

Calixarene Functionalized Supramolecular Liquid Crystals and Their Diverse Applications

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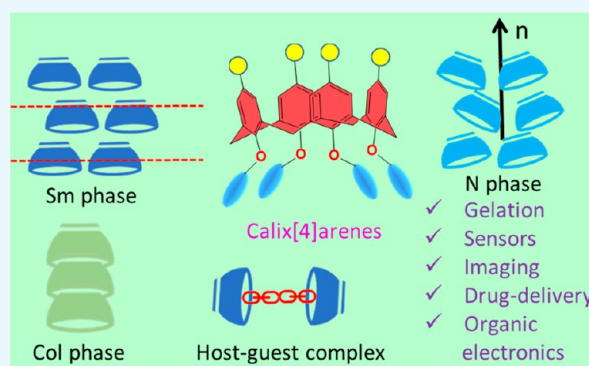
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ABSTRACT: Liquid crystals are considered to be the fourth state of matter with an intermediate order and fluidity in comparison to solids and liquids. Calixarenes are among one of the most versatile families of building blocks for supramolecular chemistry due to their unique vase-like structure that can be chemically engineered to have different shapes and sizes. During the last few decades, calixarenes have drawn much attention in the field of supramolecular chemistry due to their diverse applications in the fields of ion and molecular recognition, ion-selective electrodes for catalysis, drug delivery, gelation, organic electronics and sensors, etc. Imbuing liquid crystallinity to the calixarene framework leads to functionalized calixarene derivatives with fluidity and order. Columnar self-assembly of such derivatives in particular enhance the charge migration along the column due to the 1D stacking due to the enhanced π - π overlap. Considering limited reports and reviews on this new class of calixarene based liquid crystals, a comprehensive account of the synthesis of calixarene liquid crystals along with their mesomorphic behavior and potential applications are presented in this review.



1. INTRODUCTION

Liquid crystal (LC) phases represent a unique state of matter that possesses mobility and order on different macroscopic, supramolecular, and molecular levels.^{1–3} The hierarchical molecular arrangement or self-assembly in liquid crystals provides a platform for developing various nanostructured materials.^{4,5} Moreover, microsegregated molecular fragments, molecular shapes with various interactions, and self-organization are the essential key factors that have led to the stabilization of various LC phases.⁶ The distinguishing feature of having order and mobility in LC phases provides multiresponsive self-healing supramolecular systems, which have given rise to many devices that impact modern day life and also have become the subject of intense investigation.^{7–11} Their application in low power consuming display devices has revolutionized industry and enhanced the human standard of living.¹² Further, liquid crystal based biosensors are also widely utilized as diagnostic tools.¹³

The liquid crystalline compounds are broadly categorized into two different classes, namely, thermotropic mesogens in which the mesophase formation is generally temperature dependent and lyotropic LCs in which the mesophase formation is concentration and temperature dependent.^{14–16} Thermotropic mesogens are mainly categorized into conventional and nonconventional liquid crystals. Rodlike (calamitic)

and disklike (discotic) mesogens are the most widely known conventional LCs. Banana-shaped, star-shaped, shuttlecock-shaped, polycatenar (dumbbell-shaped), and hockey-stick-shaped mesogens are some examples of nonconventional LCs (Figure 1).^{17–20} Calamitic LCs usually stabilize nematic (N) phase and smectic (Sm) phases, which are formed by the parallel alignment of the molecules along the director without any positional order or by the presence of both positional and orientational orders (layered structure) respectively. Smectic phases are classified into many based on intralayer ordering. Equivalent mesophase structures are found in the case of discotic molecules, where they organize to form nematic and columnar phases.²¹ Columnar (Col) phases are classified again based on the organization of these columns into different lattices, namely, hexagonal (Col_h), rectangular (Col_r), oblique (Col_{ob}), helical (H), and tetragonal (Col_{tet}), respectively (Figure 2).^{22,23} In recent years, more attention has been

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Figure 1. Schematic diagram showing conventional and nonconventional molecular shapes used for the stabilization of LC phases.

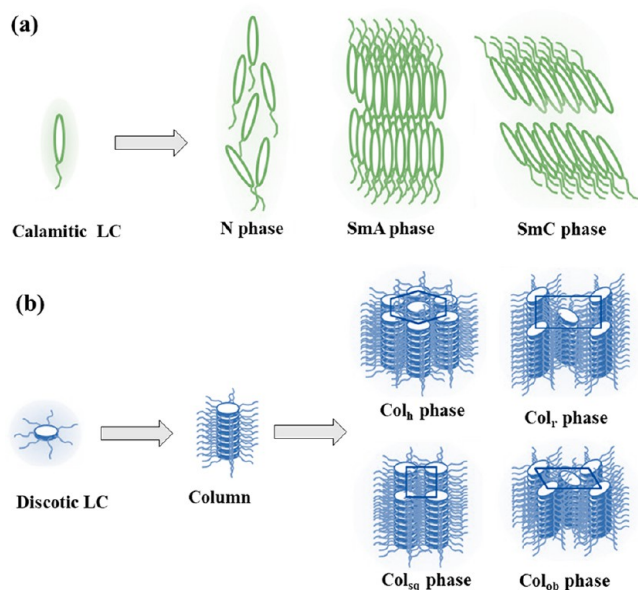


Figure 2. Schematic diagram showing mesophases stabilized by conventional liquid crystals: (a) calamitic LC phases and (b) discotic LC phases.

focused on discotic LCs, especially the Col phase due to its potential in organic electronics.^{24–30}

Calixarenes are an important class of supramolecules that can be chemically prepared by the simple reaction of *p*-tert-butylphenol and formaldehyde.^{31–34} By the judicious choice of base, reaction temperature, and reaction time, calixarenes with various shapes and ring sizes can be synthesized with good yield and purity.^{35,36} The framework of calixarene entails the presence of a wide hydrocarbon rim that contains methylene bridges along with a narrow rim having phenolic groups to give rise to three-dimensional supramolecules (Figure 3). Resorcinarenes are a type of calixarenes formed by the condensation of resorcinol with aldehyde.

The calixarenes can be readily functionalized at the lower and upper rims with a wide variety of functional groups to make versatile receptors for cations, anions, and neutral species and thus can be utilized for the sensing of the same. However, the development of such materials possessing LC properties has not been explored much.³⁷ Importantly, LC material based on a calixarene core possesses some interesting properties such as good stability across a wide thermal range and a reduced

tendency for crystallization. In addition, the functionalization of calixarene with flexible alkyl side chains can be carried out by linking the core with different functional units. The various possibilities to form calixarene based LCs by chemical functionalization on a calixarene core are represented in Figure 3. It has also been noted that some of the calixarene based functional LCs exhibit excellent mesomorphic properties with emissive behavior, columnar self-assembly, electrochemical behavior, electroluminescence, molecular switch properties, emissive gelation properties, and ion-selective behavior, respectively. Their application in ion and molecular sensing, as fluorescent probes, and as drug delivery agents has been discussed in earlier elaborate reviews.^{38–40}

However, there are few reports on the preparation and applications of calix[4]arene and resorcin[4]arene core based functionalized mesogens. This review provides a brief account of the synthesis of calixarene based LCs, their mesomorphic behavior, and their potential in diverse applications.

2. CALIXARENE BASED LIQUID CRYSTALS

2.1. Calixarene Ethers and Esters.

Initial functionalization of calixarenes to self-assembling structures started with the etherification and esterification of the hydroxyl groups. In subsequent years the flexible chain was introduced through the aldehyde component that takes part in the formation of the calixarene unit to improve the solubility. In 1992, Dalcanale and co-workers reported LC calixarenes for the first time.⁴¹ The acid catalyzed condensation of pyrogallol with 1,1-diethoxyethane in ethanol yielded a bowl-shaped macrocyclic precursor in a good yield. The free hydroxyl groups were esterified later with long chain carboxylic acids of different lengths to get the final compounds. They have also prepared calixarene derivatives by treating pyrogallol and paraformaldehyde in the presence of HCl at 85 °C. The crude compound was treated with butyryl chloride to give pure **1b** in a yield of 53%. Further hydrolysis of the same yielded compound **1a** in pure form, which was treated with appropriate alkanoyl chlorides to get the corresponding dodecaacylated compounds **1c–1k** (Scheme 1). The compounds bearing chains with 12 carbon units onward (**1d–1g**) exhibited the Col_h phase (Figure 4),⁴² while the branched chain esters did not show any LC phase due to the increased steric bulk preventing 1D packing. Compounds **1b**, **1c**, **1h**, **1i**, and **1j** were crystalline, and **1k** turned out to be liquid. The bowl shape of the core in these compounds leads to the net dipole moment of the compounds directed along their C₄ symmetry axis. Thus, the orientation of both molecular and columnar dipoles can lead to

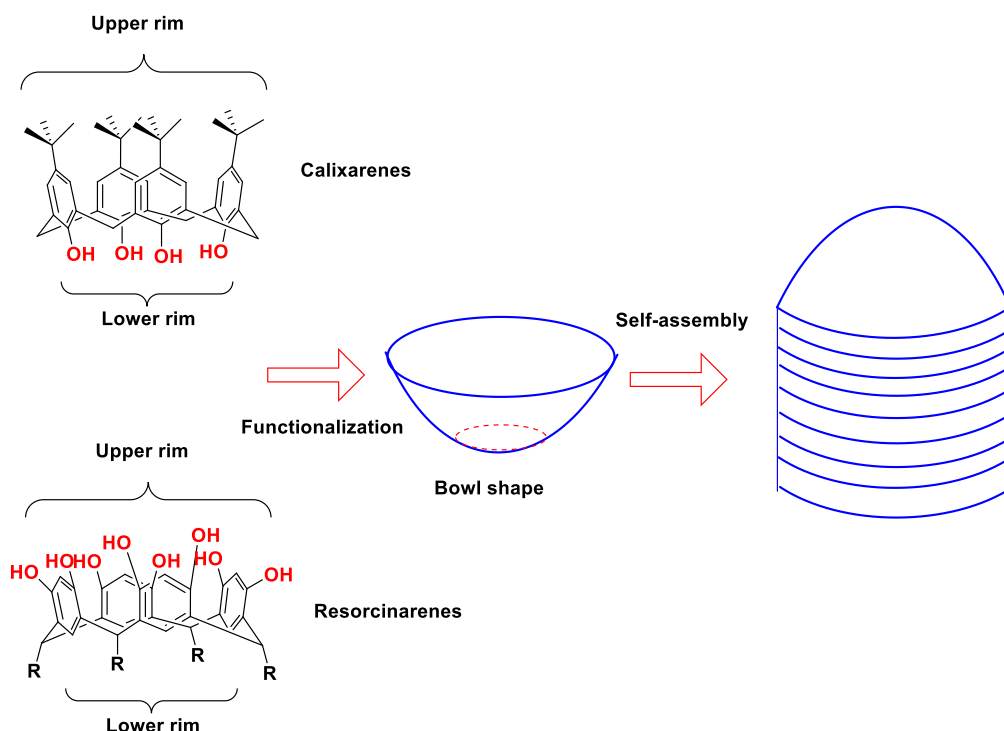
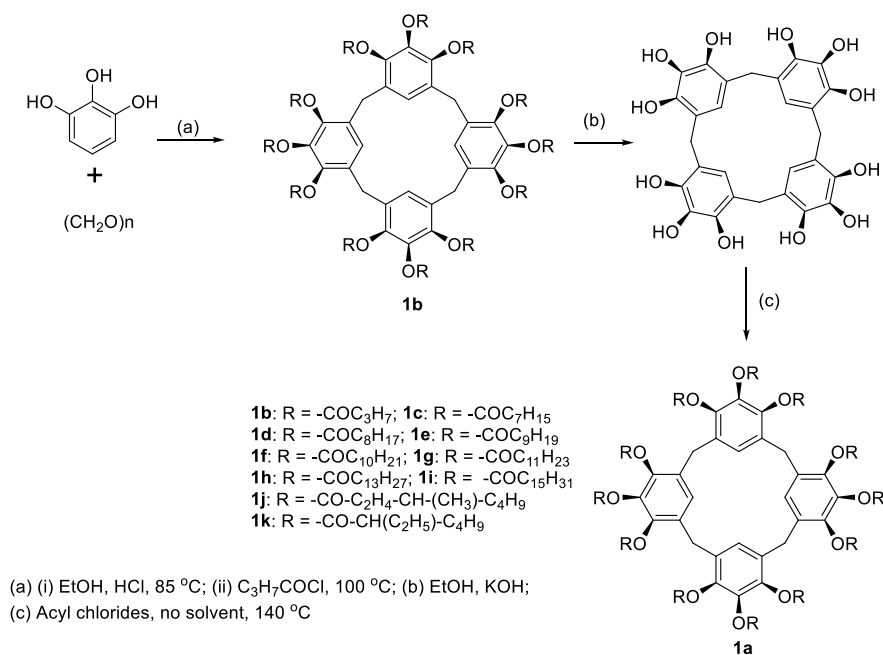


Figure 3. Basic molecular structures of calixarene and resorcinarene cores and their self-assembly on functionalization.

Scheme 1. Bowl-Shaped Liquid Crystalline Derivatives of Calixarene



a potential ferroelectric or antiferroelectric switchable Col phase in an appropriate molecular design.

The same group also developed columnar mesogens with bowl-like structures formed from conformationally mobile macrocyclic cores (Scheme 2). Compounds with methyl groups in the upper rims and eight chains in the lower rims

(**2a–2m**) were non liquid crystalline.⁴³ However, the compounds with methyl groups in the upper rims and 12 chains in the lower rims (**3a–3k**) exhibited improved liquid crystalline behavior. Out of the 10 derivatives, four compounds (**3e–3h**) exhibited a Col_h mesophase.⁴² The aromatic esters (**2j–2m**, **3k**) were non-LC due to the out-of-plane orientation

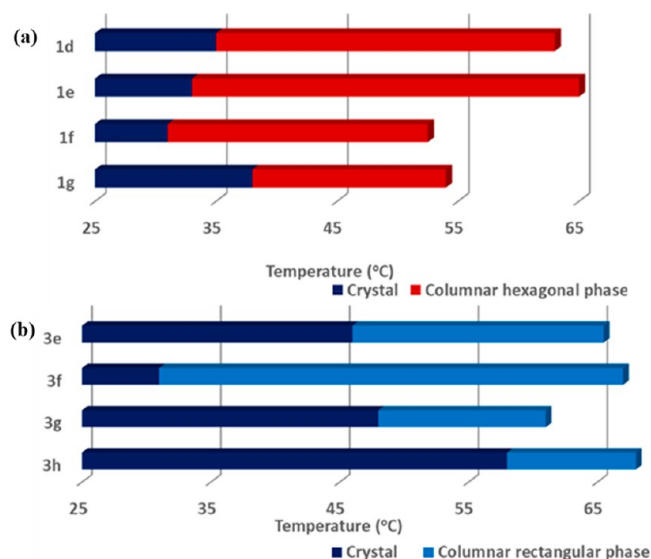


Figure 4. Graphical representation of the thermal behavior of bowl-shaped liquid crystalline derivatives (1d–1g, 3e–3h) (considered the cooling scan).

of phenyl groups hindering the 1D packing of calixarene cores. Deuterium NMR spectroscopy of deuterated benzene added as a probe to compound 3f showed the formation of the uniaxial Col phase, with domain directors perpendicular to the magnetic field.⁴⁴ This also showed that the mesogen forms a cavity with strong host properties toward the guest. The CPK model of compound 3f showed the conelike conformation of

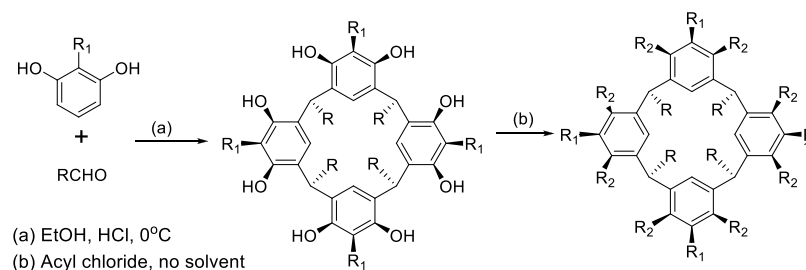


Figure 5. CPK model of compound 3f showing the hollow side view. Reproduced with permission from ref 43. Copyright 1990 Taylor & Francis.

the macromolecule (Figure 5). Calixarene derivatives with ethyl groups in the upper rims and 12 peripheral chains in the lower rims (4b–4e) turned out to be crystalline.⁴³ These studies provided the effect of structural and conformational alterations by the length of the chains in the upper rim and lower rim of the macrocyclic core and the effect on the liquid crystallinity by the number and type of chains in calixarene derivatives.

Gajjar et al.⁴⁵ synthesized calix[4]resorcinarene derivatives (5a–5c) bearing alkoxy chains, which were prepared by the reaction of cinnamaldehyde and resorcinol (Scheme 3). These compounds exhibited a Col_h phase, with the lower chain homologues exhibiting a wider mesophase range while the higher alkyl chain derivatives exhibited a lower mesophase

Scheme 2. Calixarene Based Liquid Crystalline Derivatives



- 2a: R = -CH₃; R₁ = H
 2b: R = -CH₃; R₁ = H, R₂ = -OCOC₅H₁₁
 2c: R = -CH₃; R₁ = H, R₂ = -OCOC₉H₁₉
 2d: R = -CH₃; R₁ = H, R₂ = -OCOC₁₁H₂₃
 2e: R = -CH₃; R₁ = H, R₂ = -OCOC₁₂H₂₅
 2f: R = -CH₃; R₁ = H, R₂ = -OCOC₁₃H₂₇
 2g: R = -CH₃; R₁ = H, R₂ = -OCOC₁₅H₃₁
 2h: R = -CH₃; R₁ = H, R₂ = -OCOC₁₇H₃₅
 2i: R = -CH₃; R₁ = H, R₂ = -OCOC₆H₄OC₇H₁₅
 2j: R = -CH₃; R₁ = H, R₂ = -OCOC₆H₄OC₁₂H₂₅
 2k: R = -CH₃; R₁ = H, R₂ = -OCOC₆H₄OC₁₆H₃₃
 2l: R = -CH₃; R₁ = H, R₂ = -OCOC₆H₄C₆H₁₁
 2m: R = -CH₃; R₁ = H, R₂ = -OCOC₆H₄C₁₀H₂₁

- 3a: R = -CH₃; R₁ = OH
 3b: R = -CH₃; R₁ = R₂ = -OCOC₃H₇
 3c: R = -CH₃; R₁ = R₂ = -OCOC₉H₁₉
 3d: R = -CH₃; R₁ = R₂ = -OCOC₁₁H₂₃
 3e: R = -CH₃; R₁ = R₂ = -OCOC₁₂H₂₅
 3f: R = -CH₃; R₁ = R₂ = -OCOC₁₃H₂₇
 3g: R = -CH₃; R₁ = R₂ = -OCOC₁₅H₃₁
 3h: R = -CH₃; R₁ = R₂ = -OCOC₁₇H₃₅
 3i: R = -CH₃; R₁ = R₂ = -COC₂H₄
 3j: R = -CH₃; R₁ = R₂ = -OCOC₂H₄CH(-CH₃)C₄H₉
 3k: R = -CH₃; R₁ = R₂ = -OCOC₆H₄OC₁₂H₂₅
 4a: R = -C₂H₅; R₁ = R₂ = OH
 4b: R = -C₂H₅; R₁ = R₂ = -OCOC₃H₇
 4c: R = -C₂H₅; R₁ = R₂ = -OCOC₁₁H₂₃
 4d: R = -C₂H₅; R₁ = R₂ = -OCOC₁₅H₃₁
 4e: R = -C₂H₅; R₁ = R₂ = -OCOC₁₇H₃₅

Scheme 3. Synthesis of Calix[4]resorcinarene Derived from Cinnamaldehyde (5a–5c)

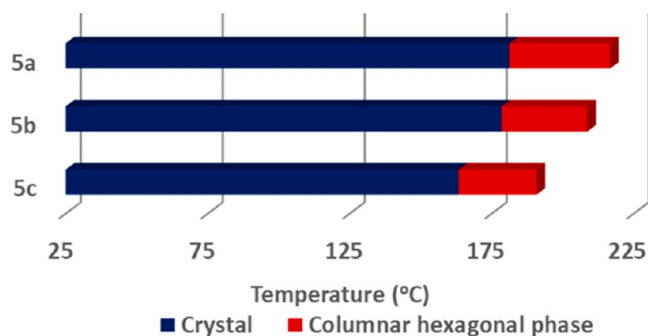
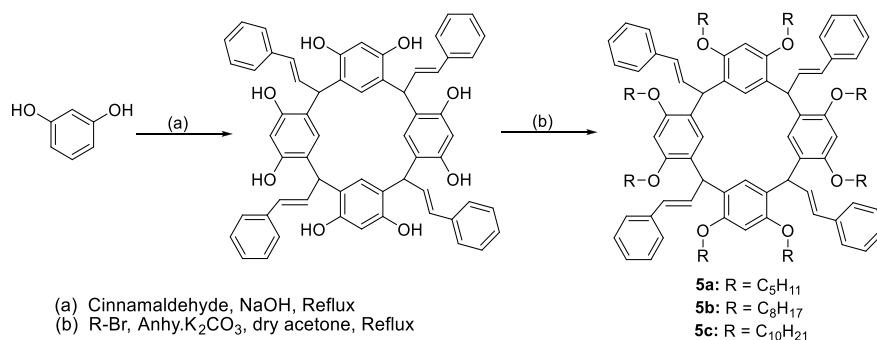


Figure 6. Graphical representation of the thermal behavior of octasubstituted resorcinarene alkyl arm functionalized derivatives (5a–5c) (considered the cooling scan).

width with lowered melting and clearing temperatures (Figure 6).

A series of lower rim functionalized octasubstituted resorcin[4]arene based compounds with variable alkoxy side chains (–OC₄H₉, –OC₆H₁₃, –OC₈H₁₇, –OC₁₀H₂₁) have been reported by Sharma et al.⁴⁶ The final compounds were prepared by a simple two-step procedure (Scheme 4). All four compounds displayed Col_h phases over a wide thermal range

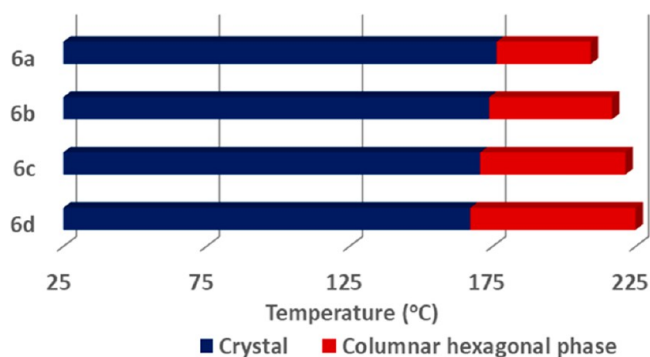
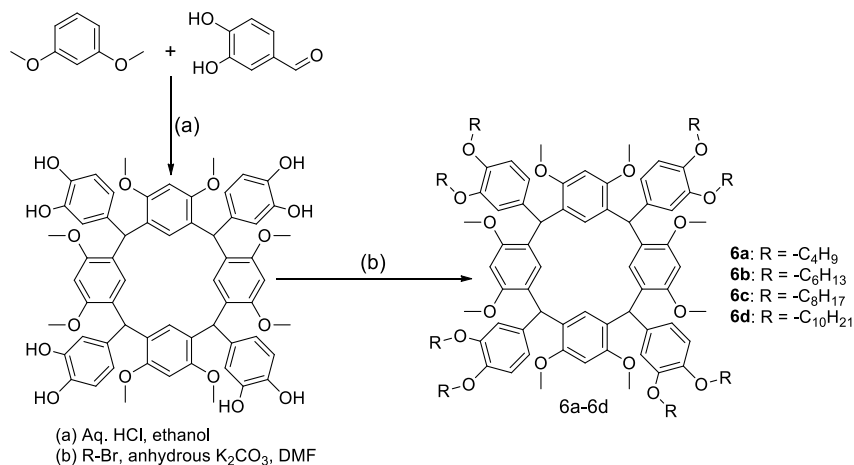


Figure 7. Graphical representation of the thermal behavior of octasubstituted resorcinarene alkyl arm functionalized derivatives 6a–6d (considered the cooling scan).

(Figure 7). Compound 6d with a decyloxy side chain was further tested for the window layer application in solar cells, especially as an alternative to the commercially available toxic Cd-based compounds which are used in solar cells. Herein, we used compound 6d as an optical window layer to achieve maximum transmittance of incident radiation toward the absorber layer and further studied it as a function of temperature. The current–voltage relation shows ohmic-type

Scheme 4. Synthesis of Liquid Crystalline Resorcinarene Derivatives (6a–6d)



Scheme 5. Synthesis of Tungsten Oxo Calix[4]arene Derivatives (7a, 7b)

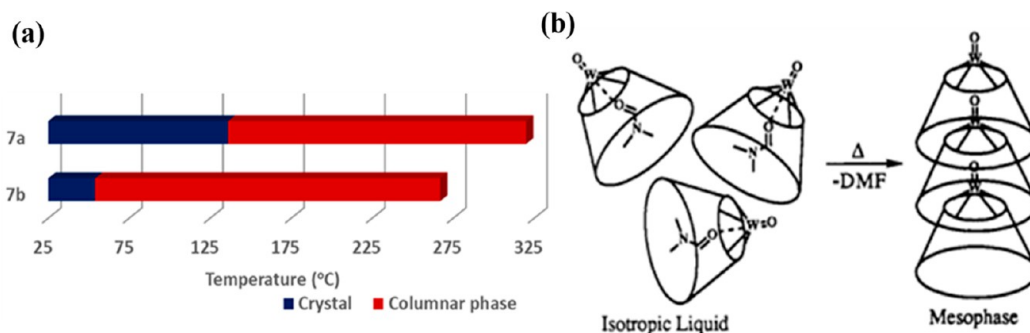
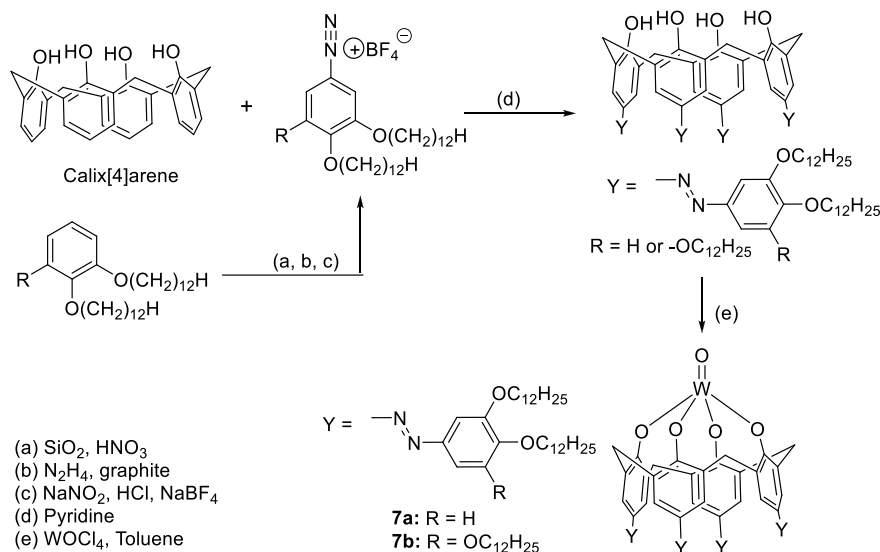


Figure 8. (a) Graphical representation of the thermal behavior of tungsten oxo calix[4]arene derivatives **7a** and **7b**. (b) Rearrangement of bowl-shaped calixarene linked tungsten core into columnar structure (**7a**, **7b**).⁴⁸ Reproduced from ref 48. Copyright 1993 American Chemical Society.

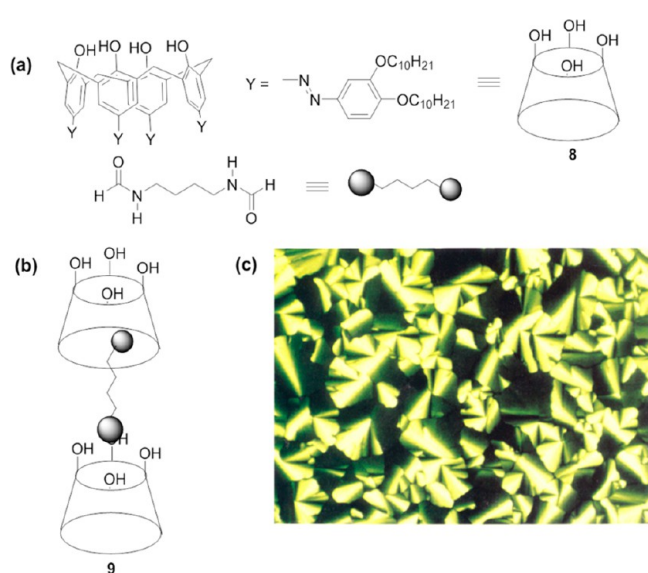


Figure 9. Structure of the azobenzene based calix[4]arene (**8**) and *N*-*n*-butylformamide (a). Schematic representation of the stacking calix[4]arenes by forming a 2:1 complex with *N*-*n*-butylformamide in the mesophase (b). Optical texture of the B_h phase stabilized by the host-guest complex in 2:1 ratio (c).⁴⁹ Reproduced from ref 49. Copyright 1995 American Chemical Society.

behavior. The optical properties display high transmittance in the visible and near IR regions at room temperature and 200 °C. The derivative showed three optical band gaps (1.61, 4.01, and 2.27 eV) at different thin film states and variable temperature which are more suitable for an eco-friendly, light absorbing window layer in solar cell applications.

