Bowlics: history, advances and applications

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ABSTRACT
There are three types of liquid crystals (LCs) in the world: rodics, discotics and bowlics, corresponding to one-, two- and three-dimensional molecules, respectively. The rodics were discovered by the Austrian, F. Reinitzer, in 1888 and is the material behind the LC display industry of $100 billion annually. The discotics were discovered by S. Chandrasekhar’s team in India, in 1977. The third type, bowlics, was proposed by a Chinese, LIN Lei (Lui LAM), in 1982 while working at the Institute of Physics, CAS, Beijing. Distinguished from the rodic and the discotic, a bowlic molecule breaks the up-down symmetry, and bowlic LCs are one of excellent candidates for switchable ferroelectrics with great potential applications in ultrahigh-density memory devices. The importance of strategic bowlic materials has recently attracted increasing attention of scientists from multiple disciplines and engineers from different backgrounds. In this review, the history of bowlics and their recent advances in molecular design, synthesis and applications are discussed.

1. Introduction
Liquid crystals (LCs) are known as the fourth state of matter after solid, liquid and gaseous states[1]. Due to the unique combination of orientational order and fluidic properties, LCs are now playing an increasingly significant role in bio-science, materials science, nanoscience and nanotechnology. The research of LCs has highly evolved from just a scientific curiosity in the beginning to the truly interdisciplinary and cutting-edge sciences that combine basic aspects of physics, chemistry, engineering and biology [2–17]. LCs have become quintessential materials in our daily life since the first discovery of LC phase in rodic (rod-like) molecules by the collaboration of Austrian botanist F. Reinitzer and German physicist Otto Lehmann in the nineteenth century (Figure 1(a)) [18,19]. LC displays (LCDs) based on rodic LCs have become one of the most important foundations of modern advanced information technology, which dominate the global market of advanced information displays with an annual worth of more than $100 billion and drastically revolutionised the way that information is presented [20–26]. In 1977, Indian chemist S. Chandrasekhar demonstrated that not only rodic molecules but also discotic (disc-like) molecules could form liquid-crystalline phases as envisioned by theoretical simulation (Figure 1(b)) [27–29]. Discotic LCs have now been considered as a new promising generation of organic semiconductors as well as mesophase semiconductors due to their remarkable electronic and optoelectronic device performances [30–32]. Interestingly, ferroelectricity was discovered in the symmetry-breaking liquid-crystalline systems including chiral rod-like molecules, chiral discotic molecules and non-chiral banana-shaped molecules, which led to a very intense research activity of polar LCs [33–35].

In 1982, Chinese physicist LIN Lei (Lui LAM) first proposed the concept of bowlic (bowl-like) LCs by considering the ‘dimensionality’ of molecules (Figure 1(c)) [36]. He pointed out that in bowlic mesophases, the steric effect of molecules makes the compensation of permanent dipoles difficult and then the \( n \rightarrow -n \) symmetry (where \( n \) is the director) valid in the rodic and the discotic may break down. Therefore, bowlic LCs may possess some special physical properties, such as genuine ferroelectricity, second-harmonic generation (SHG) etc. [37–40]. The experimental existence of bowlic monomers (Figure 2(a)) was soon reported in cyclotri-teravatylene (CTV)-based bowlic molecules by European scientists in 1985 (also called pyramidal [41] or cone-shaped [42]), and X-ray structural study of these mesophases was carried out [43]. Furthermore, bowlic polymers were also predicted by Lin in 1988 [44] and synthesised by Er-Man Zeng, a Chinese PhD student while doing his PhD thesis at Georgia Institute of Technology, USA [45]. Distinguished from the rodic...
and discotic molecules, a bowlic molecule is truly three dimensional (3D); bowlic molecules are asymmetric in the up and down direction. Bowlic molecules may have different symmetries as shown in Figure 2(b) and the corresponding phases could be either uniaxial or biaxial. The packing of bowls into columns may have specific features. For example, when all molecules in the column are oriented bottom down, then the head-to-tail symmetry is broken and the column has conical, i.e. polar symmetry C∞v (Figure 2(c)). Only polar columns may form ferroelectric or antiferroelectric phases shown in Figure 2(d) [46]. In the bowlic columns, the cones are embedded into one another with the same orientation, making the column axis polar. Such mesophases might therefore be ferroelectric, if all the columns adopted the same polarisation direction within a macroscopic domain [47]. The unprecedented characteristics of bowlic LCs could lead to new types of LCD with very fast response times and open a brand-new door for the development of ferroelectric or antiferroelectric soft materials with great potential applications in ultra-high-density memory devices and beyond. Since the discovery, a large number of bowlic molecules with different LC phases have been designed and synthesised. In 1996 at the 16th International Liquid Crystal Conference in Kent, Ohio, the Glenn Brown Award for best PhD thesis was awarded to Bing Xu from Timothy Swager’s group at University of Pennsylvania, for his work on bowlic LCs [48]. Recently, switchable ferroelectric columns have been demonstrated in bowlic LCs.
and liquid-crystalline behaviours of colloidal bowl-shaped nanoparticles have been investigated [50]. The term bowlic or bowlic LC is now recognised officially by the IUPAC [51] and formally in Handbook of Liquid Crystals [52].

In this review, we will start with the CTVs-based bowlic LCs, where the effects of functional moieties such as flexible chains, mesogenic groups and dendritic molecules on the liquid-crystalline behaviours are discussed. We then introduce the design, synthesis and properties of calixarene-based bowlic LCs with calamitic and discotic substitutions. We also address the new advances in bowlic LCs including supramolecular bowlics, corannulene LCs, subphthalocyanine LCs, liquid-crystalline peptidic macrocycles and colloidal bowl-shaped nanoparticles. The last section of this review provides a perspective for the future scope of these emerging areas of bowlic LCs. It should be noted that this work will not include all accomplishments in this research field but rather points to important developments by selecting representative examples from different research topics. We hope that this review will arouse increasing attentions of more researchers to such promising topics and future efforts would not only broaden our knowledge of soft matter but also promote their diverse applications as intelligent advanced functional materials.

