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### 1. Introduction

Liquid crystals (LCs) are fascinating soft materials which can build highly complex chemical structures through supramolecular self-assembly.<sup>1</sup> The development of functional soft materials has gained a huge momentum in recent years.<sup>2</sup> The columnar phase is a class of mesophase in which molecules assemble into cylindrical structures to act as mesogens.<sup>3–5</sup> The columnar structures formed by the one-dimensional stacking of disc-like mesogens are often termed as molecular wires and have the potential to be exploited as active layers in organic electronic devices. In the case of disc-shaped and bowl-shaped columnar LCs, the central core, which can facilitate pathways for charge-transfer carriers and the substitution of alkyl chains,

# Columnar self-assembly, electrochemical and luminescence properties of basket-shaped liquid crystalline derivatives of Schiff-base-moulded *p-tert*-butyl-calix[4]arene<sup>+</sup>

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A new family of supramolecular liquid crystalline compounds with a calix[4]arene core and two linking groups appended on four sides, exhibiting a wide range of hexagonal columnar phases, has been synthesised and well characterised. The liquid crystal behaviour of the novel materials was studied by using polarising optical microscopy (POM), differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA), and was further confirmed using high-temperature powder X-ray diffraction (XRD). An electrochemical study was carried out using cyclic voltammetry (CV) and the results were compared with theoretical values obtained from a DFT study. These compounds showed light sky-blue luminescence in solution and as a thin film under long-wavelength UV light. It was observed that all the prepared target compounds exhibited enantiotropic mesophases with good thermal stability. The structural and conformational characterisation of these new compounds was achieved using various spectroscopic techniques, including FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and MALDI-TOF. The relationship between the structure and the mesomorphic behaviour of the compounds containing an ethyl bridge with linked ester groups (**5a–5d**) is discussed. This new class of supramolecular derivatives is promising, especially considering the emissive nature and stabilisation of their columnar hexagonal mesophases, and their high range of thermal stability.

acts as an insulating mantle.<sup>6,7</sup> The self-assembly of relatively simple building blocks into complex ordered structures is a subject of increasing research towards gaining a fundamental understanding of soft-matter self-organisation.<sup>8</sup> This selfassembly is driven by shape anisotropy of the molecules, strong  $\pi$ - $\pi$  interaction and nano-segregation of incompatible molecular subunits, such as a central rigid core and peripheral flexible side chains.<sup>9</sup> Luminescent liquid crystalline materials have gained much interest recently owing to the inevitable need for white-light-emitting diodes in self-organisation, lighting and display applications.<sup>10</sup>

Calixarenes are cyclic oligomers obtained by the condensation reaction of 4-*tert*-butylphenol and formaldehyde.<sup>11</sup> Calixarenes can be obtained with different sizes and in good yields, by the judicious choice of base, reaction time, and temperature. Calixarenes are conformationally mobile; the four isomers of calix[4]arene are termed as the cone, partial cone, 1,3-alternate, and 1,2-alternate conformations. Calixarenes that are further functionalised at the upper and lower rim are useful for the encapsulation of metal ions and the formation of molecular assemblies.<sup>12</sup> Recent studies on calixarenes have shown that they possess specific self-assembly ability resulting from intermolecular



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forces, including coordination bonds,<sup>13</sup> hydrogen bonds,<sup>14</sup> ionic bonds and gelation.<sup>15</sup>