2.2. Calixarene Derivatives with Azobenzene Moieties. Azobenzenes have the ability to photoisomerize in the presence of UV light of a particular wavelength from the thermodynamically stable *trans* form (*E*-form) to the metastable *cis* form (*Z*-form). The reverse isomerization can occur by thermal back relaxation or by the irradiation of visible light. This reversible isomerization brings about a large change in the molecular shape and dipole moment, and when incorporated as a part of the mesogen, it will lead to the light controlled switchability of the mesophase, thus adding a new functionality to the system. Thus, the combination of photoswitchable azobenzene with mesogens is an active area of research.⁴⁷

Swager et al. for the first time reported the synthesis of bowl-like tungsten oxo calix[4]arenes functionalized with azobenzene moieties (**7a**, **7b**) which differ by the number of alkoxy chains on the peripheral phenyl ring (Scheme 5).⁴⁸ These compounds exhibit an ordered Col_h phase (Figure 8a). They also form host-guest complexes with DMF and pyridine solvents. The host-guest complexes do not show any

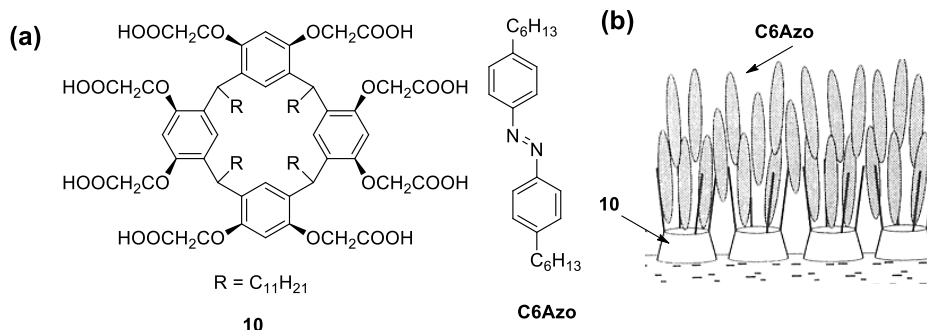


Figure 10. Structures of calix[4]arenes reported by Oh et al.⁵⁰ (a). Presentation of molecular organization of compound **10** and **C6Azo** in the form of a mixed monolayer on a water surface (b).⁵⁰ Reproduced with permission from ref 50. Copyright 2001 The Royal Society of Chemistry.

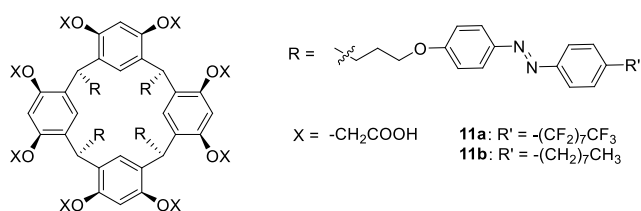


Figure 11. Structures of perfluoro-octylazobenzene (**11a**) or octylazobenzene (**11b**) functionalized *O*-octacarboxymethylated calix[4]arene derivatives.

mesophase, while the removal of guests allows the molecules to pack in a column by the incorporation of tungsten oxo groups inside the cavity leading to the stabilization of ordered Col_h phase as shown in Figure 8b.

Swager et al. also reported a bowl-shaped conformationally stable calixarene derivative (**8**) stabilizing the Col_h phase by

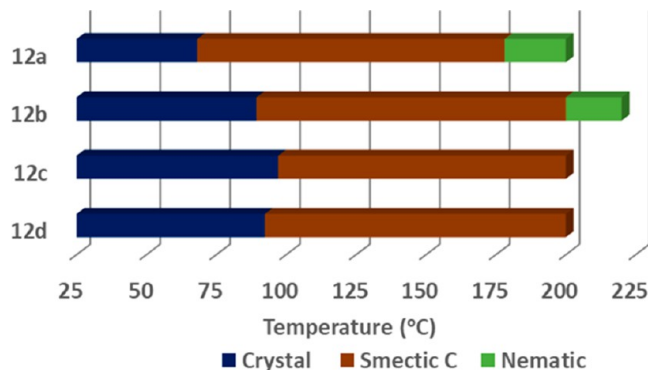
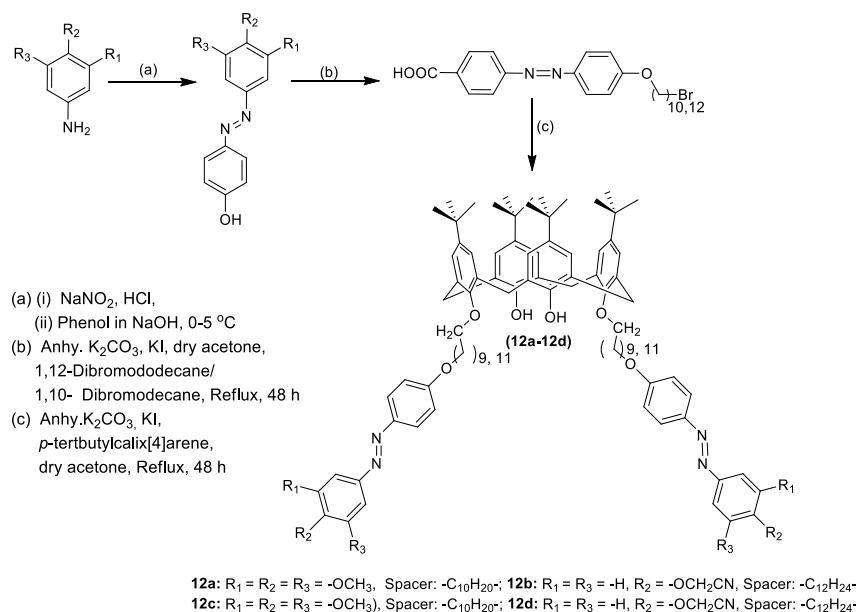


Figure 12. Graphical representation of the thermal behavior of azocalix[4]arene derivatives (**12a–12d**) (considered the heating scan).

Scheme 6. Synthesis of Lower Rim Azocalix[4]arene Derivatives (**12a–12d**)



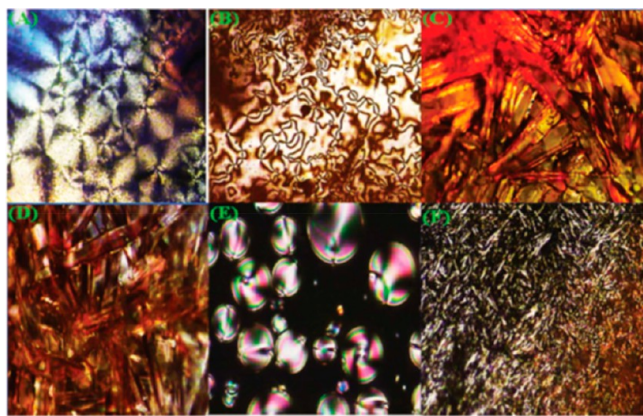


Figure 13. Polarized optical textures: (A) focal conic for compound **12a** at 85 °C; (B) schlieren type for compound **12a** at 175 °C; (C) rodlike domains obtained for SmC for compound **12c** at 97 °C; (D) rodlike domains obtained for SmC for compound **12b**; (E) nematic droplets for compound **12b** at 200 °C; (F) needlelike pattern of SmC obtained for compound **12d** at 92 °C. Reproduced with permission from ref **52**. Copyright 2013 The Royal Society of Chemistry.

host–guest interactions (Figure 9).⁴⁹ They found that these conformationally flexible materials displayed an unusual transient mesophase which was mainly detected during initial heating. Further, heating up to 163 °C showed a normal liquid

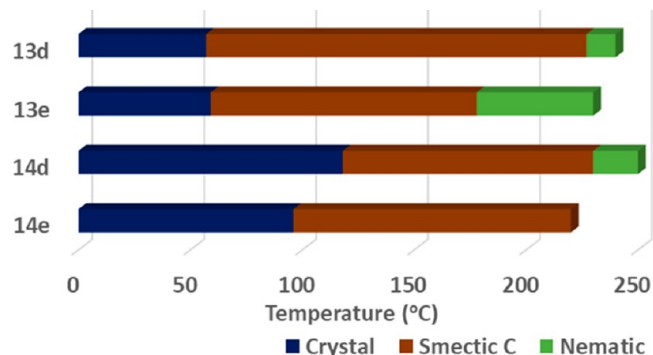
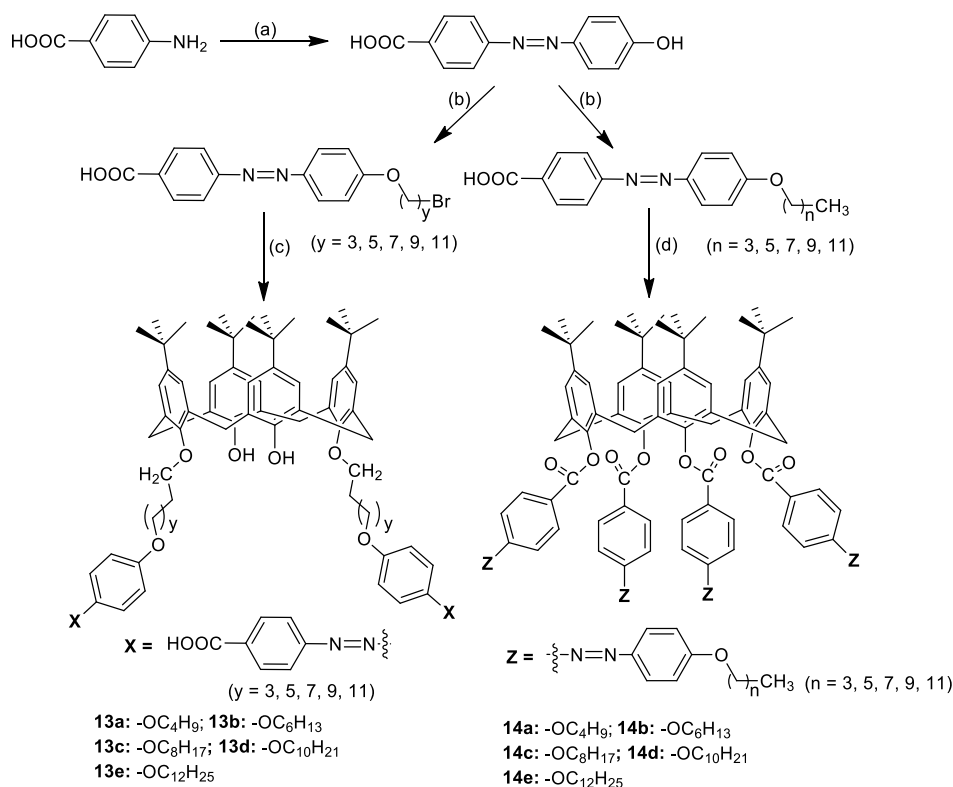


Figure 14. Graphical representation of the thermal behavior of azo-ester linked lower rim substituted calixarene derivatives (**13d**, **13e** and **14d**, **14e**) (considered the cooling scan).

type isotropic phase and, upon cooling, produced a solid crystalline compound with no birefringence. However, X-ray diffraction (XRD) analysis pointed toward an ordered arrangement. This ordered phase was confirmed to be a cubic lattice, which is reliable due to the absence of any birefringence.

After recrystallization, the initial crystal phase was found in methanol/tetrahydrofuran solvent. Upon melting of the crystallized bowl-shaped calix[4]arene, the molecules organized into a B_h phase with a head-to-tail order type arrangement

Scheme 7. Azo-Ester Linked Lower Rim Substituted Calixarene Derivatives (**13a–13e** and **14a–14e**)



(a) (i) NaNO_2 , HCl , (ii) Phenol in NaOH , 0–5 °C; (b) Anhy. K_2CO_3 , KI , dry acetone, Dibromoalkane, Reflux, 48 h; (c) *p*-tert butylcalix[4]arene, anhy. K_2CO_3 , KI , dry acetone, Reflux, 48 h; (d) *p*-tert butylcalix[4]arene, DCC, DMAP, THF, 48 h, RT.

Scheme 8. Structures of LC Calixarenes Reported by Shinkai and Co-workers

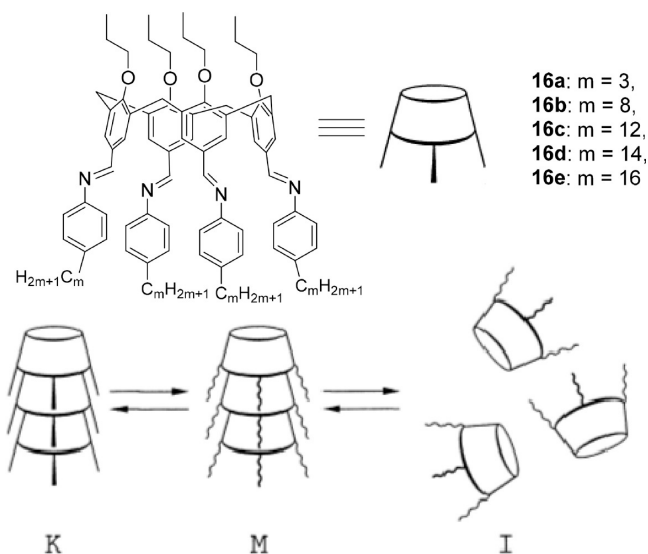
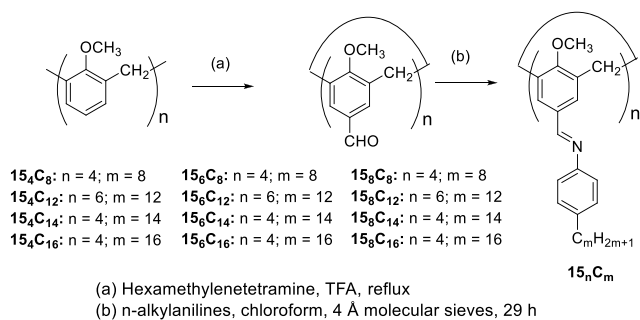


Figure 15. Schematic representation of the phase transitions of cone-shaped calix[4]arenes. In K, the molecular motion of the aliphatic chains is frozen, whereas in M it is allowed.⁵⁵ Reproduced with permission from ref 55. Copyright 1993 CSJ Publisher.

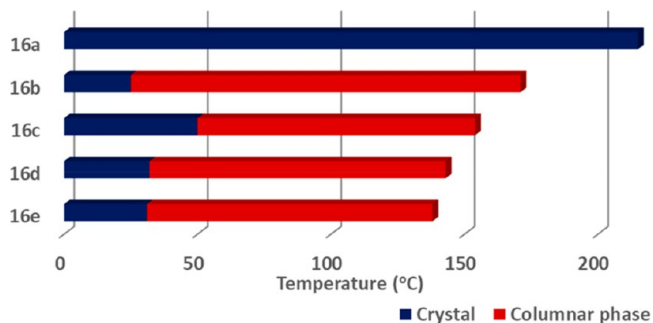


Figure 16. Graphical representation of the thermal behavior of cone-shaped calix[4]arenes derivatives (**16a–16e**) (considered the heating scan).

and dipole–dipole interactions. They found that this mesophase can be stabilized by forming a complex (**9**) with a guest containing two formamide units separated by a butyl spacer. Here, the one amide binds in the cavity and enforces the cone formation while the other one forms hydrogen bonds with the nearest neighbor, thereby leading to head-to-tail

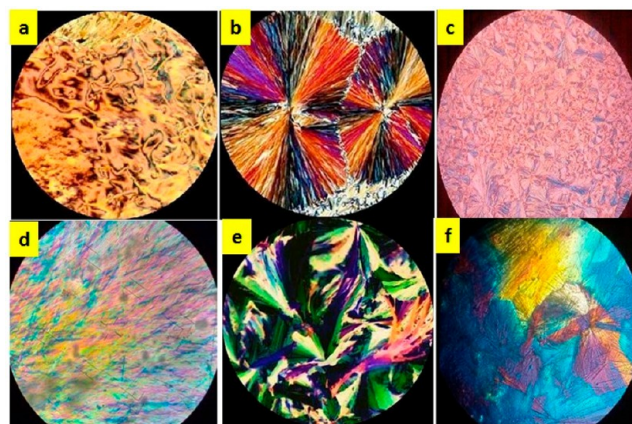


Figure 17. Compound **17c** nematic phase at 185 °C (a). SmA phase at 139 °C (b). SmC phase at 88 °C (c). Compound **18c** nematic phase at 176 °C (d). SmA phase at 130 °C. (e) SmC phase at 90 °C (f). Reproduced with permission from ref 56. Copyright 2010 Springer.

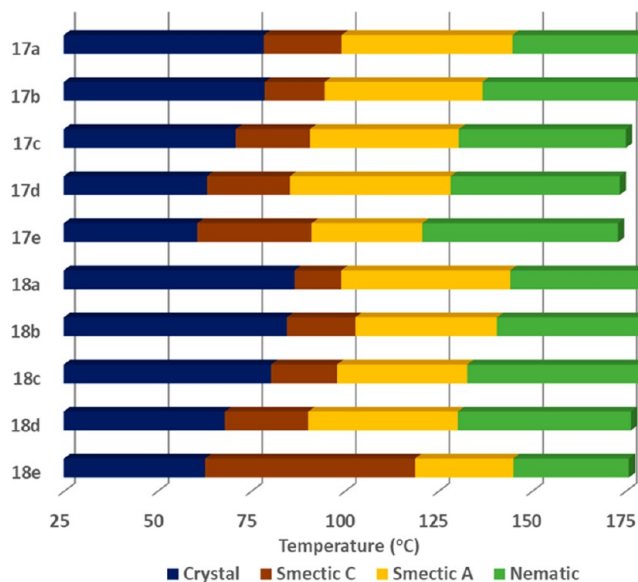


Figure 18. Graphical representation of the thermal behavior of Schiff base calixarene derivatives (**17a–17e** and **18a–18e**) (considered the heating scan).

organizations (Figure 9b). It is interesting to note that only a small amount of guest is required to stabilize a B_h phase, suggesting the cooperative nature of the guest induced transition (Figure 9c).

Along similar lines, Oh et al.⁵⁰ reported the perpendicular orientation of a nematic LC azobenzene (**C6Azo**, 4,4'-dihydroxy azobenzene) on a water surface when mixed with O-octacarboxymethylated calix[4]resorcinarene (**10**) as a host. A host–guest mixed monolayer of **C6Azo** with O-octacarboxymethylated calix[4]resorcinarene exhibited the formation of a double-layered structure by further compression. Hence compound **10** acts as an excellent host for the **C6Azo** LC compound (Figure 10).

Besides host–guest interactions, Matsuzawa et al.⁵¹ investigated the relationship between nematic orientation and the wetting qualities of mixed monolayers generated by the

Scheme 9. Synthesis of Calixarene Schiff Base Derivatives (17a–17e and 18a–18e)

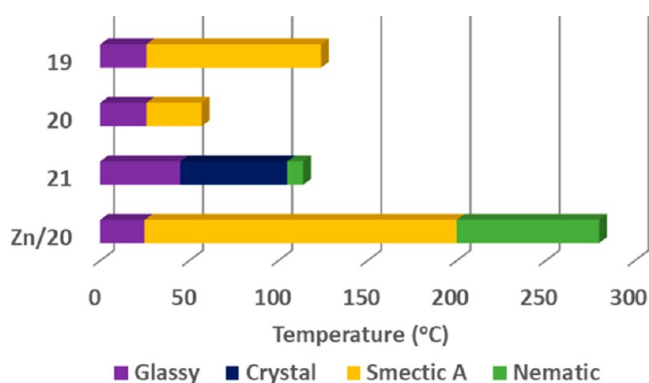
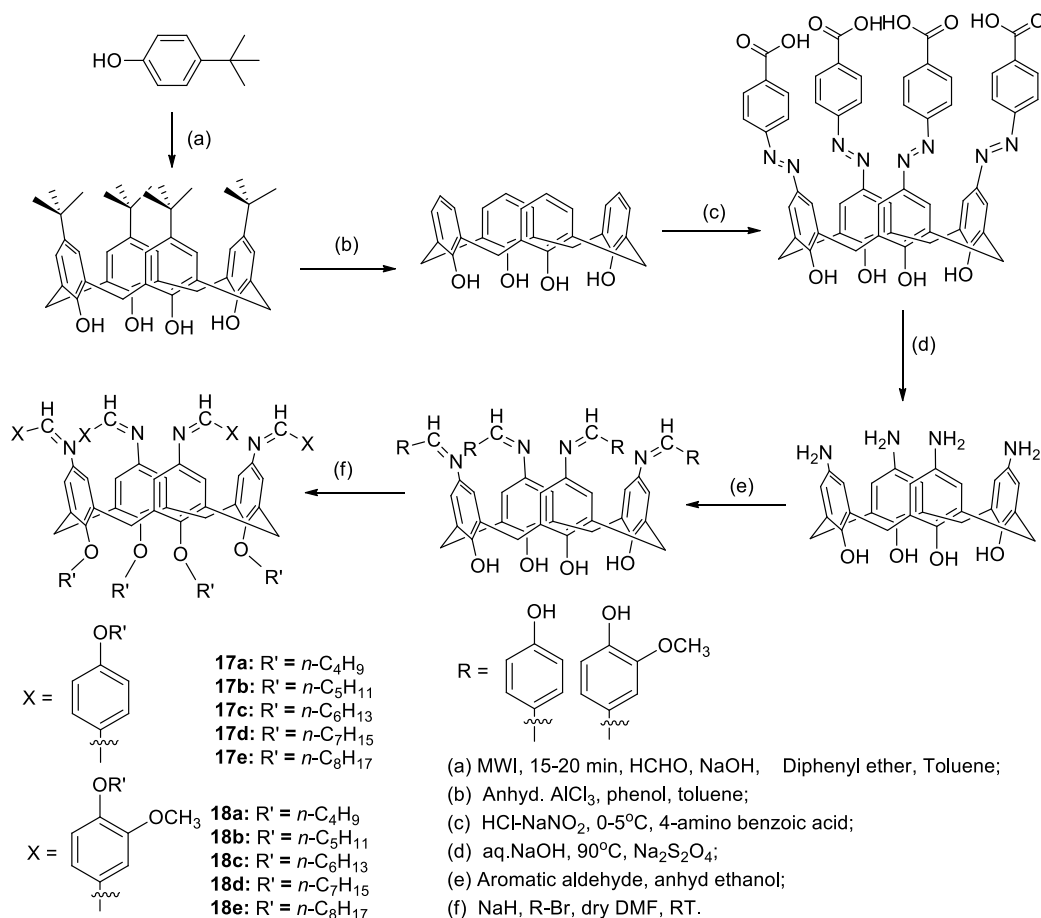


Figure 19. Graphical representation of the thermal behavior of Schiff base calixarene derivatives (19, 20, 21, and Zn/20) (considered the heating scan).

coadsorption of two *O*-octa substituted carboxymethylated calix[4]resorcinarenes (11a, 11b) with perfluorooctyl or octyl linked azobenzene groups (Figure 11). In addition, they also looked at photoirradiation of 11a and 11b monolayers, which caused a reversible *trans*–*cis* photoisomerization of the surface azobenzenes, which causes changes in the LC alignment and wettability of the monolayers. The photogenerated LC alignments are influenced by the surface compositions of the mixed monolayers. They also discovered that when LC cells

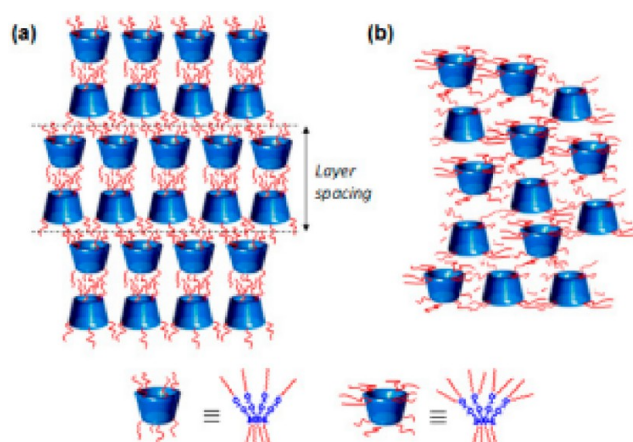


Figure 20. Proposed arrangements of compounds 19 and 20 in SmA phase (a) and compound 21 in nematic phase (b). Reproduced with permission from ref 58. Copyright 2017 Wiley.

produced using single-component monolayers of compounds 11a and 11b containing *p*-octylazobenzenes are exposed to oblique nonpolarized UV light, the orientation of the LC molecules switches from homeotropic to homogeneous, tilting toward the direction of light propagation. In contrast, single-component and mixed monolayers of the above calix[4]-

resorcinarenes with *p*-perfluorooctylazobenzenes cause homeotropic alignments and tilted homeotropic alignments with high pretilt angles, respectively.

In 2013, Sutariya et al. reported basket-shaped supra-molecules constructed by introducing two azo-ether groups on the bottom side of calix[4]arene as shown in Scheme 6.⁵² These compounds (12a–12d) exhibited enantiotropic mesomorphic properties with good thermal stability. Azo materials 12a and 12b showed smectic C and nematic phases, while oligomers 12c and 12d exhibited smectic C phase exclusively (Figures 12 and 13). Further, these supramolecules exhibited promising results in a dielectric study, which was carried out between 100 Hz and 2 MHz in the temperature range 50–110 °C. Figure 12 represents the thermal behavior of all four calixarene–azobenzene oligomers.

The same group prepared two homologous series based on azo-ether (13a–13e) and azo-ester (14a–14e) linked calixarene LC oligomers (Scheme 7).⁵³ Among all the derivatives, 13d, 13e, 14d, and 14e with decyloxy and dodecyloxy terminal chains showed smectic C and nematic phases with characteristic optical textures (Figure 14). Further, dielectric studies were reported for the synthesized materials.

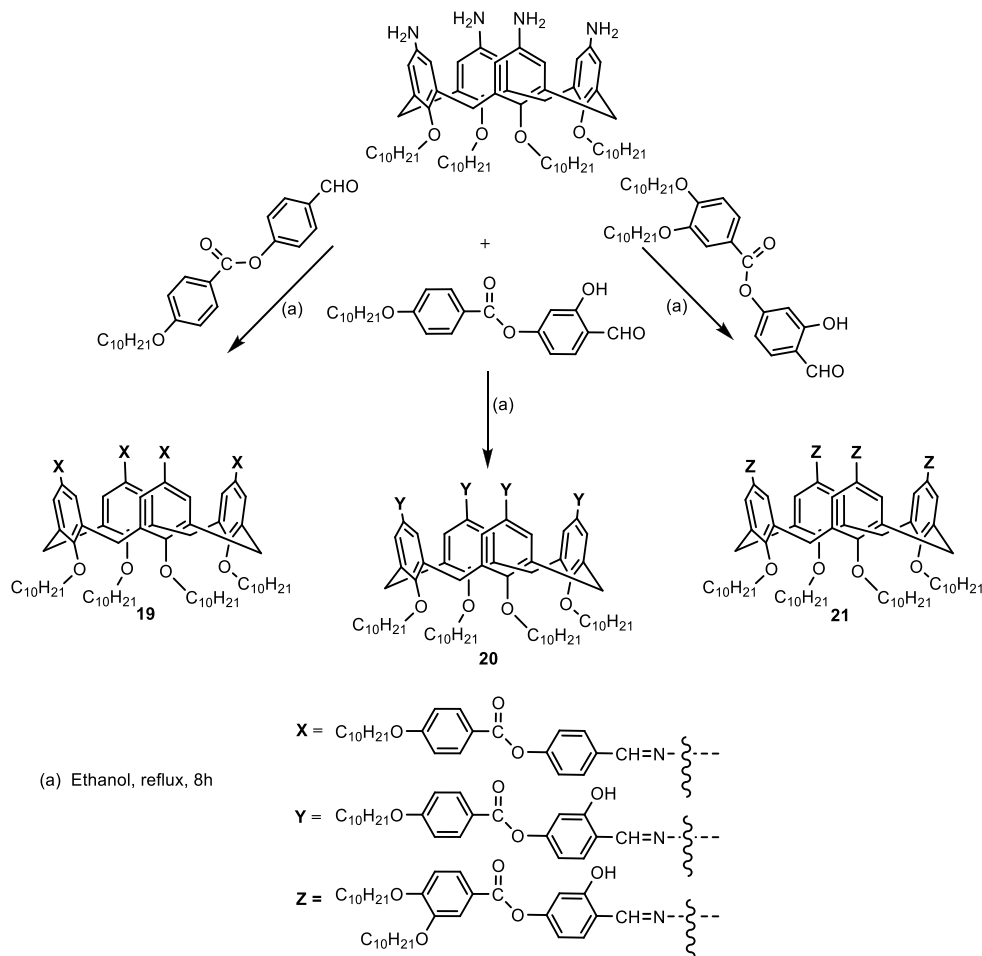
The lamellar type molecular packing of smectic C phase was confirmed by XRD studies.

2.3. Calixarene Derivatives with Schiff Base Moieties.

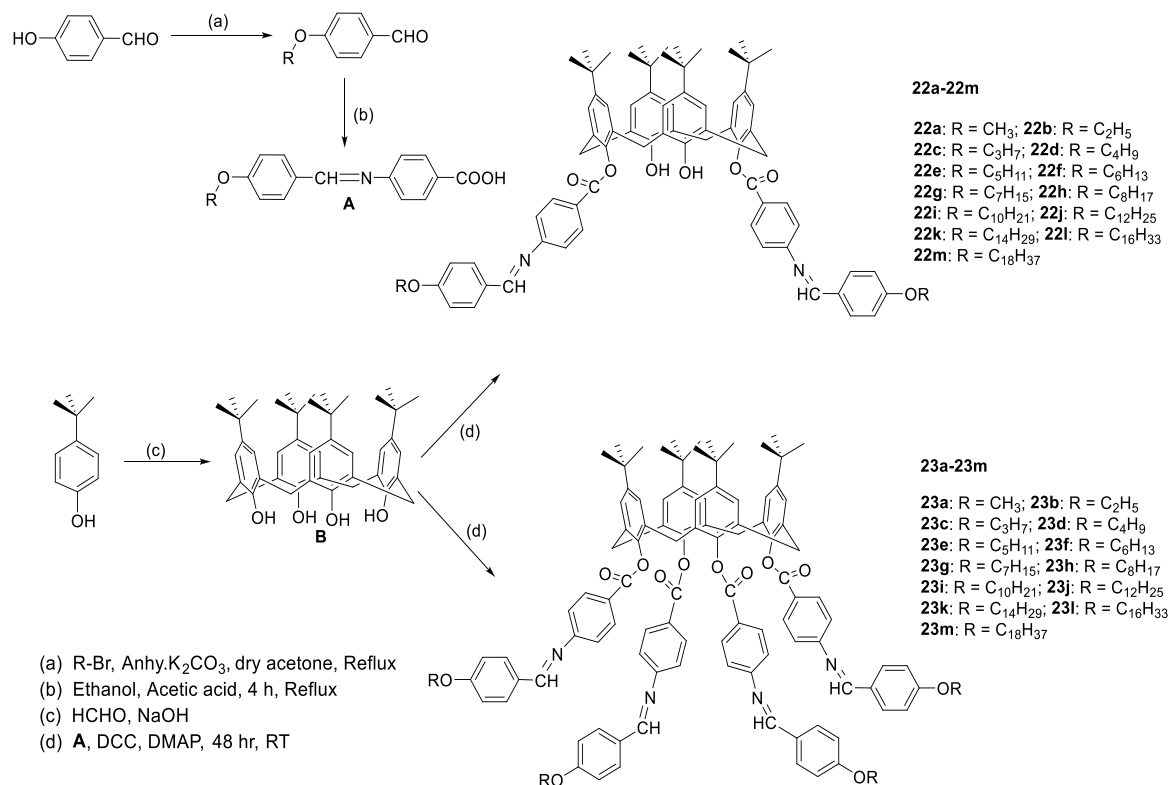
Schiff bases formed by the condensation of aldehyde and amine functionalized molecules provide an easy access to variety of mesogens in a rapid way, though they have moderate hydrolytic stability. Utilizing this approach, Shinkai et al.⁵⁴ reported *O*-methylated calix[*n*]arenes (*n* = 4, 6, and 8) coupled to 4-alkylbenzene through a Schiff base linkage, where the alkyl chain length was varied with octyl, dodecyl, tetradecyl, and hexadecyl (Scheme 8). All compounds exhibited flow birefringence with broad melting points. The nature of the mesophase is not clearly illustrated; however, the broad diffused peak in the wide angle for compound 15₈C₁₆ suggested the liquidlike packing of alkyl chains that is characteristic of a liquid crystalline phase. This phase existed from 20 to 55 °C.

