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"A New Class of Supramolecular LCs derived from Azo Calix[4]arene Functionalized 1,3,4-thiadiazole derivatives"

Vinay S.Sharma[a*], Akshara P.Shah[b], Anuj S.Sharma[c]

[a*]: *Department of Chemistry, Faculty of Basic and Applied Science, Madhav University, Sirohi, Rajasthan.*
[b]: *Department of Chemistry, Mumbai University, Santacruz, Mumbai.*
[c]: *Department of Chemistry, School of Science, Gujarat University, Ahmedabad, Gujarat.*
Corresponding author: vinaysharma3836@gmail.com

Abstract

A new class of bowl-shaped supramolecular LCs derived from calix[4]arene substituted with 1,3,4-thiadiazoles derivatives inbuilt with schiff base and ester on lower rim while azo group on upper rim with presence of alkyl side chain ($-OC_3H_7$, $-OC_8H_{17}$). In the present investigation, we have synthesized total six newly supramolecular based derivatives having three linking unit with substituted 1,3,4-thidiazole ring and variable trisubstituted side alkoxy chain on the lower rim of calix[4]arene. These supramolecular compounds were investigated by polarizing optical microscope (POM), differential scanning calorimetry (DSC), thermo gravimetric analysis (TGA) and high temperature X-ray diffraction studies (XRD). All synthesised compounds exhibited good blue fluorescences in solution under long wavelength UV light. The present compounds are promising to stabilize the hexagonal columnar phase over a broad thermal range. The bowl shaped calixarene based LCs packs into columns with enhanced intermolecular interactions. The liquid crystalline properties were influenced by the structures of the spacers on calix[4]arene skeleton to enhance the phase transition temperatures.

Key words: Calixarene, 1,3,4-thiadiazole, liquid crystals, azo, schiff-base.

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1. Introduction

Calixarenes and their based derivatives are the most attractive compounds for the third generation supramolecular chemistry after crown ether and cyclodextrin[1.] Calixarenes, possessing tunable 3D-shaped hydrophobic cavities belong to the important building blocks in supramolecular chemistry after crown ether and cyclodextrin[2]. The bowlic LCs may possess some special physical properties, such as genuine ferroelectricity and second-harmonic generation[3].The calixarenes broaden functionalized at the upper and lower rim affords them with suitable binding sites for guest encapsulation and molecular assembly[4]. Importantly, the four hydroxyl groups present in calix[4]arene interact by hydrogen bonding and also stabilize the cone conformation[5]. In recent years, the calixarene core was also successfully used as a rigid core to prepare liquid crystalline compounds[6].

In the recent reports, there has been a renewed interest in the incorporation of heterocycles in the molecular design of mesogens due to the wide variety of structures and hence the resultant properties. Hetero atoms like nitrogen, oxygen and sulfur provide a reduced molecular symmetry, strong lateral and/or longitudinal dipoles and a donor-acceptor interaction within the molecule, which in turn affects the LC self-assembly and electronic behavior of the mesogens[7]. Additionally, the mesogens with heterocyclic moieties in their molecular structures provide emission color tunability and also enable a polarized emission. This is the most important property which finds application in the area of OLEDs[8]. In this regard, many LCs bearing a heterocyclic moiety in their molecular structures are well reported in literature. There are relatively more reports on 1,3,4-Oxadiazole based LCs as compared to their sulfur analogues 1,3,4-thiadiazole based LCs. Unfortunately, oxadiazole based mesogens shows some drawbacks such as high melting point and also clearing temperatures, narrow mesophase range and poor solubility which render their applications in certain region. Reports on their sulfur analogues, *i.e.*

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1,3,4-thiadiazole based mesogens are well reported limited in literature[9-15]. It is anticipated that, the substitution of oxygen atom by sulfur atom which increases the dipole moments, packing of molecules, viscosity, melting and clearing temperatures. There are various types of LCs like Calamitic LCs, banana shaped LCs, hydrogen bonded LCs and polymeric LCs based on 1,3,4-thiadiazole are well reported in literature [16-20]. However, very few compounds based on supramolecular bowl-shaped calix[4]arene are reported for only their biological and sensing application till the present date [21-22]. Thus, we wish to report azo functionalized bowl-shaped supramolecular LCs based on trisubstituted 1,3,4-thiadiazole derivatives and calix[4]arene connected with two linking unit. As part of our effort to combine trisubstituted 1,3,4-thiadiazole derivatives on the lower rim of azo functionalized calix[4]arene for searching new supramolecular room temperature LCs with high temperature range. Azo functionalized materials are well known for their effectiveness in optoelectronic devices, food additives, indicators, dyes, photochemical molecular switches and therapeutic agents. The photochromic behavior of azo compounds improves the activity of enzymes and polypeptides in biological systems[23].

Liquid crystalline materials based on calix[4]arene rigid core was first reported in 1990[24]. Calixarene based liquid crystalline compounds which are the significant part of macrocycles based liquid crystals were investigated in some literature[25-26]. For instance, the calixarene liquid crystals with substitution of long aliphatic side chains were prepared and displayed interesting liquid crystalline behaviours[27]. Yonetake et al. synthesized two liquid crystal based on *tert*-butyl calix[8]arene to displayed smectic and nematic mesophase [28]. Yang et al. reported mesomorphic property in calix[4]arene cholesterol derivatives. They studied the mesophase appeared with the presence of columnar type molecular arrangement of calixarene

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with cholesterol derivatives[29]. In another reports, Yang et al. synthesized and studied the liquid crystalline behavior of calixarene-linked triphenylene derivatives[30]. Later, his group reported the mesomorphic properties of gallic-calixarene derivatives with stable cone conformation[31]. Previouslly, Yang et al. reported calix[4]resorcinarene cholesterol based columnar liquid crystals having schiff-base linking group[32]. Marcos and his coworkers synthesized and studied the mesomorphic property of calixarene schiff base derivatives which have binding recognition and selectivity towards Zn^{+2} ion[33]. Recently, our group reported the two liquid crystalline series of calix[4]arene based on schiff-base and ester linking group and also studied their biological behaviour[34].

A comprehensive literature reports reveals that the azo functionalized 1,3,4-thiadiazole supramolecular bowl-shaped LCs based on calix[4]arene are never be reported till the date. In this present investigation, we have designed new bowl-shaped supramolecular LCs in which calix[4]arene was chosen as rigid core which is functionalized by azo group on upper and schiff base-ester on lower rim with presence of tri-alkyl substituted 1,3,4-thiadiazole derivatives. The present bowl-shaped supramolecular LCs based on 1,3,4-thiadiazole calix[4]arene showed good photophysical properties, which may establish as promising materials for applications in photomechanics, instant displays, reversible holographic storage, and digital storage due to their high resolution and sensitivity.

