

Liquid Crystal Organization of Calix[4]arene-Appended Schiff Bases and Recognition towards Zn²⁺

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Abstract: The synthesis and liquid crystalline behavior of new calixarene Schiff base derivatives are reported. The materials were obtained by reaction of a tetraaminocalix[4]arene derivative with three aldehydes as mesogenic promotor moieties: 4-(4'-decyloxybenzoyloxy)benzaldehyde (**A**), 4-(4'-decyloxybenzoyloxy)salicylaldehyde (**B**) and 4-(3',4'-didecyloxybenzoyloxy)salicylaldehyde (**C**). All of the compounds exhibit liquid crystalline properties and these were studied by optical microscopy, DSC and X-ray diffraction. The relationship between the structure and the mesomorphic behavior of the compounds is discussed. The binding recognition and selectivity towards cations have been studied by absorption and fluorescence spectroscopy

Introduction

Calixarenes are an important class of macrocycles that have been extensively used as a core in supramolecules due to their unique 'bowl-like' structure, high functionality, persistent shape and size and their easy chemical modification.^[1] Several books and reviews concerning the synthesis, properties and applications of calixarenes have been published.^[2]

Taking into account the structure of the calixarene unit there are two main sites that can be modified and these can be addressed independently: substitution of the phenolic hydroxy groups (substitution on the narrow rim) and substitution in the position *para* to the OH-groups (substitution on the wide rim). In this way it is possible to introduce different functional groups pointing in opposite directions. Such modified calixarene derivatives have additional binding sites that augment the binding abilities when compared to the parent calixarenes and provide an ideal platform for the development of receptors towards ions depending on the functionalization. In particular, a series of

salicylideneimine-functionalized *para-tert*-butylcalixarene-core dendrimers have been synthesized.^[3] These systems are able to form complexes with a large number of metals.^[4] Among them, zinc is one of the essential trace elements and is the second most abundant transition metal ion present in the human body. In particular, in proteins Zn²⁺ presents a wide range of biochemical activities.^[5] Moreover, phosphates are one of the target anions as they play significant roles in many biological processes.^[6] It has been reported that the structural and geometrical flexibility of the metal-based receptor can organize the phosphate groups in the coordination sphere and hence these systems exhibit fluorescence sensing behavior.^[7] Despite the sizeable number of zinc complexes reported to date, fluorescent probes for phosphate anions^[8] such as monophosphorylated H₂PO₄⁻ species are still rare.^[9]

In the early eighties, Lin Lei (Lui Lam) formally proposed the concept of liquid crystals formed by bowl-like molecules.^[10] Thus, if calixarene cores (bowl-like molecules) are functionalized with promesogenic units they could self-organize into bowl-like liquid crystalline mesophases.^[11] Liquid crystal (LC) calixarenes represent an attractive option for the design of functional materials that combine the inherent properties of calixarenes with the anisotropic properties provided by the LC state, thus achieving the preparation of materials with a variety of new applications.

In 1990, Dalcanale et al. reported the preparation of the first calixarene liquid crystal, which self-organized to give a new class of mesophase, namely the bowl-shaped columnar liquid crystals.^[12] Since then, several families of liquid crystals based on calixarene derivatives have been reported by different groups, e.g., Shinkai and Komori,^[13] Xu and Swager,^[14]

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Tschierske et al.,^[15] Ichimura et al.,^[16] Yonetake et al.^[17] and Kohmoto et al.^[18] In recent years Menon et al.^[19] and Yang et al.^[20] have advanced the studies of liquid crystalline calixarenes. In 2014, Yang et al. published an interesting review on the synthesis and properties of all kinds of calixarene liquid crystals reported up to that date.^[11b] In this review the authors proposed two methods to prepare this kind of liquid crystal. One approach is to introduce the corresponding functional groups with long alkyl chains, which usually afford columnar liquid crystals with a rigid bowl core. Another method is to introduce a triphenylene unit to obtain bowl-like calixarene columns with triphenylene units as ancillary lateral columns or triphenylene columns with calixarene units on the ancillary lateral side.^[19c]

Menon et al.^[19b] studied a series of new LCs based on Schiff base calix[4]arene and these compounds showed smectic and nematic phases. These materials were also studied for their dielectric properties at various temperatures. The results indicated that the linking groups in the wide part have a great influence on the mesogenic properties of calixarene LCs.

Our group has extensive experience in the preparation and study of liquid crystal dendrimers.²¹ In our first works we described liquid crystal dendrimers derived from PAMAM and PPI dendrimers (with 4, 8, 16, 32 and 64 amino terminal groups) as a core and Schiff-bases as mesogenic units made by reaction of the amino terminal groups of dendrimer with the aldehydes: 4-(4'-decyloxybenzoyloxy)salicylaldehyde (B) and 4-(3',4'-didecyloxybenzoyloxy)salicylaldehyde (C) as mesogenic promoter moieties.^{21a,b}

Thus, the aim of the work described here was the design, synthesis and mesomorphic properties of three calix[4]arene-appended salicylidene imine derived from the same aldehydes, 4-(4'-decyloxybenzoyloxy)salicylaldehyde (B) and 4-(3',4'-didecyloxybenzoyloxy)salicylaldehyde (C) used in our previous work, and also 4-(4'-decyloxybenzoyloxy)benzaldehyde (A) to study the correlation between molecular structure and liquid crystalline properties. Zn polymer of Schiff base calix[4]arene derived from B aldehyde was also synthesized and the effect of the complexation on mesomorphic properties was also studied. Moreover, a recognition study was carried out with the prepared calixarenes and selectivity towards both cations and anions was also studied.

