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"Columnar self-assembly of bowl shaped fluorescent liquid crystals based on calix[4]arene with schiff base units" Vinav S. Sharma^{a*}, Anuj S.Sharma^b, Rajesh H.Vekariya^c

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Abstract

A new family of bowlic-shaped molecules with a calix[4]arene rigid core appended four-side displaying wide range of hexagonal columnar phase have been synthesised and well characterized. The thermal behaviour of the present compounds was established using a combination of optical polarising microscopy (POM), differential scanning calorimetry (DSC) and high-temperature powder X-ray diffraction method (XRD). It is found that all the synthesised materials show enantiotropic hexagonal columnar liquid crystal phase. The structural and conformation characterization of these newly synthesised compounds had been achieved by FT-IR, ¹H NMR, and ¹³C NMR spectroscopy. All synthesised compounds exhibited good blue luminescence in solution under long wavelength UV light. To explore the structure property correlations, the alkoxy side chain group has been varied from lower alkyl spacer to higher alkyl spacer on the lower rim of calix[4]arene. The present research specified that the introduction of linking groups on the lower rim with n-alkoxy side group is an influence approach to obtain supramolecular bowl shape liquid crystal with contains good thermal and photophysical behaviour.

Key words: - Calix[4]arene, Enantiotropic, Liquid crystal, Schiff-base

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Graphical Abstract:



1. Introduction

Study of the liquid crystalline state is a multidisciplinary subject and useful to mankind and numerous industrial applications through scientist and technologists due to its exceptional property to flow as liquid and optical properties as crystals¹. Emissive organic semiconductors are getting more attention nowadays in the development of electronic devices such as, in fabricating white organic light-emitting diodes (WOLEDs), field effect transistors and other display applications^[2]. The literature reports indicate that the red and green emissive materials are broadly synthesised. However, blue emitting materials are rarely reported. Blue light emitting materials are received an increasing consideration nowadays because of their inevitable need in producing white light emitting diodes used for lighting and other display applications 3 . The invention of the efficient blue LED based on inorganic semiconductors has contributed for creating white light but most of the inorganic semiconductors suffer from high cost and low efficiency⁴. Later, this problem can be resolved by using polymers which shows luminescent property but due to its low solubility, high purity and stability. In this regard, the molecule which shows columnar self-assembly form which enhance the applicability of emissive molecules in OLED applications ⁵⁻⁶. Calixarenes, possessing tunable 3D-shaped cavities are belonging to the important building blocks in supramolecular chemistry after the discovery of crown ether and cyclodextrin⁷. The calixarenes broaden functionalization at the upper and lower rim affords them with suitable binding sites for guest encapsulation and molecular assembly⁸. Current studies on calixarene have shown to dominate specific self-assembling ability resulting from intermolecular forces, including coordination bonds, hydrogen bonds and ionic bonds⁹⁻¹⁵.

Liquid crystalline materials based on calix[4]arene rigid core was first reported in 1990¹⁶. Calixarene based liquid crystalline compounds which are the significant part of

macrocycles based liquid crystals were investigated in some literature ¹⁷⁻¹⁸. For instance, the calixarene liquid crystals with substitution of long aliphatic side chains were prepared and displayed interesting liquid crystalline behavior ¹⁹⁻²⁰. Yonetake et al. synthesized two liquid crystal based on *tert*-butyl calix[8]arene to display smectic and nematic mesophases ²¹. Yang et al. reported mesomorphic property in calix[4]arene-linked cholesterol derivatives. They studied the mesophase appeared with the presence of columnar type molecular arrangement of calixarene with cholesterol derivatives ^[22]. In another report, Yang et al. Synthesized and studied the liquid crystalline behavior of calixarene-linked triphenylene derivatives²³. Later, his group reported the mesomorphic properties of gallic-calixarene derivatives with stable cone conformation²⁴. Menon et al. reported a review on lower rim substituted calixarenes and their various applications²⁵. Later, her group reported calix [4]arene schiff base and azoester based liquid crystalline materials and studied their dielectric properties at various temperatures ²⁶⁻²⁸. Fang et al. synthesised calix[4]arene based dimeric cholesteryl derivative with the presence of naphthalene linker²⁹. Recently, Yang et al. reported calix[4]resorcinarene cholesterol based columnar liquid crystals having schiff-base linking group³⁰. Marcos and his co-workers synthesized and studied the mesomorphic property of calixarene Schiff base derivatives, which have binding recognition and selectivity towards Zn⁺² ions ³¹. In our recent report, we have reported the two liquid crystalline series of calix[4]arene based on schiff-base and ester linking group and also studied their biological behaviour ³².