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2. Result and Discussion

2.1 Synthesis and characterization

The synthetic approach for the preparation of calix[4]arene and thiadiazole derivatives are presented in Scheme-1. Calix[4]arene **(1)** is prepared by the deterbutylation reaction of p-tert-butyl calix[4]arene[27]. The diazo derivatives of calix[4]arene **(2)** were prepared by the reported method in literature[35]. 3,4,5-trialkoxy benzohydrazide **(4)** was synthesized from the reaction of a compound **(3)** with hydrazine hydrate in the presence of n-butanol[36]. 3,4,5-trimethoxy-(4'-nitro benzoyl) benzohydrazide **(5)** is prepared from compound **(4)** with 4-nitro benzoyl chloride in the presence of pyridine. This intermediate **(5)** upon heating in the presence of phosphorous pentasulfide (P_2S_5) provided the thiadiazole derivative **(6)**[36]. Compounds **(6)** were reduced by using catalytic hydrogenation to yield the corresponding amine derivatives **(7)**, which on further heated with 4-formylbenzoic acid in the presence of a few drops of acetic acid in ethanol to form compound **(8)** respectively[37]. Scheme-2 shows the synthetic routes of the final target calixarene derivatives. The final target compounds **(9a-9f)** were prepared by the reaction of a compound **(8a-8c)** and compound **(2a-2b)** in DCM with the presence of DCC and a catalytic amount of DMAP respectively[38]. The resultant crude residue was purified by using column chromatography on silica gel eluting with methanol: dichloromethane as eluent (1:4). From the ^1H NMR, the cone confirmation of final targets compounds was confirmed by the presence of –CH_2- peaks at 3.26 ppm and 4.12 ppm respectively. The ^1H NMR, ^{13}C NMR, MALDI-TOF and IR results also well supported to the corresponding structures of derivatives and final target compounds are shown in ESI (supporting information).

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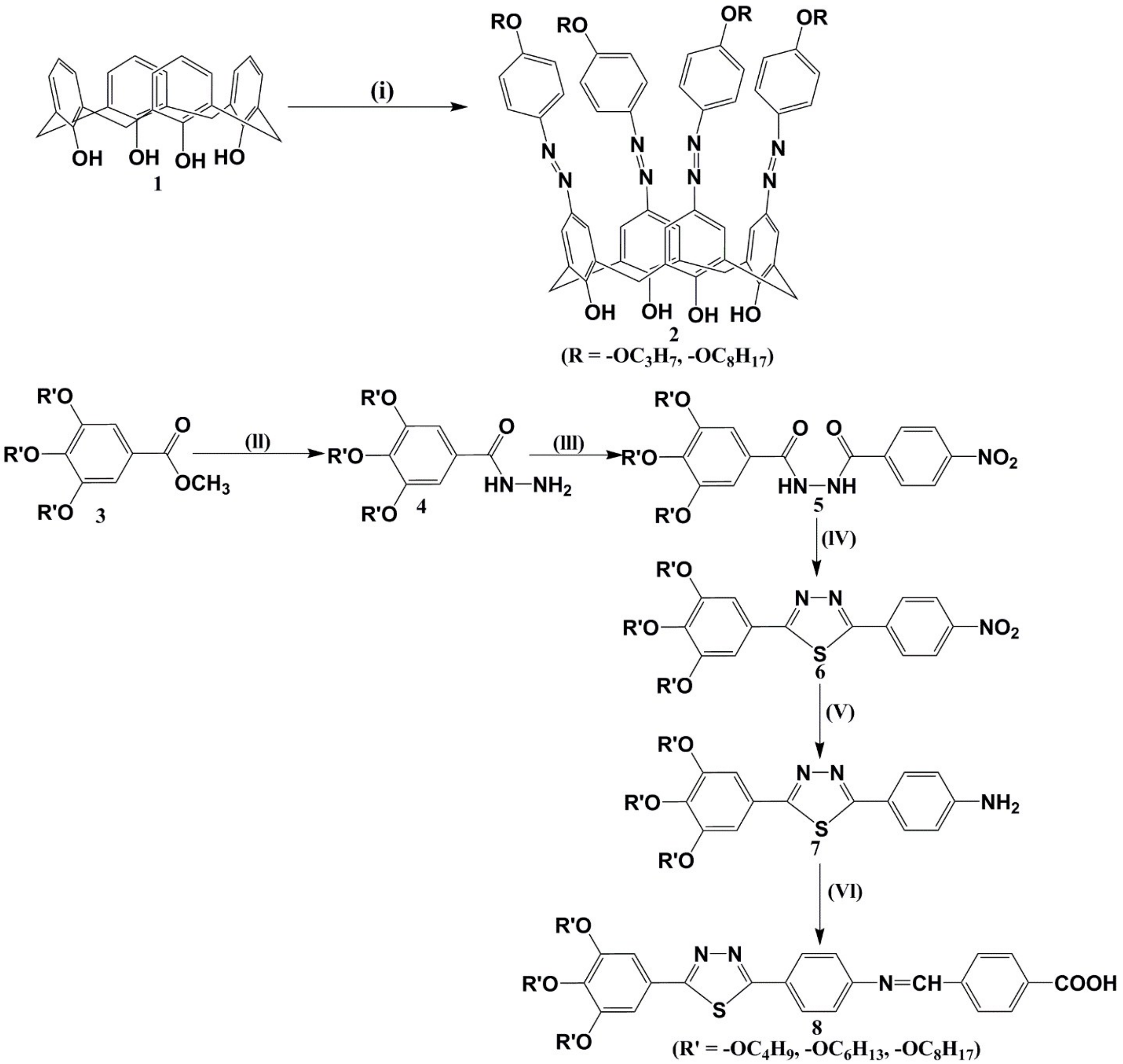

Scheme 1: (i) HCl-$NaNO_2$, 4-alkoxy amino benzene, 0-5˚C; (ii) $NH_2NH_2.H_2O$, n-butanol, reflux, 24 hr; (iii) 4-nitrobenzoyl chloride, pyridine, 60˚C, 10 hr; (iv) P_2S_5, THF, 60˚C, 18 hr; (v) 10% Pd-C, H_2 (balloon, 1 atm), THF, rt, 10-12 hr; (vi) 4-hydroxy benzaldehyde, few drops of glacial acetic acid, EtOH, 2 hr.