Results and Discussion

Synthesis of the precursors.

The tetraamino-25,26,27,28-tetradecyloxy-calix[4]arene (Cx)

The starting compounds **2**, **3**, and **Cx** were synthesized in several steps according to Supporting Information Scheme S1 by following a procedure described in the literature.^[22]

Firstly the phenolic hydroxy groups (substitution on the lower rim) of *para-tert*-butylcalix[4]arene were alkylated with decyloxy bromide to give the corresponding ether (**2**), which leads to restriction of the conformational mobility of the macrocycle and the cone shape is favored. Secondly, cleavage of the *tert*-butyl groups by reaction with AlCl₃ in toluene in the presence of phenol provided free *para*-positions, which were then available for electrophilic substitution (nitration). The tetranitrocalix[4]arene derivatives **3** were reduced to the corresponding tetraamines (**Cx**) by hydrogenation over palladium-charcoal catalyst according to a literature method.

Typical procedure for the synthesis of the calix[4]arene Schiff bases and Zn (II) metal polymer.

The preparation of the calix[4]arene Schiff bases was carried out as shown in Scheme 1. The appropriate benzaldehyde (**A**, **B** or **C**) was added to a solution of the tetraamino-25,26,27,28-tetradecyloxy-calix[4]arene (**Cx**) in ethanol (15 mL) and the mixture was heated under reflux for 8 h. The reaction mixture was cooled and yellow precipitates were obtained. The crude products were recrystallized from ethanol.

The synthesis of Zn (II) metal polymer was carried out by reaction of calix[4]arene Schiff base (**Cx-B**) with Zn(CH₃COO)₂ in ethanol in a 1:2 ratio. A polymer was obtained as deduced from the structural characterization by NMR (Supporting Information S13-S15) and MALDI (Supporting Information S28). These studies reveal the formation of a polymeric species instead of a discrete complex.

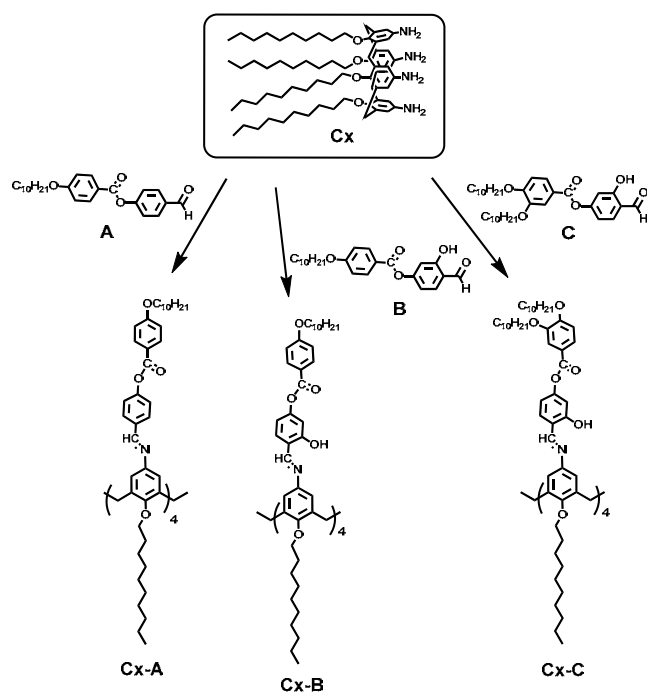
Nomenclature.

The calix[4]arene Schiff bases synthesized are denoted as **Cx-A**, **Cx-B** and **Cx-C** where **Cx** indicates calix[4]arene unit, **A**, **B**, **C** refer to the promesogenic units 4-(4'-decyloxybenzoyloxy)benzaldehyde (**A**), 4-(4'-decyloxybenzoyloxy)salicylaldehyde (**B**) and 4-(3',4'-didecyloxybenzoyloxy)salicylaldehyde (**C**), respectively.

Zn polymer derived from **Cx-B** calix[4]arene are denoted as **ZnCx-B**.

Structural characterization

The structural characterization of the compounds **Cx-A**, **Cx-B** and **Cx-C** was carried out by elemental analysis and spectroscopic methods, namely Fourier transform infrared spectroscopy (FTIR) and NMR spectroscopy. The data are gathered in the Supporting Information. The results confirmed the proposed structures of these materials.



Scheme 1. Synthetic route for calix[4]arene Schiff bases.