In another interesting report, Komari and Shinkai reported columnar liquid crystals (16a–16e) based on conformationally rigid calix[4]arenes were coupled to C₆H₄-*p*-C_{*m*}H_{2*m*+1} (*m* = 3, 8, 12, 14, and 16) via a Schiff base linkage. It was found that compounds with octyl and higher chain lengths exhibited a Col

Scheme 10. Synthetic Route of Schiff Base Molded Calix[4]arene Derivatives (19–21)



Scheme 11. Synthetic Route of Schiff Base Ester Calixarene Derivatives (22a–22m and 23a–23m)



phase (Figure 16).⁵⁵ As shown in Figure 15, the crystal to mesophase transition involves the melting of aliphatic chains, while the mesophase to isotropic transition involves the unsettling of calixarene cores.

Menon and co-workers prepared six mesogens based on upper/lower rim functionalization on a calix[4]arene core through a Schiff base unit by treating four different types of aldehydes (2-vanillin, 4-vanillin, 4-hydroxy benzaldehyde, and 2-hydroxy naphthaldehyde) with a tetraaminocalix[4]arene core. Further, these compounds were also tested for their dielectric behavior.⁵⁶ The synthetic route of Schiff base molded calixarene derivatives (17a–17c and 18a–18c) from calix[4]arene (1) is shown in Scheme 9. All six calix[4]arenes exhibited smectic A, smectic C, and nematic mesophases with a wide thermal range (Figure 18). From polarized optical microscopic (POM) texture images, a broken focal conic texture was observed for smectic C, a needle/lancet or fanlike texture was observed for smectic A, and schlieren type textures were observed for nematic phases of these compounds (Figure 17). Subsequently, the same group reported the dielectric properties of calixarene based Schiff base LCs (17a, 17b, 18a, and 18b).⁵⁷

Romero et al.⁵⁸ prepared calixarene Schiff base derivatives by the reaction of three different promesogenic aldehydes with tetraaminocalix[4]arene as the rigid core. In this study, all three compounds (19–21) displayed an SmA or nematic mesophase depending on the number of terminal alkyl chains (Figure 19). The synthetic route to prepare calixarene linked Schiff base derivatives is given in Scheme 10. Furthermore, the compounds displayed Zn²⁺ binding and selectivity. Complexation with the Zn²⁺ ion increased the ligand's emission intensity, and a mass study confirmed the presence of 1:2 and

1:1 complexes, respectively. The possible arrangement to form smectic and nematic mesophases is shown in Figure 20.

Sharma et al.⁵⁹ reported two series of lower rim functionalized calixarene Schiff base derivatives. These two homologous series were synthesized from the Schiff base derivatives of 4-amino benzoic acid and 4-*n*-alkoxy benzaldehyde at the bottom side of the *p*-*tert*-butylcalix[4]arene rigid core (Scheme 11). In this work, they noted that compounds 22g–22m in series 1 and 23d–23m in series 2 showed both smectic and nematic phases over a wide temperature range in heating and cooling conditions. Compounds 22f and 23c showed nematic phases exclusively. Lower homologues in both series turned out to be crystalline (Figure 21). Compounds 22c, 22g, 23f, 23g, 23i, and 23j were tested *in vitro* against two Gram-positive bacteria (*Staphylococcus aureus*, *Streptococcus pyogenes*), two Gram-negative bacteria (*Escherichia coli*, *Pseudomonas aeruginosa*), and three fungal strains (*Candida albicans*, *Aspergillus niger*, *Aspergillus clavatus*). These compounds exhibited good antibacterial and antifungal activity.⁵⁹

Blue light emitting materials have received considerable attention as they find potential use in the production of white organic light emitting diodes (WOLEDs) utilized in display systems. Calixarene attached with Schiff base units based on 4-*n*-alkoxy aniline in the lower rim with varying terminal alkyl chain lengths were prepared as shown in Scheme 12.⁶⁰ All seven bowl-shaped compounds exhibited columnar hexagonal phases with good thermal stability. In comparison to higher alkyl chain analogues, the compounds with shorter chains showed a wider temperature range of the mesophase (Figure 22). All the materials displayed cyan colored fluorescence on exposure to long wavelength UV light, which is promising for their application in OLEDs.

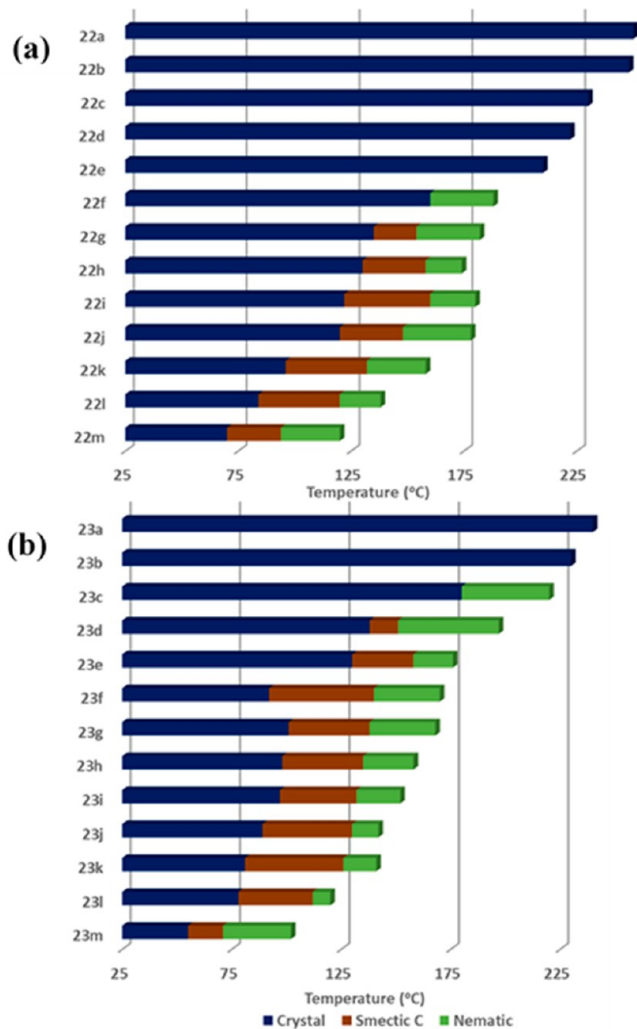


Figure 21. Graphical representation of the thermal behavior of Schiff base ester calixarene derivatives (a) 22a–22m and (b) 23a–23m (considered the heating scan).

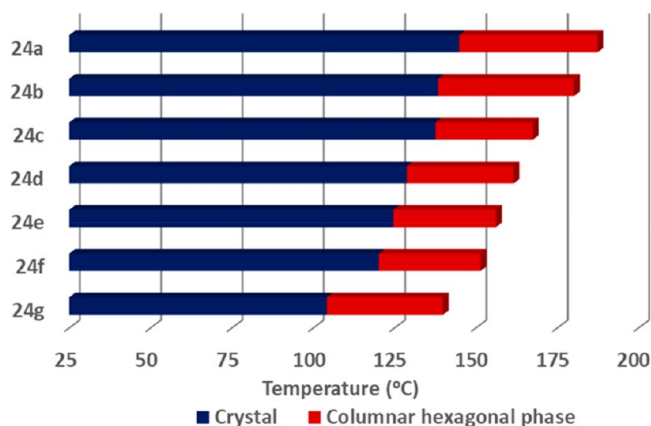


Figure 22. Graphical representation of the thermal behavior of Schiff base derivatives (24a–24g) (considered the cooling scan).

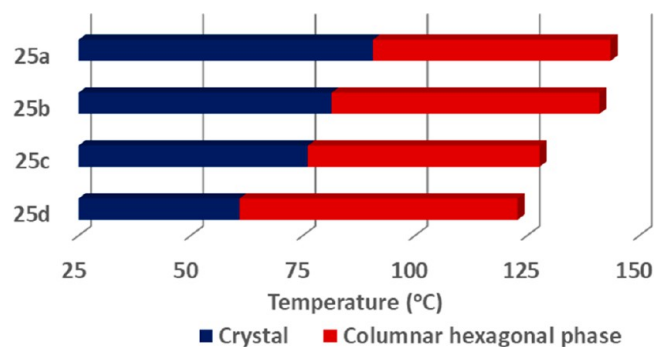


Figure 23. Graphical representation of the thermal behavior of Schiff base ester derivatives (25a–25d) (considered the cooling scan).

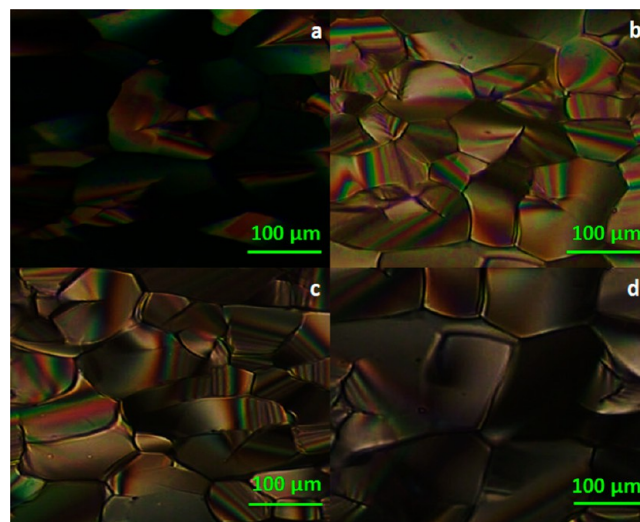


Figure 24. Photomicrographs of 25a at 93.1 °C (a), 25b at 84.2 °C (b), 25c at 76.4 °C (c), and 25d at 66.6 °C (d) on heating from the solid crystalline state as seen under cross polarizers.⁶¹ Reproduced with permission from ref 61. Copyright 2020 The Royal Society of Chemistry.

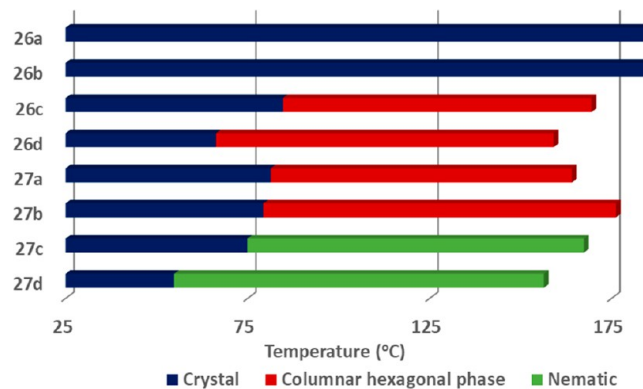


Figure 25. Graphical representation of the thermal behavior of quinoline armed thiacalix[4]arene derivatives (26a–26d and 27a–27d) (considered the cooling scan).

Scheme 12. Synthetic Route of Lower Rim Substituted Calixarene Derivatives (24a–24g)

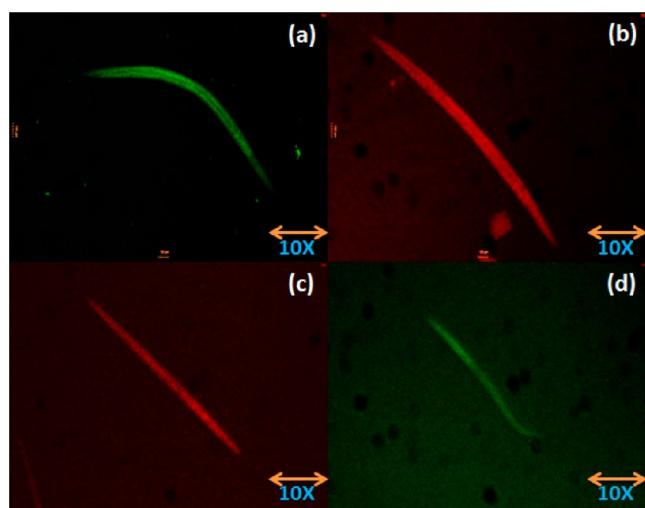
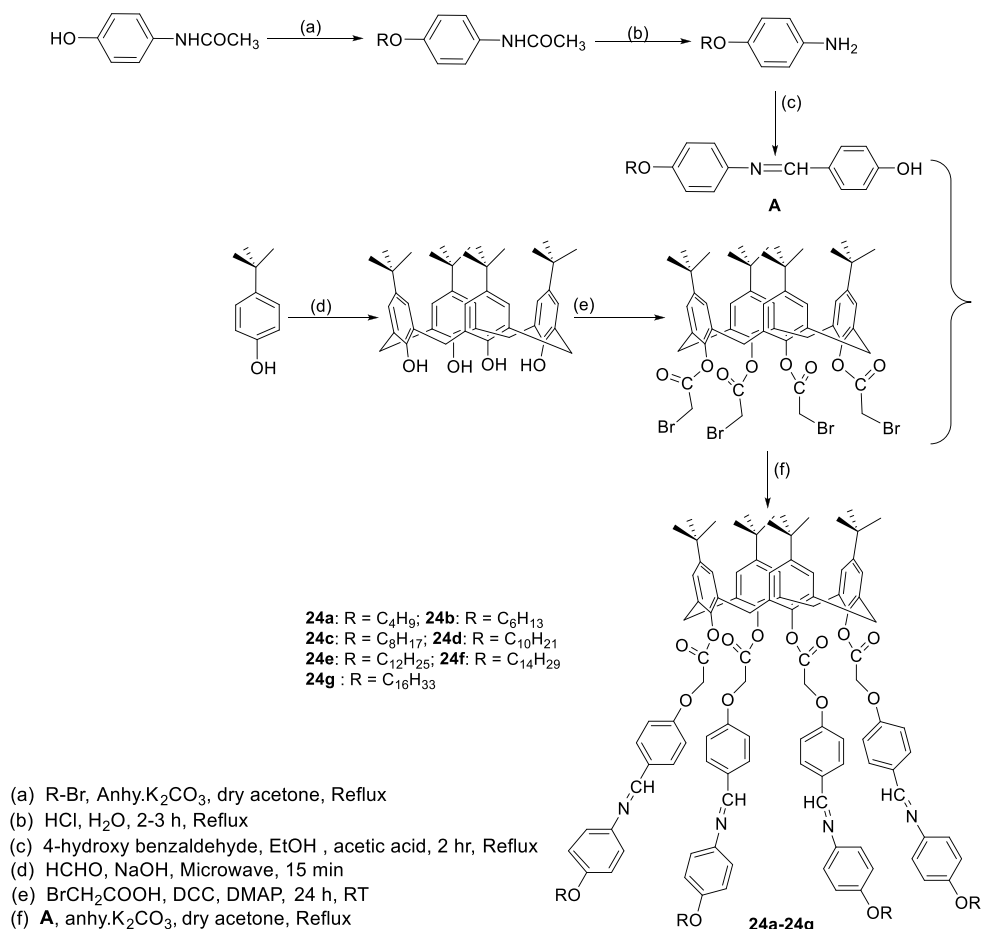


Figure 26. Distribution of parent calixarene linked quinoline derivative (27d) in nematodes (*Caenorhabditis elegans*) (5 μ M). (a) Nematode exposed with aqueous THF solution in the blue filter; (b) nematode exposed with aqueous THF solution in green filter; (c, d) nematode exposed with compound 27d in THF solvent.⁶² Reproduced with permission from ref 62. Copyright 2022 Elsevier.

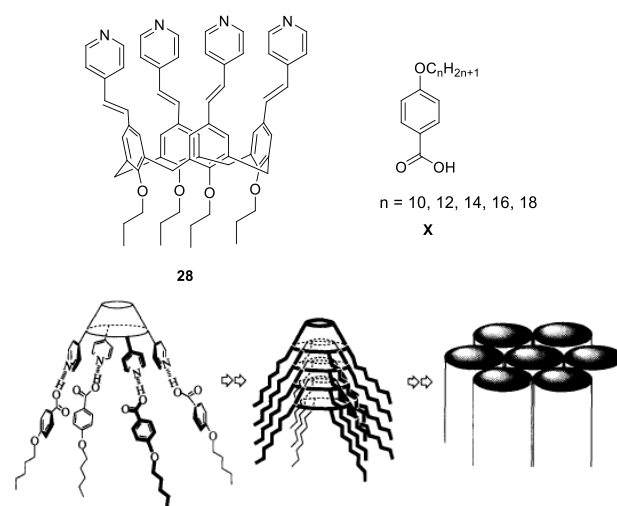
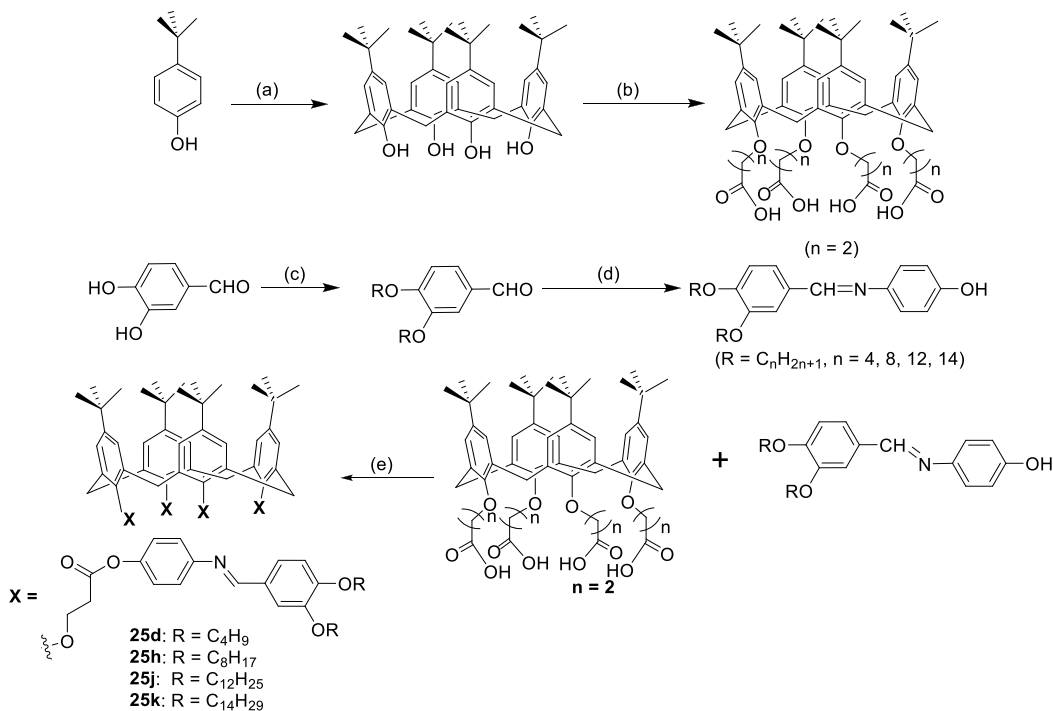


Figure 27. Structures of calix[4]arenes and 4-*n*-alkoxybenzoic acids and schematic representation of stacking calix[4]arenes to form Col phase (for chain length 12 and above).⁶³ Reproduced with permission from ref 63. Copyright 1995 Elsevier.

Scheme 13. Preparation of Lower Rim Substituted Schiff Base Ester Derivatives (25a–25d)



- (a) HCHO, NaOH, microwave, 15 min; (b) Br(CH₂)₂COOH, Anhyd.K₂CO₃, dry acetone, Reflux;
 (c) RBr, Anhyd. K₂CO₃, dry acetone, (R = C_nH_{2n+1}, n = 4, 8, 12, 14);
 (d) 4-amino phenol, EtOH, few drops of acetic acid, Reflux; (e) EDC-HCl, DMAP, DCC, 24 h, RT

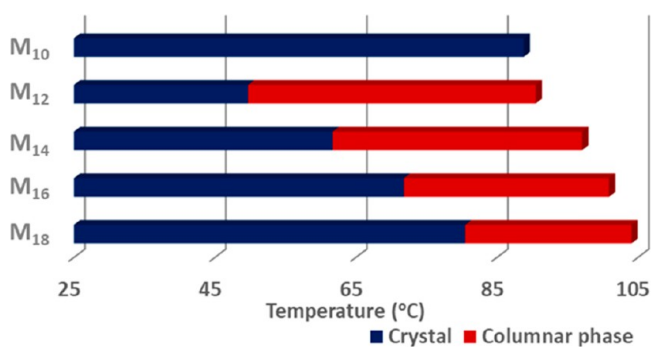


Figure 28. Graphical representation of the thermal behavior of calix[4]arene derivatives (M₁₀, M₁₂, M₁₄, M₁₆, and M₁₈) (considered the heating scan).

Sharma et al.⁶¹ reported a calixarene linked with Schiff bases that stabilize the enantiotropic Col_h phase with good photophysical and electrochemical properties. The synthetic route of calixarene derivatives (25a–25d) is shown in Scheme 13. In Figure 23, bar graphs represent the thermal behaviors of supramolecular mesogens. An increase in the terminal chain witnessed a lowering in the melting and clearing points of these mesogens. A characteristic mosaic texture was observed for the Col_h phases of these compounds (Figure 24). In addition, they exhibited sky-blue fluorescence both in solution and in the thin film state with good quantum yields.

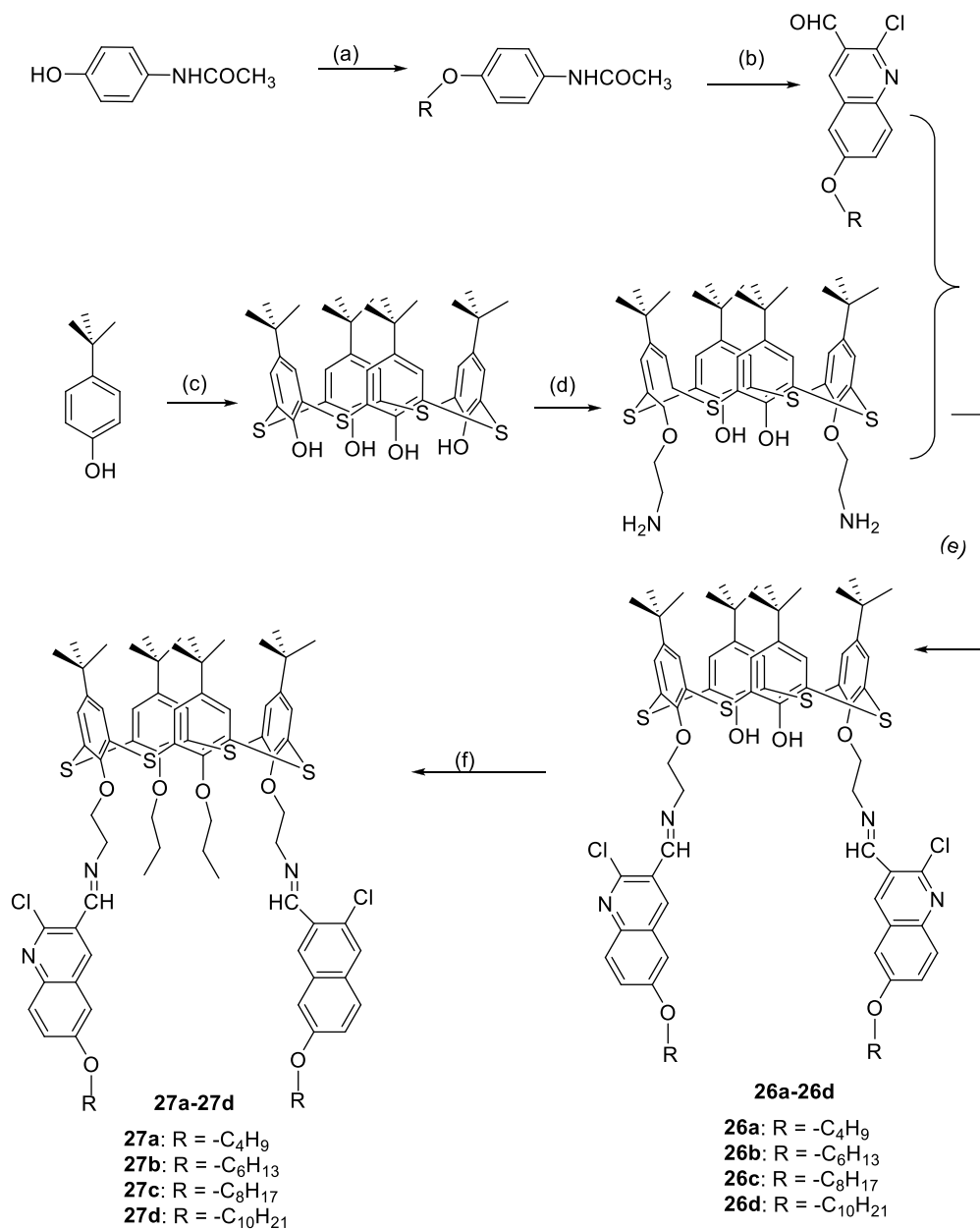
Rathod et al. reported a cone-shaped thiacalix[4]arene appended with quinoline moieties that were stabilizing liquid crystallinity (Scheme 14).⁶² The thiacalixarene core bearing

bisubstituted quinoline units stabilized the Col_h phase, when the other two hydroxyl groups were free (26c and 26d) and where the terminal chains were *n*-octyloxy and *n*-decyloxy units. In the case of tetrasubstituted thiacalix[4]arene derivatives, lower chain homologues exhibited Col_h phases while the higher chain substituted compounds showed nematic phases (Figure 25). Thus, in the class of cone-shaped supramolecules, the number of substitution and the length of the peripheral alkoxy chains affect the phase transition temperature including self-organization of the molecules, which is contrary to traditional disk-shaped mesogens. These materials showed blue fluorescence in solution and in the thin film state under a long UV irradiation. The introduction of quinoline substituted arms on the lower rim of the thiacalix core enhances the intermolecular interactions by enhancing the mesophase width. These compounds can be used for bioimaging applications, which was evidenced by the translocation of the fluorescent molecules in nematodes (Figure 26).