2. CTV-based LCs

2.1. CTVs with flexible chains

CTVs were first synthesised by Gertrude Robinson in 1915 but misdiagnosed as the dimer [53]. In 1965, Lindsey identified the correct structure and coined CTV as the name for the compound [54]. CTVs could exhibit either a crown conformation or a saddle conformation [55]. Its crown conformation provides a bowl-shaped structure, giving the molecule C₃ symmetry [56,57]. In 1985, Zimmermann et al. [41] and Malthete et al. [42] first reported the liquid-crystalline behaviours of CTV-based bowlic molecules. Zimmermann et al. designed and synthesised two series of mesogenic compounds consisting of a rigid CTV central core and six equal flexible side chains, and their mesomorphic properties were studied by calorimetry and optical microscopy [41]. Two series of compounds are 1-hexaalkyloxytribenzocyclononene (compounds 1–10 in Table 1) and II-hexaalkanoyloxytribenzocyclononene (compounds 11–18 in Table 1). In series I, thermodynamically stable mesophases began to appear when the number of carbon atoms in each side chain, n, is equal to or larger than six (n ≥ 6), while for series II, all the compounds were found to exhibit mesomorphism (n = 8–15). They called these mesophases pyramidal mesophases (P), which are in fact bowlic mesophases. They claimed that the mesophases P_A and P_C were optically uniaxial, while P_B and P_D were biaxial. Enantiotropic pyramidal mesophases were further observed in another homologous series of hexasubstituted tribenzocyclononene derivatives [19–22] [58]. Interestingly, these mesophases were found to exhibit an uncommon feature in that their optical anisotropy changed sign as function of temperature within the mesophase region. They assumed that these phases had columnar structures similar to those occurring in the conventional columnar discotics, which were confirmed by X-ray characterisations [43,59,60].

Budig et al. investigated the influence of heteroatoms and branchings on the liquid-crystalline properties of CTV derivatives [23–36] by incorporating heteroatoms (O or S) in different positions in the lateral chains (Table 2) [61]. Owing to the high melting points of compounds 23 and 24, no mesophase was detected for these short-chain derivatives. All other esters displayed columnar mesophases, and the mesophase stability of the 3-oxaalkanoates was found to increase in comparison to the corresponding alkanoates. For example, compound 29 exhibits a clearing temperature which is ~30°C higher than that of the corresponding n-alkanoate 17. Compound 31 that incorporated a divalent sulphur atom displayed approximately the same clearing temperature as the corresponding carbon analogue. Compounds 31–34, in which the ether oxygens are shifted to the fourth positions, were found to exhibit a lower mesophase stability than the corresponding nalkanoates and the compounds with oxygen atoms in the third positions of the lateral chains. The cyclotribenylenes derivatives 35 and 36, with bromine atoms or cyano groups at the termini of the side chains, did not display any liquid-crystalline phase. Moreover, it is particularly remarkable that branches in the middle of the lateral chains not only widened the mesophase range but also stabilise the mesophases significantly. The clearing temperatures of the branched compounds 30 and 34 are significantly higher than those of the comparable non-branched compounds. The mesophases of these cyclotribenzenes were studied by polarising microscopy and X-ray diffraction (XRD) measurements. For example, Figure 3 shows the liquid-crystalline textures of compounds 25 and 29 and the corresponding XRD patterns. The pattern of 25 displays a large number of interferences in the small-angle region (Figure 3(c)), which could be evaluated only on the base of an oblique cell (i.e. oblique
columnar phase D_{ob}). The pattern of compound 29 proves the existence of a hexagonal lattice (i.e. hexagonal columnar phase D_{hd}).

2.2. CTVs with mesogenic moieties

Lunkwitz et al. reported two homologous series of CTV-based bowlic LCs 37–55 in which six calamitic cyanobiphenyl or phenylthiadiazole rigid cores were introduced via flexible spacers of different length to the macrocyclic cyclotribenzylene unit (Table 3) [62]. In the series of 4-cyanobiphenyl derivatives 37–41, the melting points and the clearing temperatures were found to decrease with increasing chain length. Owing to the high melting points of the compounds with short spacers, no mesophases could be detected for compounds 37 and 39, and only monotropic phases were found for 38. The other cyanobiphenyl derivatives 40 and 41 with long chains exhibited enantiotropic liquid-crystalline properties. The smectic A (S_A) phase was observed in these bowlic LCs as confirmed by the textural observations and the XRD pattern. Compared these compounds with related monomeric 4-cyanobiphenyl LCs (e.g. C_6H_13O–C_6H_4–C_6H_4–CN: Cr 57°C N 75.5°C I), it was found that appending the cyanobiphenyl mesogens to the cyclotribenzylene unit led to a significant mesophase stabilisation and the nematic phase of the monomeric 4-cyanobiphenyl LCs was replaced by S_A phases in the CTV derivatives. In addition, S_A phases were found to be easily supercooled to −30°C without crystallisation. Replacing one of the rigid mesogens with a methyl group resulted in a mesophase destabilisation (42–44), and the melting points and the crystallisation tendency were

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>R</th>
<th>Transition temperature (T/°C) and enthalpies (T/°C/kmol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C_2H_5O⁻</td>
<td>K, 232 I</td>
</tr>
<tr>
<td>2</td>
<td>C_3H_7O⁻</td>
<td>K, 135.6 (22.1) I</td>
</tr>
<tr>
<td>3</td>
<td>C_4H_9O⁻</td>
<td>K, 68.4 (21.7) K, 103.8 (16.0) I</td>
</tr>
<tr>
<td>4</td>
<td>C_5H_11O⁻</td>
<td>K, 40.9 (15.7) P, 92.2 (14.4) I</td>
</tr>
<tr>
<td>5</td>
<td>C_6H_13O⁻</td>
<td>K, 25.0 (21.1) P, 79.9 (9.3) I</td>
</tr>
<tr>
<td>6</td>
<td>C_7H_15O⁻</td>
<td>K, 24.9 (24.8) P, 71.5 (6.9) I</td>
</tr>
<tr>
<td>7</td>
<td>C_8H_17O⁻</td>
<td>K, 18.7 (28.6) P, 66.1 (6.9) I</td>
</tr>
<tr>
<td>8</td>
<td>C_9H_19O⁻</td>
<td>K, 25.5 (40.4) P, 63.2 (6.7) I</td>
</tr>
<tr>
<td>9</td>
<td>C_10H_21O⁻</td>
<td>K, 34.8 (56.0) P, 44.2 (7.2) P, 62.0 (5.7) I</td>
</tr>
<tr>
<td>10</td>
<td>C_11H_23O⁻</td>
<td>K, 48.3 (76.0) P, 61.6 (6.2) I</td>
</tr>
<tr>
<td>12</td>
<td>C_13H_27O⁻</td>
<td>K, 23.9 (28.2) P, 152.6 (30.2) I</td>
</tr>
<tr>
<td>13</td>
<td>C_14H_29O⁻</td>
<td>K, 18.2 (22.1) P, 32.7 (14.8) P, 146.2 (29.2) I</td>
</tr>
<tr>
<td>14</td>
<td>C_15H_31O⁻</td>
<td>K, 31.5 (22.0) P, 38.6 (17.3) P, 131.6 (3.7) P, 140.8 (18.8) I</td>
</tr>
<tr>
<td>15</td>
<td>C_16H_33O⁻</td>
<td>K, 58.1 (48.4) P, 118.8 (3.1) P, 140.6 (20.2) I</td>
</tr>
<tr>
<td>16</td>
<td>C_17H_35O⁻</td>
<td>K, 67.4 (67.0) P, 99.5 (2.3) P, 139.2 (20.9) I</td>
</tr>
<tr>
<td>17</td>
<td>C_18H_37O⁻</td>
<td>K, 73.4 (81.0) P, 81.4 (1.4) P, 136.2 (18.5) I</td>
</tr>
<tr>
<td>18</td>
<td>C_19H_39O⁻</td>
<td>K, 80.5 (118.4) P, 134.6 (19.1) I</td>
</tr>
<tr>
<td>19</td>
<td>C_20H_41O⁻</td>
<td>K, 33.0 (8.4) P, 57.3 (0.2-2) P, 149.1 (9.6) I</td>
</tr>
<tr>
<td>20</td>
<td>C_21H_43O⁻</td>
<td>K, 12.0 P, 21.3 (8.2) P, 156.5 (13.8) I</td>
</tr>
<tr>
<td>21</td>
<td>C_22H_45O⁻</td>
<td>K, 43.0 (7.8) P, 162.0 (15.9) I</td>
</tr>
<tr>
<td>22</td>
<td>C_23H_47O⁻</td>
<td>K, 50.6 (4.8) P, 100.0 (16.0) P, 190.2 (20.4) I</td>
</tr>
</tbody>
</table>