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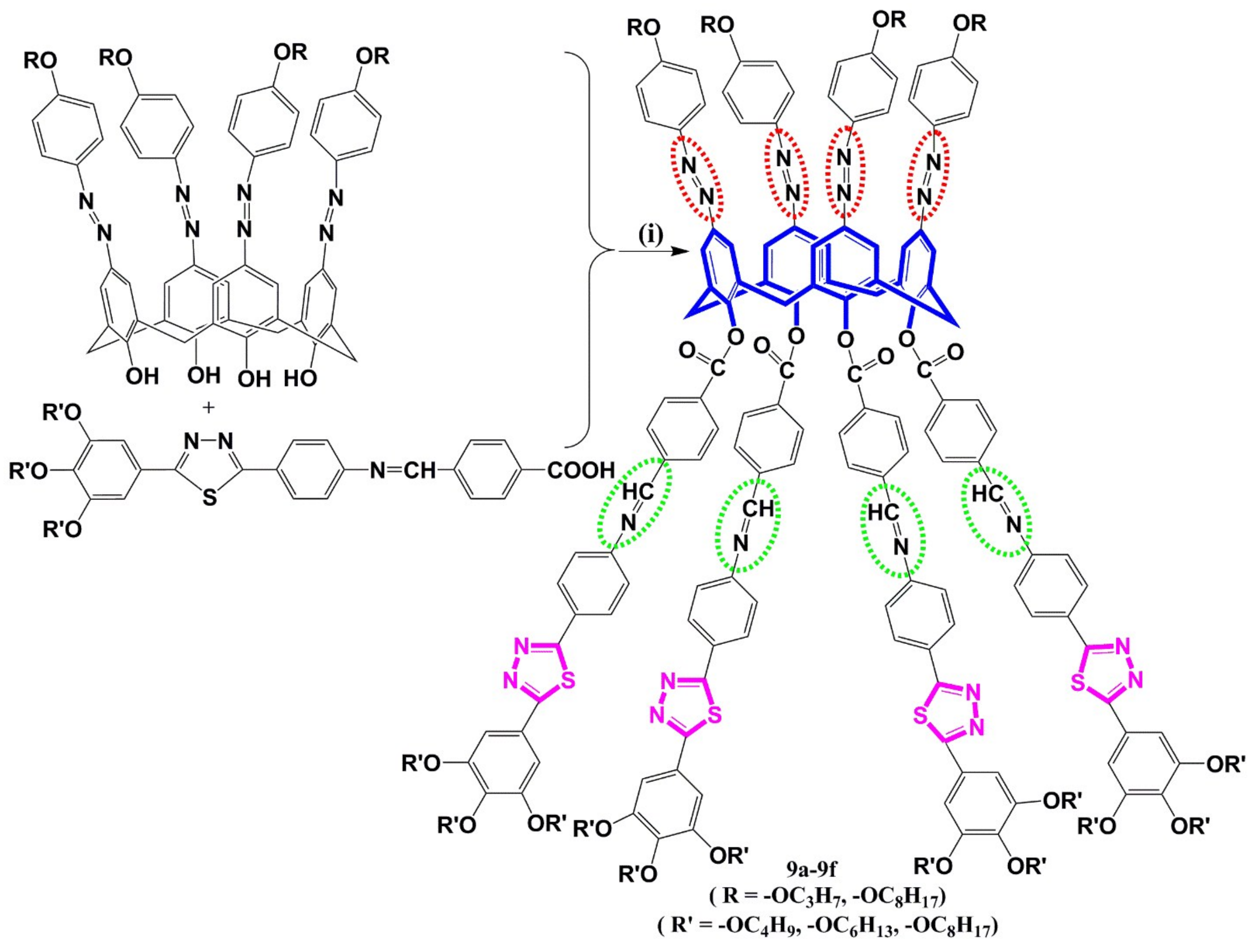

Scheme 2: (i) DCC/DMAP, DCM, 24 hr, RT.

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2.2 DSC investigation

The mesomorphic behavior of compounds 9a-9f were preliminarily studied by using differential scanning calorimetry (DSC) analysis. The transition temperatures and the associated enthalpy changes obtained from the DSC scans of second heating-cooling cycles are mentioned in Table-1 and Figure-1 respectively. Figure-2 summarizes the thermal behavior of these synthesized samples in the heating cycle. All the synthesized compounds (**9a** to **9f**) display two thermal peaks on heating and cooling cycles. Comp.**9a** with shortest alkyl chain (-OC_4H_9) on upper rim, exhibited enantiotropic columnar mesophase spanning a higher thermal range of 41.2 degrees in heating cycle after passing through crystal to phase transition to isotropic at 144.1 ˚C to 185.3 ˚C with an enthalpy change of 24.2 kJ/mol respectively as evidenced by DSC thermograms which was further confirmed by using POM study. Similarly, Compound **9f** with higher alkyl chain (-OC_8H_{17}) on upper rim showed two endothermic peaks at 114.4 ˚C and 138.8 ˚C on heating cycle which is corresponding to Cr-Col_h and Col_h-I phase transition. Also, these two thermal peaks appeared at 134.3˚C and 108.8 ˚C on cooling process which indicated the reversible phase transition process of I-Colh, Colh-Cr phase upon second heating and cooling condition. Compound **9b** with butyloxy chain group on upper rim and trisubstituted hexyloxy chain on lower rim traced two endothermic peaks at 141.3 ˚C and 177.3 ˚C on heating cycles; these exothermic peaks were observed at 173.8 ˚C and 139.6 ˚C on cooling cycle. It could observe that, compound **9a** with the butyloxy chain group on upper rim and trisubstituted on lower rim showed broad temperature range of mesophase as compare to other compounds which contain a higher alkyl chain group on the upper and lower rim. The thermal range of mesophase in compounds **9a**, **9b**, **9c**, **9d**, **9e** and **9f** is founds as 41.2 ˚C, 36.0 ˚C, 30.7 ˚C, 25.6 ˚C, 21.4 ˚C and 24.4˚C respectively. The result obtained from DSC study is further confirmed by POM and

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XRD analysis, respectively. The DSC thermograms of compounds **9e** and **9f** are shown in Figure S$_1$ (ESI).

