive site of complex systems during the electrophilic and nucleophilic reactions.

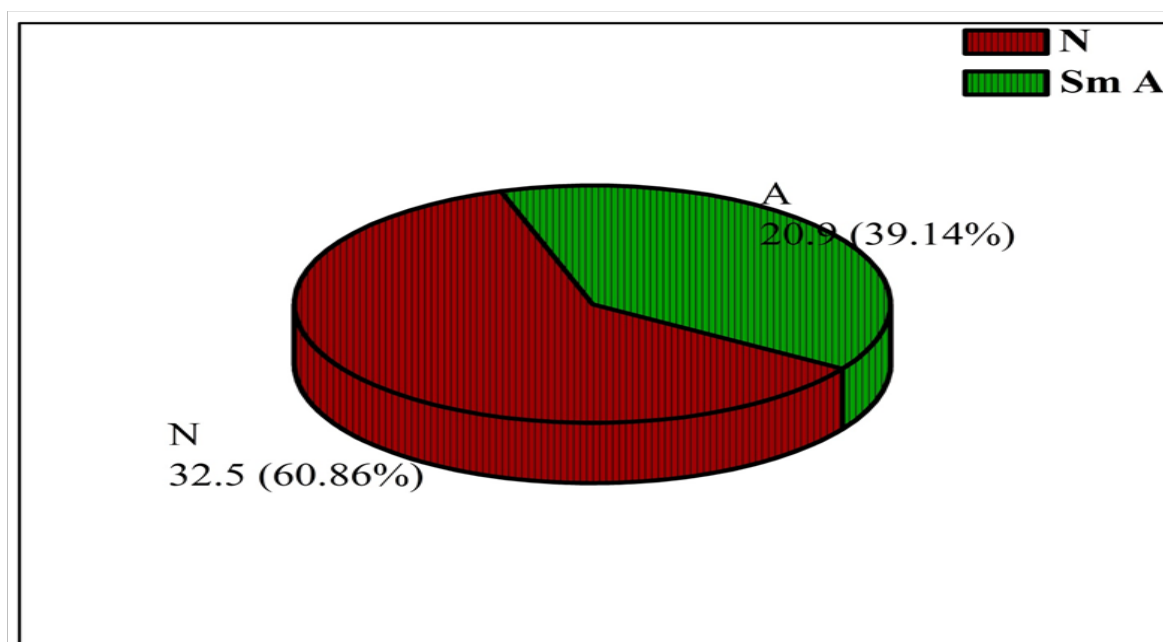


Fig.6

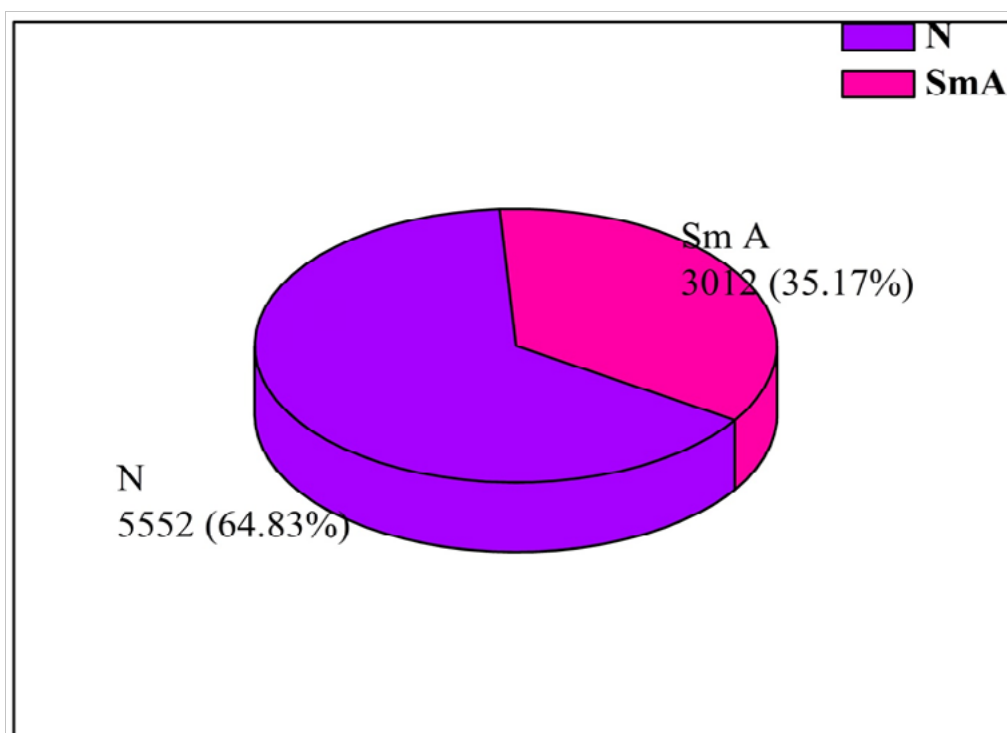


Fig.7

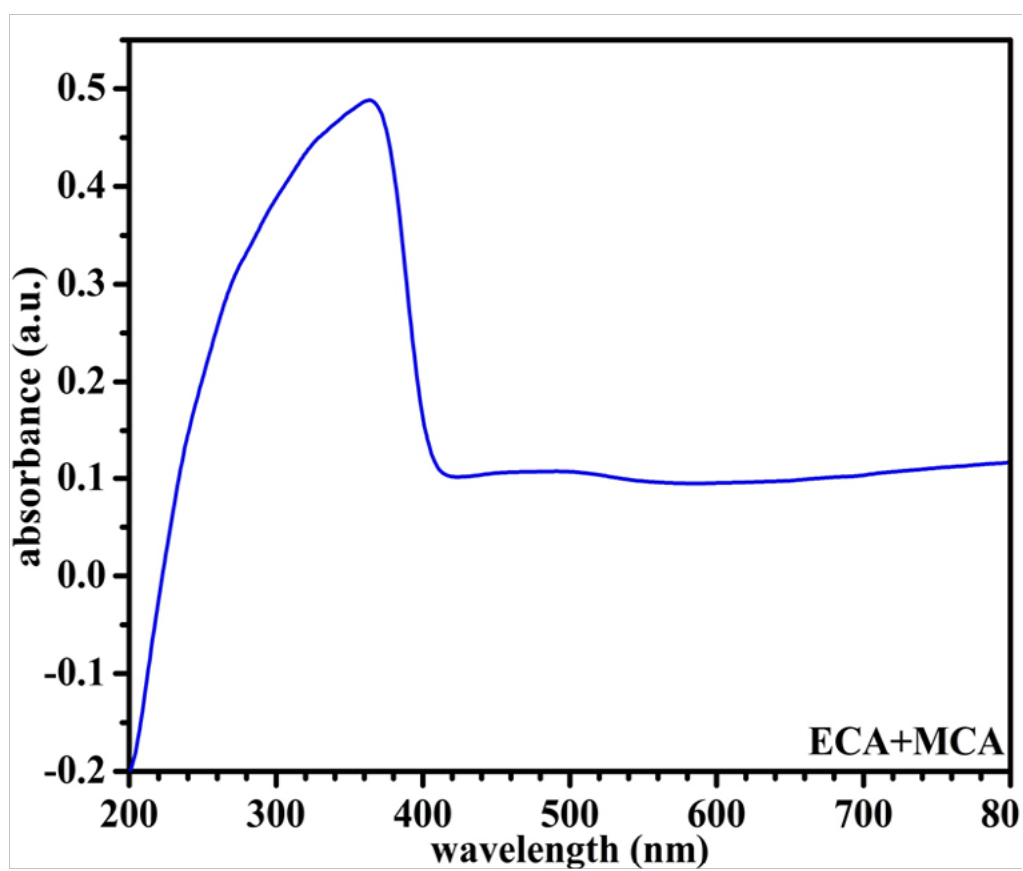


Fig.8

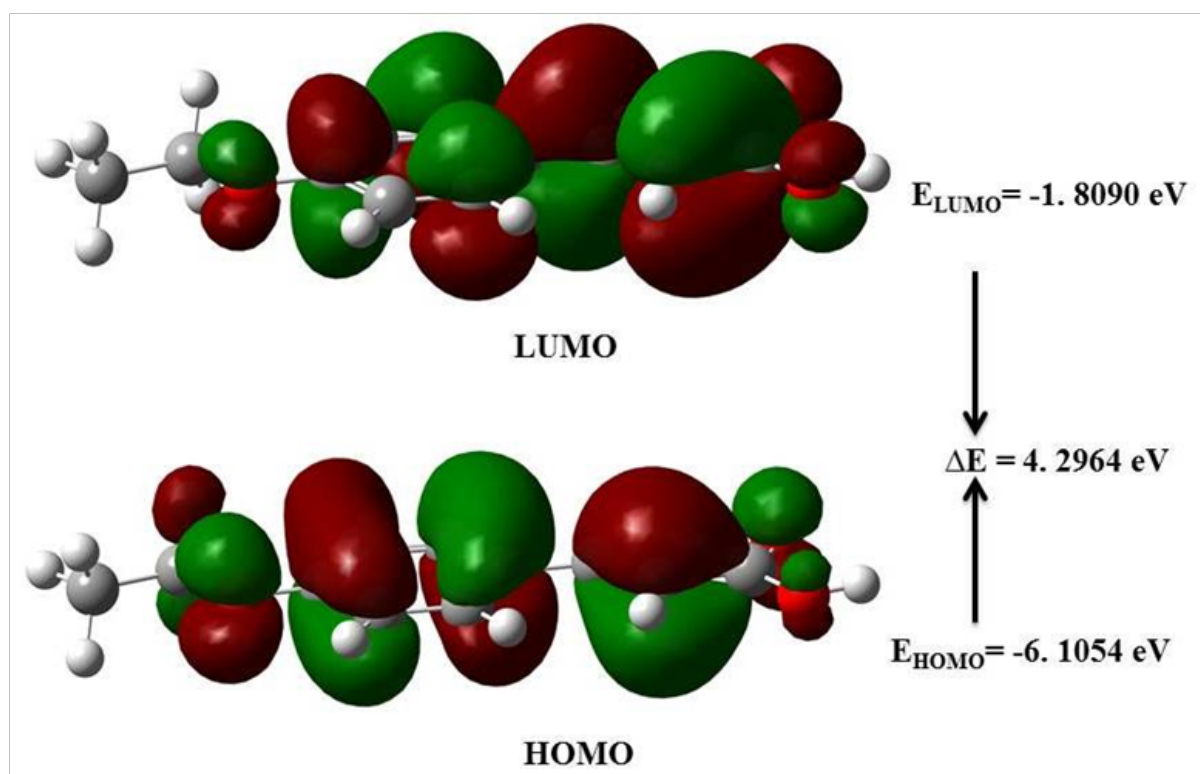


Fig.9

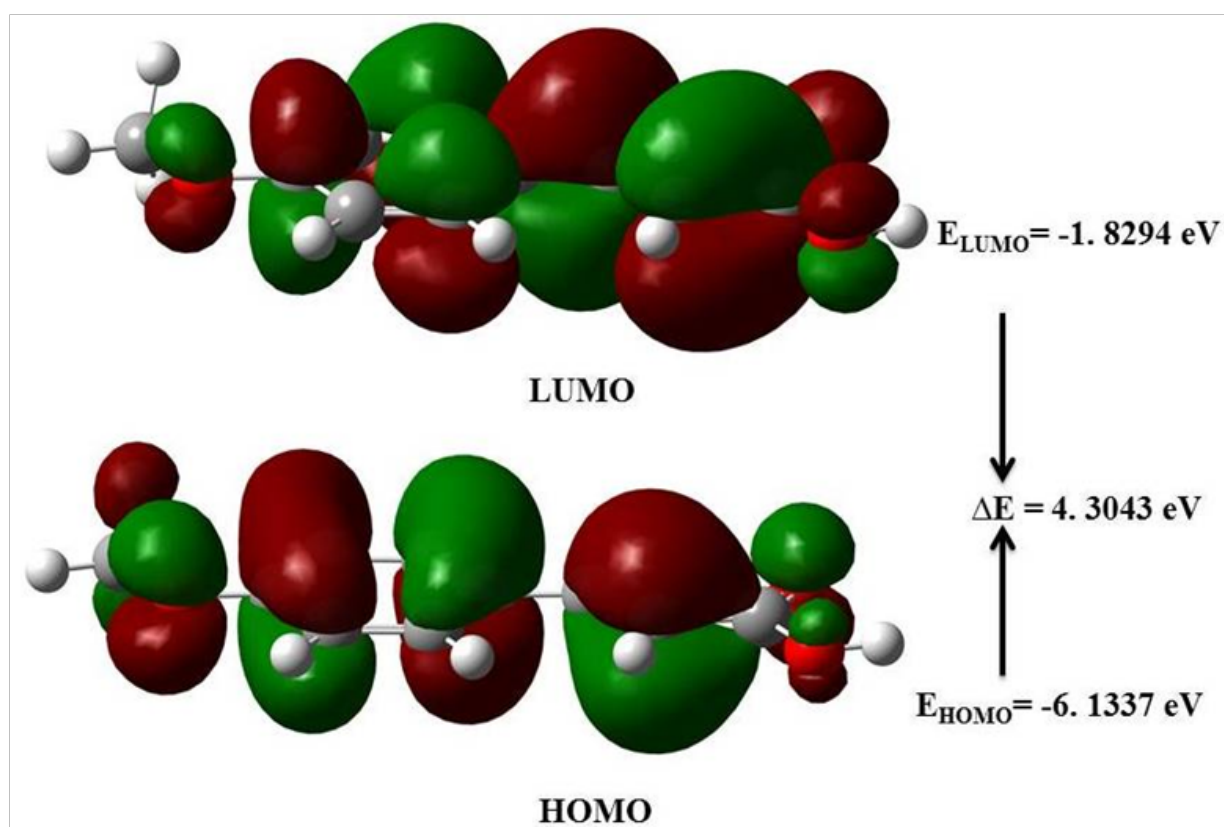


Fig.10

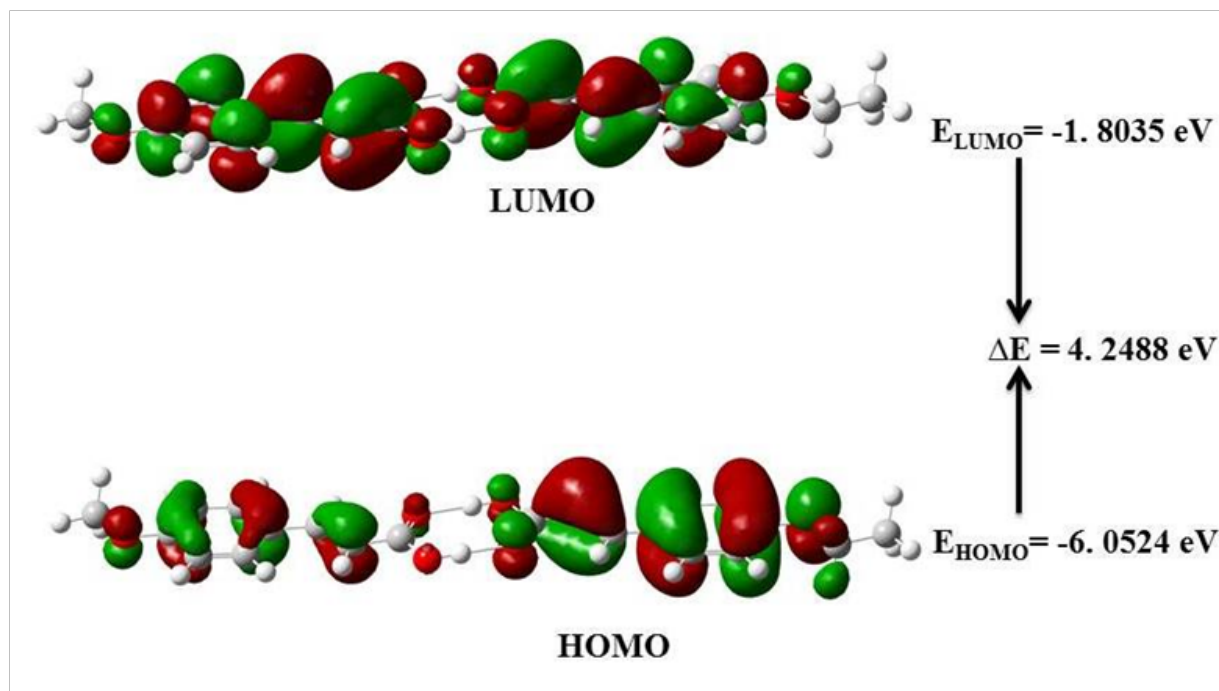


Fig.11

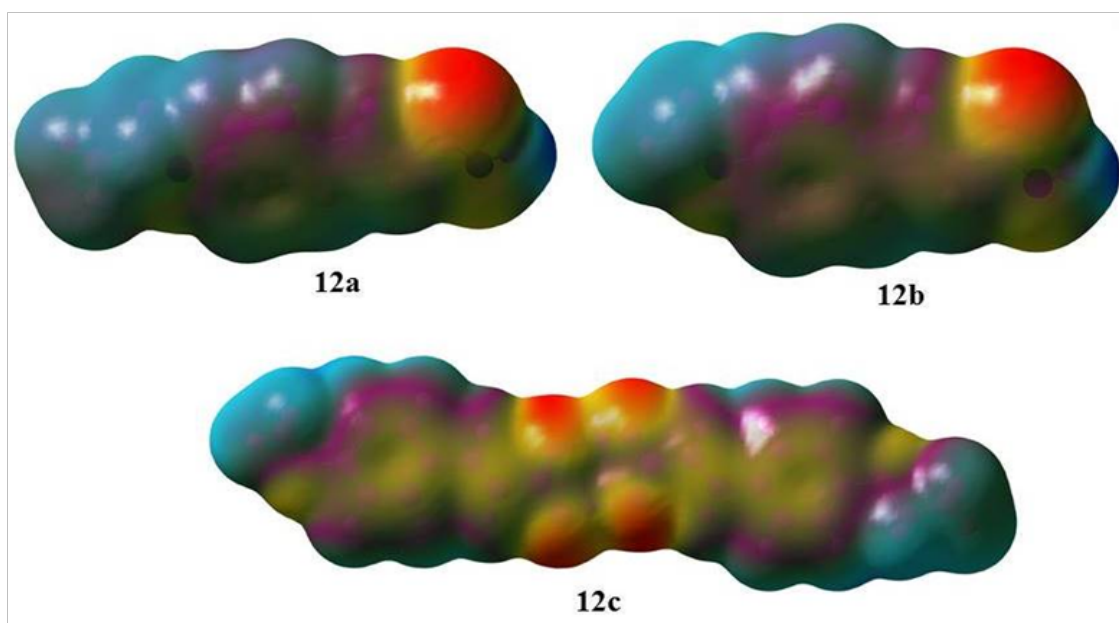


Fig.12

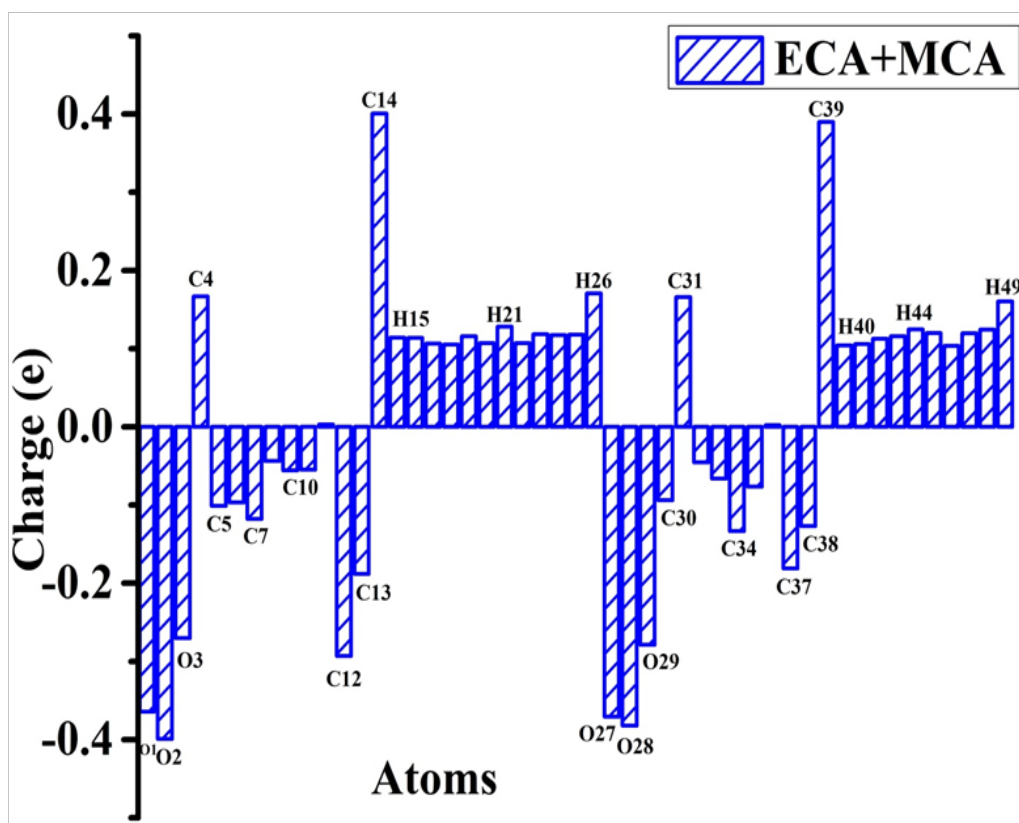


Fig.13

Table 1