**Table 1.** Phase transition temperatures (in °C) and (in brackets) enthalpies (in kJ/mol) of CTV-based bowlic compounds 1–22 first reported by Zimmermann et al. In the table, K stands for crystal and P for pyramidal mesophases, i.e. bowlic mesophases.
decreased by this desymmetrisation of the molecules. A monotropic \( S_A \) phase was observed by cooling the cyclotribenzylene derivative \( 42 \) which is a desymmetrised analogue of the non-liquid-crystalline compound \( 37 \). In the series of the thiadiazole derivatives \( 45-55 \), the phase behaviours were found to depend on the spacer length and differed significantly from that of the above 4-cyanobiphenyl derivatives. The clearing temperatures decreased with the elongation of the spacer units, but the melting points of compounds kept nearly constant. The mesomorphic properties were only observed for the short chain derivatives and were lost on increasing the spacer length. The

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>( R )</th>
<th>Transition temperature (( T/°C )) and enthalpies (( AH/\text{kJmol}^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>( \text{C}_6\text{H}_5\text{OCH}_2\text{C}(\text{O})\text{O}- )</td>
<td>K 175 I</td>
</tr>
<tr>
<td>24</td>
<td>( \text{C}_6\text{H}_5\text{OCH}_2\text{C}(\text{O})\text{O}- )</td>
<td>K 161-163 I</td>
</tr>
<tr>
<td>25</td>
<td>( \text{C}_6\text{H}_5\text{OCH}_2\text{C}(\text{O})\text{O}- )</td>
<td>K 140 (11.7) ( D_{\text{A}} ) 156 (13.9) I</td>
</tr>
<tr>
<td>26</td>
<td>( \text{C}_6\text{H}_5\text{OCH}_2\text{C}(\text{O})\text{O}- )</td>
<td>K 130 (14.8) ( D_{\text{A}} ) 154 (8.9) I</td>
</tr>
<tr>
<td>27</td>
<td>( \text{C}_6\text{H}_5\text{OCH}_2\text{C}(\text{O})\text{O}- )</td>
<td>K 123 (14.5) ( D_{\text{A}} ) 160 (11.1) I</td>
</tr>
<tr>
<td>28</td>
<td>( \text{C}_6\text{H}_5\text{OCH}_2\text{C}(\text{O})\text{O}- )</td>
<td>K 109 (14.2) ( D_{\text{A}} ) 165 (13.3) I</td>
</tr>
<tr>
<td>29</td>
<td>( \text{C}_6\text{H}_5\text{OCH}_2\text{C}(\text{O})\text{O}- )</td>
<td>K 93 (11.1) ( D_{\text{A}} ) 164 (12.9) I</td>
</tr>
<tr>
<td>30</td>
<td>( \text{C}_6\text{H}_5\text{CH}(_2\text{CH})_2\text{OCH}_2\text{C}(\text{O})\text{O}- )</td>
<td>K ? ( D_{\text{A}} ) 188 (32.1) I</td>
</tr>
<tr>
<td>31</td>
<td>( \text{C}_6\text{H}_5\text{SCH}_2\text{C}(\text{O})\text{O}- )</td>
<td>K 59 (8.0) ( D_{\text{A}} ) 138 (14.0) I</td>
</tr>
<tr>
<td>32</td>
<td>( \text{C}_6\text{H}_5\text{O}(\text{CH})_2\text{C}(\text{O})\text{O}- )</td>
<td>K 63-65 I</td>
</tr>
<tr>
<td>33</td>
<td>( \text{C}_6\text{H}_5\text{O}(\text{CH})_2\text{C}(\text{O})\text{O}- )</td>
<td>K 20 (6.7) ( D ) 179 (2.2) I</td>
</tr>
<tr>
<td>34</td>
<td>( \text{C}_6\text{H}_5\text{CH}(_2\text{CH})_2\text{O}(\text{CH})_2\text{C}(\text{O})\text{O}- )</td>
<td>K -8 (1.4) ( D ) 105 (13.3) I</td>
</tr>
<tr>
<td>35</td>
<td>( \text{Br}(\text{CH})_2\text{O}(\text{CH})_2\text{C}(\text{O})\text{O}- )</td>
<td>K 78 I</td>
</tr>
<tr>
<td>36</td>
<td>( \text{NC}(\text{CH})_2\text{O}(\text{CH})_2\text{C}(\text{O})\text{O}- )</td>
<td>K 63 I</td>
</tr>
</tbody>
</table>

**Figure 3.** Optical photomicrographs under crossed polarisers of the mesophases of cyclotriveratrylene derivatives as obtained by cooling from the isotropic melt: (a) \( D_{\text{ob}} \) phase of compound 25 at 155°C (b) \( D_{\text{hd}} \) phase of 29 at 138°C. The corresponding X-ray diffraction pattern of \( D_{\text{ob}} \) phase (c) and \( D_{\text{hd}} \) phase (d).
Table 3. Transition temperatures (in °C) and associated enthalpy values (in kJ/mol, in brackets) of CTV-based bowlic LCs linked with six calamitic phenylthiadiazole or cyanobiphenyl rigid cores 37–55. In the table, Cr stands for crystal, S\textsubscript{A} for smectic A phase, S\textsubscript{x} for unidentified smectic phase and Col for columnar mesophase.