Table 1: Phase transition temperatures (˚C) and corresponding enthalpies (kJ/mol) of synthesised compounds

Compound	Phase sequence	
	Heating	Cooling
9a	**Cr 144.1 (31.7) Col$_h$185.3 (24.2) I**	**I 181.4 (29.4) Col$_h$ 142.9 (40.9) Cr**
9b	**Cr 141.3 (30.3) Col$_h$ 177.3 (28.1) I**	**I 173.8 (31.2) Col$_h$ 139.6 (37.8) Cr**
9c	**Cr 136.5 (28.6) Col$_h$ 167.2 (16.5) I**	**I 163.6 (25.9) Col$_h$ 131.2 (32.2) Cr**
9d	**Cr 132.6 (24.8) Col$_h$ 158.2 (12.9) I**	**I 154.5 (19.6) Col$_h$ 127.7 (29.5) Cr**
9e	**Cr 124.8 (31.9) Col$_h$ 146.2 (9.5) I**	**I 141.4 (14.5) Col$_h$ 119.5 (34.7) Cr**
9f	**Cr 114.4 (23.9) Col$_h$ 138.8 (8.2) I**	**I 134.3 (12.3) Col$_h$ 108.8 (28.3) Cr**

[a] Peak temperatures in the DSC thermograms obtained during the first heating and first cooling cycles at 10˚C/min; Col$_h$ = columnar hexagonal phase.

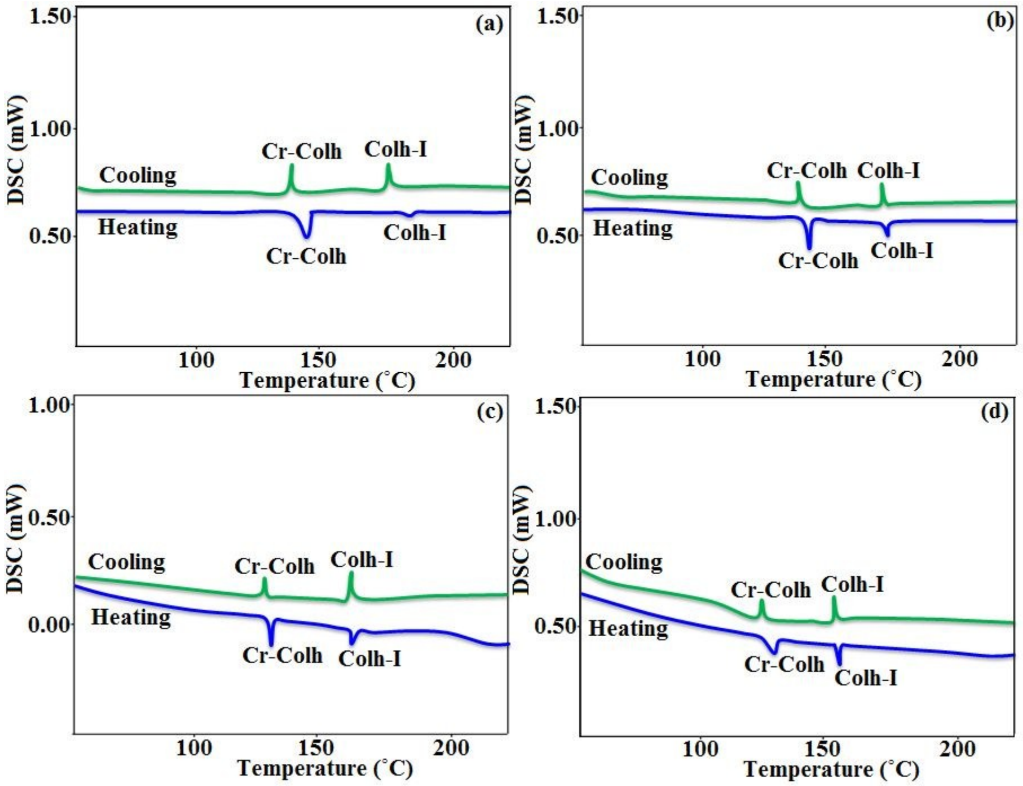

Figure 1: The DSC traces of compounds **9a** (a), **9b** (b), **9c** (c), **9d** (d) on second heating and cooling (scan rate 10˚C/min).

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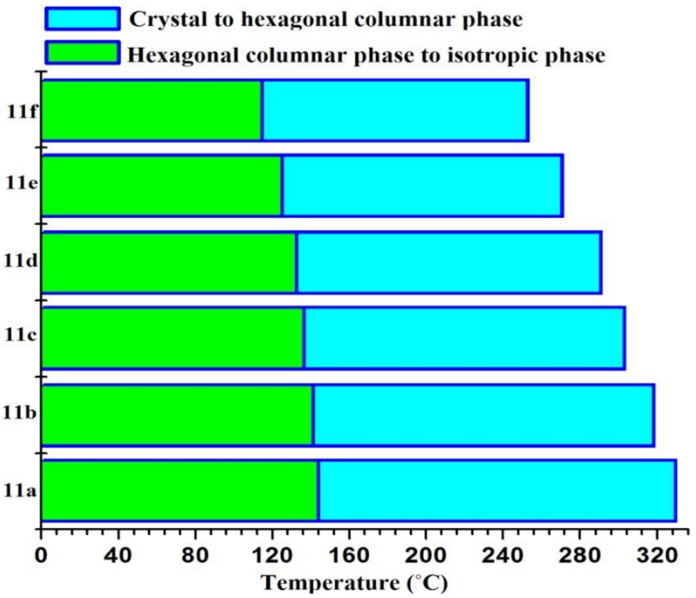

Figure 2: Thermal behaviour of comp.**9a-9f** (based on heating scans from DSC).

2.3 POM investigation

The phase transition temperatures of newly synthesized compounds were further carried out by using of polarizing optical microscope (POM) by observing the textures when the sample was sandwiched between a clear glass slide and a cover slip. The all synthesized bowl-shaped supramolecular azo calix[4]arene derivatives display a texture pattern of columnar phase. It can be noted that, the observed defect texture images pattern of hexagonal columnar phase, which is commonly observed for Colh phase. The observed texture pattern of compounds **9a**, **9b**, **9c** and **9f** are shown in Figure-3. Compound **9a** and **9c** showed similar texture pattern of hexagonal columnar phase at 142.6 ˚C and 133.8 ˚C on heating condition (Fig.2a, 2d), but having different isotropic temperature range. Similarly, compounds **9f** and **9e** showed same texture pattern of hexagonal columnar mesophase at 112.9 ˚C and 121.2 ˚C with different temperature range of mesophase on heating condition (Fig.3b, 3c). On cooling condition, same textural pattern of Colh mesophase was observed before forming the solid crystal. Thus, an enantiotropic mesomorphic behaviour over a broad thermal range of mesophase was seen for the present synthesized bowl-

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shaped supramolecules based on calixarene core. The texture pattern of compound **9b** and **9d** at 139.1 ˚C and 129.8˚C are shown in Figure S_2 (ESI). This proposal was further confirmed by XRD analysis.