In 1990, Dalcanale and his group made the first liquid crystalline materials based on a calixarene core.<sup>16</sup> Calixarenebased liquid crystalline compounds represent a significant subgroup of macrocycle-based liquid crystals and have been investigated in several studies.<sup>17,18</sup> Yang et al. reported columnar liquid crystals based on a calix[4]arene core with inbuilt cholesterol moieties, which showed excellent mesomorphic properties with a good mesophase temperature range.<sup>19</sup> They also studied the mesophase, which exhibited a columnar-type molecular arrangement of calixarene and cholesterol derivatives.<sup>20,21</sup> Yang et al. synthesised and studied the liquid crystalline behaviour of calixarene-linked triphenylene derivatives.<sup>22</sup> Later on, his group reported the mesomorphic properties of gallic-calixarene derivatives, which exhibit a stable cone conformation.<sup>23</sup> Some calixarene derivatives based on Schiffbases showed smectic and nematic phase behaviour.<sup>24</sup> Later on, two groups reported calix[4]resorcinarene-based columnar liquid crystals containing a Schiff-base linking group.<sup>25,26</sup> In our previous study, we reported various luminescent liquid crystals based on calixarene with inbuilt thiadiazole- and oxadiazole-based derivatives, which exhibited excellent mesophase properties.<sup>27-29</sup> Very recently, our research group reported a bluelight-emitting thiacalix[4]arene core based on supramolecular liquid crystals which exhibited gelation and OLED properties.<sup>30</sup> Further, we also reported bowl-shaped fluorescent liquid crystals based on calix[4]arene and trans-cinnamic-acid derivatives, which showed smectic- and nematic-type mesophases.31

As part of our research program that focuses on developing new luminescent liquid crystals, we were interested to synthesise new basket-shaped supramolecular columnar liquid crystals to understand their structure-property relationship. Herein, we report the synthesis, characterisation, luminescence and thermal behaviour of calix[4]arene as a rigid core in supramolecular LCs, as well as discotic LC compounds. In this paper, we have prepared calix[4]arene-appended Schiff-base ester derivatives and studied their mesomorphic, electrochemical and photophysical properties.

### 2. Experimental and instrumentation

#### 2.1 Materials

4-*tert*-Butylphenol, 3,4-hydroxybenzaldehyde, 4-aminophenol, anhydrous  $K_2CO_3$ , and alkyl bromides (R-Br) were purchased from S. R. L., Mumbai. 1-Bromopropionic acid, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC-HCl), 4-dimethylaminopyridine (DMAP) and formaldehyde were purchased from Merck. Solvents were dried and purified in the usual manner.

#### 2.2 Measurements

The FT-IR spectra were recorded using KBr pellets on a Shimadzu FT-IR spectrophotometer in the range of 3800–600 cm<sup>-1</sup>. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on a Bruker Advance 400 MHz

spectrometer using tetramethylsilane as the internal standard. The synthesis of *p-tert*-butyl-calix[4]arene was carried out using a Discover Benchmate System 240 V microwave synthesiser (CEM corporation). The mesophase type was identified by visual comparison with known phase standards using a Nikon Eclipse LV-100 POL polarising optical microscope (POM) fitted with a hot-stage temperature-controlled LTSE 420 heating stage (Linkam Scientific Instruments, Tadworth, Surrey, UK) with a temperature control accuracy of 0.1 K. The phase transition temperatures were measured using a Shimadzu DSC-50 at heating and cooling rates of 10 °C min<sup>-1</sup>. The X-ray diffraction (XRD) measurements were performed on a Rigaku-Ultima IV powder diffractometer equipped with a Cu K $\alpha$  source ( $\lambda$  = 1.5418 Å and 1.6 kW, X-ray tube with applied voltage and current values of 40 kV and 30 mA power) and a Philips X'PERT MPD. The absorption spectra were obtained using a Jasco V-570 UV-Vis recording spectrophotometer with a variable wavelength between 200 and 800 nm. The fluorescence spectra were recorded on a Jasco FP-6500 spectrofluorometer.