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>R\textsubscript{1}</th>
<th>R</th>
<th>Transition temperature (T/°C) and enthalpies (ΔH/ kJmol\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>37</td>
<td>R</td>
<td>CN–O(CH\textsubscript{2})\textsubscript{3}CO\textsubscript{2}–</td>
<td>Cr 220 (75.8) I</td>
</tr>
<tr>
<td>38</td>
<td>R</td>
<td>CN–O(CH\textsubscript{2})\textsubscript{3}CO\textsubscript{2}–</td>
<td>Cr 165 (76.6) [S\textsubscript{A} 133 (6.6)] I</td>
</tr>
<tr>
<td>39</td>
<td>R</td>
<td>CN–O(CH\textsubscript{2})\textsubscript{3}CO\textsubscript{2}–</td>
<td>Cr 159 (83.9) I</td>
</tr>
<tr>
<td>40</td>
<td>R</td>
<td>CN–O(CH\textsubscript{2})\textsubscript{3}CO\textsubscript{2}–</td>
<td>Cr\textsubscript{1} 65 (18.8) Cr, 112 (7.0) S\textsubscript{A} 123 (8.2) I</td>
</tr>
<tr>
<td>41</td>
<td>R</td>
<td>CN–O(CH\textsubscript{2})\textsubscript{3}CO\textsubscript{2}–</td>
<td>Cr\textsubscript{1} 95 (58.3) S\textsubscript{A} 116 (21.3) I</td>
</tr>
<tr>
<td>42</td>
<td>CH\textsubscript{3}</td>
<td>CN–O(CH\textsubscript{2})\textsubscript{3}CO\textsubscript{2}–</td>
<td>Cr 163 (40.4) [S\textsubscript{A} 145] I</td>
</tr>
<tr>
<td>43</td>
<td>CH\textsubscript{3}</td>
<td>CN–O(CH\textsubscript{2})\textsubscript{3}CO\textsubscript{2}–</td>
<td>Cr 80 S\textsubscript{A} 118 I</td>
</tr>
<tr>
<td>44</td>
<td>CH\textsubscript{3}</td>
<td>CN–O(CH\textsubscript{2})\textsubscript{3}CO\textsubscript{2}–</td>
<td>Cr 78 (48.3) S\textsubscript{A} 107 (18.1) I</td>
</tr>
<tr>
<td>45</td>
<td>R</td>
<td>CH\textsubscript{3}–N=O(CH\textsubscript{2})\textsubscript{3}CO\textsubscript{2}–</td>
<td>Cr 152 (10.7) Col 182 (54.0) I</td>
</tr>
<tr>
<td>46</td>
<td>R</td>
<td>CH\textsubscript{3}–N=O(CH\textsubscript{2})\textsubscript{3}CO\textsubscript{2}–</td>
<td>Cr 117 S\textsubscript{A} 159 I</td>
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<tr>
<td>47</td>
<td>R</td>
<td>CH\textsubscript{3}–N=O(CH\textsubscript{2})\textsubscript{3}CO\textsubscript{2}–</td>
<td>Cr 151 (30.6) Col 155 (65.8) I</td>
</tr>
<tr>
<td>48</td>
<td>R</td>
<td>CH\textsubscript{3}–N=O(CH\textsubscript{2})\textsubscript{3}CO\textsubscript{2}–</td>
<td>Cr 156 (144.9) I</td>
</tr>
<tr>
<td>49</td>
<td>R</td>
<td>CH\textsubscript{3}–N=O(CH\textsubscript{2})\textsubscript{3}CO\textsubscript{2}–</td>
<td>Cr 158 (135.6) I</td>
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<tr>
<td>50</td>
<td>R</td>
<td>CH\textsubscript{3}–N=O(CH\textsubscript{2})\textsubscript{3}CO\textsubscript{2}–</td>
<td>Cr 142 I</td>
</tr>
<tr>
<td>51</td>
<td>R</td>
<td>CH\textsubscript{3}–N=O(CH\textsubscript{2})\textsubscript{3}CO\textsubscript{2}–</td>
<td>Cr 152 S\textsubscript{A} 160 I</td>
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<tr>
<td>52</td>
<td>R</td>
<td>CH\textsubscript{3}–N=O(CH\textsubscript{2})\textsubscript{3}CO\textsubscript{2}–</td>
<td>Cr\textsubscript{1} 102 (87.1) Cr, 143 (0.9) S\textsubscript{A} 155 I</td>
</tr>
<tr>
<td>53</td>
<td>R</td>
<td>CH\textsubscript{3}–N=O(CH\textsubscript{2})\textsubscript{3}CO\textsubscript{2}–</td>
<td>Cr 80 Col 162 I</td>
</tr>
<tr>
<td>54</td>
<td>CH\textsubscript{3}</td>
<td>CH\textsubscript{3}–N=O(CH\textsubscript{2})\textsubscript{3}CO\textsubscript{2}–</td>
<td>Cr ≈20 S\textsubscript{A} 126 S\textsubscript{A} 142 I</td>
</tr>
<tr>
<td>55</td>
<td>CH\textsubscript{3}</td>
<td>CH\textsubscript{3}–N=O(CH\textsubscript{2})\textsubscript{3}CO\textsubscript{2}–</td>
<td>Cr 62 Col 148 I</td>
</tr>
</tbody>
</table>
compounds with an even number of methylene groups showed small focal conic fan textures, which can be homeotropically aligned on shearing the samples to give optically isotropic regions. These textural features are typical for \( S_A \) phases. The derivatives with an odd number of methylene groups were found to form highly viscous mesophases and display spherulitic flower textures which are typical of columnar mesophases (Col). Many other research also reported that depending on the length of the spacers connecting the central bowlic CTV unit to the rod-like rigid cores, either columnar or smectic phases can be formed \([63,64]\). Lunkwitz et al. also investigated the liquid-crystalline properties in cyclotetravera
tylene (CTV) derivatives \( 56–58 \) (Table 4), where CTTVs are much more flexible and sometimes are regarded as being disc-shaped molecules on the average \([62]\). In contrast to the CTV derivatives with \( S_A \) phases, the cyanobiphenyl derivative \( 56 \) is a nematic LC as is obvious from the typical nematic schlieren texture. A spherulitic texture was observed for the thiadiazole derivative \( 57 \) on cooling from the isotropic melt, which confirmed the absence of an \( S_A \) phase. The pyrimidine derivative \( 58 \) is a crystalline solid with no mesophase. Interestingly, in the case of the CTTV derivatives, columnar mesophases can be observed for compounds with an odd number of connecting atoms in the spacers. In the columnar phase, the CTTV core is believed to adopt the sofa form with \( C_{2v} \) symmetry \([65,66]\).