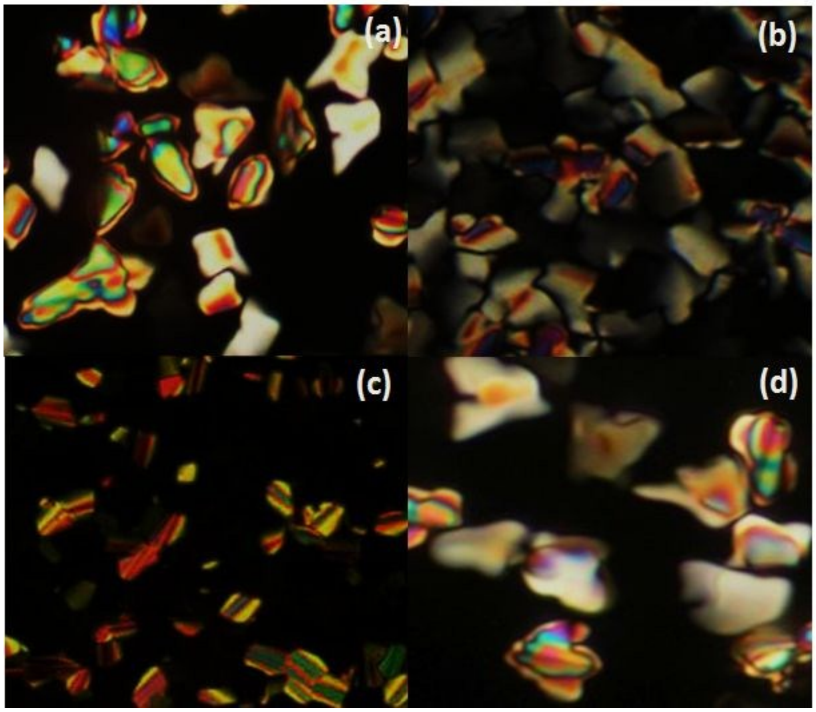

Figure 3: POM texture image of compound **9a** at 142.6 ˚C (a) compound **9f** at 112.9 ˚C (b) compound **9e** at 121.2 ˚C (c) and compound **9c** at 133.8 ˚C (d) on heating condition from solid crystalline state as seen under cross polarizers.

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2.4 XRD analysis

To confirm the mesophase observed through a polarising microscope (POM) and differential scanning calorimetry (DSC), XRD studies have been performed to confirm the liquid crystalline phase. The liquid crystalline behavior of supramolecular azo based calixarene LCs (**9a-9f**) were further confirmed by using X-ray scattering studies of unoriented samples filled in Lindemann capillaries. All the samples have been studied for their LC phase at their transition temperature. The sample was filled by melting as isotropic state and cooled down to their LC state and scanned for X-ray studies. The X-ray patterns of LC phases of all the supramolecular calix[4]arene derivatives showed three reflections at small angle region and to two diffuse scattering peaks in the wide angle region as shown in Figure-4 (a-d) and Figure S_3 (a,b) respectively. Compound **9a** at 2.71˚, 4.81˚ and 5.53˚, compound **9b** at 2.76˚, 4.82˚ and 5.57˚, compound **9c** at 2.51˚, 4.86˚ and 5.68˚, compound 9d at 2.02˚, 3.51˚ and 4.06˚, compound 9e at 2.06˚, 3.58˚ and 4.09˚, compound **9f** at 2.04˚, 3.51˚ and 4.08˚ in the small angle region and the single small reflection appeared at 19.08˚, 19.07˚, 18.73˚, 19.01˚, 19.78˚ and 19.83˚ for compounds **9a**, **9b**, **9c**, **9d**, **9e** and **9f** in the wide angle region. In addition, one more reflection peak was appeared at 21.18˚, 21.20˚, 21.18˚, 21.29˚, 21.63˚ and 21.29˚ for compounds **9a**, **9b**, **9c**, **9d**, **9e** and **9f** in the wide angle region. The d-spacing value for compound **9a** is 32.57 Å, 18.36 Å, 16.49 Å in small angle region. Similarly, 31.98 Å, 18.32 Å and 15.86 Å for compound **9b**, 35.16 Å, 18.17 Å and 16.98 Å for compound **9c**, 43.70 Å, 25.15 Å and 21.75 Å for compound **9d**, 42.84 Å, 24.66 Å and 21.59 Å for compound **9e**, 43.27 Å, 25.15 Å and 21.75 Å for compound **9f**. The ratio of these present reflections agreed with $1:1/\sqrt{3}:1/\sqrt{4}$, signifying the d[100], d[110] and d[200] plane of hexagonal lattice. The presence of small diffuse peak at wide angle region at 21.18˚, 21.20˚, 21.18˚, 21.29˚, 21.63˚ and 21.29˚ with d-spacing 4.54 ~ 4.82 Å for

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compounds **9a** to **9f** due to the presence of core-core interactions of calixarene to form ordered hexagonal phase in addition of self-assembly organizations. The literature survey indicated that the similar XRD traces were reported for supramolecular calix[4]arene liquid crystals with different substituted derivatives on lower rim[30]. The estimated molecular length of present synthesised compounds is nearer to the observed molecular length. It can be noted that the presence of broad halos at 2Θ = 18.63~19.83° indicating the ordering of the peripheral alkyl chain group at lower and upper rim of calix[4]arene core. The proposed mechanism (Figure 5) of present synthesized compounds indicated the arrangement of the bowlic shape calixarene column with substitution on lower and upper rim by schiff-base ester and azo group with presence of variable aliphatic alkyl chain on lower terminal end while propyloxy and octyloxy chain on the upper terminal end of calix[4]arene core unit. Based on all the data of DSC, POM and XRD, it is confirmed that all the synthesised azo schiff base-ester 1,3,4-thiadiazole calix[4]arene derivatives display hexagonal columnar liquid crystalline mesophase respectively.