### 3. Results and discussion

#### 3.1 Synthesis and characterisation

Scheme 1 shows the synthetic routes for the newly synthesised calixarene derivatives. The synthesis of *p-tert*-butyl-calix[4]arene (1a) was carried out using a microwave-assisted method.<sup>32</sup> *p-tert*-Butyl-calix[4]arene *tetra*-propionic acid (2a) was prepared according to a reported method.<sup>33</sup> 3,4-Di-*n*-alkoxybenzaldehyde derivatives (3a-3d) were prepared by refluxing a reaction mixture of 3,4-hydroxybenzaldehyde with various alkyl halides (R-Br) in the presence of anhydrous K<sub>2</sub>CO<sub>3</sub> and dry acetone using a reported method.<sup>34</sup> The 4-(3',4'-di-*n*-alkoxybenzylidene) aminophenol (4a-4d) was prepared by treating of 3,4-di-nalkoxybenzaldehyde (3a-3d) and 4-aminophenol in ethanol in the presence of a few drops of glacial acetic acid.<sup>35</sup> The <sup>1</sup>H NMR spectrum shows a singlet peak of -CH = N ( $\delta = 8.18$  ppm, -CH $\equiv$ N). In the FT-IR spectrum, the peak found at 1626 cm $^{-1}$ signifies the presence of an imine linking group (CH=N stretch). The final target compounds (5a-5d) were prepared by using EDC HCl and DMAP as catalysts in DCM solvent for 24 hours.<sup>36</sup> The resultant crude residue was purified using column chromatography on silica gel with methanol:chloroform (1:4) as the eluent. The *tetra* substitution on the lower rim of *p-tert*-butyl-calix[4]arene is evidenced by the absence of -OH groups in the <sup>1</sup>H NMR and FT-IR studies. In the ESI,<sup>†</sup> we show the synthesis and characterisation part of the final target derivatives: 5a, 5b, 5c and 5d. From the <sup>1</sup>H NMR spectra, the cone shapes of the compounds were confirmed by the presence of two singlets at 3.28 ppm and 4.23 ppm, respectively. All the analytical results are well supported by the corresponding structures of the final target compounds (5a-5d) and can be found in the ESI.<sup>†</sup>

#### 3.2 DSC analysis

The mesomorphic behaviours of compounds **5a**, **5b**, **5c** and **5d** were preliminarily investigated by differential scanning calorimetry

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Scheme 1 (i) HCHO, NaOH, microwave, 15 min; (ii) Br– $(CH_2)_n$ –COOH, (n = 2), anhydrous K<sub>2</sub>CO<sub>3</sub>, dry acetone; (iii) R-Br, anhydrous K<sub>2</sub>CO<sub>3</sub>, dry acetone (R = C<sub>n</sub>H<sub>2n+1</sub>, n = 4, 8, 12, 14); (iv) 4-aminophenol, EtOH, few drops of glacial acetic acid (as a catalyst); (v) EDC·HCl, DMAP, DCM, 24 h stirring at room temperature.

(DSC). The transition temperatures and the associated enthalpy changes obtained from the DSC scans of the second heating– cooling cycles are shown in Table 1 and Fig. 1. Fig. 2 summarises the thermal behaviour of these synthesised samples in the heating cycle. All of the synthesised compounds exhibit three endothermic peaks on heating and two exothermic peaks on cooling.

Table 1	Phase transition	temperatures (°	C) <sup>a</sup> and	corresponding	enthalpies	(kJ mol <sup>-1</sup>	<sup>L</sup> ) of synthesised	compounds
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	Phase sequence					
Compound	Heating	Cooling				
5a	Cr 25.3 (62.2) Cr <sub>1</sub> 89.8 (73.2) Col <sub>b</sub> 146.4 (34.2) I	I 143.6 (31.3) Col <sub>b</sub> 90.6 (57.1) Cr				
5b	Cr 23.2 (51.2) Cr <sub>1</sub> 86.2 (73.4) Col <sub>h</sub> 138.9 (30.6) I	I 141.1 (19.7) Col <sub>h</sub> 81.4 (53.5) Cr				
5 <b>c</b>	Cr 18.9 (67.2) Cr <sub>1</sub> 70.6 (86.9) Col <sub>b</sub> 126.2 (24.3) I	I 127.8 (34.2) Col <sub>b</sub> 76.1 (46.4) Cr				
5d	Cr 13.6 (40.1) Cr <sub>1</sub> 62.5 (68.2) Col <sub>h</sub> 120.7 (44.8) I	I 122.9 (30.6) Col <sub>h</sub> 60.9 (41.6) Cr				

<sup>a</sup> Peak temperatures in the DSC thermograms obtained during the second heating and cooling cycles at 10 °C min<sup>-1</sup>.