FT-IR characterization

The carbonyl band at 1735–1738 cm^{-1} attributed to aldehydes disappears and is replaced by a new band corresponding to the imine group (C=N) in the range 1605–1620 cm^{-1} . The $\nu(\text{C}=\text{O})$ band of the ester group appears at 1732–1734 cm^{-1} and this indicates the formation of **Cx-A**, **Cx-B** and **Cx-C** depending on the promesogenic unit. The bands observed at 3424 cm^{-1} and 3434 cm^{-1} correspond to the hydroxyl group (–OH) of compounds **Cx-B** and **Cx-C**, respectively. The IR data are collected in Table S1.

NMR characterization

The chemical structures of the new calix[4]arenes were confirmed by one-dimensional ^1H and ^{13}C NMR spectroscopy and by two-dimensional ^1H - ^1H COSY, ^1H - ^{13}C HSQC and ^1H - ^{13}C HMBC experiments. The ^1H and ^{13}C spectra of the

calix[4]arenes synthesized, as well as all their assignments, and two-dimensional ^1H COSY spectrum of **Cx-C**, ^1H - ^{13}C HSQC spectrum of **Cx-B** and ^1H - ^{13}C HMBC spectrum of **Cx-A** are provided in the Supporting Information (Figures S1–S12). The ^1H and ^{13}C NMR data for the calix[4]arene-imines are consistent with cone conformations.^[23]

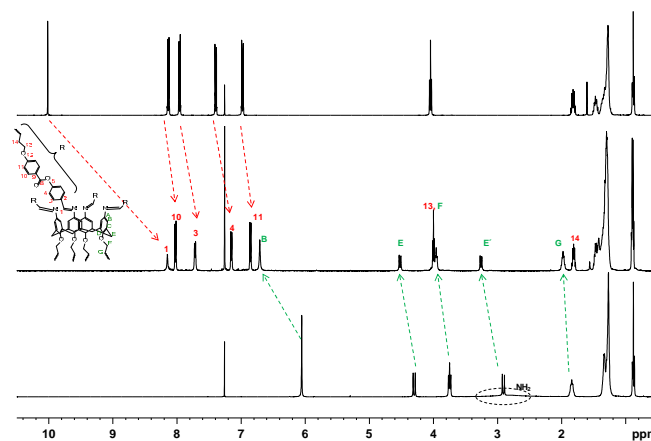


Figure 1. Proton assignment for **Cx-A** (middle) and its precursors **Cx** (bottom) and **A** (top). (500 MHz, CDCl_3 , 25 $^\circ\text{C}$).

The ^1H NMR spectra recorded on samples in CDCl_3 solution clearly show the formation of the imines. The main evidence is the change in the ^1H shift of the precursor aldehyde protons (signals around 10 and 9.88 ppm) to imine signals (8.15 and 8.3 ppm) and the associated shift in the ^{13}C NMR spectra: from 191.1 and 195.7 ppm to 157.3 and 159.8, respectively. Comparative ^1H and ^{13}C spectra of **Cx-A** and **Cx-B** are shown in **Figures 1** and **2**, respectively.

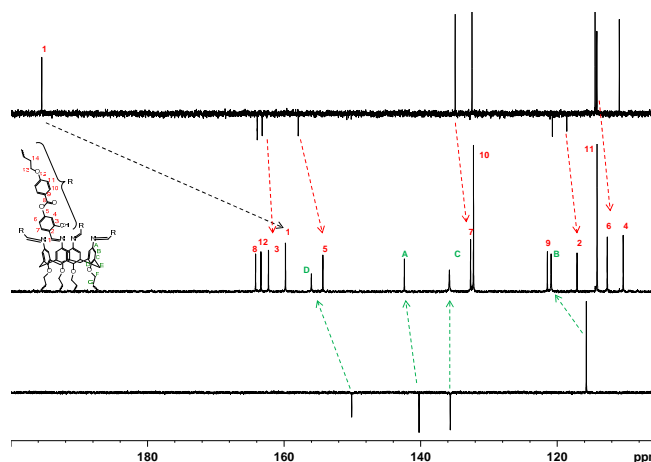


Figure 2. Expansions of ^{13}C NMR spectra and assignment for **Cx-B** and its precursors: **Cx** (bottom) and **B** (top). (125 MHz, CDCl_3 , 25 $^\circ\text{C}$).

In most cases the proton signals for the cone of the calix[4]arene (**Cx**) and the chemical shifts of their ^{13}C signals are shifted

downfield upon imine formation, whereas the aromatic signals due to protons closer to the imine experience shielding.

Evidence for intermolecular association or interdigitation in chloroform solution was not observed, as deduced from the NOE experiments. The ROESY spectrum of **Cx-A** is shown in the Supporting Information (Figure S12).

Thermal stability of the calix[4]arene Schiff bases

The thermal stability of the calix[4]arene Schiff bases was studied by thermogravimetric analysis (TGA) under a nitrogen atmosphere. All of the studied compounds exhibited good thermal stability and in all cases the 2% weight loss point was detected at temperatures more than 40 °C above the isotropisation process. The calix[4]arene Schiff base derived from 4-(4'-decyloxybenzoyloxy)benzaldehyde **Cx-A** is more stable than the homologs derived from the salicylaldehyde (**Cx-B**, **Cx-C**). Furthermore, the calix[4]arene Schiff base bearing two decyloxy terminal chains in the upper ring **Cx-C** is thermally more stable than the calix[4]arene Schiff base bearing only one **Cx-B** (Table 1).