2.3. CTVs with dendritic molecules

Collet et al. first reported the CTV-based mesogenic triester \( 59 \) which was functionalised with dendritic molecules \([67]\). The hexagonal columnar phase was observed in both racemic and optically active forms (Figure 4). Percec and co-workers synthesised a series of dendritic CTVs and their self-organised supramolecular nanostructures were investigated by a combination of XRD methods and CD experiments \([68,69]\). The dendrimers \( 60–65 \) are representative examples (Figure 5), where the dendrimers include both hexa and tris substituted CTV cores with either chiral or achiral alkyi chains \([69]\). Interestingly, the dendritic CTVs could self-organise into bowlic columns with a hexagonal lattice and/or into chiral supramolecular spheres (Figure 6). Different dendrimer types were found to exhibit different self-assembly behaviours. For example, only bowlic

Table 4. Transition temperatures (in °C) and associated enthalpy values (in kJ/mol, in brackets) of cyclotetravera
tylene (CTTV) derivatives \( 56–58 \). In the table, Cr stands for crystal, N for nematic phase and M for mesophase.

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>R</th>
<th>Transition temperature (T/°C) and enthalpies (( \Delta H/\text{kJmol}^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>56</td>
<td></td>
<td>Cr, 174(53.8) Cr, 222(63.6) N 220 I</td>
</tr>
<tr>
<td>57</td>
<td></td>
<td>Cr, 142(70.3) Cr, 204(10.6) M 222(44.5) I</td>
</tr>
<tr>
<td>58</td>
<td></td>
<td>Cr 241 I</td>
</tr>
</tbody>
</table>

Figure 4. CTV-based mesogenic triester \( 59 \) which was functionalised with dendritic molecules.
columns were observed for both the achiral (60) and chiral (61) dendrimers, whereas dendrimers 64 and 65 were able to form only spherical assemblies. The dendrimers 62 and 63 showed different behaviour at different temperature according to whether the alkyl groups are chiral or achiral. The achiral 62 formed bowlic columns at 100°C and chiral supramolecular spheres at 130°C, while its chiral analogue 63 formed only the supramolecular spheres. This new self-assembly process is expected to provide access to new mechanisms for the transfer and amplification of structural information from the molecular to supramolecular level and to generate new fundamental and technological concepts mediated by chiral supramolecular dendrimers.

3. Calixarene-based LCs

3.1. Calixarenes with calamitic moieties

Calixarenes are well-established building blocks as important as crown ethers and cyclodextrins in supramolecular chemistry [70–72]. They could be easily modified at the upper and lower rims with a large variety of functional groups and unique structures and work as novel receptors for binding all kinds of guests which may find potential applications in various fields such as ion and molecular recognition with fluorescent sensing, amino acid sensors, ion-selective electrode and chiral molecule recognition. A calix[4]arene with 4 units in the ring is known to exhibit a bowlic conformation as shown in Figure 7 [73,74]. If LC groups are introduced onto the calixarene skeleton, the
resulting derivatives are anticipated to show interesting bowlic liquid-crystalline behaviours [75,76].

Cometti et al. first investigated the mesomorphic properties of bowlic calix[4]arene core symmetrically surrounded by 12 flexible alkyl chains with variable length, and columnar mesophases were observed [77]. Tschierske et al. developed the exocalix[4]arenes 66-70 in which different calamitic rigid cores were linked to the macrocyclic calix[4]arene unit (Table 5) [78]. Upon incorporating the phenylthiadiazole units, these compounds were found to form a layered smectic A-type (S_A) mesophase. They claimed that in these derivatives of exo-calix[4]arene, the calamitic rigid units determined the mesophase type. A columnar stacking of the molecules is not possible, but the calamitic units can adopt a parallel packing, which leads to the smectic self-organisation.

Yonetake et al. designed and synthesised calix[4]arene derivative 71, and the liquid-crystalline properties were investigated [79]. As shown in Figure 8(b), a typical nematic schlieren texture with $s = \pm 1$ and $+1/2$ disclinations was observed at 76°C upon cooling. When the sample was further cooled, some stripes appeared immediately on the schlieren texture, and the stripe pattern became clear at room temperature (Figure 8(c)). Figure 8(d) shows the XRD pattern of 71 taken at room temperature. The sample was cooled from the isotropic and annealed at 70°C for 1 h. It exhibited two diffuse halos at the $2\theta$ of approximately 5 and 20°. The d-spacings of the two halos at low and wide angles are about 1.5 and 0.43 nm, respectively. The halo at wide angle corresponds to the average distance between the neighbouring mesogens. The rings for the small angle area could be associated with the smectic layer structure. The layer spacing is estimated as 5.11 nm. Accordingly, the mesogen 71 exhibited nematic and smectic phases. The oriented XRD pattern under a magnetic field further revealed a smectic A phase with a layer spacing of 5.11 nm (Figure 8(e)).

Lo et al. reported a novel series of cone-conformed end-functionalised oligophenylene-substituted calix

---

**Table 5.** Transition temperatures (in °C) and associated enthalpy values (in kJ/mol, in brackets) of calix[4]arene derivatives 66-70. In the table, Cr stands for crystal and S_A for smectic A phase.

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>Transition temperature (T/°C) and enthalpies (ΔH/ kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>66</td>
<td>CH₃</td>
<td>H</td>
<td></td>
<td>Cr 159 (113) [S_A 149 (54)] I</td>
</tr>
<tr>
<td>67</td>
<td>CH₃</td>
<td>H</td>
<td></td>
<td>Cr 196 (49) [S_A 211 (29)] I</td>
</tr>
<tr>
<td>68</td>
<td>C₂H₅</td>
<td>H</td>
<td></td>
<td>Cr 126 (126) I</td>
</tr>
<tr>
<td>69</td>
<td>C₂H₅</td>
<td>H</td>
<td></td>
<td>Cr 150 [S_A 165] I</td>
</tr>
<tr>
<td>70</td>
<td>CH₃</td>
<td>H</td>
<td></td>
<td>Cr 168 (107) I</td>
</tr>
</tbody>
</table>
Figure 8. (a) Chemical structure of calix[4]arene derivative 71; optical textures of 71 taken at (b) 76°C and (c) room temperature upon cooling using polarised optical microscope with crossed polarisers. XRD patterns of 71 (d) annealed at 70°C and (e) oriented in a magnetic field of 2.8 T.

Figure 9. Chemical structures of end-functionalised oligophenylene-substituted calix[4]-arenes 72 and 73.
[4]-arenes 72 and 73 (Figure 9) [80]. In contrast to the corresponding monomers, cyano-phenyl-calix[4]arene and methyl-biphenyl-calix[4]arene derivatives were found to exhibit highly ordered smectic supramolecular organisation as evidenced by the polarised optical microscopy and XRD studies. The optical textures of 73 were found to exhibit typical fanlike or mosaic texture, which suggest the ordered smectic mesophases (Figure 10(a–d)). Figure 10(e) shows the XRD measurements of 73 with \( n = 9-16 \), which further confirms the formation of the smectic layered structure. It was also found that the presence of the strong dipoles in the rigid calixarene segments not only facilitates and stabilises the formation of the highly ordered smectic structure but also enhances the optical properties of calix[4]arene derivatives. These findings provide a new guideline to design interesting 3D bowlic mesogenic materials.