Molecular property	ECA	MCA	ECA+MCA
Chemical formula	$C_{11}H_{12}O_3$	$C_{10}H_{10}O_3$	$C_{21}H_{22}O_6$
Molecular weight (g/mol)	192.11	178.185	370.396
Energy (KJ/mol)	-36.009	-27.3495	-125.137
Dipole moment (D)	3.851	3.618	0.278
Number of atoms	26	23	49
Number of bonds	26	23	49
LUMO energy (eV)	-1.8090	-1.8294	-1.8035
HOMO energy (eV)	-6.1054	-6.1337	-6.0524
Band gap energy (eV)	4.2964	4.3043	4.2488
Electron negativity χ (eV)	3.9572	3.9815	3.9279
Chemical potential μ (eV)	-3.9572	-3.9815	-3.9279
Global hardness η (eV)	2.1482	2.1521	2.1244
Global softness S (eV)	0.2327	0.2323	0.2353
Global electrophilicity index ω (eV)	3.6447	3.6829	3.6311
Maximum electronic charge (ΔN_{max})	1.8421	1.8500	1.8489

Table 2

LC mixture (in degree)	Intermolecular H-bond length (Å)		Intermolecular H-bond angle	
ECA+MCA	O2-H26...O29	1.660	O2-H26...O29	110.15
	O3...H49-O28	1.656	O3...H49-O28	110.16

Table 3

LC mixture	Phase	Variance	Technique	Cycle	Unit	Crystal-Melt	Nematic	Sm A	K
ECA+MCA	NA	POM		(h)	°C	146.1	192.5	160.2	