Table 1. Thermal stability, transition temperatures (°C), mesogenic behavior of Schiff base calix[4]arenes.

	T _{2%} ^a	Thermal data ^b (T °C, ΔH J/g)	Structural parameter
Cx-A	290	g 26 SmA 124 (3.6) I	Layer spacing 51.9 Å
Cx-B	264	g 26 SmA 57 (1.8) I	Layer spacing 52.0 Å
Cx-C	267	g 45 C 63 (-3.4) C' 105 N° 114 (7.9) I	Mean lateral separation 32 Å
ZnCx-B	334	g 25 SmA 200 N° 280 I	-

^a Temperature (°C) at which 2% of the initial mass is lost. ^b Data obtained by DSC in the second heating process, and taken at the maximum of the peak obtained at 10 °C min⁻¹. g = glass; C = crystal, SmA = Smectic A mesophase, N = Nematic mesophase, I = isotropic liquid. ^c optical data.

Mesogenic properties

The mesomorphic behavior of the compounds was analyzed by polarized optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD).

All of the calix[4]arenes synthesized exhibit a mesophase; the identification of the liquid crystal phase was carried out on the basis of polarizing optical microscopy (POM) by observing the textures when the sample was sheared by sliding the upper glass plate, and the assignment was confirmed by X-ray diffraction. Some microphotographs of the mesophase taken after submitting the samples to mechanical stress are shown in Figure 3 and Figure S16.

The phase transitions of the functionalized calix[4]arene Schiff bases were measured by differential scanning calorimetry (DSC)

at a heating and cooling rate of 10 °C min⁻¹ (Figures S17–S19 in the Supporting Information). All samples were dried in a vacuum desiccator prior to analysis. Three cycles were carried out in DSC experiments and data were taken from the second cycle. The results are gathered in Table 1

The three calix[4]arene Schiff bases synthesized exhibit mesogenic properties and the thermal behavior is different depending on the compound. Comparison of the thermograms corresponding to the second heating indicates that for **Cx-A** a glass transition to the mesophase occurs at 26 °C and an endothermic peak at 124 °C corresponds to the mesophase to isotropic liquid transition. In the case of **Cx-B** a glass transition to the mesophase occurs at 26 °C and an endothermic peak at 57 °C corresponds to the mesophase to isotropic liquid transition. For **Cx-C** a glass transition at 45 °C is followed by an exothermic peak at 63 °C (crystal to crystal transition) and an endothermic transition at 114 °C corresponding to the mesophase to isotropic liquid transition. For this compound a change in the color of the texture from black to yellow was observed by optical microscopy at the same temperature as the exothermic peak 63 °C observed in DSC and the sample becomes a birefringent viscous liquid at 105 °C. This last transition was not observed in the DSC thermogram. In contrast to calix[4]arenes **Cx-A** and **Cx-B**, when a sample of calix[4]arene **Cx-C**, derived from 4-(3',4'-didecyloxybenzoyloxy)salicylaldehyde, was observed by POM the transition from the isotropic to a birefringent mesophase was observed on cooling (Figure 3c).

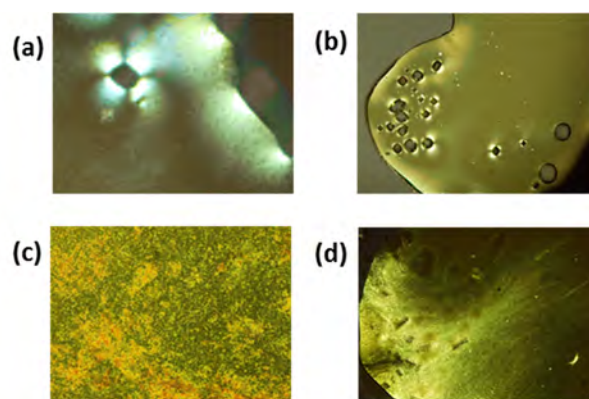


Figure 3. Microphotographs of the optical textures observed by polarizing microscopy (magnification × 20).for: (a) **Cx-A** taken at 27 °C in the cooling process from the isotropic phase ; (b) **Cx-B** taken at 47 °C in the third cooling process; (c) **Cx-C** taken at 110 °C in the third heating process (d) 200°C (magnification ×50) in the first heating process during the SmA to N transition.

ZnCx-B polymer exhibits thermotropic liquid crystal behavior with two different phases on heating. These phases were observed under POM, and identified as SmA and N mesophases because of the similarity with the textures observed for the calix[4]arene Schiff bases described above. The first mesophase exhibits a homeotropic texture and was observed birefringence when the sample was sheared by sliding the upper glass plate. A second transition to a birefringent phase was observed at 200°C and was identified as N mesophase. Figure 3d shows a microphotography of the texture corresponding to the SmA-N transition. The transition temperatures are gathered in Table 1.