2.4. Calixarene Derivatives with Stilbene Moieties.

Stilbene is a widely investigated fluorophore with linear geometry and photoswitchability, thus finding applications in many organic materials and liquid crystals. Shinkai et al.⁶³ prepared thermotropic liquid crystals (28) stabilized by intermolecular hydrogen bonds formed between a pyridyl linked calix[4]arene core and four *p*-alkoxy benzoic acids of different chain lengths (C_nH_{2n+1}, n = 10, 12, 14, 16, 18) (Figure 27). Except for the complex with 4-*n*-decyloxybenzoic acid, all the complexes showed Col phases. The increase in the chain length led to an increase in the melting and clearing points (Figure 28). The proposed columnar stacking model for these calixarene based compounds is shown in Figure 27.⁶³

Scheme 14. Preparation of Lower Rim Substituted Schiff Base Ester Derivatives (26a–26d and 27a–27d)

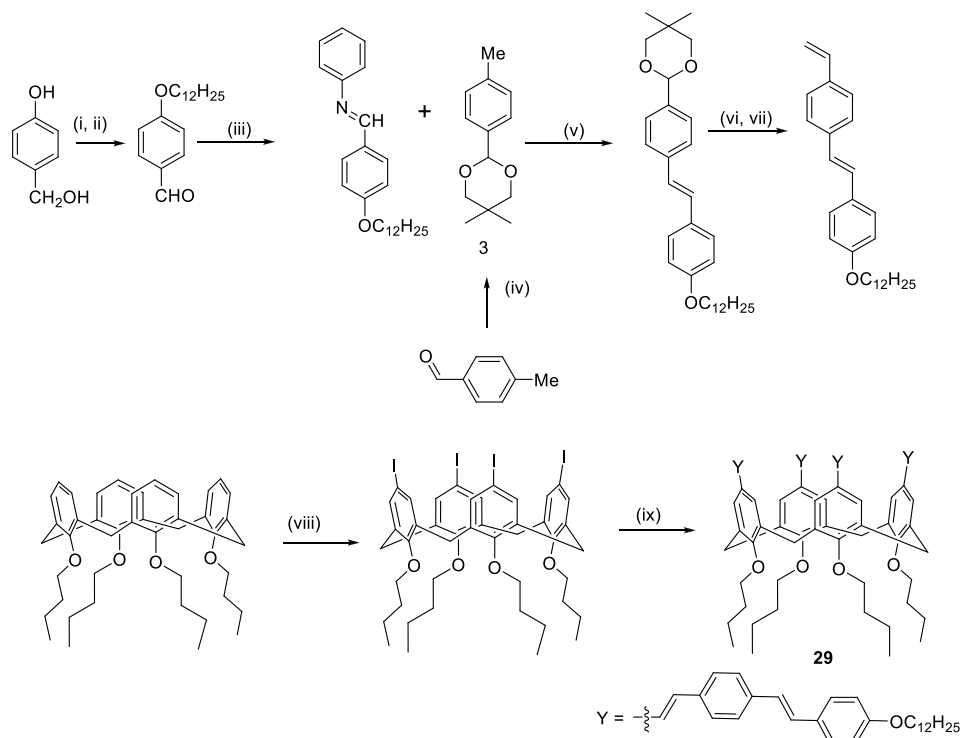


(a) R-Br, anhydrous K₂CO₃, dry acetone; (b) POCl₃, DMF; (c) Sulphur powder, NaOH, diphenyl ether
 (d) Bromo ethylamine, anhydrous K₂CO₃, CH₃CN; (e) EtOH, drops of acetic acid
 (f) Propyl bromide, anhydrous K₂CO₃, KI, CH₃CN

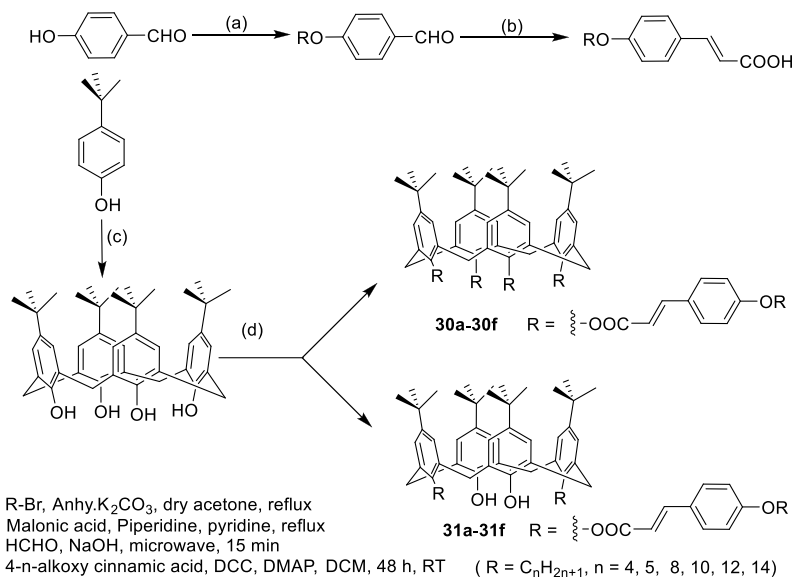
Nierengarten et al.⁶⁴ developed π -conjugated liquid crystalline derivatives where a calix[4]arene core is connected to four oligophenylenevinylene (OPV) moieties (Scheme 15). Photophysical investigations also revealed strong electronic coupling between the four OPV fragments of the calix[4]OPV derivative. From the XRD studies it was shown that the compound exhibits a liquid crystalline phase with a bilayered arrangement spanning from 140 to 180 °C. However, the corresponding oligophenylacetylene derivative was non liquid crystalline. Such compounds are useful in optoelectronic applications and in the field of host–guest chemistry.

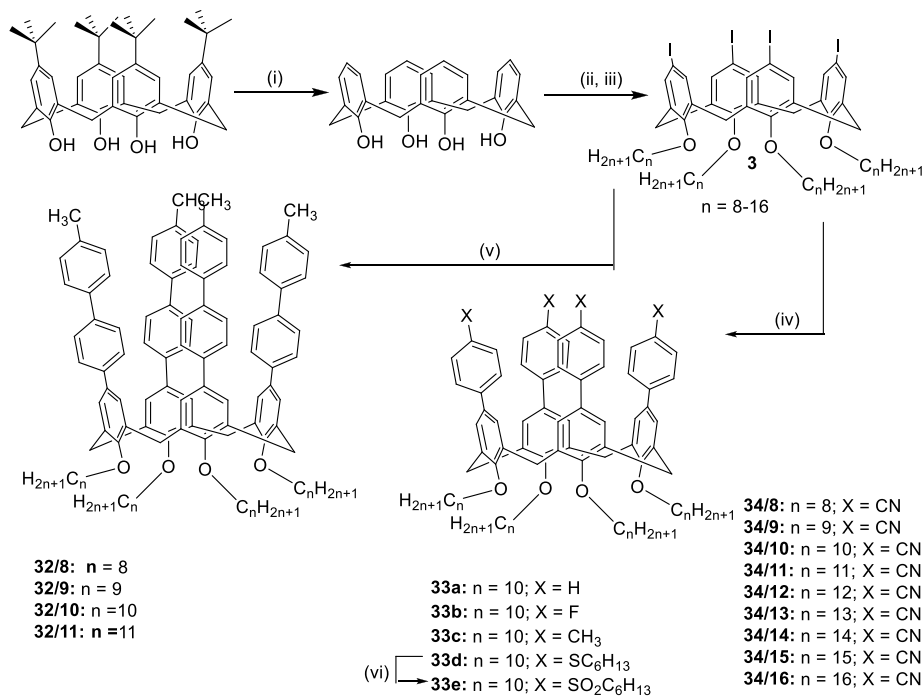
2.5. Calixarene Derivatives with Cinnamic Ester Moieties. Sharma et al.⁶⁵ reported bowl-shaped molecules with a calix[4]arene connected with 4-*n*-alkoxy cinnamic acids at four sides (30a–30f) or two sides (31a–31f) of the calix[4]arenes (Scheme 16). All the compounds turned out to be enantiotropic LCs. The disubstituted derivatives showed higher thermal stability of the mesophase as compared to the tetrasubstituted derivatives. The lower ($n = 4$) and middle member ($n = 5, 8, 10,$ and 12) derivatives from both series showed smectic C and smectic A phases, while the higher member derivatives ($n = 14$) displayed only the nematic phase without displaying any smectic properties (Figure 29).⁶⁵

Scheme 15. Synthetic Route for Oligophenylenevinylene Functionalized Calixarene Derivatives (29)



- (i) 1-Bromododecane, K₂CO₃, DMF, 70 °C, 24 h (80%); (ii) MnO₂, CH₂Cl₂, rt, 3 h (83%)
 (iii) Aniline, C₆H₆, heat, 24 h (80%); (iv) 2,2-dimethylpropane-1,3-diol, *p*-TsOH, C₆H₆, heat, 24 h (96%)
 (v) *t*-BuOK, DMF, 80 °C, 2 h (50%); (vi) CF₃COOH, H₂O, CH₂Cl₂, RT, 5 h (99%)
 (vii) Methyltriphenylphosphonium bromide, *t*-BuOK, THF, RT (80%); (viii) CF₃COOAg, I₂, CHCl₃, Heat, 3 h (91%)
 (ix) Stilbene derivative, Pd(OAc)₂, tri-*o*-tolylphosphine, Et₃N, Xylene, heat, 48 h (68%)

Scheme 16. Synthesis of Bowl-Shaped Calixarene Derivatives Bearing *trans*-Cinnamic Acid Derivatives (30a–30f and 31a–31f)

Scheme 17. Synthesis of Tetraoligophenylene Substituted Luminescent Calix[4]arene Derivatives (32/8–32/11, 33a–33e, and 34/8–34/16)


(i) Phenol, AlCl_3 , toluene, 3–4 hr, RT (70–80%); (ii) (a) NaH , DMF, 0°C , 1 h, (b) $\text{C}_n\text{H}_{2n+1}\text{Br}$, 75°C , overnight; (iii) (a) AgCF_3COO , CHCl_3 , 75°C , 30 min; (b) I_2 , CHCl_3 , 30 min (60–95%);
 (iv) $\text{X-C}_6\text{H}_4\text{-B(OH)}_2$, $\text{Pd(OAc)}_2/2\text{P(o-tol)}_3$, K_2CO_3 , Toluene and methanol, overnight (50–80%)
 (v) $\text{CH}_3\text{-C}_6\text{H}_4\text{-B(OH)}_2$, $\text{Pd(OAc)}_2/2\text{P(o-tol)}_3$, K_2CO_3 , Toluene and methanol, overnight (60–62%)
 (vi) *m*CPBA, CH_2Cl_2 , RT, 1 h

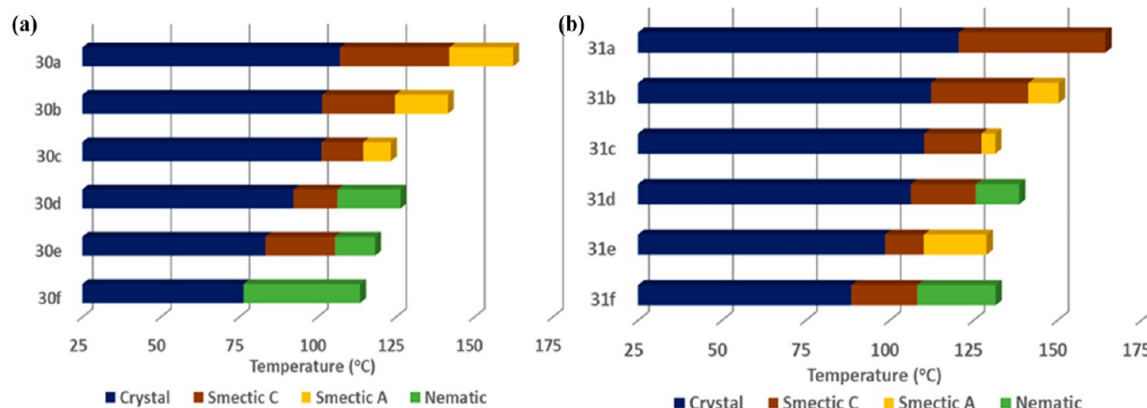


Figure 29. Graphical representation of the thermal behavior of bowl-shaped calixarene derivatives bearing *trans*-cinnamic acid: 30a–30f (a) and 31a–31f (b) (considered the cooling scan).

2.6. Calixarene Derivatives with Oligophenylene Moieties. Calixarene units were directly functionalized with aromatics or through spacers to stabilize macromolecules stabilizing liquid crystallinity. Wong et al. reported two series of tetraoligophenylene substituted luminescent calix[4]arene derivatives (32a–32d and 33a–33f) prepared by Suzuki reaction of arylboronic acid and tetraiodocalixarene and investigated their liquid crystalline properties (Scheme 17).⁶⁶ Thus, in contrast to the conventional rodlike 4-cyano-4'-alkoxybiphenyl mesogens, which exhibit nematic and/or

smectic A phases, cyano-phenyl-calix[4]arene and methyl-biphenyl-calix[4]arene derivatives exhibit highly ordered smectic phases with interdigitated antiparallel packing (Figure 30). The observed POM images of synthesized compounds are shown in Figure 31. These studies proved that the presence of strong dipoles in the calixarene framework is important to stabilize the formation of highly ordered layered structures.

Yonetake et al.⁶⁷ developed new calixarene LCs (35 and 36), which were synthesized by reaction of calixarene, *tert*-butylcalix[8]arene and *C*-methyloctakis(2-hydroxyethyl)calix-

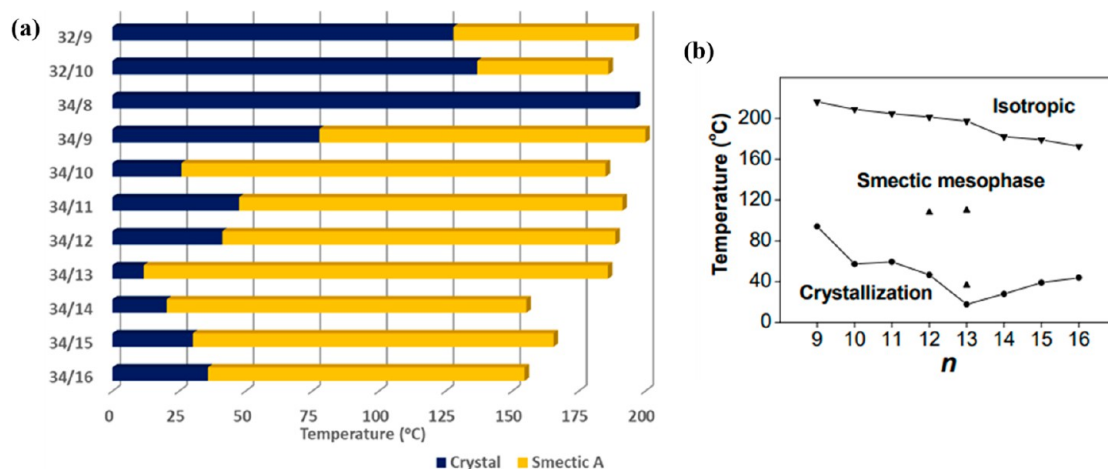


Figure 30. (a) Graphical representation of the thermal behavior of tetraoligophenylene substituted luminescent calix[4]arene derivatives (32/9, 32/10, and 34/8–34/16) (considered the cooling scan). (b) Phase diagram showing the smectic phase in the 34/ n compounds series versus the tail alkoxy carbon number $n = 9–16$ measured from the second heating cycle. Reproduced from ref 66. Copyright 2006 American Chemical Society.

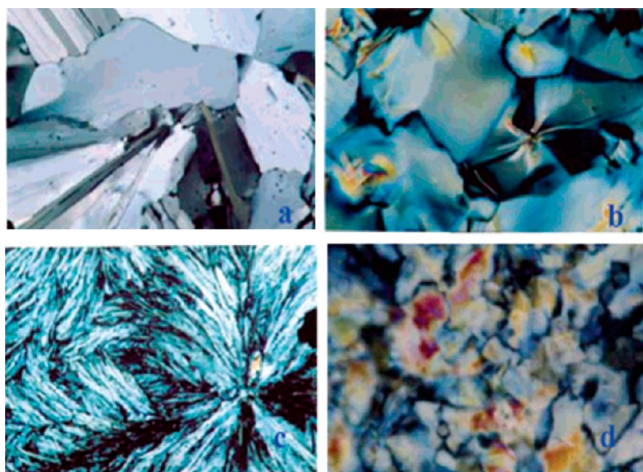


Figure 31. Some representative polarized optical microscope textures (magnification 200X): (a) 34/11 at 168 °C, mosaic and lancet texture with some homeotropic area; (b) 34/14 at 148 °C, mosaic texture; (c) 34/15 at 153 °C, grasslike and fanlike texture; (d) 31/9 at 150 °C, mosaic texture. Reproduced from ref 66. Copyright 2006 American Chemical Society.

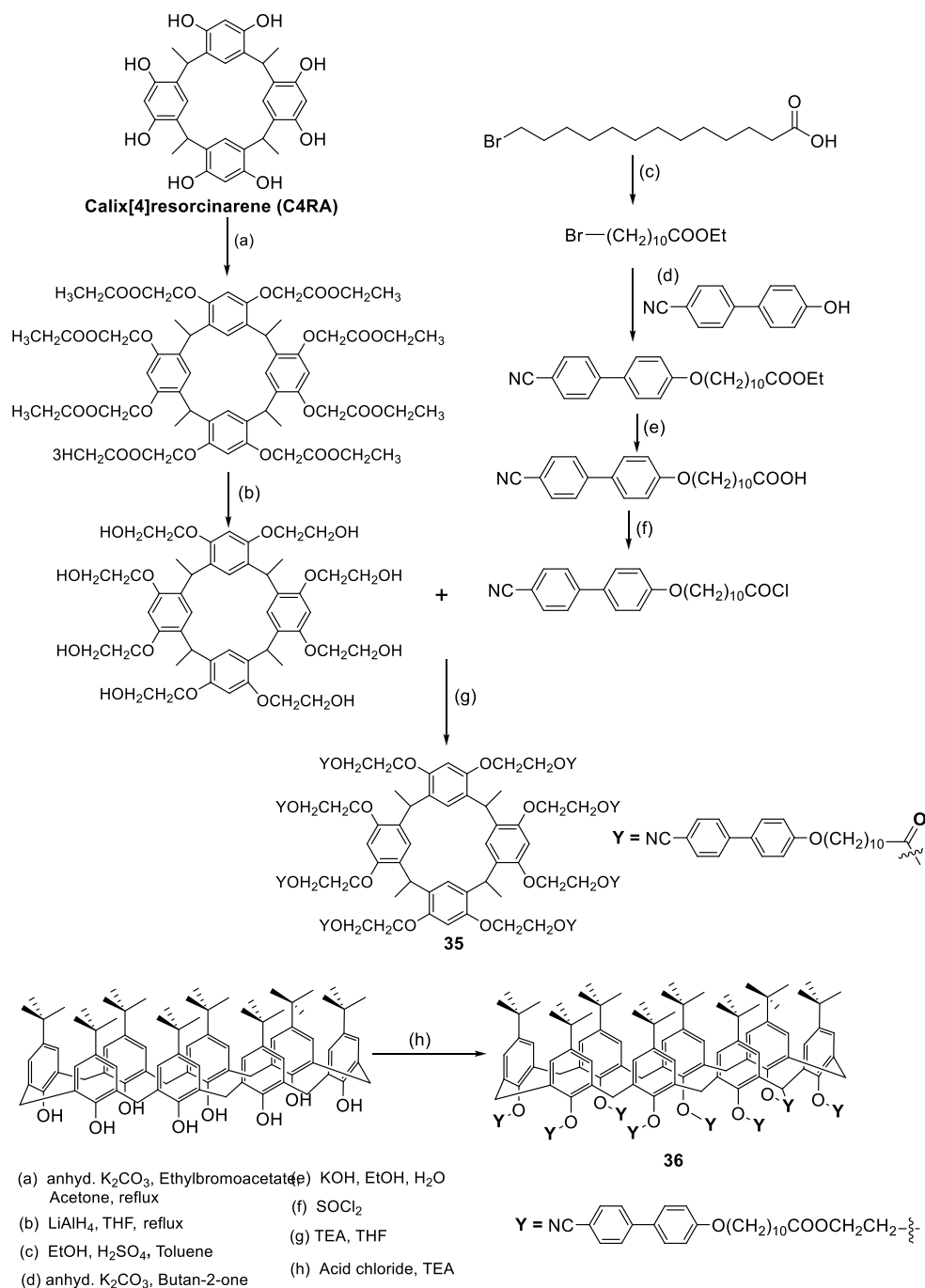
[4]resorcinarene, and 11-[(4'-cyano-1,1'-biphenyl-4-yl)oxy]-decanoyl chloride in the presence of triethylamine as a base (Scheme 18). Both compounds exhibited smectic mesophases. Compound 35 with *tert*-butylcalix[8]arene exhibited a highly ordered SmA phase. Compound 36 was found to adopt a specific molecular structure due to the rigid bowl-like calix[4]-resorcinarene core, *i.e.*, a conelike structure with mesogenic units aligned within the molecule. In addition to SmA phase, this compound also exhibited a nematic phase. The supercooling observed for this compound during the phase transition was very small due to the rigid molecular structure. Such compounds usefully have a memory effect due to their high glass transition temperatures as in the case of side chain polymers.

Yonetake et al. introduced calix[4]resorcinarene based mesogenic compounds and their composites with dendrimers (Figure 32) for magneto processing.⁶⁸ They used photocurable liquid crystals and fixed homogeneous, homeotropic, and bend oriented structures. The LC monomers were irradiated by UV light through a photomask under the influence of a magnetic field. Molecular orientation was used to record the pattern in the film successfully. Using this technique, low viscous branched LCs based on calix[4]resorcinarene 35 and dendrimer (LCD2 decorated with CN-C6) could be aligned under the magnetic field. Through this finding they could align the vapor grown carbon fiber and polycarbonate nanocrystal under the magnetic field.

2.7. Octahomotetraoxacalix[4]arene Based Derivatives. Octahomotetraoxacalix[4]arene derivatives are less studied but provide a wider rim and enhanced flexibility. Kohmoto et al.⁶⁹ prepared octahomotetraoxacalix[4]arene based derivatives (37a–37c and 38a–38c) containing long alkyl chains on the lower rim and studied their mesomorphic properties. Scheme 19 depicts the synthesis of target compounds. Among them, compound 38c with an octadecyloxy group showed a smectic A phase (Figure 33). It was also shown that homocalixarenes (38a–38c) formed LC phases with longer layer distances when 2 equiv of 1,2-ethylenediamine was added as a linker. It was interesting to note that, in these cases, 1,2-ethylenediamine played a catalytic role to form the smectic LC phase. An addition of 1,2-ethylenediamine assisted the conformational fixation of cone conformation via the salt formation during equilibrium (38a/EN, 38b/EN, 38c/EN). The cone conformation thus formed was stable and did not revert to other conformations. These are schematically represented in Figure 34.

2.8. Amphiphilic Calix[4]arene Derivatives. Calixarenes provide the option to functionalize the upper and lower rims with different types of flexible chains (of different miscibilities) to facilitate nanosegregation of incompatible molecular units driving to different kinds of thermotropic and lyotropic self-assemblies. Along similar lines, amphiphilic calix[4]arene compounds with carboxylic acid (39a, 39b) and trimethylammonium moieties (40a, 40b) and variable alkyl chains were prepared by Strobel et al.⁷⁰ They have investigated the self-

Scheme 18. Synthetic Route of Calix[4]resorcinarene and Calix[8]arene Based Derivatives (35, 36)



assembly of these compounds in an aqueous solution. The carboxylated calixarene mesogens formed vesicles in dilute solutions and stable monolayers on water. On the other hand, calixarene derivatives with ammonium head groups had high water solubilities without showing any aggregation. All calixarene amphiphiles formed lyotropic LCs at high concentrations. This proves that the nature of the ionic head group of amphiphilic calixarenes is a key parameter to control and tune the self-assembly in aqueous solution. It was also shown that the symmetry of the assemblies was independent of the concentration of the calixarene amphiphiles, *i.e.*, carboxylated derivatives exhibited vesicles and lamellar LCs, whereas trimethylammonium derivatives formed micelles below 50 Å

diameter that aggregate at higher concentrations into rectangular lyotropic LCs. The synthetic route of calixarene linked derivatives is illustrated in Scheme 20.

Zakharova et al.⁷¹ prepared amphiphilic calix[4]arene derivatives (Figure 35) which are oxyethylated at the lower rim and studied their behavior in water and aqueous-organic solutions (41a, 41b). From POM and XRD studies they established the liquid crystalline organization of these compounds. Analysis of the phase diagram obtained reveals that the parameters of the existence of LC phases are significantly influenced by the structure of substituents at both the upper and lower rims, as well as by the nature of the solvent. It is noteworthy that the LC systems are formed within

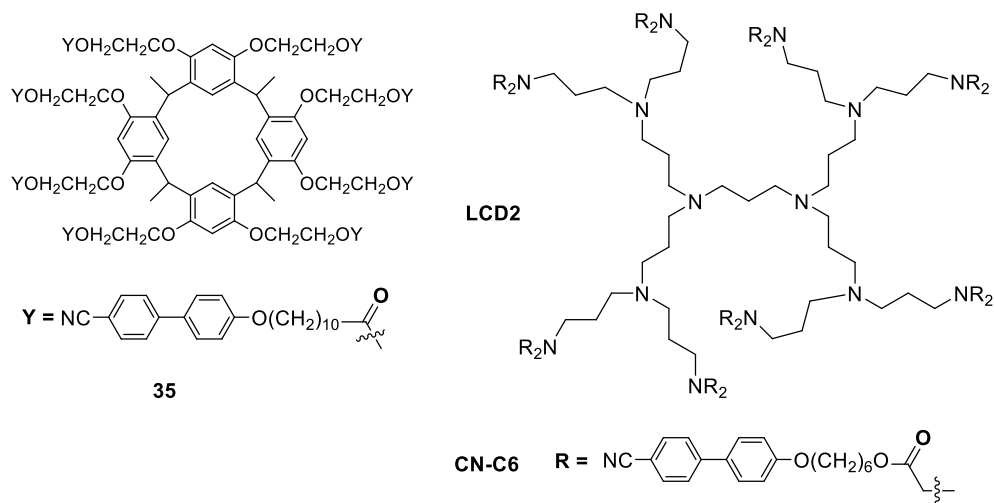
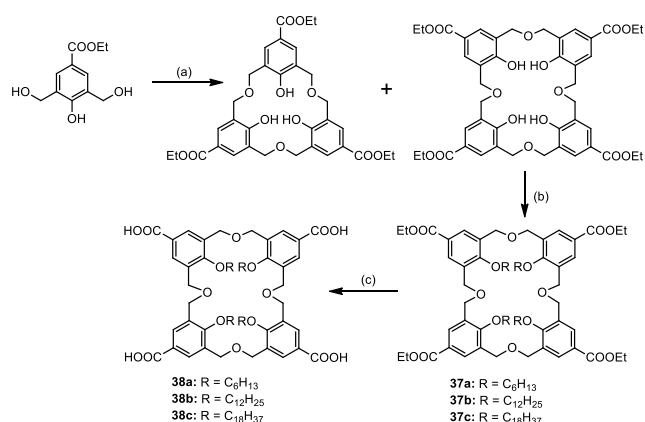


Figure 32. Structural formula of calix[4]resorcinarene derivative (35) and LC dendrimer.

Scheme 19. Synthesis of Octahomotetracalix[4]arene Derivatives (37a–37c and 38a–38c)



(a) Xylene, Reflux; (b) R-Br, Anhyd.K₂CO₃, KI, Reflux; (c) KOH, EtOH/H₂O, 60 °C

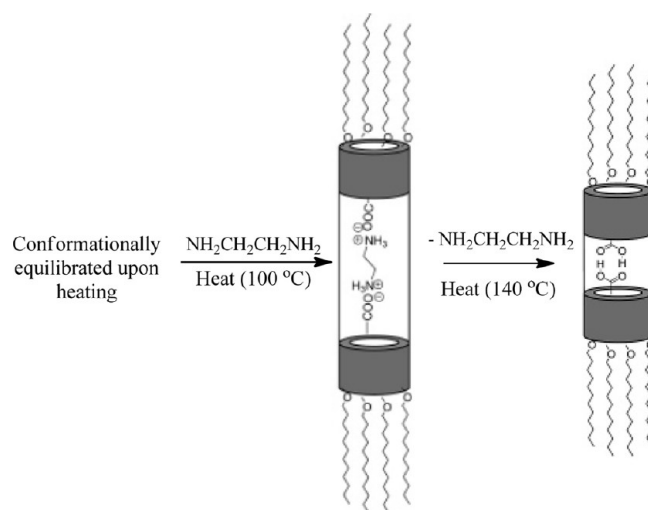


Figure 34. Schematic representation of the proposed conformational change of 38 with 1,2-ethylenediamine.⁶⁹ Reproduced from ref 69. Copyright 2006 American Chemical Society.

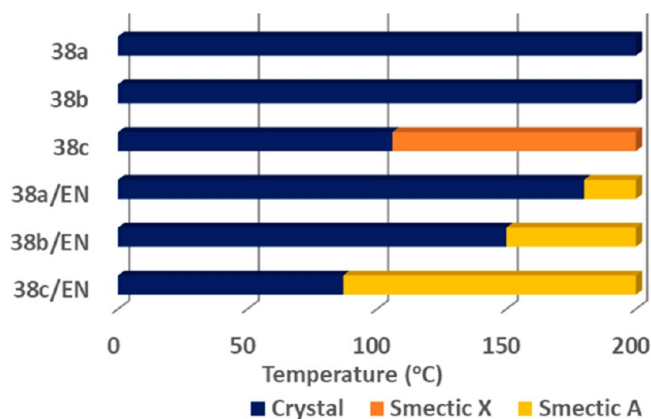


Figure 33. Graphical representation of the thermal behavior of octahomotetracalix[4]arene derivatives (38a–38c and 38a/EN–38c/EN) (considered the cooling scan).

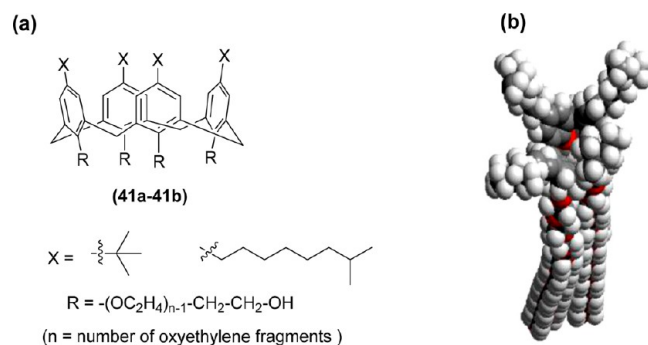


Figure 35. (a) Chemical structure of amphiphilic oxyethylated calix[4]arene. (b) Molecular model of 9CO16; gas phase energy minimized structure optimized by MM method with MM2 force field; Chem3D program.⁷¹ Reproduced with permission from ref 71. Copyright 2010 Elsevier.

Scheme 20. Synthetic Route of Amphiphilic Calixarene Derivatives (39a, 39b; 40a, 40b)

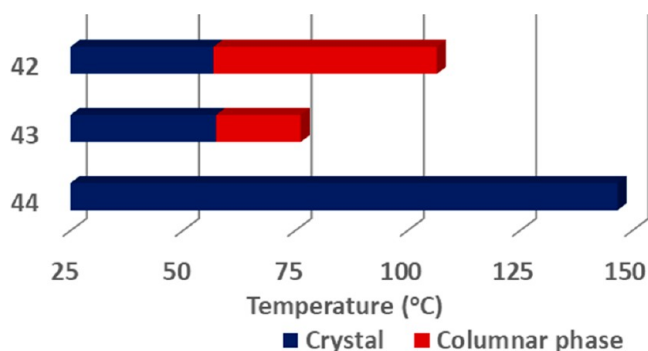
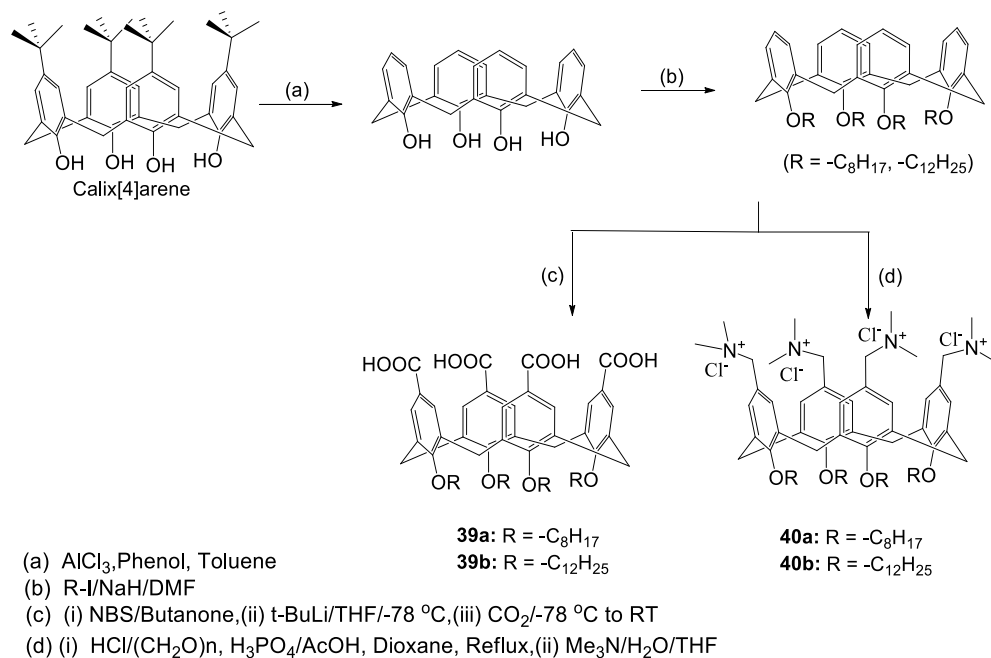


Figure 36. Graphical representation of the thermal behavior of gallic-calixarene derivatives (42–44) (considered the cooling scan).

a wide concentration range of lanthanum ions. This is of high importance from the viewpoint of the template design of novel supramolecular materials with magnetic, luminescent, and catalytic activities.