Fig. 1 The DSC traces of compounds 5a (a), 5b (b), 5c (c) and 5d (d), on second heating and cooling (scan rate 10 °C min<sup>-1</sup>).



Fig. 2 Bar graphs showing the thermal behaviour of compounds 5a-5d on (a) heating cycle and (b) cooling cycle.

Compound 5a with a butyloxy group shows three endothermic peaks corresponding to crystal-to-crystal (Cr-Cr<sub>1</sub>), crystal-tomesophase (Cr1-Colh) and mesophase-to-isotropic liquid (Colh-I) transitions. The observed mesophase spans over a good thermal range of 64.5 degrees with an isotropic temperature of 146.4 °C. The isotropic liquid on cooling showed the commencement of a columnar mesophase at 90.6 °C, which was further confirmed by POM analysis. Further, three endothermic peaks appear at 23.2 °C, 86.2 °C and 138.9 °C for compound 5b, 18.9 °C, 70.6 °C and 126.2 °C for compound 5c, and 13.6 °C, 62.5 °C and 120.7 °C for compound 5d on heating. Two exothermic peaks appear at 81.4  $^\circ$ C and 141.1  $^\circ$ C for compound 5b, 76.1 °C and 127.8 °C for compound 5c, and 60.9 °C and 122.9 °C for compound 5d upon cooling. It can be seen that the compounds 5a-5c show a higher temperature range for the mesophase compared to compound 5d, which is substituted by a dodecyloxy tail group. These phenomena

suggest that the lower alkyl chain substitution on the lower rim of calix[4]arene is more favourable for increasing the phase transition temperature and further enhancing the scope of the mesophase temperature. The results obtained from the DSC study were further confirmed by POM and XRD analysis.

#### 3.3 POM investigation

The transition temperatures of the newly synthesised compounds were further investigated using polarising optical microscopy (POM) by observing the texture when a sample was sandwiched between a glass slide and a cover slip. All of the synthesised materials under crossed polarisers display a texture pattern of a columnar-type mesophase. It is interesting to note that the texture pattern images show a hexagonal columnar phase (Colh), which is commonly observed for columnar-type mesophase materials. The observed texture patterns for compounds **5a**, **5b**, **5c** and **5d** are shown in Fig. 3. Compounds **5a**, **5b**, **5c** 



Fig. 3 Photomicrographs of **5a** at 93.1 °C (a), **5b** at 84.2 °C (b), **5c** at 76.4 °C (c) and **5d** at 66.6 °C (d) on heating from the solid crystalline state as seen under cross polarisers.

and **5d** show similar texture patterns of their hexagonal columnar phase (Colh) at 88.4 °C, 84.2 °C, 72.4 °C and 66.6 °C and become isotropic liquids at 148.7 °C, 144.2 °C, 129.6 °C and 124.1 °C on heating. Moreover, one can see that compound **5b** shows a higher mesophase temperature range compared to the other synthesised derivatives. This result indicates that the mesophase temperature range is largely dependent on the substitution of lower alkyl chains in the synthesised compounds. On cooling, the same textural pattern of the Colh phases was observed before the formation of solid crystals at lower temperature. Thus, an enantiotropic mesomorphic behaviour over a broad thermal range of the mesophase was seen for the synthesised basket-shaped supramolecular calixarene derivatives.

#### 3.4 XRD analysis

The liquid crystalline behaviour of two supramolecular calixarene-based LCs (5a and 5c) was further confirmed by X-ray scattering studies of unoriented samples filled in Lindemann capillaries. Powder XRD measurements were performed at the transition temperatures observed using POM to confirm the mesophases exhibited by the compounds 5a-5d. One can see that all four derivatives showed three reflections in the small-angle region and another two diffuse peaks at the highangle region (Fig. 4 and Fig. S1, ESI†). The XRD pattern of compound 5a at 88.0 °C shows three reflections at 3.2°, 5.3° and  $6.7^{\circ}$  in the small-angle region and the observed *d*-spacing values are 27.59 Å, 16.67 Å and 13.20 Å, respectively. Similarly, compound 5c exhibits three reflections at  $2.8^{\circ}$ ,  $5.8^{\circ}$  and  $7.1^{\circ}$ and the observed d-spacing values are 31.53 Å, 15.24 Å and 12.45 Å, respectively. There are three reflections at  $3.1^{\circ}$ ,  $5.1^{\circ}$  and  $6.5^{\circ}$  for compound **5b**, and  $2.4^{\circ}$ ,  $5.01^{\circ}$  and  $6.3^{\circ}$  for compound 5d in the small-angle region, and the observed *d*-spacing values are 28.48 Å, 17.34 Å and 13.60 Å for compound 5b and 36.78 Å, 17.63 Å and 14.03 Å for compound 5d, respectively. The ratio of these present reflections agrees with  $1:1/2:1/\sqrt{3}$ , suggesting