Supramolecular organization in the mesophase

The mesophases of compounds **Cx-A**, **Cx-B** and **Cx-C** were studied by powder X-ray diffraction at room temperature in their frozen states. Prior to the X-ray measurements, each sample was heated up to the isotropic liquid, cooled down to the mesophase and then further cooled down to room temperature. The X-ray diffractograms confirmed in all cases that the mesophase freezes and crystallization does not take place, as suggested by the DSC thermograms and the POM observations.

The X-ray patterns of **Cx-A** and **Cx-B** recorded under these conditions are very similar (Figures 4a and 4b). The patterns contain in the low-angle region a set of three (two in the case of **Cx-B**) equally spaced sharp maxima that can be respectively assigned to the first, second and third order reflections from a lamellar structure. In the high-angle region a broad, diffuse halo

is detected and this corresponds to a mean distance of about 4.5 Å. This kind of X-ray diffractogram is characteristic of a smectic mesophase without positional order within the layer. Given the orthogonal character of these mesophases deduced from the presence of homeotropic domains in the textures observed by POM (*vide supra*), this supports the assignment of the mesophase of **Cx-A** and **Cx-B** as smectic A.

The spacings measured in the low-angle region of the patterns for **Cx-A** are 51.9, 25.9 and 17.4 Å. These values give a layer periodicity (lamellar thickness) of 51.9 Å. For **Cx-B** the measured spacings are 51.9 and 26.1 Å, giving a layer period of 52.0 Å (Table 1). The practically identical layer thickness measured for both compounds is not unexpected in view of the similarity of the chemical structures of their molecules, the only difference being the presence of the extra laterally attached OH groups in **Cx-B**, which do not affect the molecular length.

The layer thickness is significantly larger than the molecular length and this suggests that the mesophase adopts a bilayer structure. This is confirmed by simple calculations based on the generally accepted assumption that the density of organic compounds is close to 1 g cm⁻³. The density ρ of a smectic mesophase is related to the molecular mass M and the layer spacing d by the formula

$$\rho = (M \times Z \times 10^{24}) / (d \times S \times N_A)$$

where Z is the number of molecules per layer extending along the director ($Z = 1$ for a monolayer and $Z = 2$ for a bilayer), S is the molecule cross-section and N_A is Avogadro's number

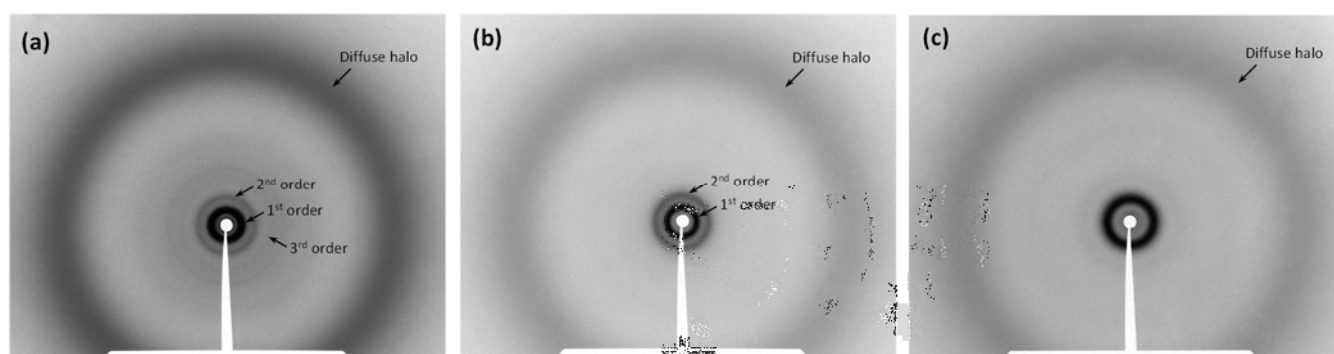


Figure 4. Room temperature XRD pattern of: (a) **Cx-A** in the SmA mesophase; (b) **Cx-B** in the SmA mesophase; (c) **Cx-C** in the N mesophase

Assuming $\rho = 1 \text{ g cm}^{-3}$, it is deduced that in the case of a monolayer structure one molecule ($Z = 1$) would fill a layer area S of about 80 \AA^2 . This would give a cross-section of 20 \AA^2 per hydrocarbon chain, a value too narrow considering that the tails are conformationally disordered in the mesophase and 20 \AA^2 would be the cross-section expected for a fully-extended all-*anti* hydrocarbon chain. The mesophase must therefore have a bilayer structure ($Z = 2$) that, with the aforementioned formula, gives a molecule cross-section of 160 \AA^2 , i.e., 40 \AA^2 per chain assuming a head-to-head association of two molecules. This value may seem too large at first sight, but it can be accounted for by the conformational disorder of the hydrocarbon chains and by the interpenetration between the tails of the two associated molecules and/or between the tails of molecules in neighboring layers. This interpenetration phenomenon is not unexpected in molecules with this peculiar geometry, which forces the tails on the wide rim apart from each other to distances larger than the usual separation between close-packed hydrocarbon chains. In the proposed bilayer structure the molecules form two sublayers with an opposite orientation: in each sublayer the narrow rim of the molecules, containing the decyloxy groups directly bonded to the macrocycle, must be oriented towards the interior of the layer and the wide rim, which contains the mesogenic units and their decyloxy groups, must be oriented towards the surface (Figure 5a). In this way, segregation of the different regions of the molecules takes place along the layer normal. A bilayer structure for the smectic mesophase of a similar calixarene was proposed by Armaroli and Nierengarten.^[28]