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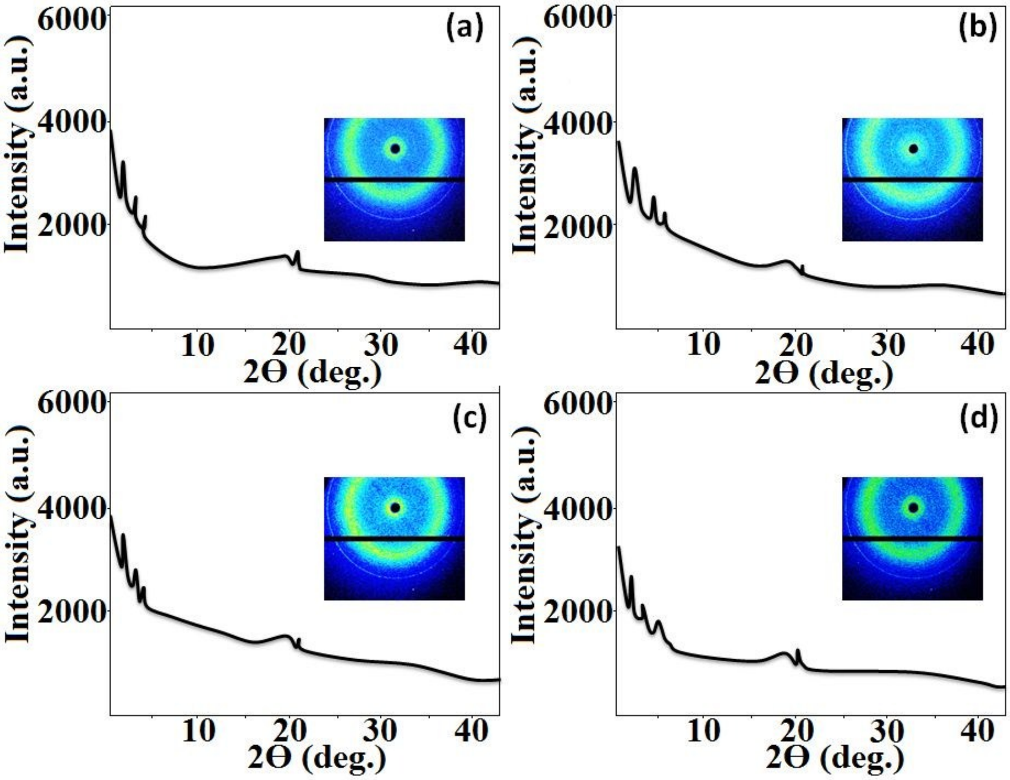

Figure 4: XRD profiles depicting the intensity against the 2*Θ* obtained for the Colh phase of compound **9d** at 131.0 ˚C (a); Colh phase of compound **9a** at 143.0 ˚C (b); Colh phase of compound **9e** at 124.0 ˚C (c); Colh phase of compound **9b** at 141.0 ˚C (d) on cooling from isotropic temperature; the insert shows the image pattern obtained.

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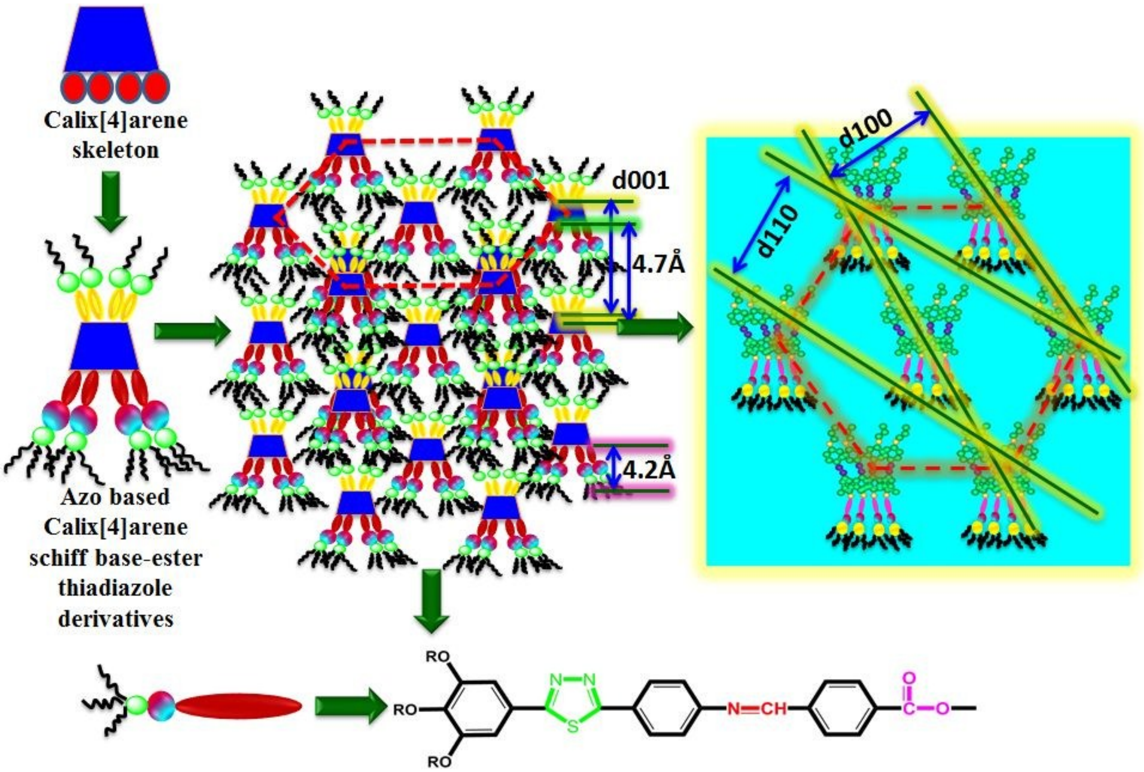

Figure 5: Schematic representations of the columnar hexagonal molecular arrangements (comp.**9a**).

2.5 Thermal stability

Thermal stability of compounds **9a-9f** were studied by thermogravimetric analysis (TGA) shown in Figure 6(a, b). All the synthesized 1,3,4-thiadiazole based supramolecular calixarene derivatives were stable at least up to ≈300˚C and complete degradation occurs at around 450˚C. As there is no loss seen up to 150 °C that means no water or other solvent entrapped in mesophase formation. All the synthesized compounds show good thermal stability.