Fig. 4 XRD patterns recorded for compound **5a** at 88.0  $^{\circ}$ C (a) and **5c** at 74  $^{\circ}$ C (b) on cooling from isotropic temperature.

the presence of [100], [110] and [200] planes of a hexagonal lattice.  $^{20}$  There are two diffuse peaks at 19.8  $^{\circ}$  and 23.7  $^{\circ}$  for compound 5a,  $18.9^{\circ}$  and  $22.6^{\circ}$  for compound 5b,  $19.4^{\circ}$  and 21.1° for compound 5c, and 19.8° and 21.3° for compound 5d, with observed *d*-spacing values in the range of 3.81–4.63 Å. In the wide-angle region, the first diffuse reflection appears, which corresponds to the ordering of bridging alkyl chains in alkoxy side groups (-OR), while the second diffused reflection favours the ordered packing arrangement of the hexagonal phase. A literature survey indicated that similar XRD traces have been reported for calixarene-based LCs on the lower and upper rim side.<sup>21-23</sup> The estimated molecular lengths of compounds 5a and 5c are approximately 29.32 Å and 32.17 Å, which almost correspond to the observed molecular lengths. The proposed mechanism of the synthesised compounds indicates the prearrangement of the self-assembly process for the novel basket-shaped supramolecular Schiff-base calixarene derivatives, which arrange to form columnar hexagonal (Col<sub>b</sub>) mesophases in compounds 5a-5d, as shown in Fig. 5.

#### 3.5 Photophysical behaviour

*p-tert*-Butyl-calix[4]arene, with various groups and possible  $\pi$ -conjugation between the long alkoxy peripheral side chains and central rigid core, exhibits promising photophysical properties, which are tabulated in Table 2. The absorption and fluorescence spectra of the compounds **5a–5d** were recorded in



Fig. 5 Schematic representations of the columnar hexagonal molecular arrangements (5a).

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

Comp.	Absorption <sup>a</sup> (nm)	Emission <sup>a</sup> (nm)	Stokes shift (nm)	Quantum yield <sup>c</sup>	$(\epsilon/10^6 \text{ L mol}^{-1} \text{ cm}^{-1})$	Absorption <sup>b</sup> (nm)	Emission <sup>b</sup> (nm)	Quantum yield <sup>b</sup>
5a	356	446	90	0.57	19.6	358	441	0.51
5b	354	441	87	0.67	22.8	361	443	0.62
5 <b>c</b>	350	438	88	0.58	23.4	366	447	0.49
5d	348	432	84	0.71	25.6	368	450	0.63

<sup>*a*</sup> Micromolar solution in THF, excited at the respective absorption maxima. <sup>*b*</sup> Emission obtained by exciting the thin films at their respective absorption maxima in solution. <sup>*c*</sup> Relative quantum yield calculated with respect to quinine sulphite solution in 0.1 M  $H_2SO_4$  with a quantum yield of 0.54.