A comprehensive literature search reveals that the supramolecular columnar liquid crystalline compounds with blue luminescence properties are rarely reported. In this present work, we report the newly functioned bowl shaped calix[4]arene derivatives based on schiff base

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and ester linking group with a variable alkoxy (-OR) side chain and studied their mesomorphic and photophysical behavior.

2. Experimental and Instrumentation

2.1 Materials

4-*tert*-butyl phenol, 4-hydroxy benzaldehyde, 4-hydroxy acetanilide, anhydrous K₂CO₃, alkyl bromides (R-Br) were purchased from S.R.L., Mumbai. 1-bromo ethanoic acid, N, N'-dicyclohexyl carbodimide (DCC), 4-dimethyl amino pyridine (DMAP), formaldehyde were purchased from Sigma Aldrich. Solvents were dried and purified in the usual manner.

2.2 Measurements

The FT-IR spectra were recorded as KBr pellet on Shimadzu in the range of 3800-600 cm⁻¹. The ¹H and ¹³C NMR spectra were obtained on a Bruker Advance 300 MHz spectrometer using tetramethylsilane as the internal standard. The synthesis of p-*tert*-butyl calix[4]arene was carried out by using a Discover Benchmate System 240 V microwave synthesizer (CEM corporation). The mesophase type was identified by visual comparison with known phase standards using a Nikon Eclipse LV-100 POL polarizing optical microscope (POM) fitted with a hot stage temperature-controlled LTSE 420 heating stage (Linkam Scientific Instruments, Tadworth, Surrey, UK) with temperature controlling accuracy of 0.1K. The phase transition temperatures were measured using Shimadzu DSC-50 at heating and cooling rates of 10 °C min⁻¹. The X-ray diffraction (XRD) measurements were performed on a Rigaku-Ultima IV powder diffractometer equipped with a Cu k α source ($\lambda = 1.5418$ A° and 1.6 kW, X-ray tube with applied voltage and current values as 40 kV and 30 mA power) and also Philips X'PERT MPD. The absorption spectra were studied by using Jasco V-570 UV-Vis recording spectrophotometer with a variable

wavelength between 200 and 800 nm. The fluorescence spectra were recorded on a Jasco FP-6500 spectrofluorometer. The mixtures in square quartz cuvettes were excited at 320 nm, and the emission spectra were collected from 320 to 600 nm.

3. Result and discussion

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3.1 Synthesis and characterization

Scheme 1 shows the synthetic routes of the present bowl shape calixarene derivatives. The synthesis of p-tert-butyl calix[4]arene (1d) was carried out by microwave assisted method ³³. P*tert*-butyl calix [4] arene tetra Bromo ethanoic acid (1e) was carried out by reporting method ³⁴. 4-n-alkoxy acetanilide (1a) was prepared by refluxing the reaction mixture of 4-hydroxy acetanilide with R-Br in the presence of anhydrous K₂CO₃ and dry acetone by using reported method ³⁵. 4-n-alkoxy aniline (1b) was prepared by hydrolysis of 4-*n*-alkoxy acetanilide (1a) in HCl with the presence of water ³⁵. 4-(4-n-alkoxy phenyl) imino methyl phenol (1c) was prepared by the reaction of comp. 1b with 4-hydroxy benzaldehyde in the presence of a few drops of glacial acetic acid in ethanol ³⁶. The ¹H NMR of shows singlet of 1H (δ = 8.43 ppm, -N=CH-). From FT-IR, the peak found at 1630 cm⁻¹ signifying the presence of -N=CH- group. The final target comp. (1f) was prepared by the reaction of comp.(1c) with comp.1e in presence of anhydrous K₂CO₃ and dry acetone ³⁷. The resultant crude residue was purified by using column chromatography on silica gel eluting with methanol: chloroform as eluent (1:4). The tetra substitution on lower rim of p-tert butyl calix[4]arene is evidenced by the absence of -OH group in ¹H NMR and FT-IR sturdy. In ESI, we have shown the synthesis and characterisation part of final target derivatives comp.1f₄, 1f₆, 1f₈, 1f₁₀, 1f₁₂ and 1f₁₄. From the ¹H NMR, the cone shapes of final compounds were confirmed by presence of bridging methylene protons appear two

doublets at 3.2 ppm and 4.2 ppm respectively. The ¹H and ¹³C NMR results also well supported to the corresponding structures of comp.1 f_4 , 1 f_6 , 1 f_8 , 1 f_{10} , 1 f_{12} and 1 f_{14} are mention in ESI.