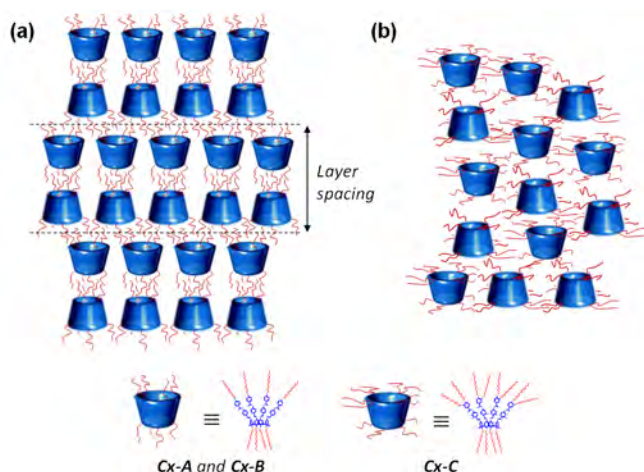


Figure 5. Proposed arrangement of: (a) **Cx-A** and **Cx-B** in the SmA mesophase, (b) **Cx-C** in the N mesophase.

For **Cx-C** the X-ray patterns are different from those obtained for **Cx-A** and **Cx-B** (Figure 4c). In the low-angle region only diffuse scattering is observed. In particular, two broad haloes corresponding to mean distances of about 32 and 16 \AA are detected. In the high-angle region a diffuse halo is observed corresponding to a mean distance of 4.5 \AA . This kind of pattern is consistent with a nematic mesophase. Indeed, the absence of Bragg reflections and the presence of diffuse intensity only indicate that there is no periodical order and thus smectic or columnar mesophases must be ruled out. The diffuse spots provide information about the mean distances between the molecules in the mesophase. The observed scattering in the low-angle region suggests that the molecules pack at a mean lateral distance of about 32 \AA (Table 1). In this case, the nematic mesophase is promoted by the presence of a total number of eight decyloxy chains in the wide rim of the molecules (Figure 5b). This precludes the adoption of an elongated shape, like the one adopted by **Cx-A** and **Cx-B**, and produces a flatter conformation.

However, in spite of this shape, **Cx-C** is unable to generate columnar mesomorphism probably because the decyloxy groups located on the narrow rim hinder the stacking.

Optical Properties.

UV/visible absorption and emission studies

The optical properties of compounds **Cx-A**, **Cx-B** and **Cx-C** were studied in chloroform [10^{-5} M] and the relevant bands are shown in the Supporting information (Table S2). The electronic absorption spectra of the ligands **Cx-A**, **Cx-B** and **Cx-C** were recorded over the 230–500 nm range and the calixarene-based ligand shows a band at 350 nm associated with azomethine $\pi \rightarrow \pi^*$ transitions.

Recognition Studies

A. Cation Recognition Studies.

The binding recognition and selectivity of calixarene derivatives **Cx-A**, **Cx-B** and **Cx-C** towards cations were studied by following their optical properties.

The absorption study was carried out in the range 230–500 nm in dichloromethane/acetonitrile solutions (1:1) by maintaining the ligand concentration at 16 μM throughout the experiment and varying the molar ratio of the added metal ion. The metal ions

studied were Li^+ , Na^+ , Cs^+ , Mg^{2+} as their perchlorate salts (2.29–2.68 mM) and Zn^{2+} and Pd^{2+} (1.70–2.59 mM) as their acetate salts. The recognition study on the ligands **Cx-A** and **Cx-C** shows that do not complex any of these cations.

The ligand **Cx-B** does not complex Li^+ , Na^+ , Mg^{2+} , Cs^+ or Pd^{2+} . (Supporting Information Figure S20). The ligand **Cx-B** complexes Zn^{2+} selectively. calix[4]arene **Cx-B** is a better chelator than calixarene **Cx-A** due to the orthophenol group of calixarene **Cx-B**.

The presence of the extra long C10 chain of calixarene Cx-C makes this molecule do not present the binding properties of calix[4]arene **Cx-B**.

The addition of Zn^{2+} to a solution of the ligand **Cx-B** is represented in **Figure 6** and changes can be observed in the absorption spectra at 261, 273, 341, 382 nm. In particular, when the calix[4]arene was titrated against Zn^{2+} , an increase was observed in the absorbance of the bands at 261, 382 nm along with a significant decrease in the bands at 273, 341 nm. Two isosbestic points were observed at 264 and 367 nm and all these indicate the coexistence of more than one complex after the zinc titration.