2.9. Calix[4]arene Derivatives with Amide Moieties.

Amides are formed by the condensation of acids and amines, which provide hydrogen bonding units to assist the self-assembly. In 2015, Fang et al.⁷² synthesized gallic-calixarene based derivatives with amide units (42–44) in yields ranging from 57 to 76% (Scheme 21). Gallic-calix[4]arene derivative and gallic-thiacalix[4]arene derivatives possess stable cone conformations, but gallic-calix[6]arene derivatives did not show any stable conformation. Thus, the first two derivatives exhibited a Col LC phase while the last one did not show any LC behavior.

Lower rim substitution on the three calixarene cores, namely calix[4]arene, calix[6]arene, and thiacalix[4]arene, yielded three supramolecular derivatives. Compounds 42 and 44 showed a stable cone shape with mesomorphic characteristics. On the other hand compound 43 did not show the expected liquid crystalline property due to the lack of a stable structure.

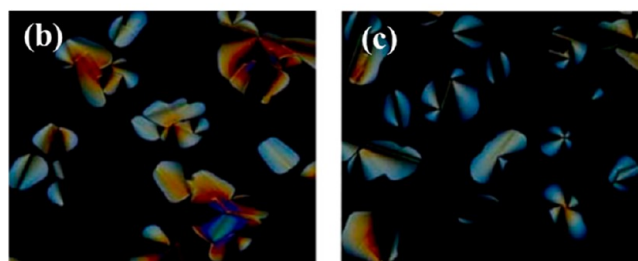
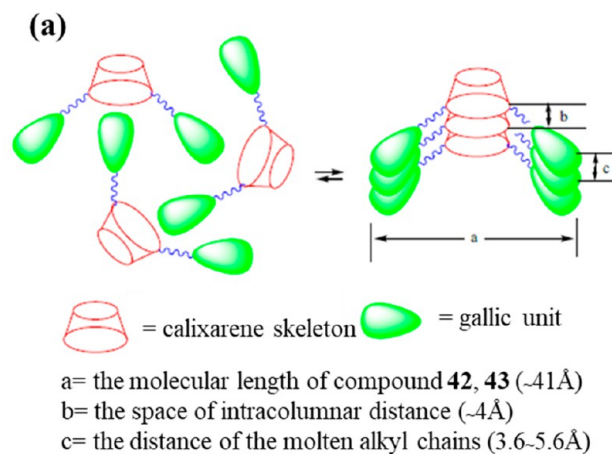
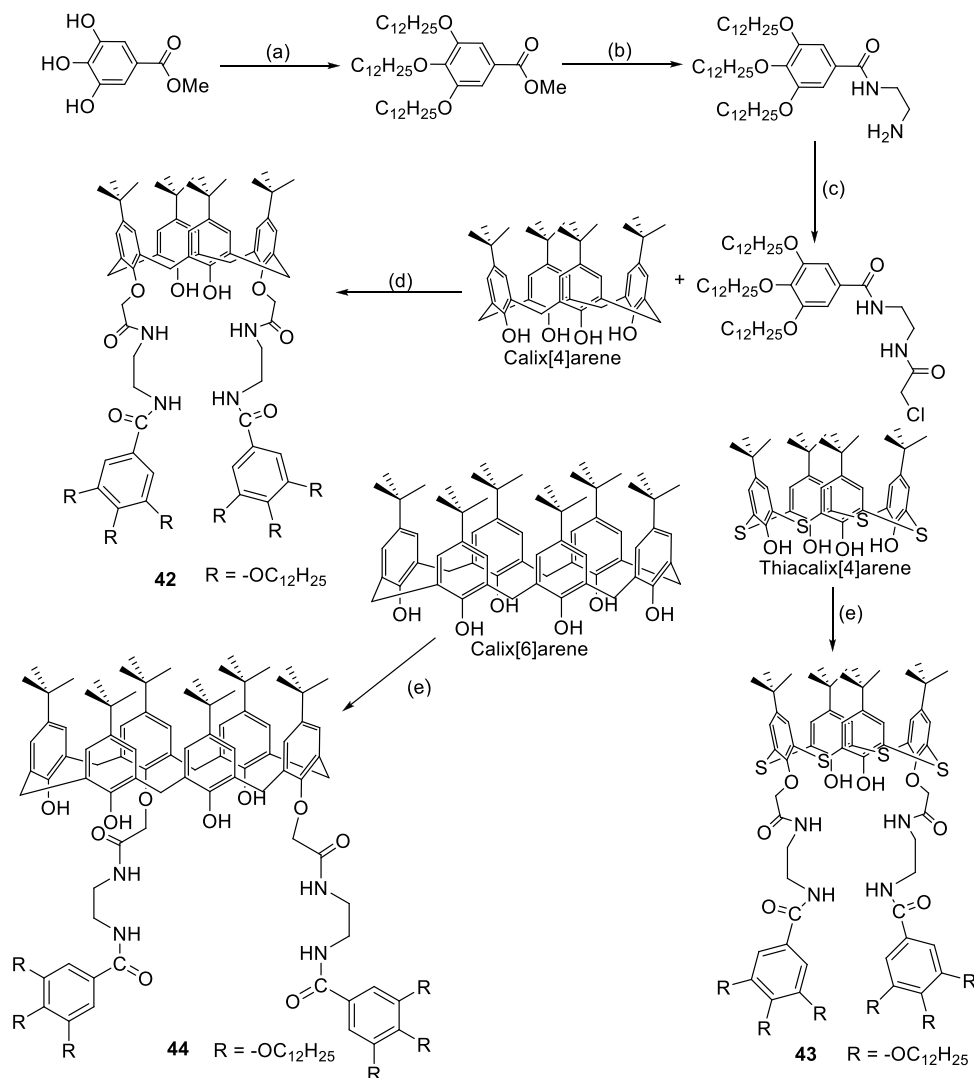


Figure 37. Schematic representations of the columnar self-assembly of compounds 42 and 43 (a). Textures of compounds 42 and 43 under POM on cooling at 70 °C (b, c). Reproduced with permission from ref 72. Copyright 2015 Elsevier.

The supramolecular derivatives (42 and 44) showed a Col_h phase, which was confirmed through POM and differential scanning calorimetry (DSC) studies (Figures 36 and 37).

In another study, six resorcinarene derivatives (45a–45f) were synthesized with excellent yields using microwave-assisted methodology (Scheme 22).⁷³ All the compounds

Scheme 21. Synthesis Route of Supramolecular Amide Linked Calixarene Derivatives (42–44)



(a) C₁₂H₂₅Br, K₂CO₃, MeCN; (b) Ethylenediamine, MeOH; (c) Chloro acetyl chloride, CHCl₃; (d) KI, K₂CO₃, MeCN; (e) KI, K₂CO₃, DMF

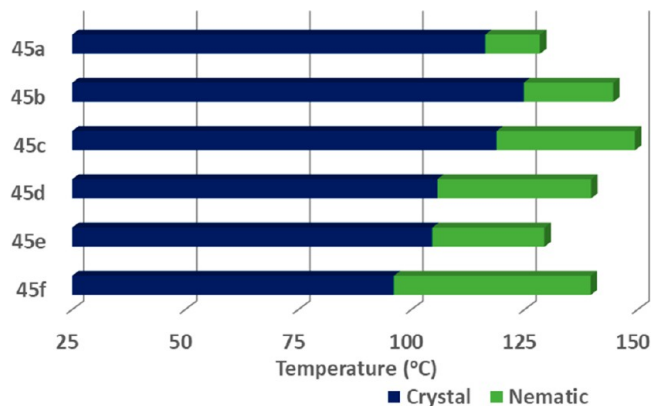


Figure 38. Graphical representation of the thermal behavior of Schiff base functionalized resorcinol[4]arene derivatives (45a–45f) (considered the cooling scan).

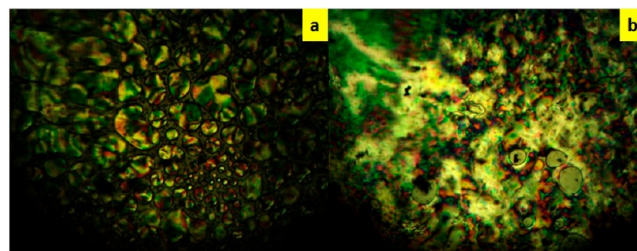
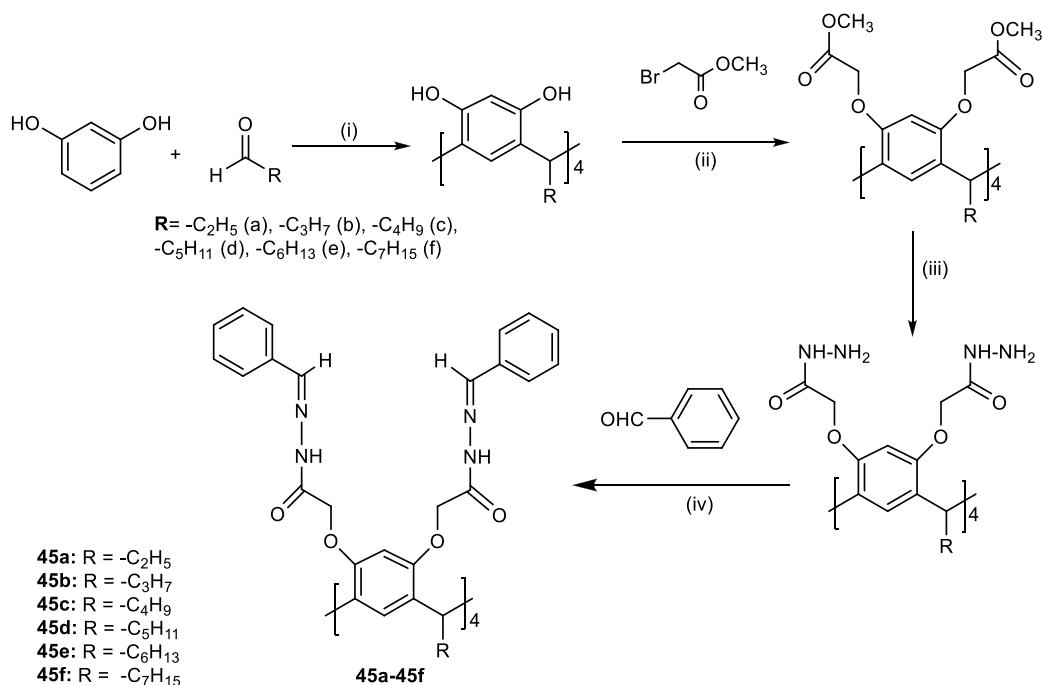


Figure 39. Nematic textures of compound 45e at 50 °C (a) and compound 45c at 70 °C (b). Reproduced with permission from ref 73. Copyright 2021 Taylor & Francis.

displayed enantiotropic nematic mesophases (Figures 38 and 39). Further, these Schiff base containing resorcinarene derivatives showed good antimicrobial potency.

2.10. Calix[4]arene Derivatives Containing Heterocycles. The introduction of heterocycles in liquid crystals is a

Scheme 22. Synthesis of Calix[4]resorcinarene Molded Schiff Base Amide Derivatives (45a–45f)



(i) Con.HCl, Ethanol, Reflux, 72 h or MWI, 300W, 3 h; (ii) K₂CO₃, Acetonitrile, Reflux, 36 h or MWI, 300W, 2 h;
(iii) Hydrazine hydrate, Ethanol, Reflux, 24 h or MWI, 300W, 1 h; (iv) Ethanol, DMF, AcOH (Catalytic), 80 °C, 72 h
or MWI, 300W, 2 h

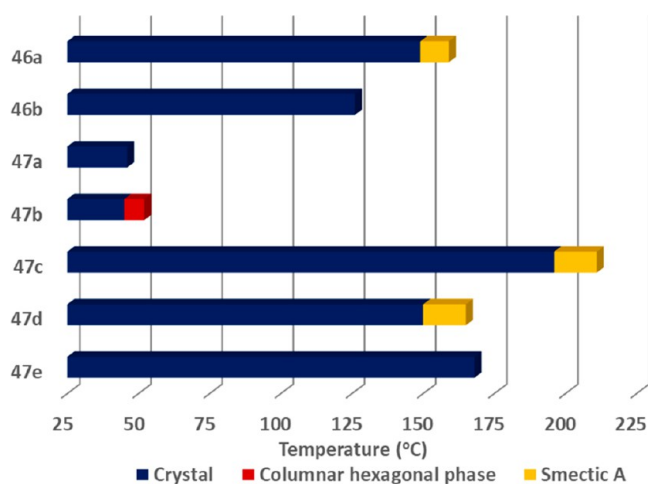


Figure 40. Graphical representation of the thermal behavior of *exo*-calix[4]arene derivatives (46a, 46b, and 47a–47e) (considered the cooling scan).

rewarding exercise often because of the extra properties they bring to the materials. Heterocycles offer lateral and/or longitudinal dipoles, a particular shape to the molecule, which can be changed based on the number and nature of the heteroatom in the ring, and optical and electronic properties they impart to the molecule. Thus, many heterocycles containing N, O, and S are utilized in the design of liquid crystals with new functional behaviors.⁷⁴ Thus many research groups combined heterocyclic moieties with calixarene moieties to stabilize liquid crystalline phases.

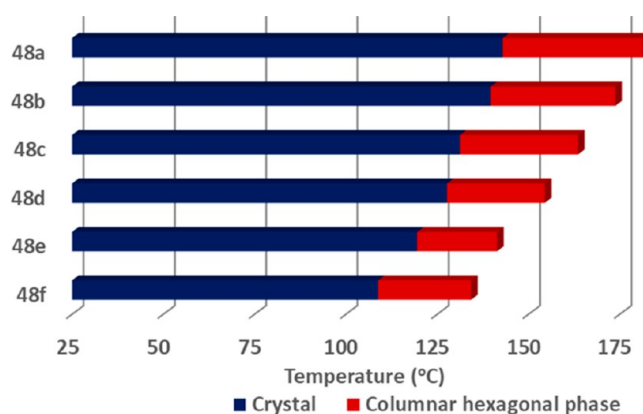


Figure 41. Graphical representation of the thermal behavior of supramolecular calix[4]arene substituted with 1,3,4-thiadiazole derivatives (48a–48f) (considered the cooling scan).

Budig et al.⁷⁵ have prepared pyrogallol substituted *exo*-calix[4]arenes (46a, 46b, and 47a–47e) with 12 3-oxaalkanoxy chains and *exo*-calix[4]arenes in which 8 or 12 rodlike phenylthiadiazole and phenylpyrimidine units were connected through spacers with the central calix[4]arene core (Scheme 23). Compound 46a showed a smectic phase, while compound 46b turned out to be crystalline. This could be due to the increase in the length of chain in the upper rim from methyl to propyl. One of the 3-oxaalkanoates (C₁₂ chain, 47b) forms a Col_h mesophase, whereas compounds 47c and 47d incorporating heterocyclic calamitic units in the lateral chains give liquid crystalline materials with a smectic A phase. Compound 47e again turned out to be crystalline (Figure 40).

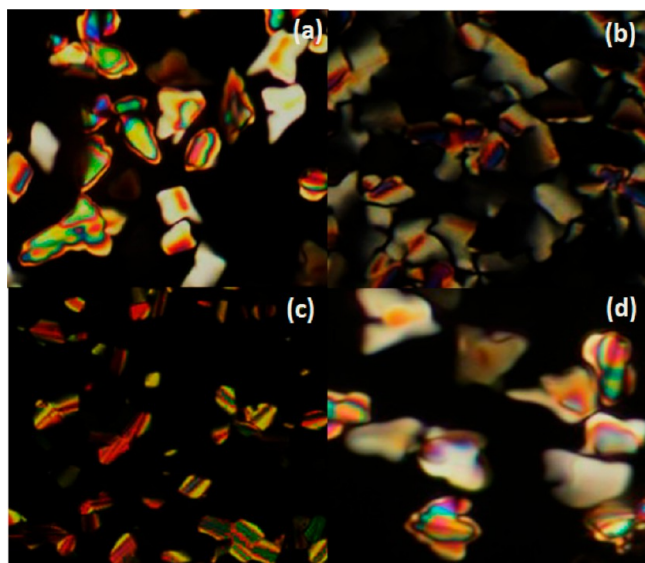
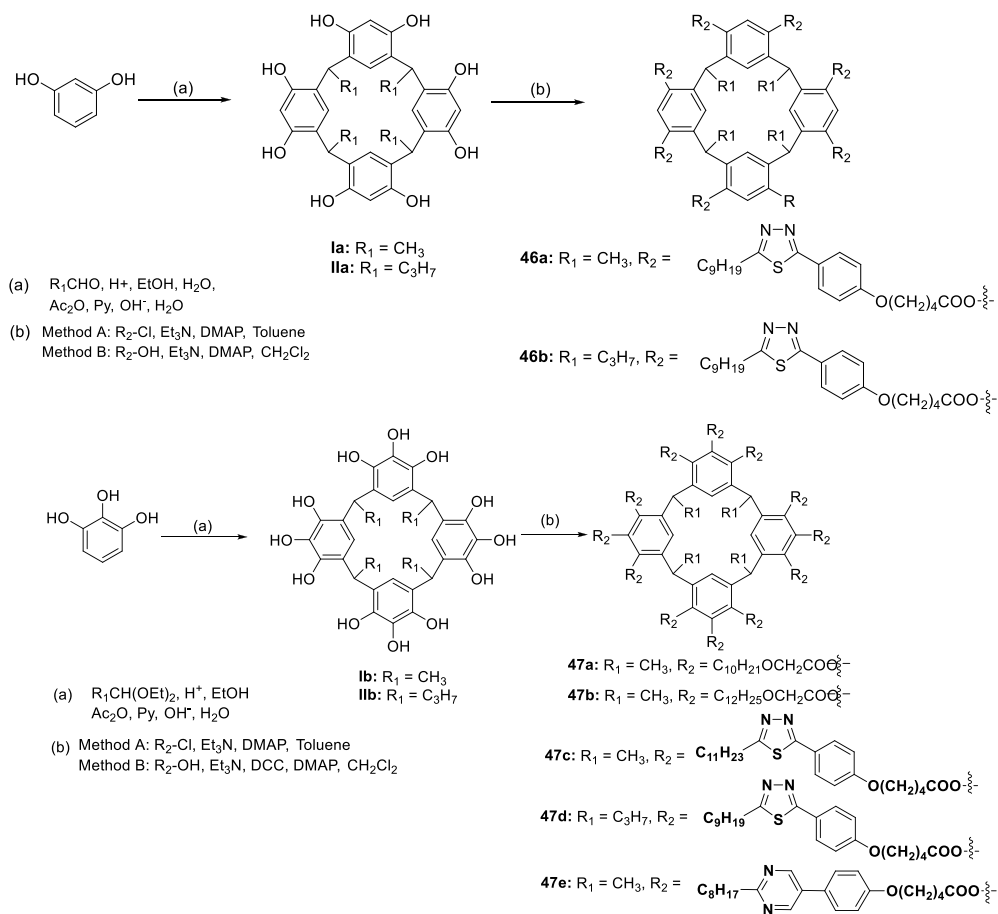
Scheme 23. Structures of *exo*-Calix[4]arene Derivatives

Figure 42. POM texture images of compound **48a** at $142.6\text{ }^\circ\text{C}$ (a), compound **48f** at $112.9\text{ }^\circ\text{C}$ (b), compound **48e** at $121.2\text{ }^\circ\text{C}$ (c), and compound **48c** at $133.8\text{ }^\circ\text{C}$ (d), obtained on heating from the solid crystalline state.⁷⁶ Reproduced with permission from ref 76. Copyright 2019 The Royal Society of Chemistry.

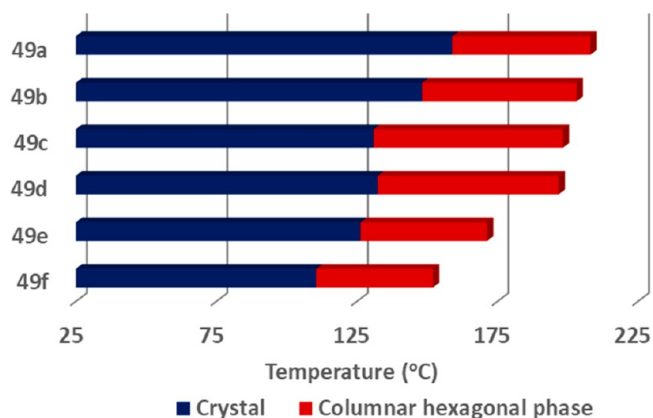
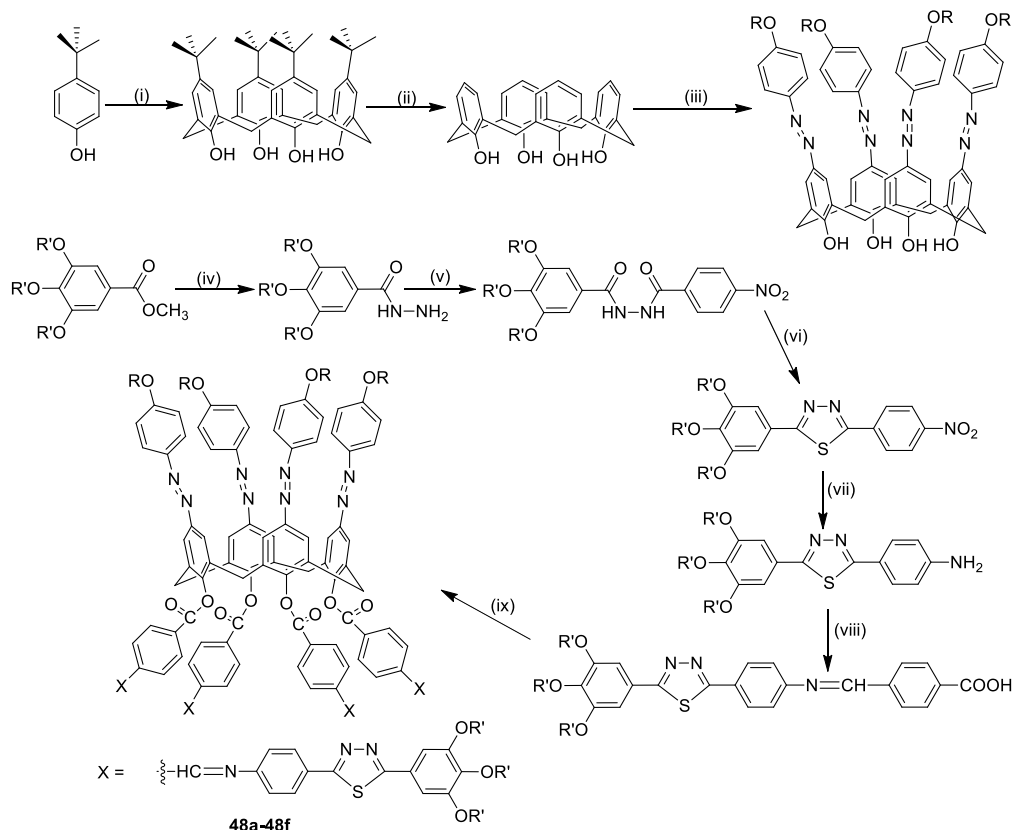


Figure 43. Graphical representation of the thermal behavior of supramolecular calix[4]arene LCs based on oxadiazole derivatives (**49a–49f**) (considered the cooling scan).

Some of the selected compounds form condensed films at the air–water interface as studied with the Langmuir technique, whereby the molecular areas at the collapse points were determined by the densely packed peripheral chains.

Recently, Sharma et al. reported calixarene based LCs with upper rims having the azo group and lower rims connected with Schiff bases through ester linking groups.⁷⁶ In this study,

Scheme 24. Preparation of Thiadiazole Linked Azo Calixarene Based Supramolecular Compounds (48a–48f)



48a: R = $-\text{C}_3\text{H}_7$, R' = $-\text{C}_4\text{H}_9$
48b: R = $-\text{C}_3\text{H}_7$, R' = $-\text{C}_6\text{H}_{13}$
48c: R = $-\text{C}_3\text{H}_7$, R' = $-\text{C}_8\text{H}_{17}$
48d: R = $-\text{C}_8\text{H}_{17}$, R' = $-\text{C}_4\text{H}_9$
48e: R = $-\text{C}_8\text{H}_{17}$, R' = $-\text{C}_6\text{H}_{13}$
48f: R = $-\text{C}_8\text{H}_{17}$, R' = $-\text{C}_8\text{H}_{17}$

(i) HCHO, NaOH, microwave, 10 min; (ii) Anhy. AlCl_3 , phenol, toluene
 (iii) HCl, NaNO_2 , 4-alkoxy amino benzene, 0–5 °C; (iv) $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$, n-butanol, reflux, 24 h
 (v) 4-nitrobenzoyl chloride, pyridine, 60 °C, 10 h; (vi) P_2S_5 , THF, 60 °C, 18 h
 (vii) 10% Pd-C, H_2 (balloon, 1 atm), THF, rt, 10–12 h; (viii) 4-hydroxy benzaldehyde, few drops of glacial CH_3COOH , EtOH, 2 h
 (ix) Acid derivatives, DCC, DMAP, DCM, 24 h, RT

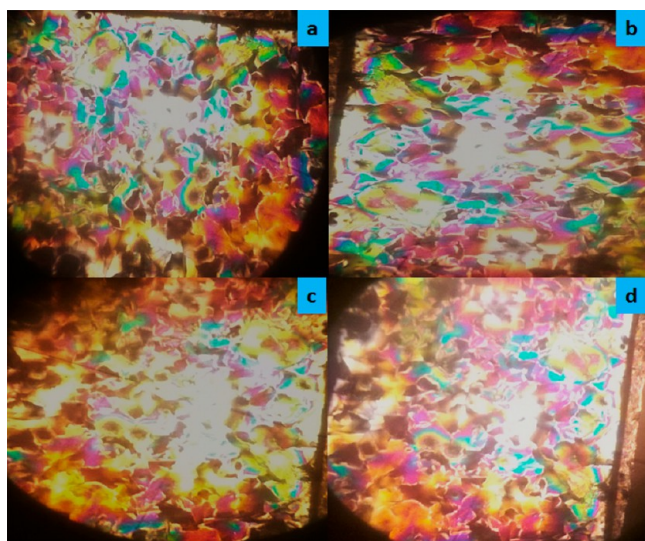


Figure 44. POM texture image of Col_h phase in compound **49c** at 131.3 °C (a), compound **49d** at 136.6 °C (b), compound **49e** at 124.8 °C (c), and compound **49f** at 104.2 °C (d), on heating condition as seen under cross polarizers. Reproduced with permission from ref 77. Copyright 2018 Elsevier.