Menon et al. reported the calix[4]arene Schiff bases 74–77 and their liquid-crystalline properties (Figure 11) [81]. All the compounds were found to exhibit nematic structure and a typical fanlike or mosaic texture, which suggests an ordered smectic mesophase. Dielectric investigations were also carried out and wide temperature range N, SmA and

---

**Figure 10.** Some representative polarised optical microscope textures (200×) (a) 73 (\( n = 11 \)) at 168°C, mosaic and lancet texture with some homeotropic area; (b) 73 (\( n = 14 \)) at 148°C, mosaic texture; (c) 73 (\( n = 15 \)) at 153°C, grass-like and fan-like texture; (d) 73 (\( n = 9 \)) at 150°C, mosaic texture; (e) XRD patterns of frozen LC samples of 73 with \( n = 9-16 \) exhibiting multiple higher order reflections in the small angle area.
SmC phases were observed. These results indicated that the linking groups in the wide part have a large influence on the mesogenic properties of calixarene LCs [82]. Romero et al. synthesised liquid-crystalline calix[4]arene-appended Schiff bases 78–80 that exhibited a smectic A mesophase or a nematic phase depending on the number of terminal chains (Figure 12) [83]. Recently, Zhang et al. developed the calix[4]arene-cholesterol derivatives 81 with Schiff-base bridges (Figure 13(a)) [84]. They were found to exhibit the mesomorphic properties with the molecular arrangement of the calixarene bowlic column and Schiff-based cholesterol unit as ancillary lateral column. The mesophases disappeared upon the complexes of 81 with AgClO₄ (Figure 13(b)), which suggests that the mesophase of compounds 81 could be tuned by the ion-complexation behaviours.

Xu and Swage demonstrated the columnar LCs with a rigid bowlic core based on oxo-tungsten calixarene complexes 82 and 83 (Figure 14(a)) [48]. The most dramatic consequence of host–guest complexation was its effect upon the mesomorphic behaviour of the complexes. While the R = H analogue exhibited a
bowlic mesophase from 136 to 320°C, its DMF complex melted directly to an isotropic phase at 115°C. Likewise, the R = OC\(_{12}\)H\(_{25}\) DMF complex melted to form an isotropic phase at 84°C. Complexes with pyridine guests were found to exhibit isotropic transitions at the same temperatures, indicating that a filled cavity is more important than the nature of the guest. With further heating (200–250°C), the DMF complex slowly dissociated to form the liquid-crystalline phase. The deleterious effect of a DMF or pyridine guest on the mesophase stability indicated that the occupation of cavity is critical to the formation of LCs (Figure 14(b)).

According to the columnar structure of the mesophases, it is assumed that the bowlic cores exhibited a head-to-tail arrangement whereby tungsten-oxo groups protrude into the cavity of the neighbouring mesogen.

Xu and Swager also investigated the host–guest mesomorphism of calixarene derivatives 84 (Figure 15) [85]. They demonstrated how host–guest principles could be used to stabilise a columnar bowlic phase of a conformationally flexible calix[4]arene. The uncomplexed conformationally flexible calix[4]arene 84a was found to display a transient columnar
bowlic mesophase which is only observed in the first heating. Further heating of 84a to 163°C produces an isotropic phase, and subsequent cooling yields a non-birefringent solid material. They found that 84b was especially effective for the formation of a host–guest mesophase with 84a. The host–guest mesophase (ratio of 84a–84b is 2:1) displayed high fluidity and thermodynamic stability over a 40°C range. They proposed that the function of 84b is as shown in Figure 15(b), where one amide hinds in the cavity and enforces the cone conformation while the other forms hydrogen bonds with the nearest neighbour, thereby inducing head-to-tail organisations.

Sutariya et al. designed series of lower rim azocalix[4]arene bowlic mesogens 85 (Figure 16) with a flexible aliphatic chain and a rigid scaffold [86]. These compounds were found to exhibit smectic C and nematic phases upon heating and cooling conditions. Interestingly, the introduction of azo groups enables them to respond upon external light irradiations. Moreover, novel gallic-calixarene derivatives with columnar phases were recently designed and synthesised (86 and 87) [87]. These mesomorphic studies suggested that the conformation plays a crucial role for bowlic calixarene LCs and the stable cone conformation is favourable for excellent mesomorphic property.

3.2. Calixarenes with discotic triphenylene moieties

Yang’s group made several efforts to develop the bowlic calix[4]arene LCs by linking discotic triphenylene
In theory, there are two possible mesomorphic staking behaviours for LCs of calix[4]arene-linked triphenylene dimers as shown in Figure 17. One way is calixarene as cores, that is calixarene bowlic column with two triphenylene units as ancillary lateral columns (Figure 17(a)). The symmetrical calix[4]arene-linked triphenylene dimer 88 (Figure 18) with a C_{10} chain was such a case that exhibited the liquid-crystalline behaviour of a calixarene bowlic column with two triphenylene units as ancillary lateral columns [88]. Another way was triphenylene as cores, that is triphenylene column with calixarene units on ancillary lateral sides as shown in Figure 17(b). Compounds 89 and 90 were such cases that exhibited interesting mesomorphic behaviour of triphenylene column with calixarene units on ancillary lateral sides [89].

Interestingly, Yang et al. synthesised symmetrical triads of triphenylene–calix[4]arene–triphenylene 91 bridged by hydrazone spacers (Figure 19) [90]. It was found that these compounds showed interesting ion-complexation-induced mesomorphic conversion between two distinct columnar phases. The neat compounds 91 showed mesophase with calixarene’s bowlic column as cores. The Ag^+ complexes of 91 exhibited mesophase with triphenylene column as cores. Recently, another calixarene-linked discotic triphenylenes 92 were synthesised via click chemistry. The neat compounds 92 showed mesophase but their complexes with metallic salts exhibited no LC behaviours [91].

4. New advances of bowlic LCs

4.1. Supramolecular bowlic LCs

Another idea to stabilise such polar bowlic structures is to use a hydrogen bonding (H-bonding). Many researchers have attempted to find the columnar LCs based on such structural concept [92–96]. Miyajima et al. reported that the fan-shaped molecules 93–95...
Figure 19. Chemical structures of triphenylene–calixarene–triphenylene 91 and 92.