1.4 (a) 350 **(b)** 1.2 THE 300 DCM Chloroform MeCN DMF THF DCM Chloroform MeCN Absorbance (a.u.) 1.0 250 Intensity (a.u.) 0.8 200 DMF 0.6 150 0. 100 0.2 5( 450 550 650 350 750 650 350 450 550 750 Wavelength (nm) Wavelength (nm) (d) (c) 350 1.4 300 1.2 Absorbance (a.u.) 250 1.0 Intensity (a.u.) 200 0.8 5c 0.0 100 0.4 50 0.2 450 550 650 750 450 550 650 750 350 350 Wavelength (nm) Wavelength (nm)

Fig. 6 (a) Absorption and (b) fluorescence spectra of compound **5a** in different solvents. (c) Absorption and (d) fluorescence spectra of compounds **5a–5d** in THF solution (5  $\mu$ M).

anhydrous THF, and are shown in Fig. 6 and 7. Solvent screenings of compound **5a** were performed in various solvents, including THF, DCM, chloroform, MeOH and DMF, revealing changes in its optical properties (Fig. 6a and b) which further confirm the proposed intramolecular charge-transfer mechanism.<sup>37</sup> Upon irradiating the solution, compound **5a** exhibits an absorption maximum centred at 356 nm, while the values are 354 nm for compound **5b**, 350 nm for compound **5c** and 348 nm for



Fig. 7 (a) Absorption and (b) fluorescence spectra of compounds **5a–5d** in solid thin film state.

compound 5d. A fluorescence maximum was observed at around 446 nm for compound 5a, 441 nm for compound 5b, 438 nm for compound 5c and 432 nm for compound 5d. The highly delocalised electronic systems exhibit  $\pi - \pi^*$  and  $n - \pi^*$ transitions from the central core to the peripheral side chains (-OR). The molar absorption coefficient was found to be in the range of  $\varepsilon$  = 19.6–25.6 × 10<sup>6</sup> L mol<sup>-1</sup> cm<sup>-1</sup> for the synthesised basket-shaped materials. The absorbance and fluorescence wavelengths cannot be affected by changing the side alkoxy chain on the lower rim of the calixarene core, but can be affected by the intensity of the absorbance and fluorescence of the parent compounds (5a-5d). As can be seen, all derivatives showed sky-blue fluorescence in solution as well as in a solid thin film. The Stokes shifts for all four derivatives are in the desirable range of 84-90 nm. The appearance of luminescence at a higher wavelength than the absorption wavelength is in good agreement with the common explanations. It can be observed that the various substitutions on the calixarene core only at the peripheral side could slightly affect their Stokes shift. The emission spectra showed one stable maximum band in the range of 432-446 nm, which is recognised as the electronic transition from lowest unoccupied molecular orbital to the highest occupied molecular orbital. The quantum yield represents the percentage photon emission and is important for assessing fluorescent molecules. Relative quantum yields of the compounds (5a-5d) were measured with respect to quinine sulphate 0.1 N sulfuric acid solution with a quantum vield of 0.54, and was found to be in the range of 0.57-0.71 (Table 2). Thin films of the supramolecules were produced by drop-casting on glass slides. The absorption and emission wavelengths of the thin films are slightly higher than the solution spectra and show redshifting, due to the presence of aggregation and intermolecular interactions.38

#### 3.6 TGA analysis

The thermal stability of compounds **5a–5d** was further studied by thermogravimetric analysis (TGA), as shown in Fig. 8. The TGA of compounds **5a** and **5b** shows only 6% weight loss from 160 °C to 240 °C. The TGA of compound **5c** and **5d** shows 8% weight loss from 180 °C to 300 °C, which demonstrates the good thermal stability of the Schiff-base-moulded calixarene compounds. One can see that there is no observed weight loss up to 150 °C, which clearly indicates that there is no water or other solvent captured in the mesomorphic state. All the derivatives exhibit good thermal stability. The thermal stability



of the lower chain substituted materials (**5a** and **5b**) showed slightly lower thermal stability as compared to the higher chain substituted materials (**5c** and **5d**). This is due to the presence of periphery higher alkyl side groups, which stabilised the mesophase more than the lower alkyl side groups. All the derivatives degrade completely at or above 300 °C.