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1f (R = C_nH_{2n+1} , n = 4, 6, 8, 10, 12, 14, 16)

Scheme 1: Reagents and conditions: (a) R-Br, Anhy.K₂CO₃, dry Acetone, Reflux; (b) HCl, H₂O, 2-3 h., Reflux; (c) 4-hydroxy benzaldehyde, EtOH, glacial acetic acid, 2 h., Reflux; (d) HCHO, NaOH, Microwave, 15 min; (e) bromo acetic acid, DCC, DMAP, DCM, 24 h. stirring at RT; (f) 1c, Anhy.K₂CO₃, dry Acetone, Reflux.

3.2 DSC analysis

The mesomorphic behaviours of compounds $1f_4$, $1f_6$, $1f_8$, $1f_{10}$, $1f_{12}$, $1f_{14}$ and $1f_{16}$ were preliminarily studied by differential scanning calorimetry (DSC). The transition temperatures and the associated enthalpy changes obtained from the DSC scans of second heating-cooling cycles are shown in Figure 1 and Table 1. Figure S_1 summarizes the thermal behaviour of these synthesised samples in heating and cooling cycle. All the synthesised compounds $(1f_4 \text{ to } 1f_{16})$ display three thermal peaks on heating and cooling cycles. Comp.1f₄ with shortest alkyl chain, exhibited enantiotropic columnar mesophase spanning a thermal range of 18 degrees in the heating cycle after passing through a crystal to crystal phase transition at 124.6 °C to 142.8 °C with an enthalpy change of 18.2 kJ/mol respectively as evidenced by DSC thermograms which was further confirmed by using POM study. Comp. $1f_6$ showed three endothermic peaks at 119.1 °C, 139.6 °C and 174.6 °C corresponding to Cr-Cr', Cr'-Col_h and Col_h-I phase transition. Also, three thermal peaks appeared at 180.1°C, 138.3°C and 117.3°C on cooling process which indicated the reversible phase transition process of I-Colh, Colh-Cr' and Cr'-Cr phase upon second heating and cooling conditions. The observed temperature range of $comp.1f_6$ was spanning over a good thermal range of 35.0 degrees with the isotropic temperature of 174.6 °C. Comp.1f₁₂ with dodecyloxy chain group traced three endothermic peaks at 98.7 °C, 122.3 °C and 151.6 °C on heating cycles, on applying cooling, these exothermic peaks were appeared at 156.1°, 124.6° and 102.1°C on cooling cycle and also it showed lower mesophase temperature range 29.3 degrees on heating as compare to other compounds. It could be seen that, compound 1f₄ with a butyloxy chain group showed broad temperature range of mesophase as compare to other compounds which contain higher alkyl side spacer chain group. The result obtained from DSC study is further confirmed by POM and XRD analysis, respectively. The DSC thermograms of compounds $1f_{12}$, $1f_{14}$ and $1f_{16}$ are shown in Figure S₂-S₃ (ESI).

Compound	Phase sequence				
	Heating	Cooling			
1f ₄	Cr 124.6 (9.2) Cr' 142.8 (18.2) Col _h	I 187.3 (7.3) Col _h 144.8 (15.1)			
	182.1 (24.2) I	Cr'121.8 (6.5) Cr			
1f ₆	Cr 119.1 (8.3) Cr' 139.6 (12.6) Col _h	I 180.1 (9.7) Col _h 138.3 (13.5)			
	174.6 (23.1) I	Cr' 117.3 (8.4) Cr			
1f ₈	Cr 112.7 (6.2) Cr' 134.5 (10.4) Col _h	I 167.4 (5.2) Col _h 137.5 (26.4) Cr'			
	169.9 (20.5) I	116.0 (9.4) Cr			
1f ₁₀	Cr 102.6 (5.1) Cr' 124.2 (14.6) Col _h	I 161.5 (9.4) Col _h 128.7 (18.6) Cr'			
	158.8 (18.2) I	108.5 (6.2) Cr			
1f ₁₂	Cr 98.7 (8.2) Cr' 122.3 (16.3) Col _h	I 156.1 (8.4) Col _h 124.6 (24.5) Cr'			
	151.6 (21.8) I	102.1(7.8) Cr			
1f ₁₄	Cr 86.8 (7.5) Cr' 118.4 (23.2) Col _h	I 151.4 (6.7) Col _h 120.1 (19.3) Cr'			
	148.6 (21.5) I	90.4 (10.6) Cr			
1f ₁₆	Cr 78.1 (5.2) Cr' 102.5 (17.3) Col _h	I 139.8 (4.9) Col _h 104.1 (11.8) Cr'			
	136.4 (15.6) I	82.5 (8.6) Cr			

Table1. Phase transition temperatures ^a(°C) and corresponding enthalpies (kJ/mol) of synthesised compounds

^a Peak temperatures in the DSC thermograms obtained during the second heating and second cooling cycles at 10° C/min; Col_h = columnar hexagonal phase.