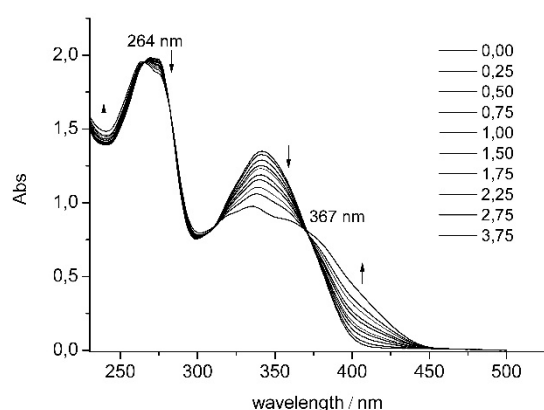


Figure 6. UV-vis spectra of **Cx-B** ($1.6 \cdot 10^{-5} \text{ mol L}^{-1}$) with different numbers of equivalents of Zn^{2+} .

In particular, when the transition metal salt of Zn^{2+} was introduced, the absorption at 341 nm was shifted to longer wavelengths due to complexation. The maximum absorption band at around 341 nm is associated with the free ligand **Cx-B** and this was shifted to 382 nm. Effectively, calix[4]arene **Cx-B** acts as a chelator due to the ortho-phenyl group and the imine of calixarene **Cx-B**.

B. Anion Recognition Studies.

Since the receptor molecules detect Zn^{2+} selectively, the *in situ* prepared zinc complexes were evaluated in an anion recognition study. The binding recognition and selectivity of these complexes towards anions were also studied by absorption and fluorescence.

The anions Cl^- , Br^- , I^- , HPO_4^{2-} and H_2PO_4^- were used as tetrabutylammonium salts. Runs were carried out in order to understand the removal of Zn^{2+} . As a result of these runs it can be stated that Zn^{2+} is not removed by the presence of the anions HPO_4^{2-} , Cl^- , Br^- and I^- . Similar results can be found in the literature¹⁹ but, in our case, the Zn^{2+} is removed selectively by the anion H_2PO_4^- .

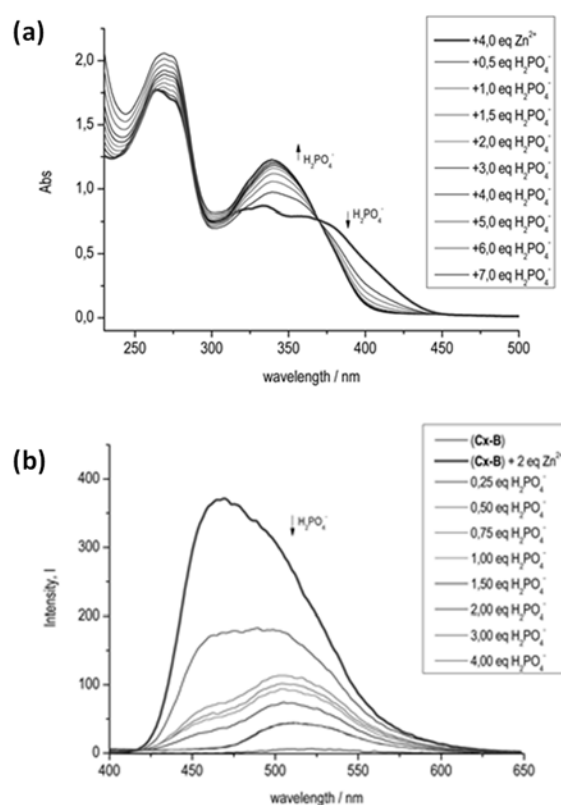


Figure 7. (a) Absorption data for the titration of zinc complexes of calixarene **Cx-B** with the addition of different quantities of H_2PO_4^- in dichloromethane/acetonitrile (1:1). (b) Fluorescence data for the titration of zinc complexes calixarene **Cx-B** with the addition of H_2PO_4^- ($5.2 \cdot 10^{-3} \text{ M}$) in dichloromethane/acetonitrile (1:1). $\lambda_{\text{exc}} = 340 \text{ nm}$.

The results of the titrations are shown in **Figure 7**, which represents the titration with H_2PO_4^- of a solution of the *in situ* prepared zinc complexes with four equivalents of Zn^{2+} . The absorption bands of the complexes observed at 382 nm were progressively shifted to 341 nm, which corresponds to the absorption of the free ligand **Cx-B**. These findings suggest the

disruption of the complexes with Zn^{2+} followed by the removal of Zn^{2+} by the H_2PO_4^- ions to result in the free ligand. The recovery of the absorption seems to be associated with a certain type of coordination between zinc and the calixarene. Indeed, the addition of the same number of equivalents of H_2PO_4^- as of zinc produces almost the same effect on the absorption as the addition of twice that number of equivalents, which is the quantity required to remove the zinc completely (Figure 7a).