#### 3.7 Electrochemical study

Cyclic voltammetry (CV) is a potentiodynamic electrochemical method which provides information about the electrochemical properties of molecules in solution. In CV studies, the observed onset of reduction and oxidation potential values estimate the HOMO and LUMO values and further provide information regarding electron band gap  $(E_g)$  of the molecules. The synthesised Schiff-base-moulded supramolecular calixarene derivatives were investigated for their electrochemical behaviour by carrying

Table 3 Electrochemical properties of compounds 5a-5d

Comp.	E <sub>oxd</sub>	E <sub>red</sub>	E <sub>HOMO</sub>	$E_{\rm LUMO}$	$\Delta E_{\rm g}$ , CV	EA	PI
5a	1.87	$-1.59 \\ -1.62 \\ -1.64 \\ -1.67$	-6.10	-2.64	3.46	6.10	2.64
5b	1.91		-6.14	-2.61	3.53	6.14	2.61
5c	1.93		-6.16	-2.59	3.57	6.16	2.59
5d	1.92		-6.15	-2.56	3.56	6.15	2.56

Experimental conditions: reference electrode (Ag/AgNO<sub>3</sub>), counter electrode (platinum electrode), working electrode (glassy carbon), supporting electrolyte (0.1 M TBAP).

out cyclic voltammetry experiments in THF solvent. For organic semiconductor materials, the highest occupied molecular orbital (HOMO) indicates the energy required to extract an electron from the molecules via oxidation and the lowest occupied molecular orbital (LUMO) means the energy required to inject an electron into the molecule via reduction. The cyclic voltammograms of compounds 5a-5d look similar, with oxidation and reduction wave potential peaks (Fig. 9). The observed values of the HOMO, LUMO, energy levels, electron affinity (EA), ionisation potential (PI) and calculated energy band gaps are tabulated in Table 3. In the present experiment, an Ag/AgNO<sub>3</sub> (0.1 M) reference electrode, platinum rod counter electrode and glassy carbon working electrode were used in a single-compartment cell. The reference electrode in this experiment was calibrated with a ferrocene/ferrocenium redox couple with an absolute energy level of -4.80 eV.<sup>39,40</sup> In this experiment, the solution of the supporting electrolyte is THF containing a 0.1 M solution of tetra-butylammonium perchlorate (TBAP). The scanning rate for recording the cyclic voltammograms was 0.05 mV s<sup>-1</sup>. The lower alkyl chain substituted Schiff-base-moulded supramolecular derivatives (5a and 5b) showed a lower band gap value as compared to higher alkoxy side chain substituted derivatives (5c and 5d), which clearly indicates the higher reactivity of the lower chain substituted



Fig. 9 Cyclic voltammograms of (a) 5a, (b) 5b, (c) 5c, and (d) 5d in anhydrous THF solution of TBAP (0.1 M) at a scanning rate of 0.5 mV s<sup>-1</sup>.



Fig. 10 Optimised geometries, HOMO and LUMO energy levels of compound **5a** (a-c), and compound **5b** (d-f), obtained by DFT calculations at the B3LYP/31G (dp) level.

calixarene materials. The LUMO and HOMO energy levels were calculated by using the formula  $E_{\text{LUMO}} = -(4.8 - E_{1/2}, \text{Fc}, \text{Fc}^+ + E_{\text{red}}, \text{onset})$  eV and  $E_{\text{HOMO}} = -(4.8 - E_{1/2}, \text{Fc}, \text{Fc}^+ + E_{\text{oxd}}, \text{onset})$  eV, respectively. All the synthesised materials (**5a–5d**) show LUMO energy levels of -2.64 eV, -2.61 eV, -2.59 eV and -2.56 eV, while the HOMO energy levels are -6.10 eV, -6.14 eV, -6.16 eV and -6.15 eV. All four derivatives (**5a–5d**) showed band gaps ( $E_g$ ) of 3.46 eV, 3.53 eV, 3.57 eV and 3.56 eV, demonstrating their good reactivity. A lower band gap is more favourable for optoelectronic device applications. The band gap values obtained from CV are in good agreement with the results from the DFT study. Further, out of all of the synthesised compounds, compound **5a** was found to be more reactive because of the lower HOMO–LUMO energy gap, while compound **5c** is more stable with its slightly higher band gap value.