Figure 1: The DSC traces of compounds $1f_4$ (a), $1f_6$ (b), $1f_8$ (c), $1f_{10}$ (d) on second heating and cooling (scan rate 10° C/min).

3.3 POM investigation

The transition temperatures of newly synthesised 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 synthesised bowl-shaped supramolecular derivatives displayed a texture pattern of columnar phase. It is interesting to note that the observed defect texture images pattern of hexagonal columnar phase which is commonly observed in Col phase. The observed texture pattern of compounds $1f_4$, $1f_8$, $1f_{10}$ and $1f_{14}$ are shown in Figure 2. Compound $1f_4$ and $1f_{10}$ showed a similar texture pattern of hexagonal columnar phase at 143.0°C and 124.0°C on heating condition (Fig.2a, 2c), but having a different isotropic temperature range. Similarly, compounds $1f_8$ and $1f_{14}$ showed same texture pattern of

columnar mesophase at 134.0° and 118.0°C with different temperature ranges of mesophase on heating condition (Fig.2b, 2d). On cooling condition, same textural pattern of Col mesophase was observed before the solid crystallization. Thus, an enantiotropic mesomorphic behavior over a broad thermal range of mesophase was seen for the present synthesized bowl-shaped Supermolecules based on calixarene core.



Figure 2: Photomicrographs of compound $1f_4$ at 145.0 °C (a) $1f_8$ at 136.0 °C (b) $1f_{10}$ at 119.0 °C (c) and $1f_{14}$ at 120.0 °C (d) on heating from the solid crystalline state as seen under cross polarizers.

3.4 XRD analysis

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To confirm the mesophase observed through a polarizing microscope (POM) and differential scanning calorimetry (DSC), XRD studies have been performed to confirm the liquid crystalline phase. The liquid crystalline behaviour of supramolecular calixarene based LCs (1f₄,

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1f₆, 1f₈, 1f₁₀, 1f₁₂, 1f₁₄) 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 the small angle region and two diffuse scattering peaks in the wide angle region as shown in Figure 3 (a, b) and Figure S_4-S_5 (a,b) respectively. Compound $1f_4$ showed three reflections at 5.08°, 9.17° and 10.21° in the small angle region. Similarly, Compound 1f₆ at 4.97°, 8.78° and 10.63°, compound 1f₈ at 4.98°, 9.32° and 10.18°, compound $1f_{12}$ at 4.08°, 8.08° and 10.01°, compound $1f_{14}$ at 4.97°, 8.03° and 10.04°, compound $1f_{10}$ at 4.93°, 8.97° and 10.21° in the small angle region and a single small reflection appeared at 17.38°, 16.58°, 17.12°, 16.01°, 19.38° and 19.91° for compound 1f₄, 1f₆, 1f₈, 1f₁₀, 1f₁₂ and 1f₁₄ in wide angle region. The d-spacing value of compound 1f₄ is 17.41Å, 9.67Å, 8.69Å in small angle region. In the same way, 17.80Å, 10.10Å and 8.36Å for compound 1f₆, 17.83Å, 9.52Å and 8.72Å for compound 1f₈, 17.94Å, 9.88Å and 8.70Å for compound 1f₁₀, 21.68Å, 10.97Å and 8.87Å for compound $1f_{12}$, 17.80Å, 11.04Å and 8.84Å for compound $1f_{14}$. The ratio of these present reflections agreed with $1:1/\sqrt{3}:1/\sqrt{4}$, signifying the [100], [110] and [200] plane of hexagonal lattice. The presence of small diffuse peak at wide angle region at 21.24°, 19.01°, 19.97°, 19.89°, 21.12° and 21.08° with d-spacing $4.25 \sim 4.73$ Å for compounds 1f₄ to 1f₁₄ due to the core-core interactions of 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 rim²⁵. 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 $2\theta = 15 \sim 20^{\circ}$ indicating the

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ordering of the peripheral alkyl chain group at the lower region of calix[4]arene. The proposed mechanism of present synthesised compounds mentions in Figure 4 which indicated the arrangement of the bowlic shape calixarene column with substitution on lower rim by schiff-base ester linking group and also aliphatic alkyl chain at the terminal and lateral side group. Based on all the data from DSC, POM and XRD, it is confirmed that all the synthesised schiff base-ester calix[4]arene derivatives display hexagonal columnar liquid crystalline mesophase respectively.