Figure 20. (a) Chemical structures of fan-shaped molecules 93–95 (phase transition temperatures in °C) and (b) illustration of their columnar assembly via hydrogen bonding. Optical textures of (c) 94 and (d) 95 at 90 and 80°C, respectively.
self-assembled conically into an umbrella, which stacks up to form a bowlic columnar LC structure (Figure 20(a,b)) [97]. The introduction of a large dipole into the focal core of such fan-shaped molecules was expected to obtain spontaneous macroscopic polarisation in the resulting LC mesophase. 4,5-Dithiaphthalonitrile derivatives 94 and 95 were thus designed and synthesised, where two H-bonding amide groups ensure their umbrella-shaped assemblies that are essential for polarised columns. They confirmed that 94 and 95 both formed the hexagonal columnar mesophases (Figure 20(c,d)). The columnar mesophase in 94 was found to possess a spontaneous macroscopic polarisation, whereas spontaneous polarisation was absent in the mesophase of H-bonded 95. Unfortunately, these LCs were not switchable ferroelectrics because its polarisation did not respond to the external electric field.

Recently, a breakthrough has been made to stabilise the bowl-shaped assembly of phthalonitrile derivatives 96 into supramolecular columns by designing appropriate molecules with hydrogen bonds as shown in Figure 21(a) [49]. Under an applied electric field, both columns and core cyano groups could be unidirectionally aligned, thereby generating an extremely large macroscopic remnant polarisation (Figure 21(b)). The non-centrosymmetry was further characterised by SHG measurements, for which polarisation switching was clearly observed (Figure 21(c)). To the best of our knowledge, this system is the first demonstration of intrinsic

![Figure 21](https://example.com/figure21.png)

**Figure 21.** The chemical structure (a) of a mesogen 96 that assembles into a hexagonal columnar phase (b). Assembly proceeds by the segregation of four mesogens into a core–shell structure, with polar phthalonitrile units inside and the aliphatic side chains outside. (c) The intrinsic ferroelectric nature of the bowlic columns is shown by the hysteresis of polarisation against electric field. (d) The cyano group in the core of the columns are either pointing up or down (according to the applied electric field) and yield a polar order parallel to the column axis (orange and green arrows for cyano groups pointing up and down, respectively). Reproduced with permission [100]. © 2015 Macmillan Publishers Limited.
ferroelectricity in a liquid-crystalline system without any
treatment of the device surface or additional processing. The
authors claimed that the phthalonitrile units instead of
the hydrogen bonds were responsible for the ferroelectricity (Figure 21(d)). Although the polar amide units
did not contribute to the ferroelectric effect, their bond polarisation ensured and maintained the unidirectional
columnar orientation. The ferroelectric properties of this
system were sensitive to several molecular parameters such as flexibility of the core, congestion of the shell
structure, molecular packing within the core and intra-
column hydrogen bonds. Interestingly, wet-processed
LC films of such bowlic columns with a high optical
quality were also found to exhibit uniform spontaneous polarisation with a directional tunability under external
electric field [98]. These features would lend superiority to the other conventional organic ferroelectrics in fabricating thin films, especially for device processing. Unlike the conventional ferroelectrics including the crystalline inorganic solids of barium titanate (BTO) and lead zirconate titanate (PZT), and polymer films of polyvinylidene fluoride, such supramolecular LCs could easily self-organise into large uniform ferroelectric domains in painted films or LC bulks, even nano-/micro-fibres and gels, which makes possible the easy fabrication of devices such as high-density memories, ferroelectric field-effect transistors and organic photovoltaic cells [99–104].

4.2. Liquid-crystalline corannulenes

Corannulene was first prepared in 1966 and charac-
terised as a bowl-shaped polynuclear aromatic hydro-
carbon. Corannulene is also known as a buckybowl
due to its unique connection and bowl shape [105–110]. Aida et al. reported the first corannulene deriva-
tives 98 and 99 that were able to form a liquid-
-crystalline assembly (Figure 22) [111]. In particular, compound 99 was found to form a hexagonal column-
ar LC assembly over a wide temperature range including room temperature. On cooling from the isotropic melt of 99, the resulting fluidic LCs in polarised optical microscopy at 115°C clearly showed a fan texture (Figure 23(c)), which indicated the characteristic hexagonal columnar LC assemblies. XRD analysis of 99 at 70°C showed diffraction peaks with d-spacings of 35.0, 20.2 and 17.5 Å (Figure 23(d)), which could be indexed as the (1 0 0), (1 1 0) and (2 0 0) reflections of a hexagonal columnar meso-
phase. A broad halo centred at 4.3 Å is typical of paraffinic domains in the molten state. Compared with 99, corannulene 98 bearing linear paraffinic side chains formed a LC mesophase only in a very narrow and much higher temperature range. The resulting fluidic material showed a LC texture at 165°C (Figure 23(a)), which was distinctively different from that of 99. XRD analysis of 98 at 165°C showed a periodic pattern composed of an intense peak with a d-spacing of 28.3 Å, indexed as the (0 0 1) reflection, followed by other peaks due to higher order reflec-
tions up to (0 0 7) (Figure 23(b)). From this character-
istic XRD pattern, 98 most likely adopts a lamellar structure in the LC state. Interestingly, it was found that the LC columns of assembled 99 can be aligned homeotropically to an ITO electrode surface under an applied electric field (Figure 23(c), inset). Furthermore, the pattern developed electrically could be main-
tained for a long period of time at 125°C even after the electric field was switched off. Recently, liquid-
crystalline behaviours were also observed in fivefold symmetric substituted corannulene derivatives [112]. These new LC materials, tailored with molecularly engineered corannulenes, are expected to open a new door for a variety of interesting applications.

4.3. Liquid-crystalline subphthalocyanines

Subphthalocyanine is a rare example of π-conjugated aromatic molecules with a rigid tetrahedral structure [113,114]. They are composed of three isoidole units condensed around a boron atom which also bears an axial ligand perpendicular to the macrocyclic core. Subphthalocyanines have recently attracted significant technological interest in the fields of organic semiconduc-
tors and optoelectronics [115,116]. Guilleme et al. reported the bowl-shaped mesogens based on the C3
-symmetric boron subphthalocyanine 100 (Figure 24) [117]. This bowl compound was found to exhibit columnar phase with permanent polar order along the columnar axis. The polarisation orientation could be developed under electric field application only when cooling the sample from the isotropic phase. The degree of polar order was large enough for device applications, not sensitive to electric fields of opposite sense, and can be conserved for weeks in the mesophase after the electric field was switched off. This unique effect was ascribed to the rigidity of the axial dipolar subphthalocyanine stacks.