				(c)			188	159.9	134.6
		DSC		(h)	°C	145.6	191.7	159.3	
					J/g	(12.52)	(4.76)	(5.19)	
				(c)			187.1	154.6	133.7
							(2.38)	(4.88)	(3.06)

h-heating, c-cooling

Table 4

Donor (i)	Acceptor (j)	E (2) Kcal/mol	E (j)-E (i) a.u	F (i,j) a.u
From unit 1 to unit 2 π (O2-H26)	π^* (O29-C39)	0.36	1.32	0.020
π (O3-C14)	π^* (O28-H49)	0.12	1.45	0.012
π (C13-C14)	π^* (O28-H49)	0.39	1.07	0.018
LP(1)O3	π^* (O28-H49)	8.35	1.07	0.085
LP(2)O3	π^* (O28-C39)	0.09	0.71	0.007
LP(2)O3	π^* (O28-H49)	22.11	0.70	0.114
From unit 2 to unit 1 π (O28-H49)	π^* (O3-C14)	0.37	1.32	0.020
π (O29-C39)	π^* (O2-H26)	0.12	1.45	0.012
π (C37-C39)	π^* (O2-H26)	0.39	1.07	0.018
LP(1)O29	π^* (O2-H26)	8.27	1.07	0.084
LP(2)O29	π^* (O2-C14)	0.09	0.71	0.007
LP(2)O29	π^* (O2-H26)	21.83	0.70	0.113

Unit 1-ECA; Unit 2-MCA

4. Conclusion

The ECA+MCA liquid crystal mixture geometry is optimized by DFT/B3LYP/6-311G (d,p) method. The DFT conformational studies are in good agreement with the experimental results. HOMO-LUMO study reveals the intermolecular charge transfer between ECA and MCA which is experimentally validated. Increasing of alkoxy chain length and its influence on liquid crystal mixture is reported. The NBO analysis confirms that the optimized LC mixture is a strong intramolecular H-bond interactions of charge transfer from lone pairs to the π^* (O-H) antibonds and structurally rigid. This may be suitable material for optical devices.

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