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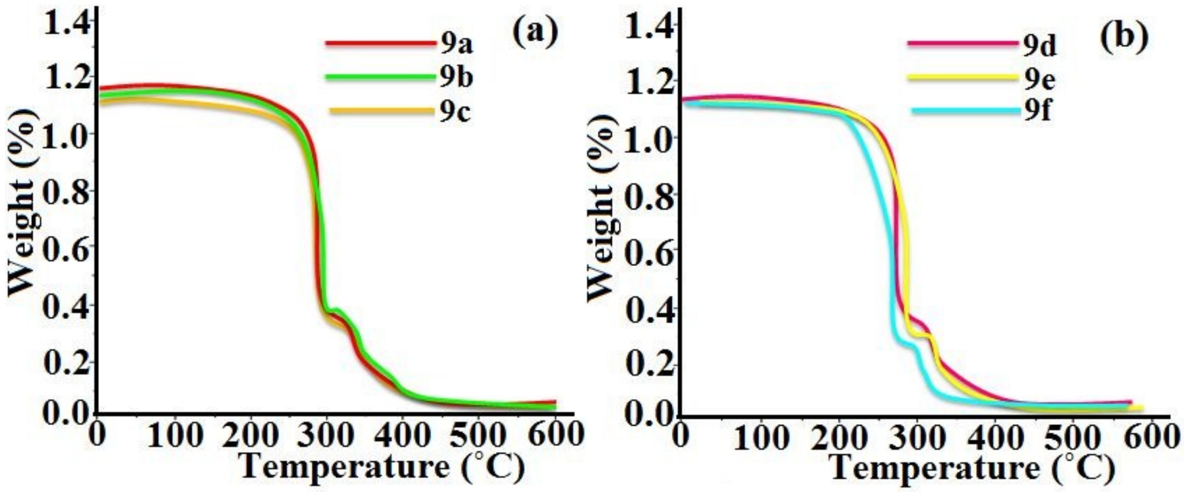

Figure 6: TGA curves of the compounds **9a-9c** (a); compounds **9d-9f** (b) carried out at a rate of 10 ˚C/min.

2.6 Photophysical behaviors

The photophysical properties of these supramolecular calix[4]arene compounds **9a**, **9b**, **9c**, **9d**, **9e** and **9f** were studied in solution. Figure-7 represents the absorption and emission spectra of compound **9a** in various organic solvents respectively. One can see that the absorbance and the emission intensities of compound **9a** are higher in organic solvents as compared to polar solvents. The absorbance and emission intensities of compound **9a** in THF is higher as compare to other organic solvents because of its moderately nature to dissolve wide range of nonpolar and polar chemical compounds[39]. Micromolar THF solutions of all supramolecular compounds **9a-9f** were used to measure the absorption and fluorescence spectra mention in Figure-8. The corresponding spectral data were depticated in Table-1. The azo linkage containing compounds was irradiated with UV light, the band corresponding to *Π-Π** and n-*Π** transitions which is decreases with increasing irradiation time[40]. The low intense short wavelength absorption maxima appeared at nearly 279 to 283 nm, this is due to the presence of *Π-Π** transition in phenyl rings respectively. However, the high intense longer wavelength absorption maxima observed at 348 to 354 nm, this is attributed to the presence of a *Π-Π**

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transition involving the π-electronic system throughout the whole mesogenic portion, with a considerable charge transfer character[40]. Compound **9a** irradiated at 364 nm, *E-Z* isomerization taking place which is decrease in the absorption band from 346 nm is ascribed to Π-Π^* transition of the trans (*E*) isomer observed in azo group respectively. The further very weak absorption band found in the visible region around at 452 nm which is represents to n-Π^* transition of cis (*Z*) isomer in the azo group was gradually increased by reaching photo stationary state at 80 sec. After that, no change observed in the absorption spectrum which is further confirms the photo-saturation of *E-Z* (trans-cis) isomerization. From figure-7 and figure-9(a,b), its clear that all the other derivatives showed n-Π^* transition at nearly 451 nm which confirmed the presence of *E-Z* (trans-cis) isomerization process in present synthesized derivatives. The highly delocalized electronic systems and Π-Π^* transitions with the presence of heteroaromatic part inbuilt with the lower rim of calixarene derivatives with high molar absorption coefficient (ε = 23.6-27.4 × 10^6 L $mol^{-1}cm^{-1}$) recognized to the maximum absorption in the present synthesised azo based supramolecular compounds. The absorption and fluorescence of the higher alkyl substituted compounds (**9d-9f**) were higher than lower alkyl substituted compounds (**9a-9c**), this is due to the variation of the side alkyl chain group which suggesting that the long alkyl substitution with electron donating oxygen and the conjugation of aromatic rings with electron accepting imide group inbuilt with azo group increases the intramolecular charge transfer efficiency which fluctuated the fluorescence and absorbance intensity. As can be seen in the Figure-8b, all the compounds showed light sky bluish fluorescence in THF solution respectively. This is promising as the blue light emitting materials are not only limited blue also their energy levels are high. They provide an efficient approach in fine-tuning the emission wavelength on combining with another dopant emitter in the construction of white OLEDs[36]. The emission spectra of all the

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compounds showed the one stable emission maxima bands at center around 436-440 nm which attributed to the electronic transition from lowest unoccupied molecular orbital (LUMO) to the highest occupied molecular orbital (HOMO) respectively. Supramolecular calix[4]arene azo-schiff-base ester derivatives exhibited a bathochromic shift in the absorption and emission maxima. Relative quantum yields were measured in solution as reported earlier[36]. The quantum yields of present synthesised compounds are in the range of 0.44-0.56 respectively.

Table 1: Photophysical properties of the supramolecular mesogens recorded in the THF (5μM) solution.

Compounds	**Absorption λ_{abs}/nm ($\varepsilon/10^6$ L.mol^{-1} cm^{-1})**	**Emission λ_{em}/nm**	**Stoke shift nm**	**Quantum yield[a]**
9a	283, 348 (23.6)	437	89	0.46
9b	281, 352 (24.2)	439	87	0.49
9c	280, 351 (24.8)	440	89	0.56
9d	279, 351 (25.8)	440	89	0.56
9e	279, 352 (26.2)	436	84	0.44
9f	279, 354 (27.4)	436	82	0.46

[a]: Relative quantum yield calculated with respect to quinine sulphite solution in 0.1 M H_2SO_4 with a quantum yield of 0.54.