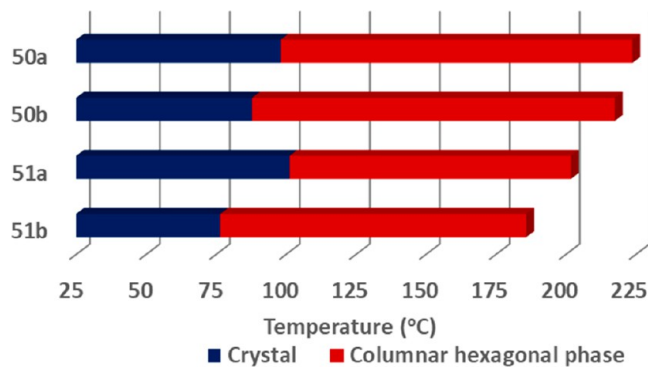
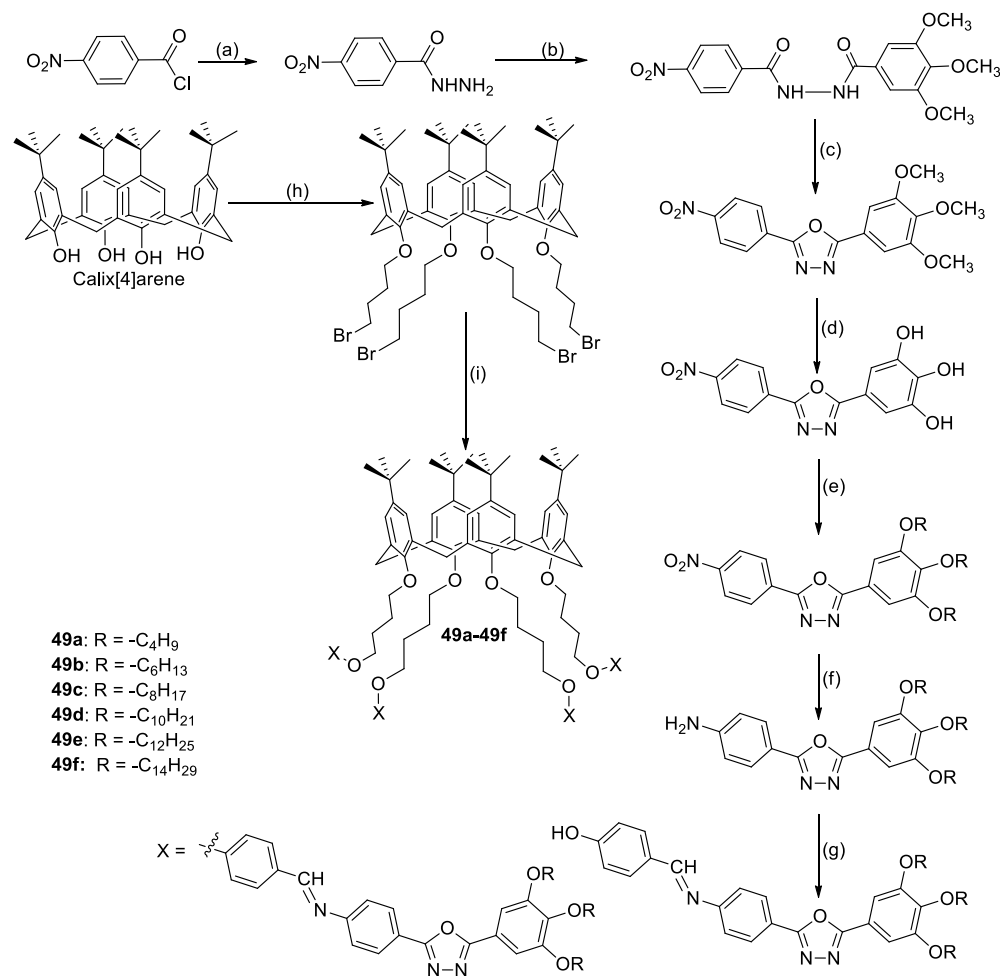


Figure 45. Graphical representation of the thermal behavior of supramolecular calix[4]arene LCs based on oxadiazole and thiadiazole derivatives (**50a**, **50b**; and **51a**, **51b**) (considered the cooling scan).

six derivatives (**48a–48f**) with propyloxy ($-\text{OC}_3\text{H}_7$) and octyloxy ($-\text{OC}_8\text{H}_{17}$) terminal chains and trisubstituted phenyl thiadiazole unit connected through an ester linkage. The synthetic route of target thiadiazole based calixarene derivatives is shown in Scheme 24. All six derivatives showed a Col_h mesophase (Figure 41). Increase in the length of the terminal chain led to a decrease in the melting and clearing

Scheme 25. Synthetic Route of Oxadiazole Linked Schiff Base Calixarene Derivatives (49a–49f)



- (a) NH_2NH_2 , RT, anhydrous acetone; (b) 3,4,5-trimethoxy benzoyl chloride, pyridine, 60 °C, 10 h;
 (c) POCl_3 , 100 °C, 4 h; (d) BBr_3 , DCM, 0 °C to RT; (e) R-Br, Anhyd. K_2CO_3 , Dry acetone, reflux, 12 h;
 (f) 10 % Pd-C, H_2 (balloon, 1 atm), THF; (g) 4-hydroxy benzaldehyde, few drops of AcOH, EtOH, reflux, 2 h;
 (h) 1,4-dibromobutane, Anhy. K_2CO_3 , Dry acetone, Reflux, 2 h;
 (i) Schiff base derivatives, Anhy. K_2CO_3 , Dry acetone, Reflux, 2 h

temperatures of the compounds. The optical textures observed for columnar self-assembly for these azo based supramolecules are shown in Figure 42. Further, these materials showed blue light emission and good electrochemical properties.

Sharma et al. synthesized 1,3,4-oxadiazole linked calixarene molecules to assess the effect on mesomorphism and thermal stability.⁷⁷ Six blue light emitting mesogenic compounds (49a–49f) were varied from each other based on the length of the alkyl chain on the phenyl group.

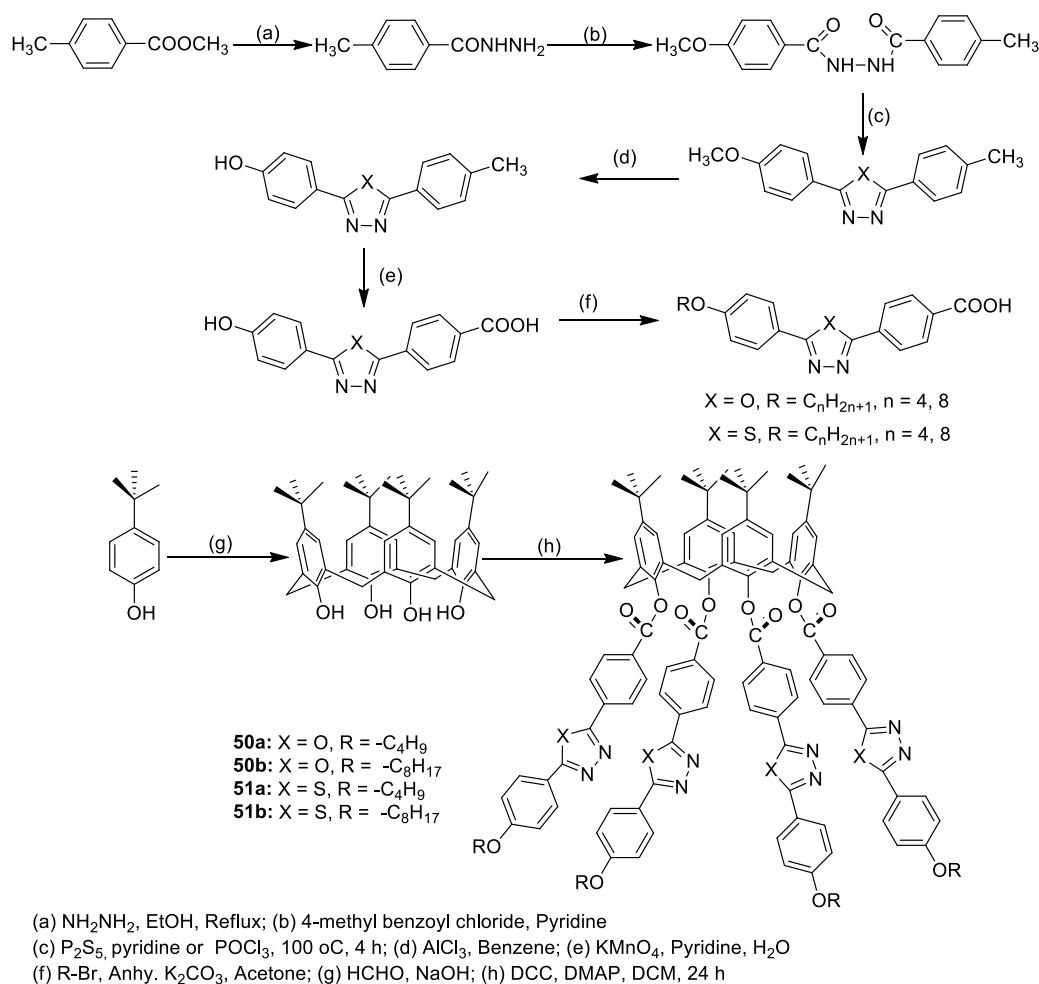
All the compounds exhibited a Col_h phase with a wide thermal range. Increase in the peripheral chain length reduced the melting and clearing temperatures (Figures 43 and 44) These compounds exhibited blue light emission in solution and in the thin film state. The synthetic scheme is given in Scheme 25.

In a continuation of our work on heterocyclic ring based calixarene LCs, we designed four supramolecular cone-shaped calixarene derivatives by linking them to 1,3,4-oxadiazole (50a, 50b) and 1,3,4-thiadiazole (51a, 51b) units.⁷⁸ The yields of the desired materials were in the range 71–76% (Scheme 26).

All the compounds exhibited a Col_h phase (Figure 45). Moreover, these materials showed excellent photophysical behavior with the exhibition of blue light emitting properties. In comparison to oxadiazole linked mesogens, thiadiazole mesogens were found to be efficient with wide range Col_h phases. Furthermore, when compared to thiadiazole compounds in solution and thin films, oxadiazole compounds emit a deep blue fluorescence under long wavelength UV radiation. These compounds were also tested for their capability to aggregate in polar and nonpolar solvents. Compounds 50b and 51b were able to form gels in a nonpolar solvent. The development of organogels was confirmed by analyzing the solution's emission spectra as a function of time and temperature (Figure 46).

Recently, we reported a new class of thiacalixarenes decorated with 1,3,4-thiadiazole derivatives and further compared them with results obtained from calixarene linked mesogens.⁷⁹ Four compounds (52a–52d) were obtained in good yield (69–76%) by reaction of thiacalixarene scaffolds and Schiff base thiadiazole derivatives. The synthetic route for

Scheme 26. Synthetic Route of Oxadiazole and Thiadiazole Linked Calixarene Derivatives (50a, 50b; 51a, 51b)



these materials is represented in Scheme 27. All derivatives showed a stable Col_h phase with a wide thermal range (Figure 47). Further, these compounds also exhibited blue fluorescence under long UV radiation. One of the compounds was used in the fabrication of a blue OLED; by doping in a CBP host it exhibited an external quantum efficiency of 0.8%. These compounds also showed the ability to form organogels in nonpolar solvents like decane and dodecane (Figure 48). The xerogel of compound 52d exhibited a columnar self-assembly, as was evident from the XRD studies.

Very recently, our group prepared four calixarene based upper/lower rim functionalized supramolecular derivatives (53a–53d) by Sonogashira coupling reaction of dibromo calixarene scaffold with 4-*n*-pentyloxy phenyl acetylene (Scheme 28).⁸⁰ The synthesis involved nine reaction steps to obtain the desired target supramolecules in good yields of 64–71%. All the calixarene based compounds showed an enantiotropic Col_h phase with a wide thermal range and with higher thermal stability (Figure 49).

2.11. Calix[4]arene Derivatives Containing Cholesterol Moieties. Cholesterol has been used extensively in the construction of supramolecular materials, liquid crystals,⁸¹ and anchors/tethers for model biological membranes⁸² due to the commercial availability, ease of functionalization, and rigid structure with high chiral purity which is conducive for the various types of self-assembly. In fact, the first reported liquid

crystal was cholesterol benzoate.⁸³ Thus, there are many reports on the oligomers formed by linking cholesterol units to calix[4]arene.

In 2015, Yang and co-workers reported the first calix[4]-arene–cholesterol oligomeric LCs (54a, 54b, 55a, 55b).⁸⁴ These di- and tetrasubstituted cholesterol linked supramolecules were prepared in good yields by treating calix[4]-arene and cholesterol esters in acetonitrile solvent (Scheme 29). All two side and four side linked cholesterol materials exhibited Col phases. The authors observed that having long spacers and more cholesterol units is more conducive to enhancing the mesophase width (Figure 50). All four derivatives showed the typical focal-conic texture of a Col LC phase (Figure 51).

Additionally, Yang et al. also prepared two oligomers bearing cholesterol and calix[4]arene skeletons (56a, 56b) having an imine bridge.⁸⁵ The complete synthesis of cholesterol–calixarene oligomers is shown in Scheme 30. They investigated the mesogenic properties of the calixarene bowl-shaped column with imine linked cholesterol unit as an ancillary lateral column. These compounds exhibited Col phases. The increase in the spacer length showed a decrease in the melting and clearing points (Figure 52). Further, they also made $AgClO_4$ complexes of these oligomers (56a, 56b); however, they were not mesogenic implying that the ion complexation process may be used to alter the mesogenic behavior of these

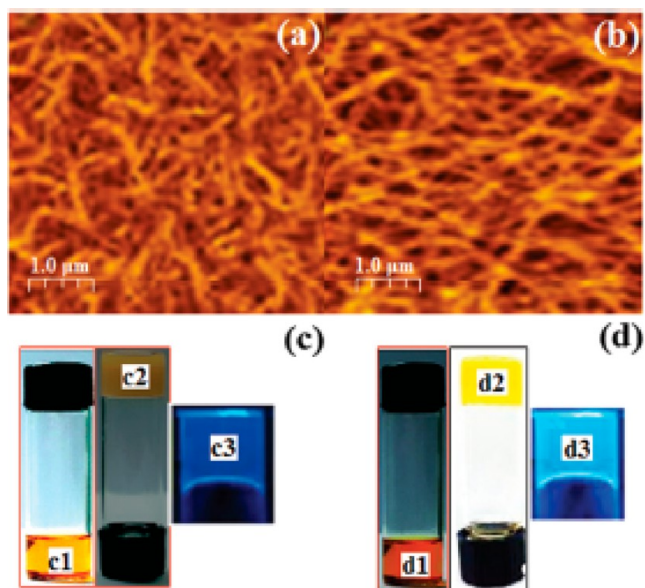


Figure 46. AFM images of the aggregates of compound **50b** (a) and compound **51b** (b) in pure dodecane (scale bar 1 μm). Images showing solutions of compound **50b** (c1) and compound **10d** (d1) in daylight. Images showing the formation of gels in daylight and UV light of compound **50b** (c2 and c3) and compound **51b** (d2 and d3). Reproduced with permission from ref 78. Copyright 2019 The Royal Society of Chemistry.

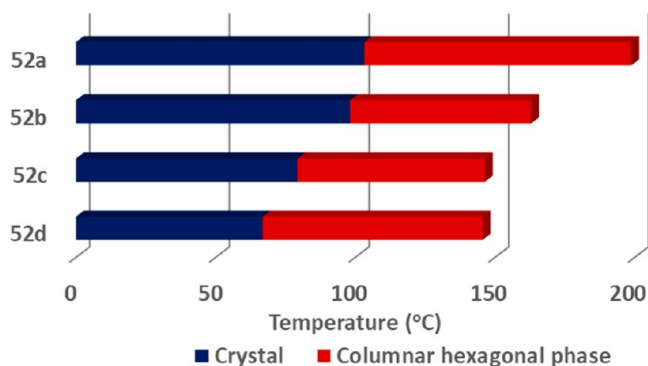


Figure 47. Graphical representation of the thermal behavior of thiadiazole linked calixarene derivatives (**52a**–**52d**) (considered the cooling scan).

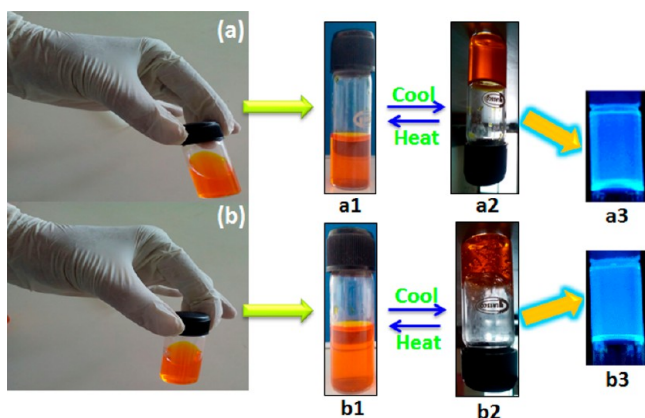


Figure 48. (a, b) Images showing solutions of compound **52c** (a1) and compound **52d** (b1) in daylight. Gels in daylight and UV light of compound **52c** (a1–a3) and compound **52d** (b1–b3). Reproduced from ref 79. Copyright 2019 American Chemical Society.

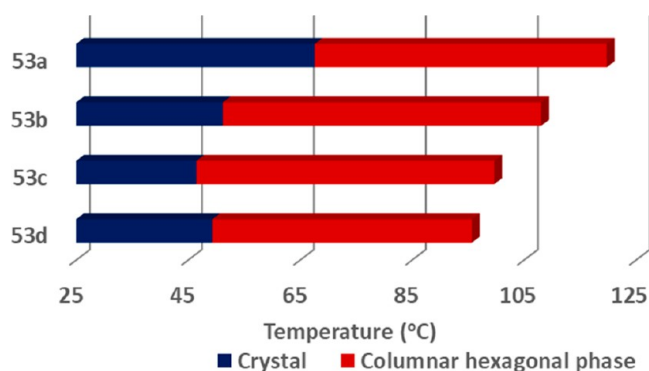


Figure 49. Graphical representation of the thermal behavior of thiadiazole linked calixarene derivatives (**53a**–**53d**) (considered the cooling scan).

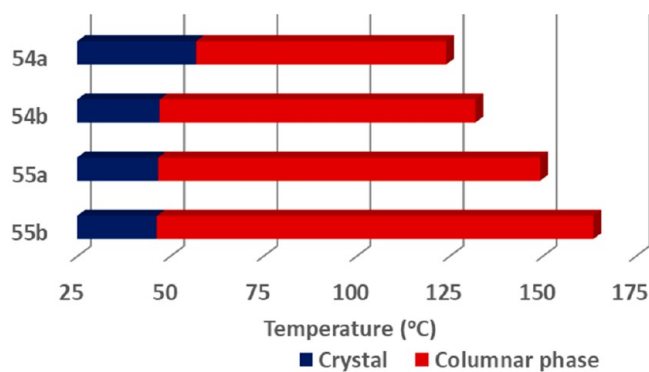


Figure 50. Graphical representation of the thermal behavior of calix[4]arene–cholesterol oligomeric LCs (**54a**, **54b**; and **55a**, **55b**) (considered the cooling scan).

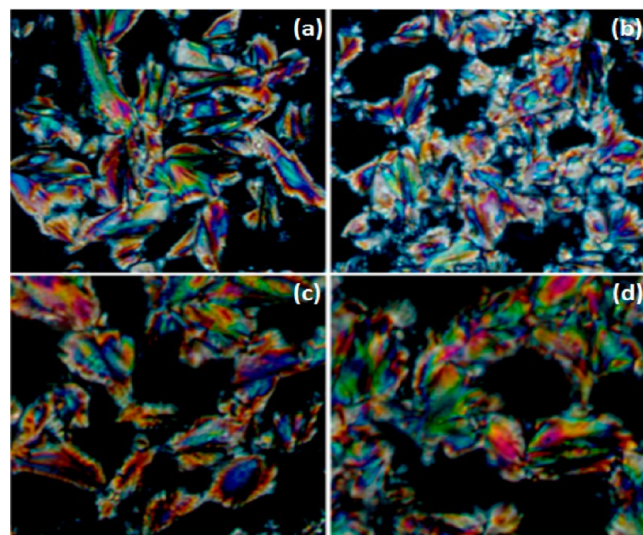


Figure 51. POM images obtained for the Col phase of compounds **54a** (a), **54b** (b), **55a** (c), and **55b** (d) obtained at 80 °C on cooling the isotropic melt. Reproduced with permission from ref 84. Copyright 2015 Elsevier.

Scheme 27. Synthetic Route of Thiadiazole Linked Thiocalixarene Derivatives (52a–52d)

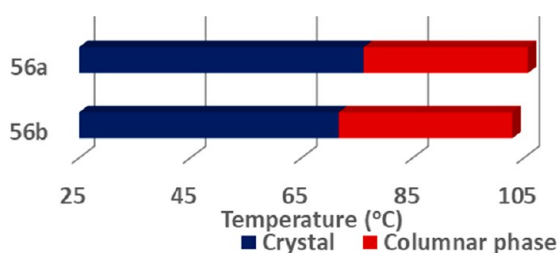
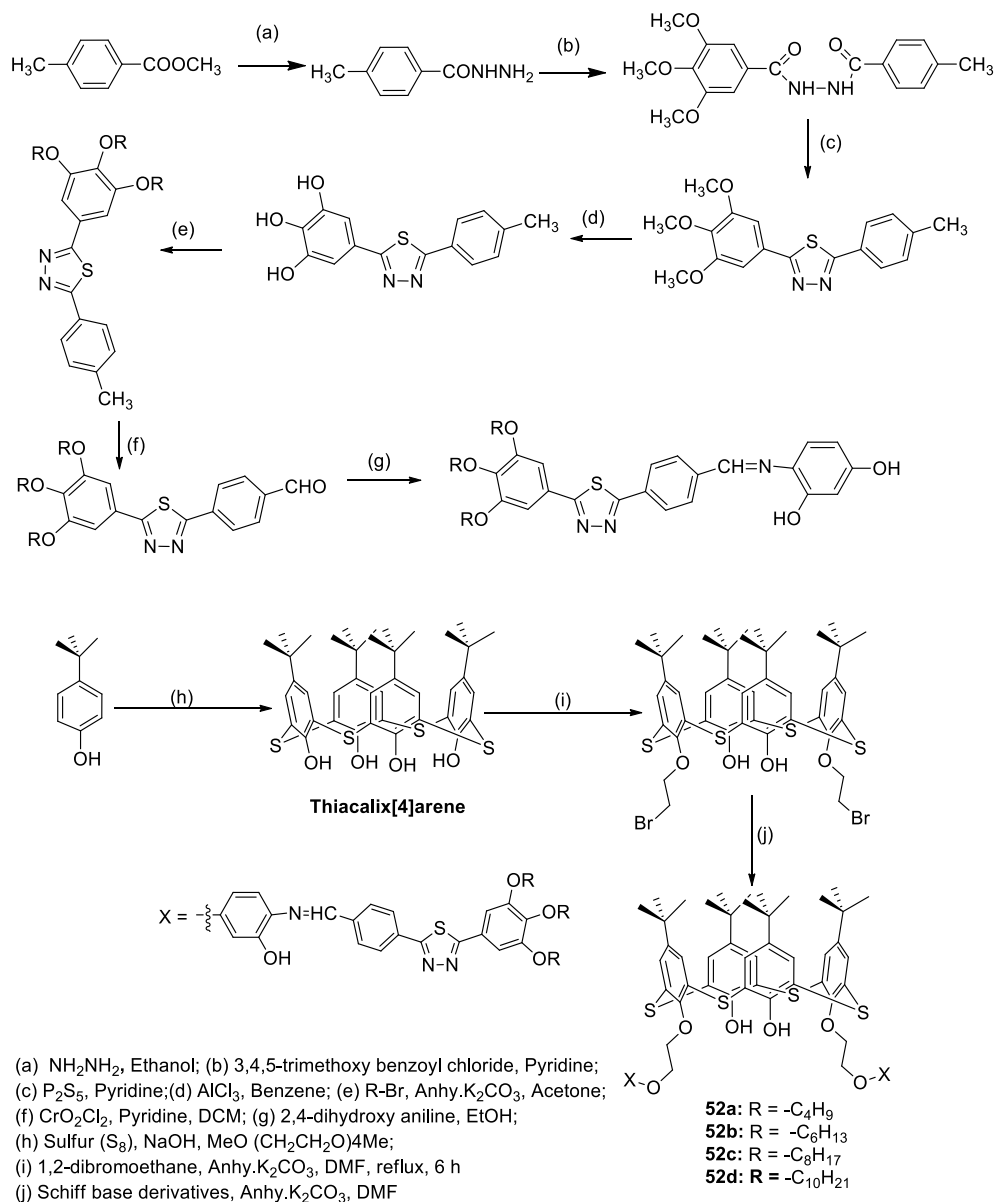


Figure 52. Graphical representation of the thermal behavior of calix[4]arene–cholesterol derivatives with Schiff base bridges (56a, 56b) (considered the cooling scan).

supramolecular LCs. Figure 53 depicts a schematic illustration of columnar self-assemblies and their behavior on ion complexation.

In another study, Guo et al.⁸⁶ linked four cholesterol units on calix[4]resorcinarene and investigated the liquid crystalline

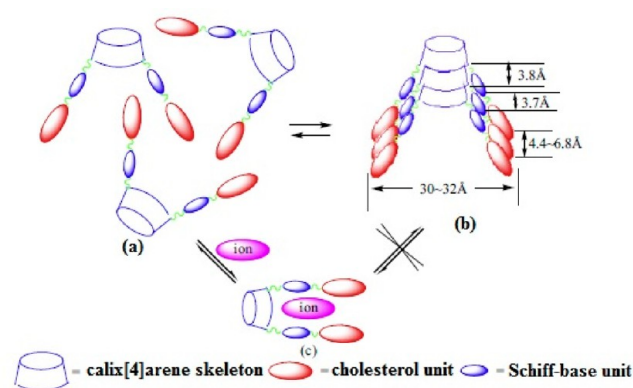
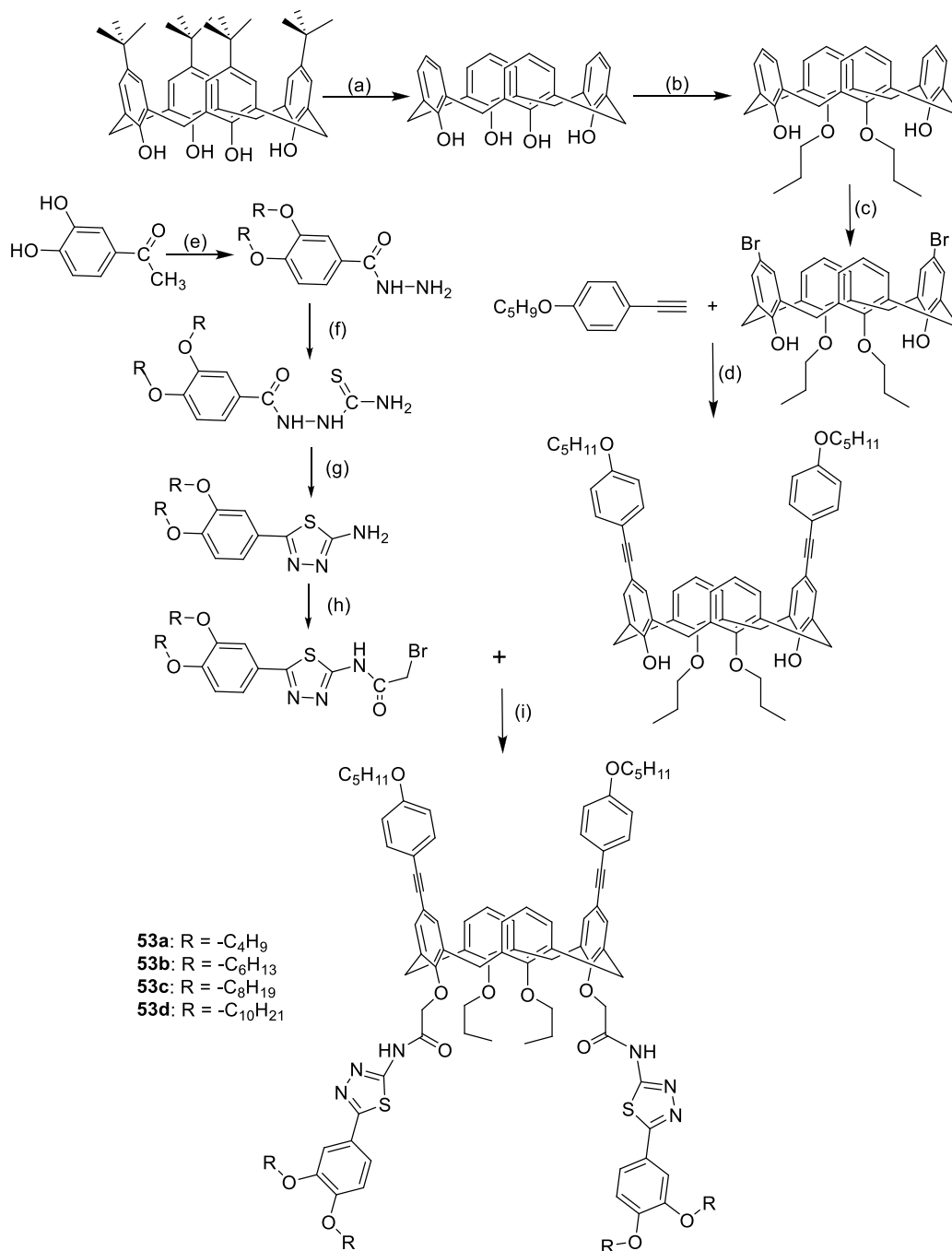


Figure 53. Schematic representation of (a) columnar layered molecular arrangements, (b) their dimensions, and (c) the complexation models. Reproduced with permission from ref 85. Copyright 2016 Elsevier.

Scheme 28. Synthetic Route of Thiadiazole Linked Calixarene Derivatives (53a–53d)



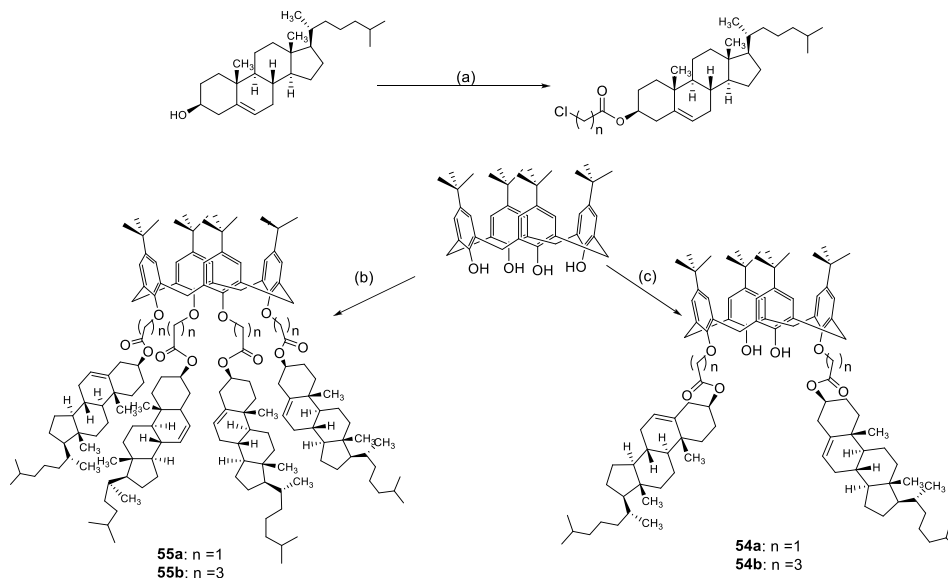
(a) Anhy. AlCl₃, Phenol, Toluene; (b) n-propylbromide, Anhyd K₂CO₃, CH₃CN, 18 h, reflux, N₂; (c) Br₂, DCM, addition at RT for 2 h; (d) Pd (PPh₃)₂Cl₂ (15 mol%), CuI (10 mol%), TEA, 80 °C, 18 h; (e) R-Br, DMF, anhyd. K₂CO₃, NH₂NH₂, EtOH; (f) NH₄SCN, HCl; (g) CH₃COCl, HCl; (h) BrCH₂COOH, EDC.HCl, DMAP, DCM, RT, 24 h; (i) Anhy. K₂CO₃, CH₃CN, Reflux, 8 h

properties. The synthetic route for the preparation of these compounds (57a, 57b) is given in Scheme 31. These compounds exhibited a Col_h phase. The mesogenic properties were dependent on the structures of the spacers. Incorporation of rigid Schiff base spacers led to the increase of phase transition temperatures and mesophase thermal ranges, while soft alkyl spacers reversed the trend by having broad transition and increased viscosity (Figure 54). The typical focal-conic

and band-type textures obtained for the Col_h phase of resorcinarene based compounds 57a, 57b, 58a, and 58b are presented in Figure 55.