#### 3.8 Cone confirmation and DFT study

The conformation of the parent *p-tert*-butyl-calix[4]arene core and its functionalised derivatives were analysed in terms of four different conformations, cone, partial cone, 1,2-alternate and 1,3-alternate, arising from different modifications on the upper and lower rims, respectively.<sup>41</sup> In the present case, all of the synthesised *p-tert*-butyl-calix[4]arene derivatives adopt a cone conformation as confirmed using <sup>1</sup>H NMR and <sup>13</sup>C NMR techniques. In the <sup>1</sup>H NMR spectroscopy results, all derivatives show two singlets (1:1) for a *tert*-butyl group substituted on the upper side, and also one pair of doublets (1:1) for a methylene bridge (-CH<sub>2</sub>) at around 3.66 ppm and 4.22 ppm, indicating

Table + Energenes and structural properties of the calivarenes	Table 4	Energetics and	structural	properties	of the	calixarenes
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Comp.	HOMO (a.u.)	LUMO (a.u.)	Gap (LUMO– HOMO) a.u. (eV)	Total energy (a.u.)	Dipole moment (Debye)
5a	-0.28871	-0.15711	0.1316 (3.581)	-6553.96	16.254
5b	-0.28865	-0.15693	0.1317 (3.583)	-6780.19	16.596
5 <b>c</b>	-0.29471	-0.16273	0.1319(3.589)	-7257.45	16.435
5d	-0.29440	-0.16229	0.1321 (3.594)	-8161.67	17.012

1 a.u. = 27.2116 eV = 627.509 kcal mol<sup>-1</sup>.

protons in different environments, such as axial and equatorial positions. In addition, the spectra show two singlets (1:1) for aromatic hydrogen, which confirm the presence of a cone conformation of the *p-tert*-butyl-calix[4]arene unit functionalised at the lower side. The symmetries of non-equivalent protons of the methylene groups in the cone conformation are called axial and equatorial by their similarity to the nomenclature commonly used for protons. The peaks for -C=O and -OCH<sub>2</sub> at nearly 158-160 and 72-74 ppm in the <sup>13</sup>C NMR spectrum confirm the cone shape of the synthesised materials.42 The optimised geometries of the target Schiffbase-moulded calixarene derivatives (5a and 5b), along with their HOMO and LUMO energy levels, were evaluated using Density Functional Theory (DFT) calculations at the B3LYP/ 6-31G(dp) level, as depicted in Fig. 10a-f. The optimised structures of all four derivatives clearly suggest that the geometries of all supramolecular compounds are basically cone shaped. The HOMO, LUMO, band gap  $(E_g)$ , dipole moment and total energies of compounds 5a-5d are tabulated in Table 4. One can see that the total energy and dipole moment of the lower alkyl chain substituted compounds (5a and 5b) is lower compared with the higher chain substituted compounds (5c and 5d). This is because of the substitution of the highly polar peripheral alkyl chain group on the terminal side.

# 4. Conclusion

We herein reported a family of novel Schiff-base supramolecular luminescent liquid crystals based on a *p-tert*-butyl-calix[4] arene core substituted with various peripheral alkoxy groups on the terminal side chains. These molecules show sky-blue emission in solution as well as in the solid thin film state with good quantum yield. The blue-light-emitting materials exhibited columnar hexagonal (Col<sub>h</sub>) liquid crystals with good thermal and photophysical properties. The Schiff-base-moulded calixarene self-assembled to form an ordered hexagonal columnar phase with a good mesophase temperature range. The length of the side alkoxy spacer had no effect on the absorption and emission properties in the solution state but did affect their intensity. All homologues show a high temperature range of the mesophase with good thermal stability. All supramolecular functionalised *p-tert*-butyl-calix[4]arene-based derivatives adopted a cone confirmation, which was proven from <sup>1</sup>H NMR, <sup>13</sup>C NMR and DFT calculations. In essence, these basket-shaped blue-lightemitting supramolecular compounds are promising due to their columnar hexagonal phase, self-assembly, electrochemical and photophysical properties and their potential for the fabrication of OLEDs, organic optoelectronic devices and solar cells.

# Conflicts of interest

There are no conflicts to declare.

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