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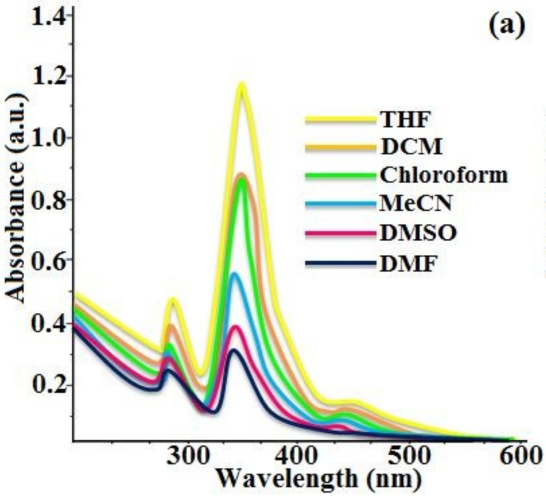

Figure 7: Absorption and fluorescence spectra of compound **9a** in 5μM different solvents.

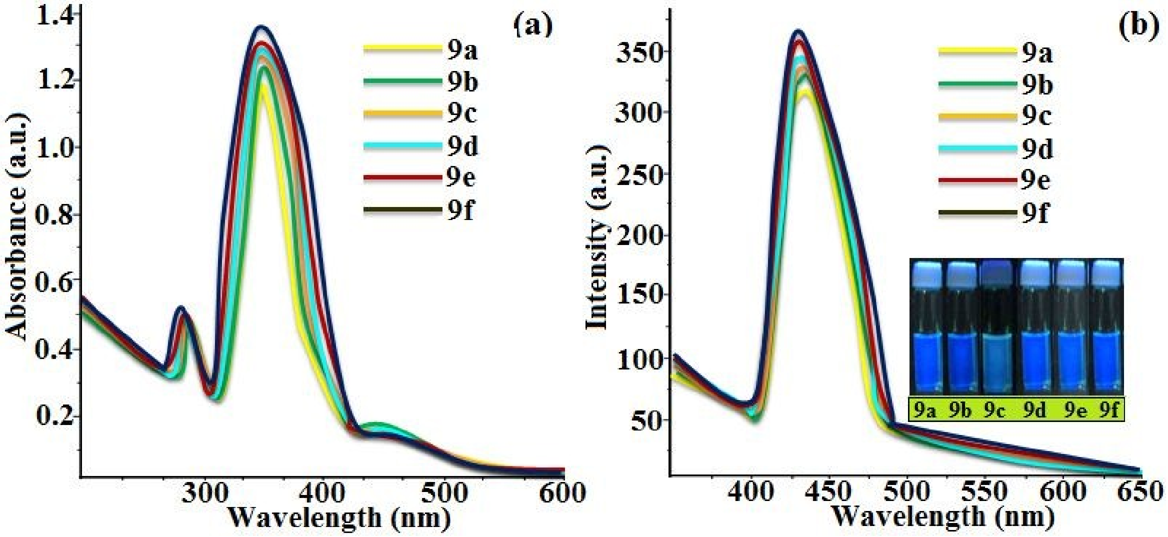

Figure 8: Absorption and fluorescence spectra of compounds **9a-9f** in 5μM THF solution.

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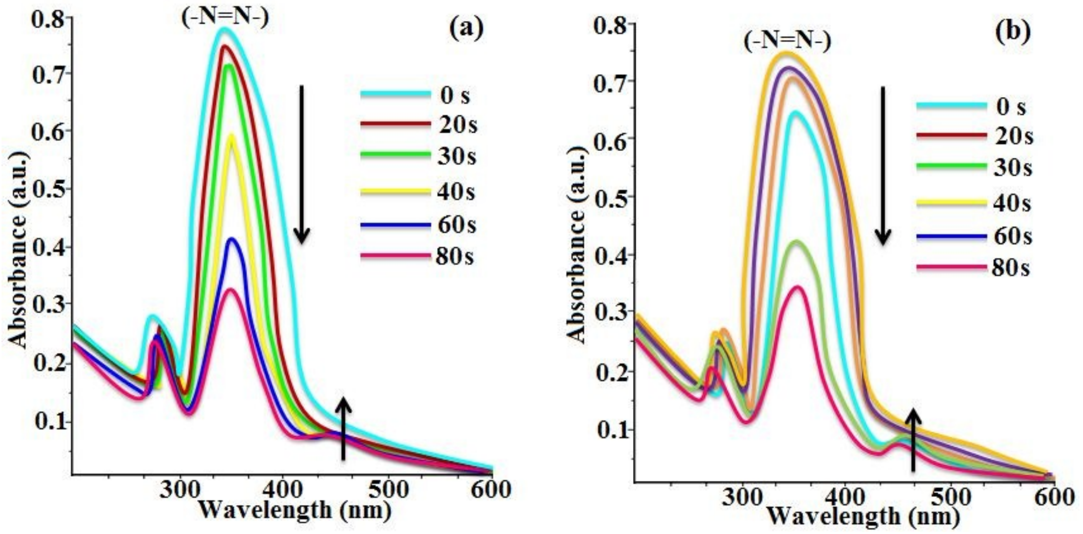

Figure 9: Absorbance spectra of compound **9a** (a); compound **9d** (b).

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3. Conclusions

In summary, we have designed and synthesized newly supramolecular azo based 1,3,4-thiadiazole calix[4] arene derivatives inbuilt with mono substituted and tri-substituted variable peripheral alkoxy side chain on the lower and the upper rim with schiff-base and ester unit are a promising class of bowlic shaped columnar liquid crystals with a good thermal stability of mesophase. These synthesized derivatives are fully characterized and investigated for their thermal and photophysical behaviour. The thermal behaviour was studied with the help of TGA, DSC, POM and XRD studies. The self-assemble of building blocks in the design to form an ordered hexagonal columnar phase with good thermal range of mesophase. The studies on photophysical properties revealed that these supramolecular derivatives exhibited good fluorescence properties. These all synthesised calix[4]arene derivatives show blue light emission in the solution. The length of the side spacer alkyl chain had no effect on the absorption and emission properties but it fluctuated the intensity of absorption and emission. The present research suggested that not only the bowl-shaped liquid crystal of calix[4]arene derivatives could be prepared by substitution on lower and upper rim, but also its enhanced by substitution of various 1,3,4-thiadiazole derivatives to achieved the stable columnar hexagonal phase, which allowed a approach to design and synthesis of newly fluorescent supramolecular liquid crystalline derivatives of calix[4]arene and also it will be of great attention to the scientific community working in the area of supramolecular columnar liquid crystal.

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