2.12. Calix[4]arene Derivatives Containing Triphenylene Moieties. Hexaalkoxy triphenylene is considered as a workhorse in the field of discotic liquid crystals. The structure can be easily modified to attain different mesomorphic behaviors. There are several oligomeric and polymeric liquid

Scheme 29. Synthetic Routes of Cholesterol Linked Calix[4]arene Derivatives (54a, 54b; 55a, 55b)



(a) $\text{Cl}(\text{CH}_2)_n\text{COOH}$ ($n = 1, 3$), DCC, DMAP, DCM; (b) Cholesterol chloroalkanoates, Anhy. K_2CO_3 , KI, MeCN; (c) Cholesterol chloroalkanoates, Anhy. K_2CO_3 , KI, MeCN

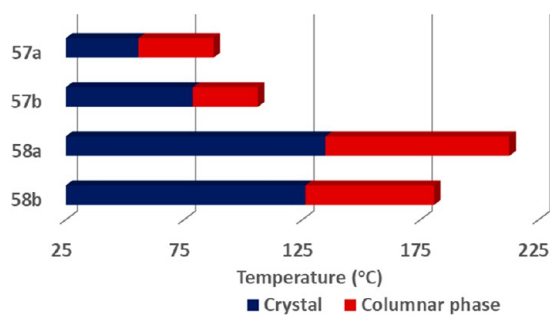


Figure 54. Graphical representation of the thermal behavior of calix[4]resorcinarene-cholesterol LCs (57a, 57b; 58a, 58b) (considered the cooling scan).

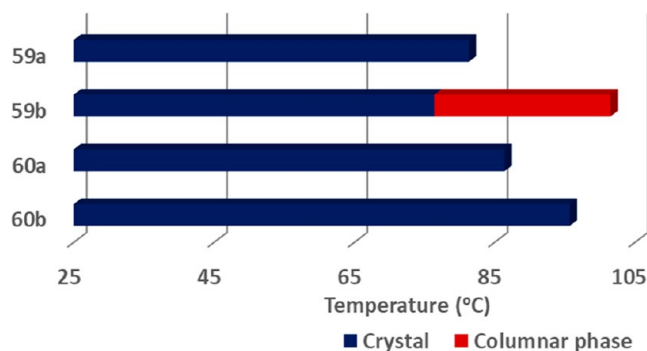


Figure 56. Graphical representation of the thermal behavior of calixarene linked discotic triphenylene derivatives (59a, 59b; 60a, 60b) (considered the heating scan).

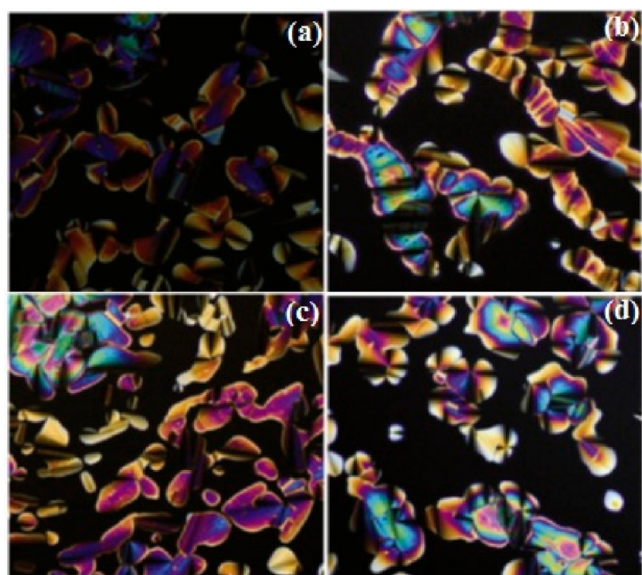


Figure 55. Mesomorphic texture of Col_h phase obtained under POM on cooling for compounds 57a, 57b, 58a, and 58b at 75, 90, 170, and 160 °C (500 \times) (a–d). Reproduced with permission from ref 86. Copyright 2017 Elsevier.

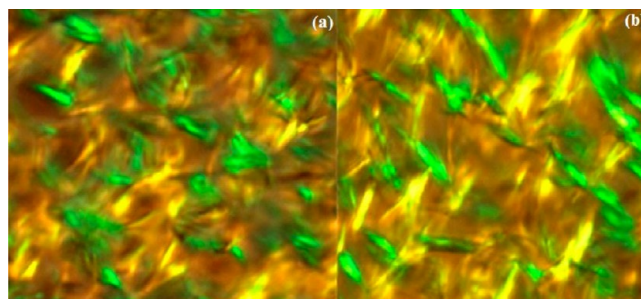
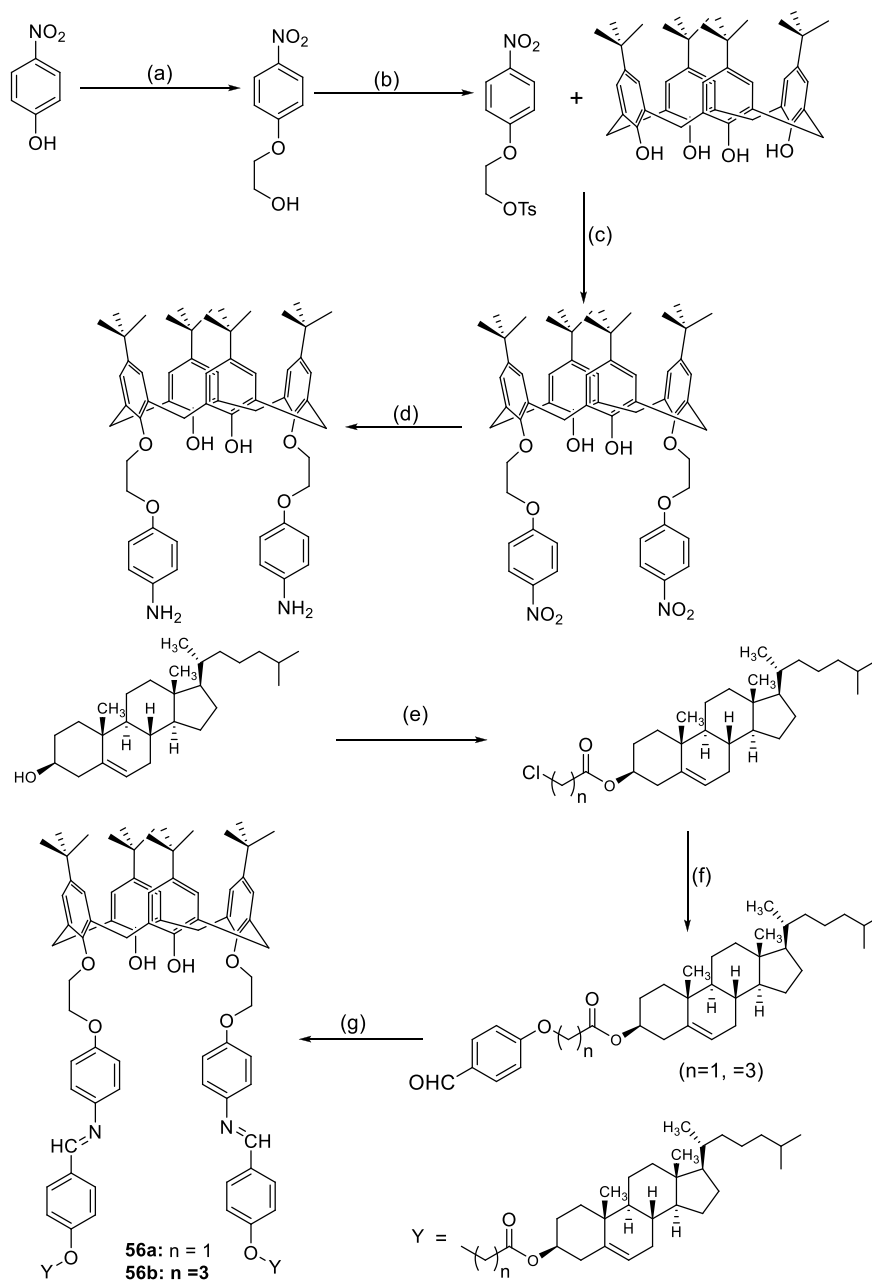


Figure 57. Textures of columnar phase of triads 61 and 62 under POM on cooling at 45 °C (400 \times) (a, b). Reproduced with permission from ref 91. Copyright 2012 Elsevier.

Scheme 30. Preparation of Cholesterol Linked Calix[4]arene Derivatives (56a, 56b)



(a) 2-chloroethan-1-ol, KOH, H₂O; (b) TsCl; (c) Anhy. K₂CO₃, MeCN; (d) N₂H₄·H₂O, Pd-C, EtOH
 (e) Cl(CH₂)_nCOOH (n = 1, 3), DCC, DMAP, DCM; (f) 4-hydroxy benzaldehyde, Anhy. K₂CO₃, MeCN
 (g) Calixarene amine derivative, MeOH/CHCl₃

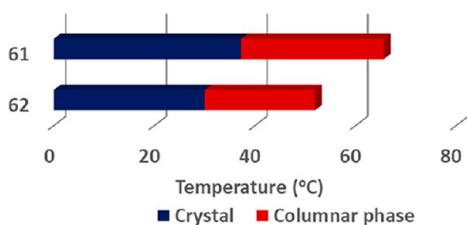
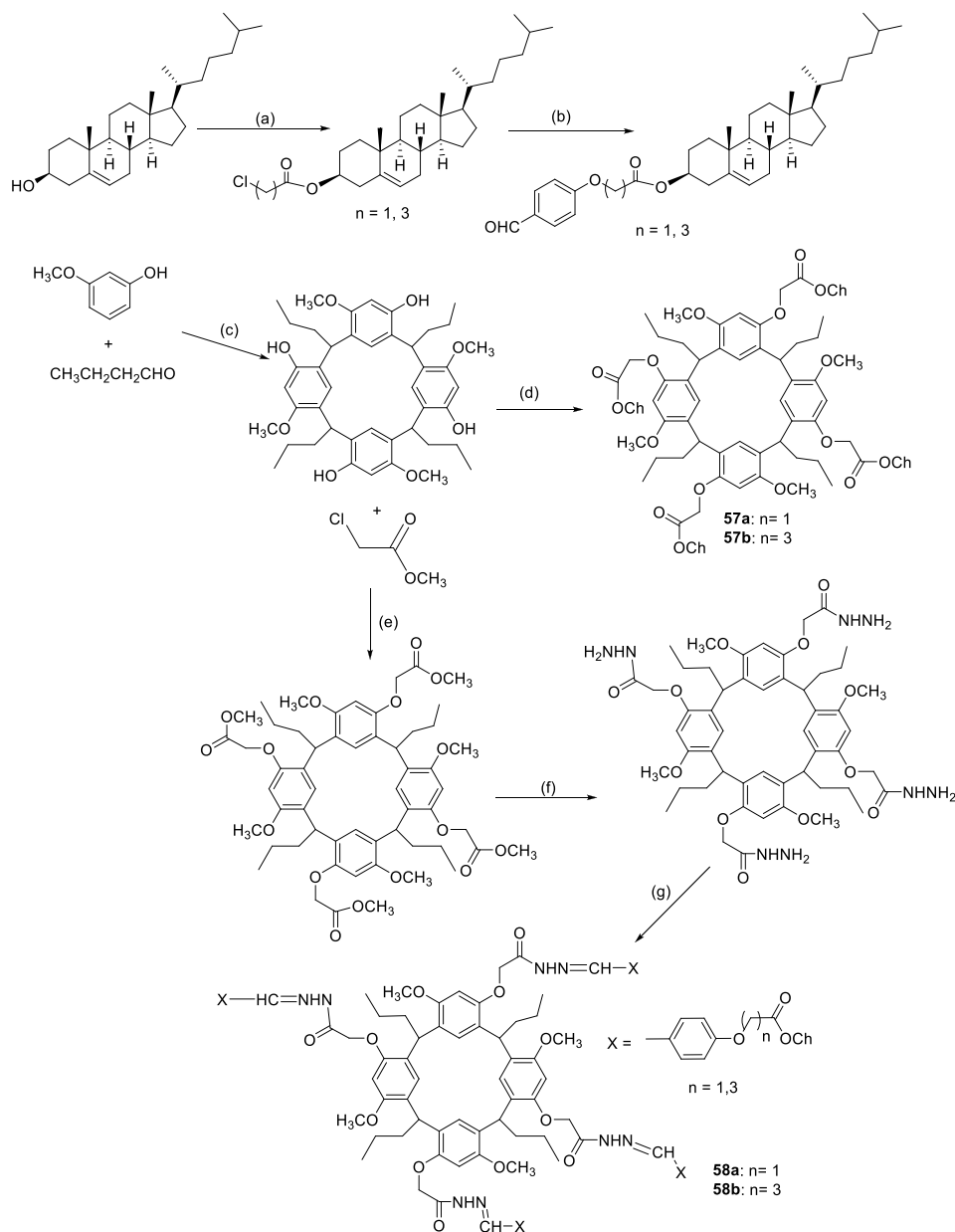


Figure 58. Graphical representation of the thermal behavior of symmetrical triads of triphenylene-calix[4]arene-triphenylene columnar LCs (**61**, **62**) (considered the cooling scan).

crystals reported, where the triphenylene acts as a major component.^{87–89} Many research groups tried to connect a calixarene core with triphenylene units with spacers of different lengths and natures. In 2011, Yang's group⁹⁰ synthesized the first macrocyclic compounds based on a calixarene core connected with a discotic triphenylene moiety in good yields by varying the spacer length (hexyl and decyl) of the triphenylene unit (**59a**, **59b**). The liquid crystalline behavior was seen in a symmetrical calix[4]arene linked triphenylene dimer with a decyl spacer (**59b**) (Figure S6). The length of the peripheral side chain, length of the spacer, molecular planarity,

Scheme 31. Synthetic Route of Calix[4]resorcinarene Linked Cholesterol Derivatives (57a, 57b; 58a, 58b)



(a) $\text{Cl}(\text{CH}_2)_n\text{COOH}$, ($n = 1, 3$), DCC, DMAP, DCM; (b) 4-hydroxybenzaldehyde, Anhy. K_2CO_3 , MeCN; (c) $\text{BF}_3 \cdot \text{Et}_2\text{O}$, CH_2Cl_2 ; (d) 2a, 2b, Anhyd K_2CO_3 , KI, MeCN; (e) Methyl 2-chloroacetate, Anhy. K_2CO_3 , KI, MeCN; (f) $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$; (g) Cholesterol aldehyde derivatives, Ethanol, reflux

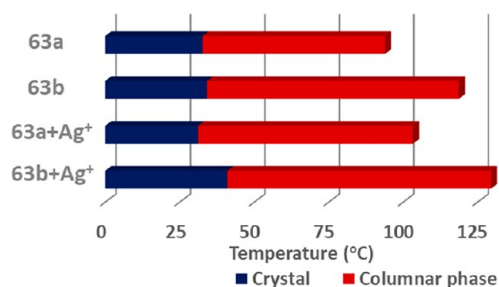
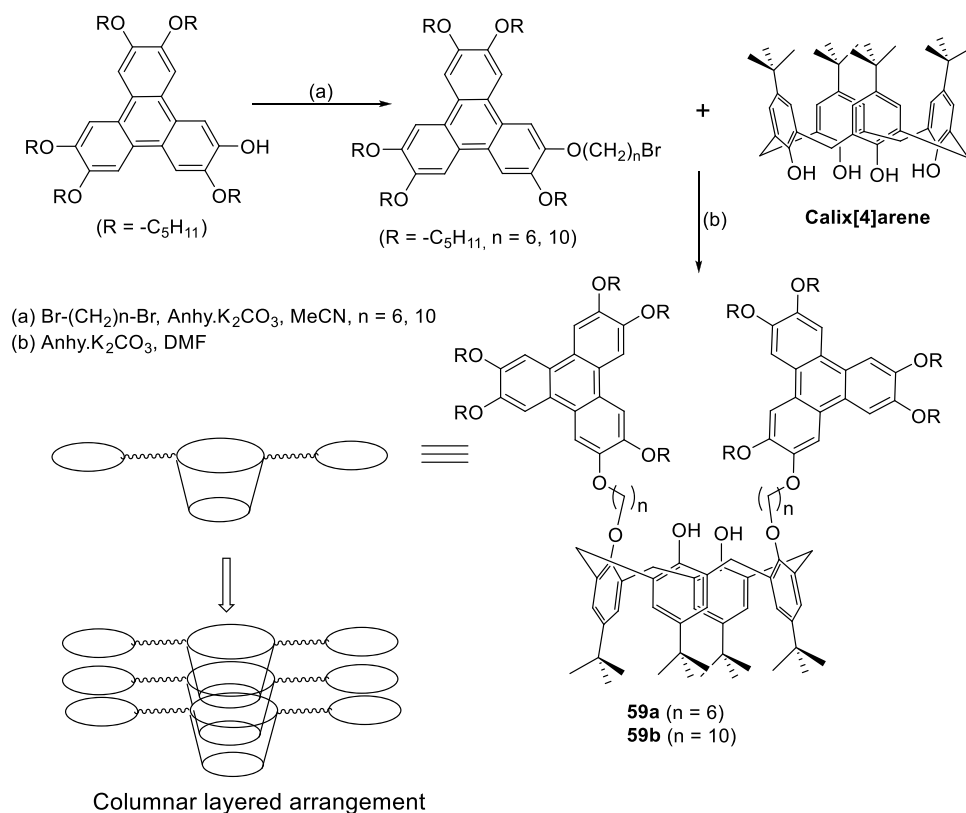


Figure 59. Graphical representation of the thermal behavior of symmetrical triads of triphenylene-calix[4]arene-triphenylene columnar LCs (63a, 63b) and their complexes (63a+Ag⁺, 63b+Ag⁺) (considered the cooling scan).

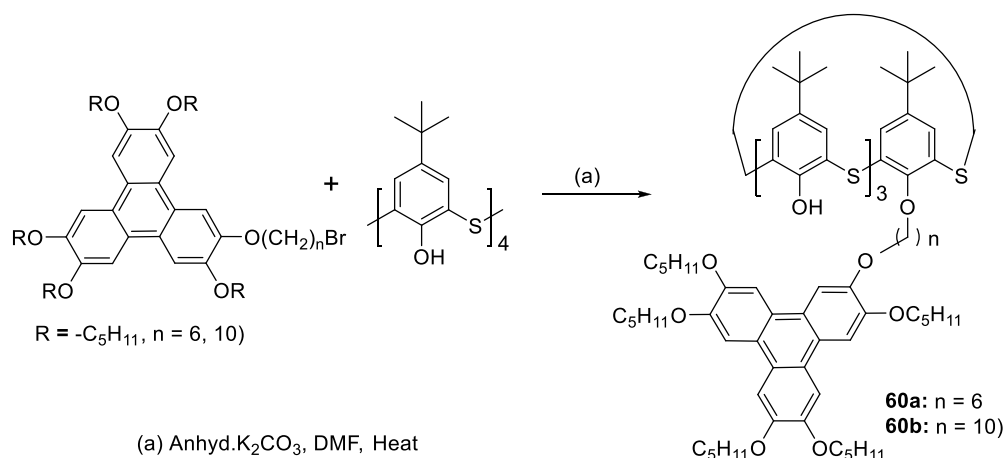
and stability of the calixarene geometry played a crucial role in the mesomorphic features of calixarene linked triphenylenes. The synthetic route to these mesogens is given in Scheme 32.⁹⁰ To study the influence of the conformation on the properties of the materials, thiacalix[4]arene, which was bridged by S groups with more flexible conformation reversal, was tried (Scheme 33). Here only monosubstituted thiacalix[4]-triphenylene derivatives were obtained, but they were crystalline. Thus, the atoms on the rim also affect the reactivity and conformational stability of the resultant molecules.

In continuation with their work on triphenylene-calix[4]arene LCs, Yang and co-workers reported calixarene linked symmetrical triphenylene dimers (61, 62) in good yields and investigated their mesomorphic properties.⁹¹ The nature of the

Scheme 32. Synthesis Route of Calixarene Linked Discotic Triphenylene Derivatives (59a, 59b)



Scheme 33. Synthesis Route of Thiacalix[4]triphenylene Derivatives (60a, 60b)



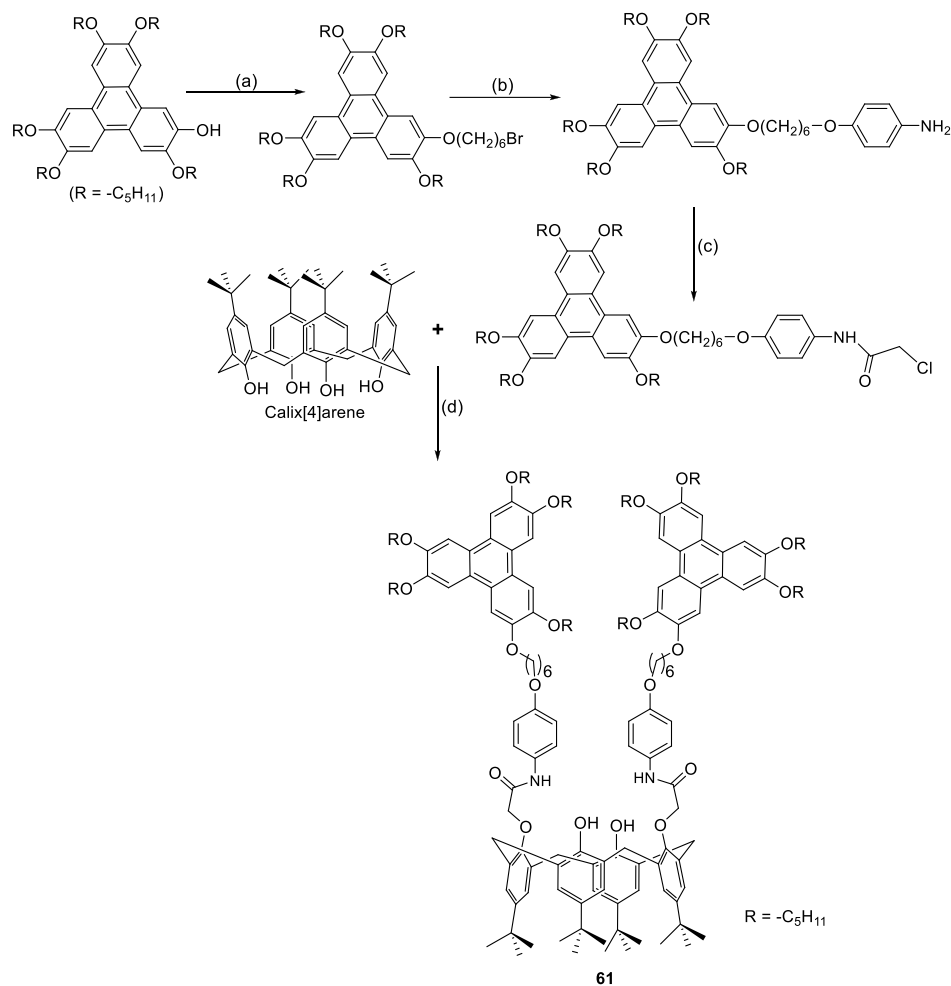
spacer was varied either by having an aromatic amido spacer or with a hydrazine spacer.

The results obtained were more promising compared to their previous work on calix[4]arene linked triphenylene mesogens. The systematic routes of syntheses of compounds **61** and **62** are shown in Schemes 34 and 35, respectively. The optical textures obtained for both compounds are presented in Figure 57. The synthesized compounds showed enantiotropic Col phases with low clearing temperatures. Further, the columnar stacking behavior of compound **61** was also confirmed by atomic force microscopy (AFM) by the tapping method. Due to the presence of amide units, compound **61**

exhibited higher melting and clearing temperatures than compound **62** (Figure 58).

Yang et al.⁹² reported another set of symmetrical triphenylene dimers bridged by a central calixarene unit (**63a**, **63b**) connected with hydrazone groups. In this study, they discovered an interesting mesomorphic change between two columnar phases caused by ion complexation. Further, they showed that the silver complexes of materials **63a** and **63b** with triphenylene moieties also displayed enantiotropic Col phases with wide thermal ranges which were higher than those of the uncomplexed compounds (Figure 59). The route of chemical synthesis of triphenylene based mesogens (**63a**, **63b**)

Scheme 34. Synthetic Route of Triphenylene Linked Amide Based Calixarene Derivatives (61)



(a) 1,6-dibromo hexane, Anhy.K₂CO₃, MeCN; (b) tert-butyl N-(4-hydroxyphenyl)carbamate, TFA
 (c) Chloro acetyl chloride; (d) Anhy. K₂CO₃, KI, MeCN

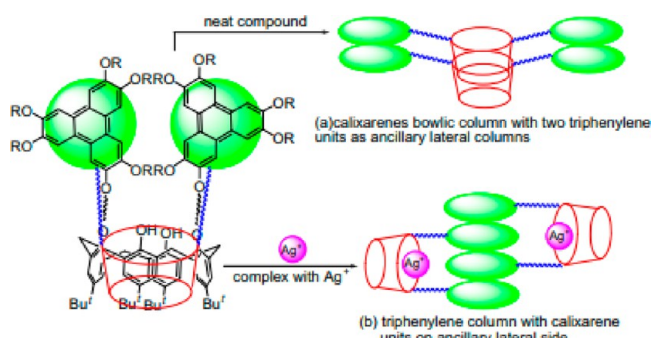


Figure 60. Two kinds of schematic representation of the columnar layered molecular arrangement for triads of triphenylene–calixarene–triphenylenes **63a** and **63b** before and after complexation.⁹² Reproduced with permission from ref 92. Copyright 2013 Elsevier.

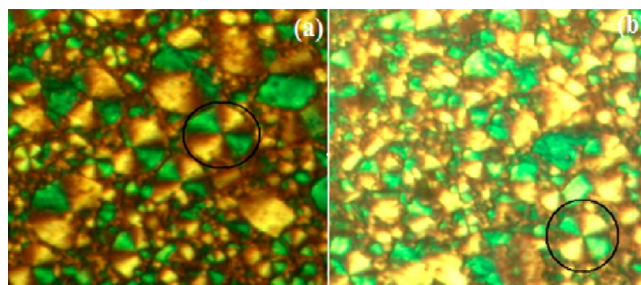


Figure 61. Fanlike textures of columnar phase in compounds **64a** and **64b** (a, b) were obtained with polarized optical microscopy on cooling at 90 °C (400×). Reproduced with permission from ref 93. Copyright 2014 Elsevier.

Scheme 35. Synthetic Route of Triphenylene Linked Hydrazone Based Calixarene Derivatives (62)

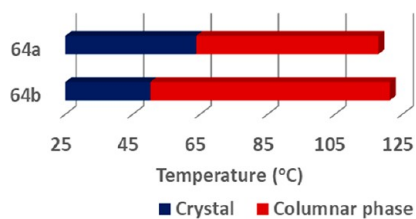
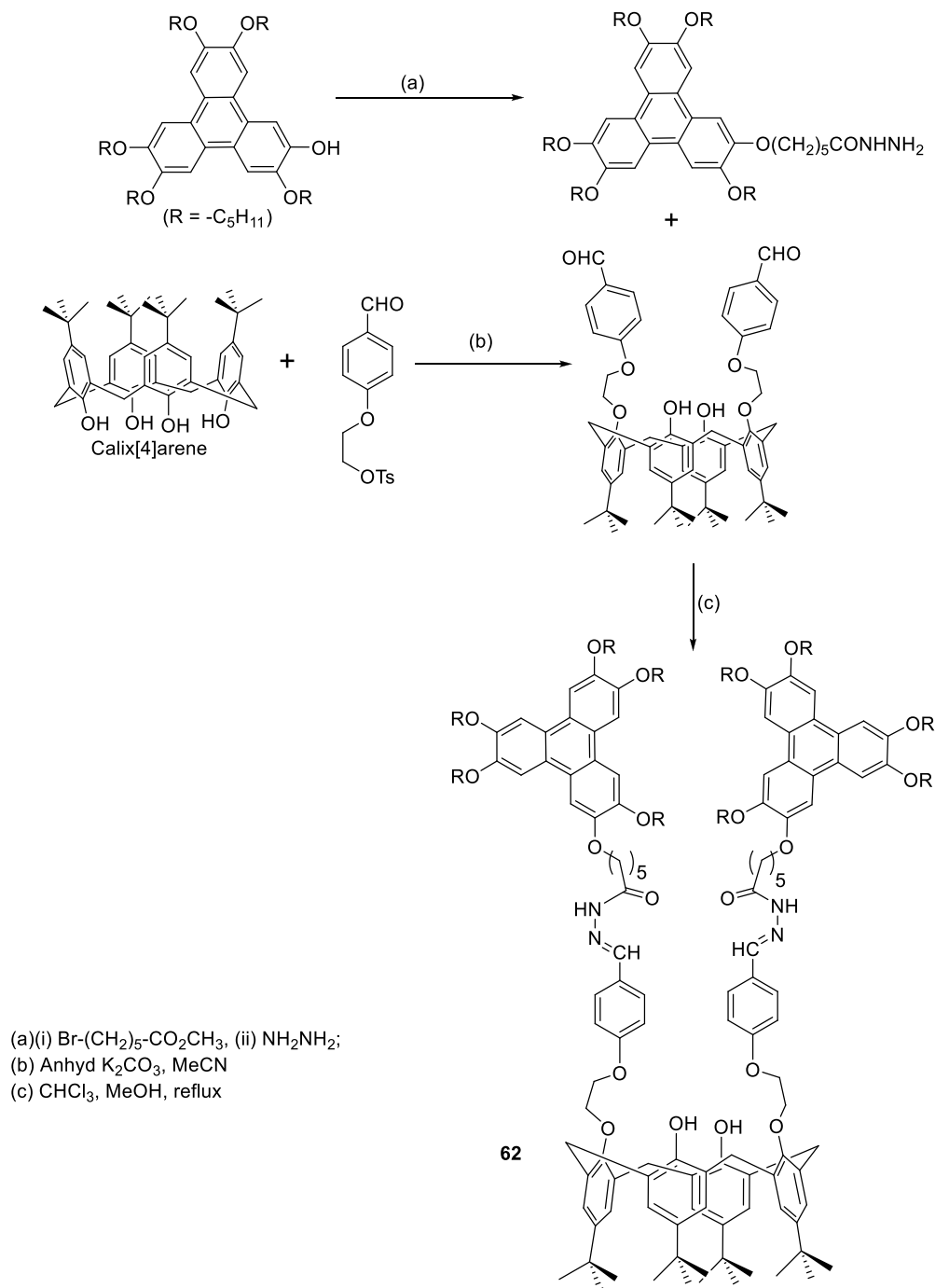


Figure 62. Graphical representation of the thermal behavior of calixarene linked discotic triphenylene columnar LCs (64a, 64b) (considered the cooling scan).

is shown in Scheme 36. A schematic representation of the self-assembly of the neat compound and the silver complex of the same to form a columnar layered phase is represented in Figure 60.