Since the receptor molecule **Cx-B** detects Zn^{2+} selectively according to UV-vis, the *in situ* prepared complexes were also evaluated in anion recognition studies using a fluorescence technique.

Firstly, the calix[4]arene **Cx-B** was excited at 340 nm and the fluorescence was studied in dichloromethane/acetonitrile (1:1) with a ligand concentration of 2.7×10^{-5} M. Two equivalents of the Zn^{2+} cation were added and the corresponding emission was measured, with a marked increase in the emission observed with respect to the free ligand. The emission band maximum (514 nm) shifted to a shorter wavelength, 470 nm, and a blue shift of 44 nm was therefore observed. The fluorescence was improved because the metal ion is chelated through a phenolic oxygen and the imine nitrogen, with the lone pair of the nitrogen used in the complexation. A subsequent titration with H_2PO_4^- led to a gradual quenching of the original fluorescence intensity of the complexes due to the photoelectron transfer (PET) process from the lone pair of the nitrogen to the salicylidene moiety. This result shows that the zinc calixarene derivatives have a high selectivity and sensitivity towards the H_2PO_4^- anion (Figure 7b).

Characterization by Maldi.

After titration of **Cx-B** with 10 equivalents of Zn^{2+} , mass spectrometry was carried out to identify the complex **Cx-B**: Zn formed. Mass spectrometry peaks corresponding to the (1:1) and (1:2) complexes were found (Figure 8a).

The metal complexes formed *in situ* were titrated with 10 equivalents of H_2PO_4^- and it can be seen from Figure 8b that there is no evidence for the formation of zinc complexes, which means that Zn^{2+} has been removed by the presence of H_2PO_4^- .

It can be concluded that the removal of Zn^{2+} is completely reversible with the anion H_2PO_4^- .

Moreover, the prepared Zn polymer has been studied by UV (Supporting Information Figure S28) and MALDI and it shows the presence of a polymer molecule with peaks which can be attributed to **(C-B)Zn** and **(C-B)Zn₂** (Supporting Information

Figure S28(a)) and also to **(C-B)₂Zn**, **(C-B)₂Zn₂**, **(C-B)₃Zn₂**, **(C-B)₃Zn₃** and **(C-B)₃Zn₄**, **(C-B)₄Zn₃**, ... and **(C-B)₅Zn₄**, ... (Supporting Information Figure S28(b)).

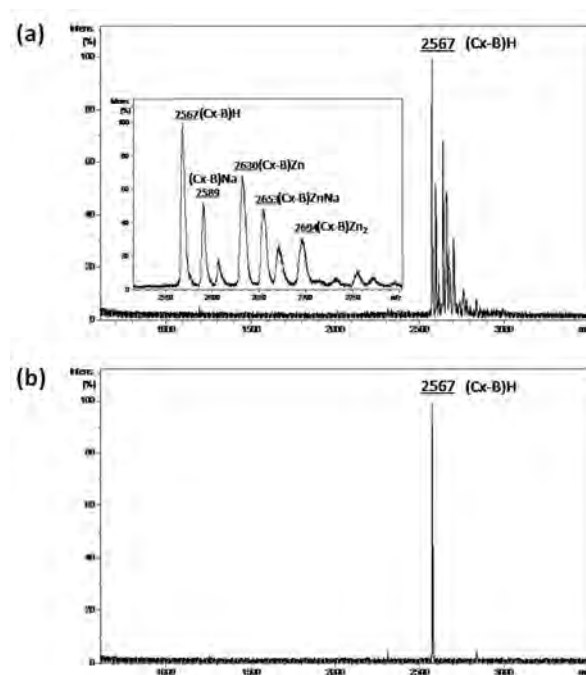


Figure 8. (a) Mass spectrum for the ligand **Cx-B** with Zn^{2+} . (b) Mass spectrum observed for calixarene **Cx-B** with Zn^{2+} after the addition of 10 equivalents of H_2PO_4^- .

Conclusions

We have successfully synthesized liquid crystalline calix[4]arene-appended Schiff bases that exhibit a smectic A mesophase or a nematic phase depending on the number of terminal chains.

XRD studies revealed interesting structural details concerning the packing of these compounds in their mesophases. On the basis of the experimental results, some supramolecular models have been proposed.

The three calix[4]arene derivatives, namely **Cx-A**, **Cx-B** and **Cx-C**, were subjected to metal complexation with different alkali, alkaline earth and transition metals. The UV-vis and emission studies show that calix[4]arene **Cx-B** shows selectivity towards Zn^{2+} . The emission intensity of the ligand was enhanced by complexation with Zn^{2+} metal and mass spectrometry indicated the coexistence of (1:1) and (1:2) complexes. In addition, a novel and effective off-on-off type dihydrophosphate derivative chemosensor has been developed based on Zn-complexes.

The preparation of Zn (II) metal complex of calix[4]arene Schiff base gives rise to the formation of a polymeric species instead of a discrete complex.

Supporting Information for this article includes: materials and general techniques, synthetic details and characterization, NMR spectra, POM microphotographs, DSC traces, Absorption and emission spectra, and MS spectra.

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