Figure 3: XRD profiles depicting the intensity against the 2Θ obtained from the Colh phase of compound 1f₄ at 141.0 °C (a); Colh phase of compound 1f₆ at136.0 °C (b) on cooling from isotropic temperature.



Figure 4: Schematic representations of the columnar hexagonal molecular arrangements in compound 1f₄.

3.5 Photophysical behaviors

The photophysical properties of these supramolecular calix[4]arene compounds $1f_4$, $1f_6$, $1f_8$, $1f_{10}$, $1f_{12}$, $1f_{14}$ and $1f_{16}$ were studied in solution. Figure 5 represents the absorption and emission spectra of compound $1f_4$ in various organic solvents. One can see that the absorbance and the emission intensities of compound $1f_4$ are higher in organic solvents as compared to polar solvents. The absorbance and emission intensities of compound $1f_4$ in THF is higher as compare to other organic solvents. Micromolar THF solutions of all supramolecular compounds were used to measure the absorption and fluorescence spectra mention in Figure 6 and Figure 7. The corresponding spectral data were collected in Table 2. As can be seen, compound $1f_4$, $1f_6$ and $1f_8$ exhibited an absorption maximum centered at 318 nm, 316 nm and 310 nm and maximum

emission at 331 nm, 333 nm and 325 nm (λ_{max}) wavelength absorption peaks. 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 ($\varepsilon =$ $11.6-24.0 \times 10^6$ L mol⁻¹cm⁻¹) recognized to the maximum absorption in the present synthesised supramolecular compounds. The absorption and fluorescence of the compounds $1f_{10}$, $1f_{12}$, $1f_{14}$ and $1f_{16}$ were higher than that of compounds $1f_4$, $1f_6$ and $1f_8$, 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 increases the intramolecular charge transfer efficiency which increased the fluorescence intensity. As can be seen in the Figure 7a-7b, all the compounds showed sky bluish fluorescence in THF solution. 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 ³⁸. The emission spectra of all the compounds showed the one stable emission maxima bands at center around 324-333 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 schiff-base ester derivatives exhibited a bathochromic shift in the absorption and emission maxima. It can be noted that the effect of alkyl substitution chain in the terminal side chain had no effect on the absorption and emission peaks, but the intensity is fluctuated as varying alkyl chain from short alkyl spacer to higher alkyl spacer. Relative quantum yields were measured in solution as reported earlier³⁹⁻⁴⁰. The quantum yields of present synthesised compounds are in the range of 0.32-0.50 respectively.

Compounds	Absorption λ _{abs} /nm (ε/10 ⁶ L.mol ⁻¹ cm ⁻¹)	Emission λ _{em} /nm	Stoke shift nm	Quantum yield ^a
$1\mathrm{f}_4$	318 (11.6)	331	13	0.32
$1f_6$	316 (12.6)	333	17	0.43
$1\mathrm{f}_8$	310 (13.4)	325	15	0.38
$1f_{10}$	319 (18.4)	332	13	0.32
$1f_{12}$	310 (20.4)	330	20	0.50
$1f_{14}$	308 (22.4)	325	17	0.43
$1f_{16}$	308 (24.0)	324	16	0.40

Table 2: Photophysical properties of the supramolecular mesogens recorded in the THF $(5\mu M)$ solution.

^a: Relative quantum yield calculated with respect to quinine sulphite solution in 0.1 M H₂SO₄ with a quantum yield of 0.54.



Figure 5: Absorption and fluorescence spectra of compound $1f_4$ in 5μ M different solvents.

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Figure 6: Absorption spectra of compounds in 5μ M THF solution.



Figure 7: Fluorescence spectra of compounds in 5µM THF solution.

5. Conclusions

Supramolecular schiff-base ester calix[4]arene derivatives inbuilt with terminal alkoxy side groups are a promising class of bowlic shaped columnar liquid crystals with good thermal stability of the mesophase. The studies on photophysical properties revealed that these supramolecular derivatives exhibited good fluorescence properties. The self-assemble to form an ordered hexagonal columnar phase with a good thermal range of mesophase. 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 in the solution state. The increase of the flexible alkyl chain length on terminal side is affected on the mesophase range. The compounds with lower alkyl chain group show the higher temperature range of mesophase as comparison to higher alkyl chain substituted compounds. In essence, these supramolecular LCs molecules are promising with respect to their photophysical properties and self-assembly behaviour to show hexagonal columnar liquid crystal phase.

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