In a similar work, Hong et al.⁹³ synthesized triphenylene substituted calixarene derivatives (64a, 64b) via the click reaction and investigated their mesogenic properties. In this study, they studied the liquid crystalline behaviors of compounds before and after complexation with metal salts like NaSCN, AgSCN, and NaCl. The synthetic route for the triazole based mesogens is shown in Scheme 37. It was observed that the compounds (64a, 64b) exhibited a

Scheme 36. Synthetic Route of Novel Triads of Triphenylene–Calix[4]arene–Triphenylenes (63a, 63b)

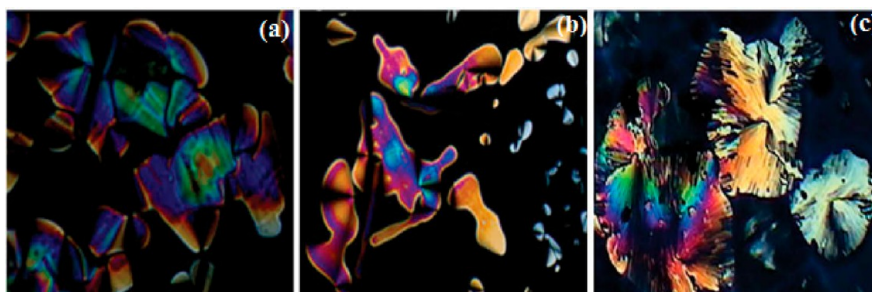
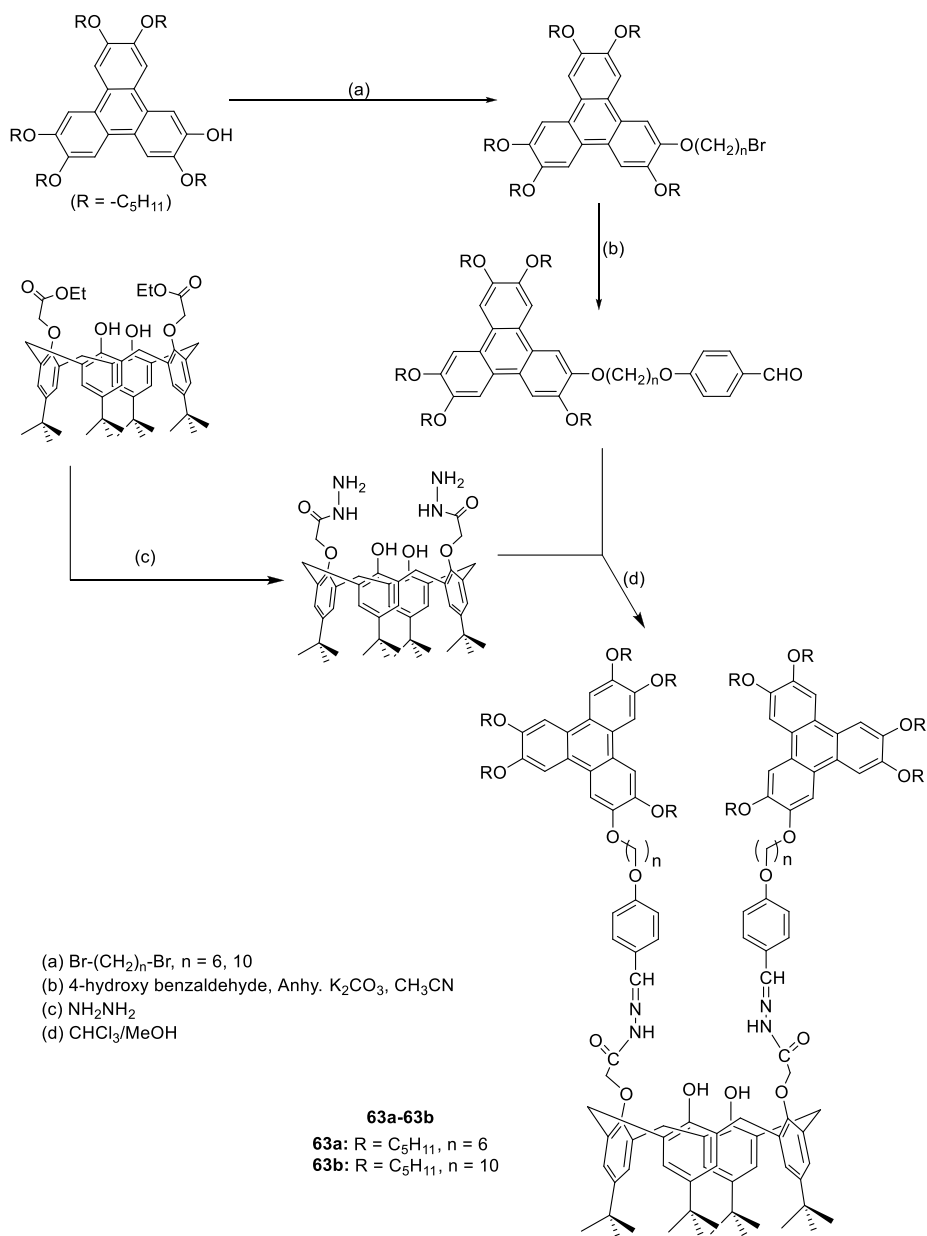


Figure 63. Mesomorphic columnar hexagonal textures of compounds 65 (a) and 66/67 (b) and distorted lamellar type columnar phase of compound 68 (c) obtained under POM on cooling at 70 °C (500 \times). Reproduced with permission from ref 94. Copyright 2017 Taylor & Francis.

Scheme 37. Synthetic Route of Calixarene Linked Azide–Triphenylene Derivatives (64a, 64b)

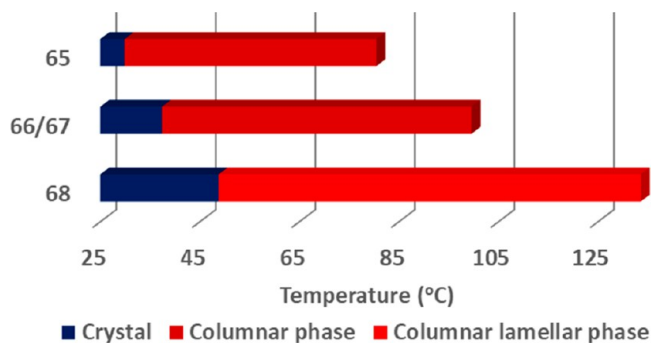
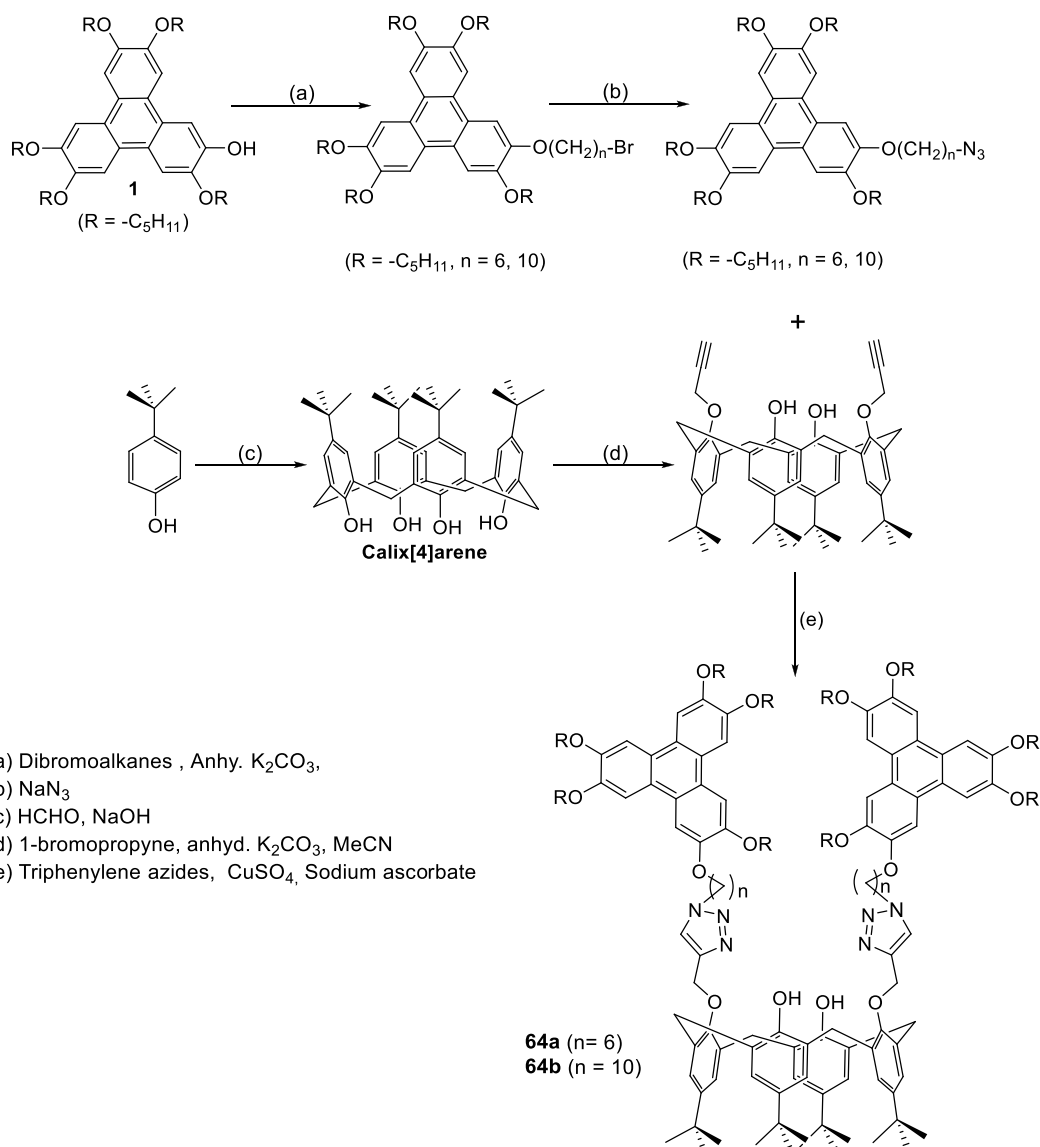


Figure 64. Graphical representation of the thermal behavior of calix[4]resorcinarene–triphenylene oligomer columnar LCs (65–68) (considered the cooling scan).

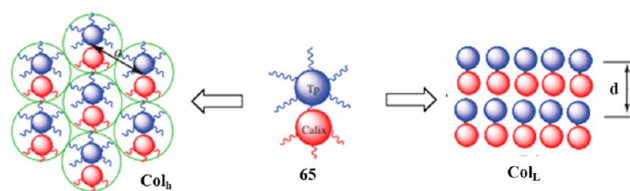
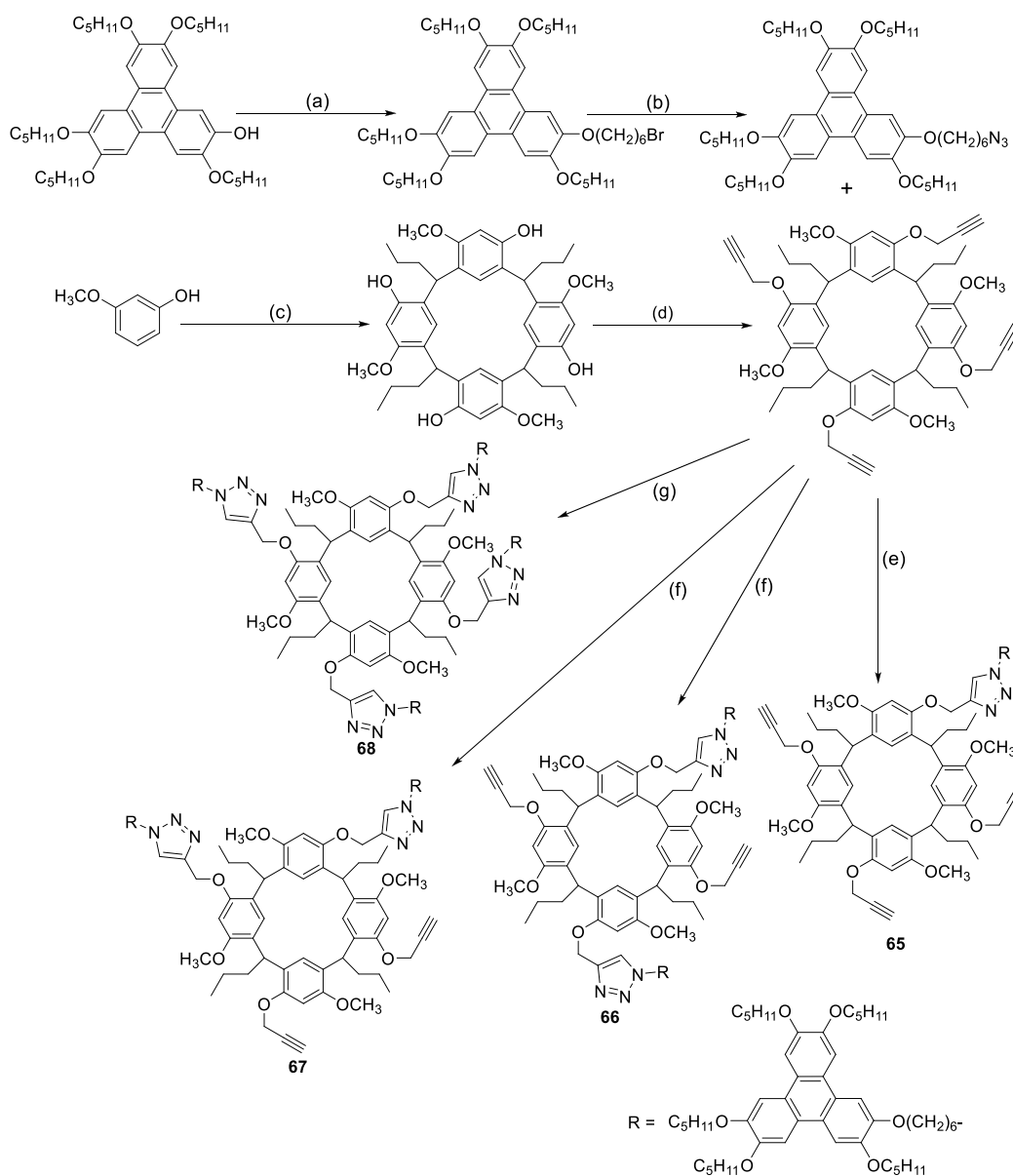


Figure 65. Two possible schematic representations of the hexagonal columnar phase and lamellar columnar structure for compound **65**.⁹⁴ Reproduced with permission from ref 94. Copyright 2017 Taylor & Francis.

Scheme 38. Synthetic Route of Calix[4]resorcinarene–Triphenylene Oligomers (65–68)



- (a) 1,6-dibromo hexane, Anhy.K₂CO₃, MeCN; (b) NaN₃; (c) Butanal, BF₃·Et₂O, DCM
 (d) 1-bromo propyne, Anhyd.K₂CO₃, MeCH; (e) 1:1 (mol ratio of reactants), CuSO₄, Sodium Ascorbate, DMF
 (f) 2:1 (mol ratio of reactants), CuSO₄, Sodium Ascorbate, DMF; (g) 4:1 (mol ratio of reactants), CuSO₄, Sodium Ascorbate, DMF

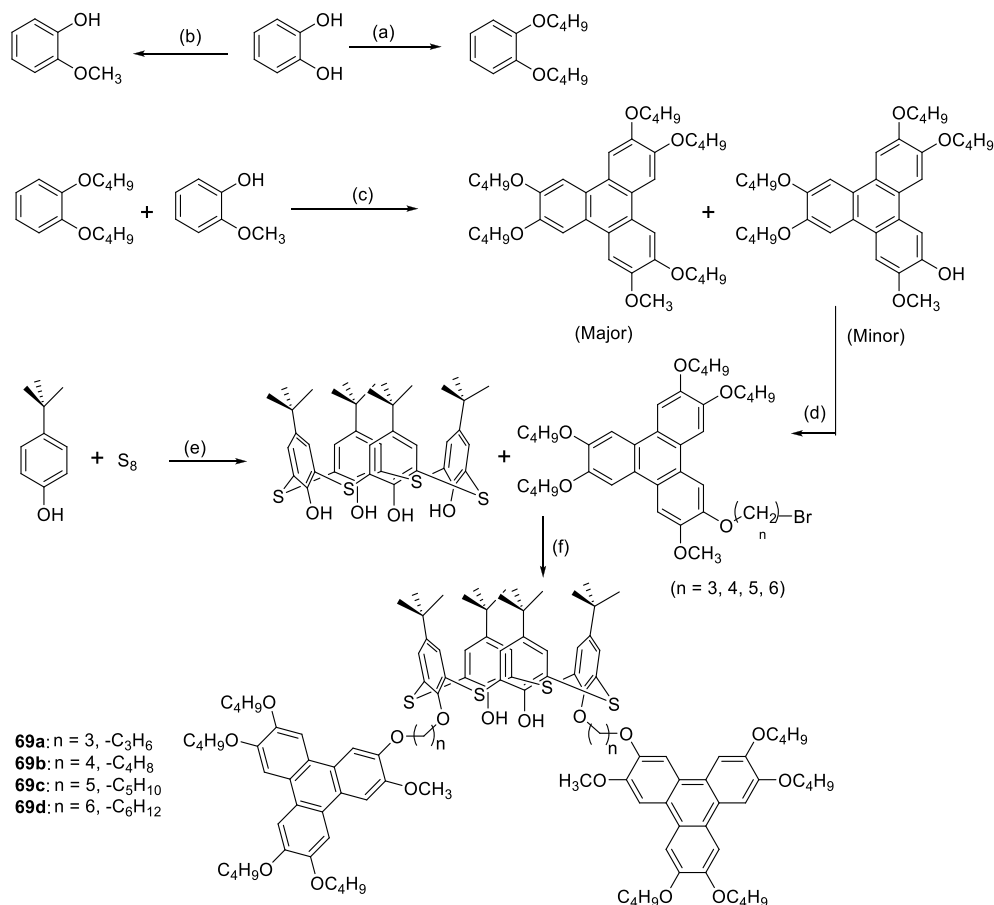
mesomorphic state, but their complexes did not display any LC properties. Figure 61 shows the POM images at specific temperatures, with both derivatives having fanlike textures. These texture patterns were similar to the well-known reported POM images of triphenylene substituted mesogens. Both compounds exhibited an enantiotropic Col phase with a wide thermal range (Figure 62).

Yang and co-workers, by controlling the molar ratios of reactants, prepared calix[4]resorcinarene–triphenylene monomer, dimer, and tetramers via click chemistry and studied their thermal behaviors (Scheme 38).⁹⁴ They summarized that an increase in the number of triphenylene moieties on the resorcinarene core provides a higher mesophase temperature range and stability. The typical focal-conic texture images of compounds 65–67 observed in the cooling condition is shown

in Figure 63. X-ray studies confirmed that the monomer (65) and dimers (66, 67) had mixed columnar mesophases with the Col_h structure and the disordered lamellar type columnar structure (Col_l), whereas compound 68 exhibited only a disordered lamellar columnar structure (Figure 64). Figure 65 represents the organization of tetramer 65 into a lamellar columnar structure.

Patel et al.⁹⁵ recently reported similar triphenylene derivatives with central thiacalixarene spacers (Scheme 39). These molecules displayed blue light emitting properties in solution as well as thin films with high good quantum yields. All the compounds exhibited a room temperature Col_h phase (Figure 66). With the increase in the spacer length, a lowering of melting and clearing temperatures was noticed. These compounds displayed excellent aggregation induced emission

Scheme 39. Synthetic Route of Thiacalixarene Linked Triphenylene Derivatives (69a–69d)



(a) C₄H₉Br, anhydrous K₂CO₃, ethanol, 24 h; (b) CH₃I, anhydrous K₂CO₃, CH₃CN, Reflux;
 (c) anhydrous FeCl₃, DCM, 6 h, RT; (d) dibromo alkane, anhydrous K₂CO₃, CH₃CN, Reflux, 24 h
 (e) Sulphur powder, NaOH, diphenyl ether, Reflux, 8 h; (f) NaH, CH₃CN, Reflux, 24 h

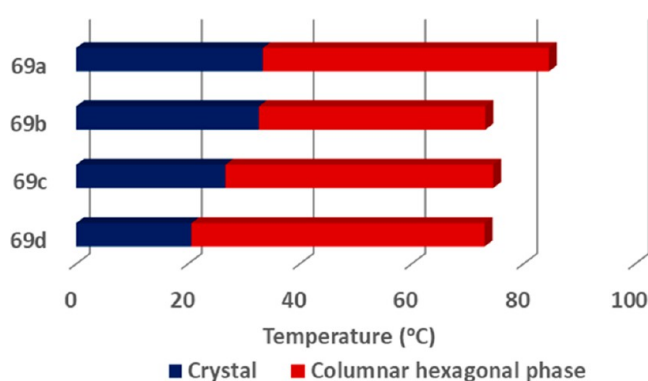


Figure 66. Graphical representation of the thermal behavior of thiacalixarene linked triphenylene based room temperature columnar LCs (69a–69d) (considered the cooling scan).

(AIE) behavior in the THF–H₂O system with addition to the intramolecular charge transfer (ICT) effect. They have also shown good electrochemical behavior as confirmed by cyclic voltammetry study and further compared with computational study results to correlate the electronic properties and reactivity.⁹⁵ These compounds were further tested for their

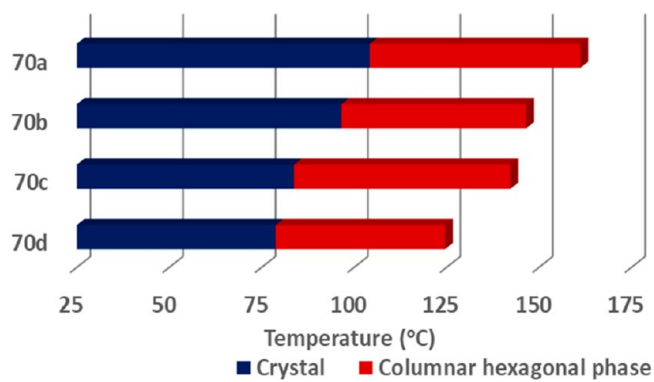
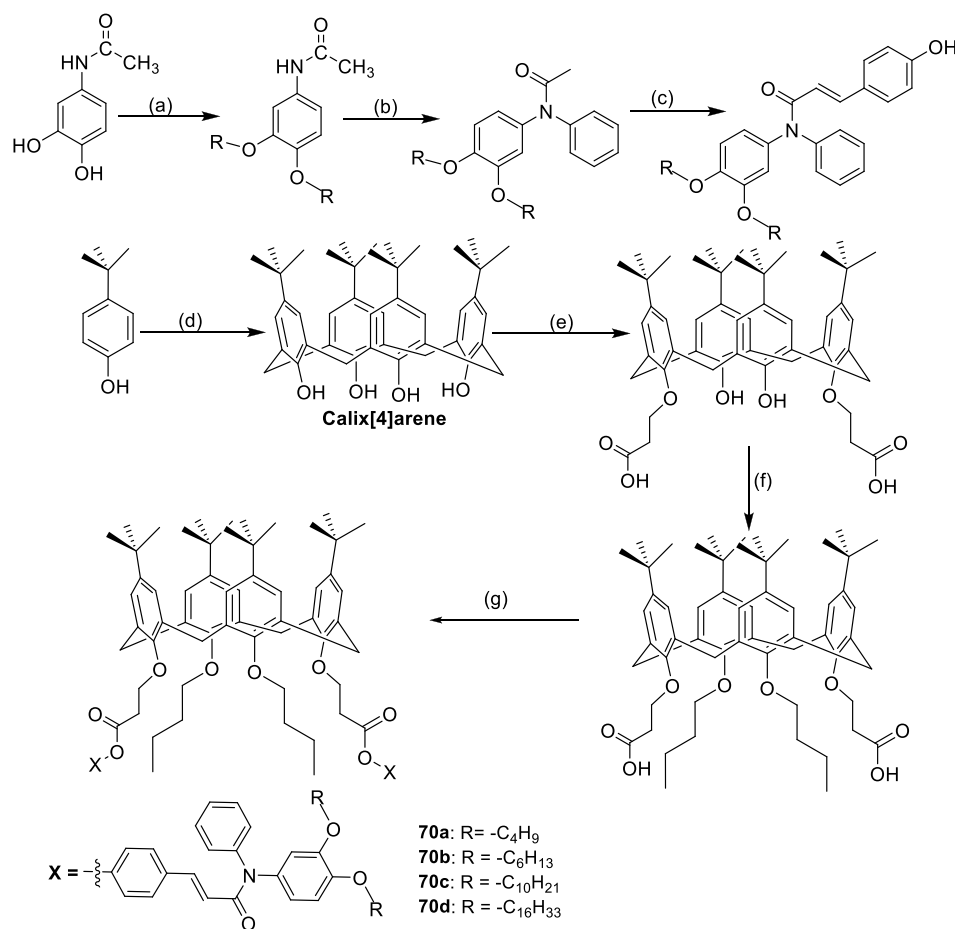


Figure 67. Graphical representation of the thermal behavior of chalcone–biphenyl amine functionalized supramolecular columnar LCs (70a–70d) (considered the cooling scan).

dielectric behavior in the frequency range from 20 Hz to 2 MHz and showed good dielectric behavior in the thermal range of 20–50 °C.

2.13. Calix[4]arene Derivatives Containing Chalcone Moieties. Chalcones are prepared by the Claisen–Schmidt base catalyzed condensation of aromatic ketones and

Scheme 40. Synthetic Route of Chalcone Linked Calixarene Derivatives (70a–70d)



- (a) R-Br, Anhyd. K_2CO_3 , Acetone, reflux, 2 h; (b) Bromo benzene, anhyd. K_2CO_3 , CuI, nitrobenzene, 15 h, reflux;
 (c) 4-hydroxybenzaldehyde, KOH, EtOH, RT, 24 h; (d) HCHO, NaOH, microwave, 15 min;
 (e) $\text{Br}(\text{CH}_2)_2\text{COOH}$, Anhy. K_2CO_3 , CH_3CN , reflux, 4 h; (f) $\text{C}_4\text{H}_9\text{Br}$, Anhy. K_2CO_3 , CH_3CN , reflux, 5 h;
 (g) EDC-HCl, DMAP, DCM, RT, 24 h

aldehydes. These compounds have extended conjugation and hence are colored. Apart from biological activity, they are also known as materials for photoalignment, photo-cross-linkers, and fluorescent dyes and as nonlinear optically (NLO) active materials. Thus, many liquid crystals were prepared by using chalcone derivatives.^{96,97}

Our research group prepared four calixarene derivatives (70a–70d) substituted by peripheral chains containing biphenyl amine chalcone moieties (Scheme 40).⁹⁸ In this report, we described seven reaction steps to obtain target compounds in good yield (64–73%) with cone confirmation as depicted in Scheme 33. All synthesized materials showed high thermal stability and a wide range enantiotropic Col_h phase (Figure 67). The compounds displayed blue light emission with good quantum yields. One of the compounds (70d) was used to fabricate blue OLEDs, as either neat or doped conditions in polyvinyl carbazole host. Compound 70d showed the best electroluminescence results in the series, with a 0.71% external quantum efficiency. Here, with the increase in the peripheral chain length, a gradual drop in the melting and clearing temperatures was noted.

3. CONCLUSION AND FUTURE PERSPECTIVES

In the past decade, calixarene based materials have garnered huge interest for various applications. Calixarene based materials are extensively used as supramolecular hosts for many guests, and also as motifs for molecular self-assembly. The substituted calixarene LC compounds can be easily prepared in good yield by the upper/lower rim functionalization of the calixarene core. These compounds stabilized the mesophases that appear for calamitic and discotic LCs over a wide thermal range with low melting and clearing temperatures. They have also shown the capability to form organogels with ordered molecular arrangements.

An understanding of the thorough structure–property relationships is required to realize their full potential and successful application in the fields of electronics and optics. Host–guest complexation is a good option to realize new modes of self-assembly and functions; further, it may unravel a new area of supramolecular polymers. Creating porous organic polymers and porous membranes is another area of application that can be investigated. Introduction of the amphiphilic nature in calixarene opens a new avenue for the utilization of this class of molecules in chemical biology and biomembrane studies. Incorporation of fluorophores in the molecular

structure also helps in bioimaging, sensing, and organic light emitting applications. Introduction of electroactive molecular units will help in the realization of self-assembling organic materials that will be useful in organic electronics. In this regard, we have summarized some of the recent developments in the synthesis of calixarene based materials and their liquid crystalline behaviors in this review. We believe that this review article will be useful for researchers working in this area of supramolecular chemistry, liquid crystals, and self-assembly.

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^{||}V.S.S. and V.K.V. made equal contributions.

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Notes

The authors declare no competing financial interest.

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