Recently, Guilleme et al. designed and synthesised another subphthalocyanine-based bowlic molecule 101 with switchable columnar nematics (Figure 25) [118]. An amide group incorporated between the central core and each of the three peripheral molecular segments were found to enhance the cohesive forces between neighbour-
boring molecules, due to strong intermolecular hydrogen-bonding interactions along the column. As a result, the material showed a hexagonal columnar mesophase Co6, in a very broad temperature range. However, the
Figure 22. Chemical structures of corannulenes 97–99 and their liquid-crystalline properties. Cr, Col, M, and I denote crystalline, hexagonal columnar, lamellar and isotropic phases, respectively.

Figure 23. (a,c) Polarised optical micrographs of 98 at 165°C and 99 at 115°C. Inset in (c) shows optical texture at 125°C of 99, sandwiched by glass plates with patterned ITO electrodes (5-μm separation) under an applied electric field of 15 V/μm. (b,d) X-ray diffraction (XRD) patterns of 98 at 165°C and 99 at 70°C. Inset in (d) shows a magnified XRD pattern at 2θ = 2°–5°.
Figure 24. (a) Top and side views of the axial dipolar subphthalocyanine macrocycle. The yellow spheres represent the arylethynyl substituents. Head-to-tail stacking leads to polarised columnar structures. (b) Chemical structure of the C₃-symmetric subphthalocyanine 100.

Figure 25. (a) Top and side views of the axial dipolar subphthalocyanine macrocycle and its packing in columns without the head-to-tail invariance. The yellow spheres represent the arylamide substituents. (b) Molecular structure of the bowlic subphthalocyanine 101. (c) Optical texture of the lyotropic phase in dodecane (10 wt%). (d) X-ray diffraction pattern recorded at room temperature. (e) Textures observed by POM for the lyotropic mesophase in dodecane (10 wt%) under a low-frequency (0.1 Hz) square-wave field: left, +40 V; centre, transient texture observed during voltage inversion; right, −40 V. Sample thickness, 5 μm.
high viscosity of the mesophase and the high temperatures of its range of stability are not ideal for processing and possible applications. Therefore, they tried to control these features by the addition of a suitable solvent. The low viscosity together with the kind of texture observed by polarised optical microscopy as shown in Figure 25(c) suggested the possibility of having a nematic phase at 10 wt%. XRD confirmed that this phase was a columnar nematic $N_{\text{Col}}$ (Figure 25(d)). Interestingly, this lyotropic $N_{\text{Col}}$ LCs exhibited polar response under the electric field (Figure 25(e)), which confirmed by texture observations and SHG methods. Since the LCs are lyotropic, uniform polar films could be easily fabricated simply by evaporating the solvent under an electric field. This could be of interest for the manufacture of thin-film electronic devices.

4.4. Liquid-crystalline peptidic macrocycles

Being inspired by naturally occurring peptidic macrocycles, Sato et al. developed liquid-crystalline compounds 102 and 103 that were capable of self-organising into hexagonal columnar mesophases over a wide temperature range that includes room temperature (Figure 26) [119]. With the help of internal H-bonds, these macrocyclic peptides adopted a highly robust, bowl-shaped conformation with a large dipole moment. Differential scanning calorimetry analysis of 102 on second heating showed an LC mesophase over the temperature range from $-12$ to $77^\circ\text{C}$, which was characterised as hexagonal columnar ($C_{\text{ol}}h$) phase by polarised optical microscopy and XRD analysis. Likewise, compound 103 was also found to self-assemble into hexagonal columnar ($C_{\text{ol}}h$) phase from $-14$ to $95^\circ\text{C}$. Interestingly, they found that upon application of an electric field, the LC columns of both 102 and 103 underwent large-area unidirectional homeotropic orientation. It is also noteworthy that even after the electric field was switched off, the large-area unidirectional columnar orientation was maintained throughout an observation period of half a year. Amorín et al. demonstrated porous liquid-crystalline phases with an internal diameter of 7 Å from self-assembling cyclic peptides decorated with mesogenic dendrons.
The strategy took advantage of H-bonding interactions involving endocyclic amide groups and mesogenic driving forces promoted by polycatenar dendron-like benzoic acid derivatives. Moreover, Kawano et al. reported the columnar liquid-crystalline metallomacrocycles by the incorporation of the metal complexes inside the liquid-crystalline macrocycles [121].

4.5. Colloidal bowl-shaped nanoparticles

Various bowl-shaped nanoparticles and colloids have been recently designed, synthesised and characterised [122–127]. Their promising applications have been investigated in many aspects such as nanocontainer [124], superhydrophobic surfaces [125] and infrared-blocking coatings [126]. Marechal et al. explored the phase behaviour of bowl-shaped nanoparticles using confocal microscopy and computer simulations [50]. Experimentally, they observed the formation of a worm-like fluid phase, where the bowl-shaped particles were believed to stack on top of each other. Additionally, they performed Monte Carlo simulations, where the stacking and phase behaviour of hard bowl-shaped particles were investigated as a function of the thickness (or equivalently deepness). Figure 27 shows the phase diagram of hard bowl-shaped nanoparticles in the packing fraction (φ) versus thickness (D/σ) representation. Different stable crystal phases could be found. In the inverted crystal (IX) and the inverted braid-like crystal (IB), the particles were stacked in columns with half of the columns flipped upside down such that the rims of the bowls could interdigitate. In the IX, the resulting columns were all aligned head to toe, while in the IB phase, the columns resemble braids with alternating tilt direction of the particles within each column. The solid hemispheres (D = 0.5σ) were found to exhibit two stable crystal structures, i.e. IX’ and paired face-centred-cubic (fcc2) phases. The IX’ phase could be regarded as a sheared version of IX with alternating orientation of the particles and where the particles are not organised in columns. In the fcc2 phase, the pairs of hemispheres joined together to form complete spheres that could rotate freely on the lattice positions of an fcc crystal. For D/σ ≤ 0.3, an isotropic-to-columnar phase transition at intermediate densities was found. It was also found that columnar phase with all the particles pointing in the same direction was more stable than a columnar phase, where half of the columns were upside down. The work provides insight in the self-organisation of bowl-shaped nanoparticles, which is expected to provide guidance for designing molecular and nano-metre-sized bowls as well as their liquid-crystalline properties and applications [128,129].

5. Conclusion and future prospects

In this review, we have outlined the history, advances and applications of bowlic LCs. Bowlics were first proposed by the Chinese physicist Lui LAM in 1982. Since the discovery of bowlic phases in CTV molecules by European scientists in 1985, a large amount of bowlic liquid-crystalline materials have been developed based on various bowlic cores including calixarenes, corannulenes, subphthalocyanines, peptidic macrocycles etc.
Different bowlic mesophases such as columnar, nematic and smectic phases have been observed in bowl-shaped molecules by linking the bowlic cores with multitudinous mesogenic groups and flexible side chains. The liquid-crystalline properties of colloidal bowl-shaped nanoparticles have also been explored. Interestingly, bowlic ferroelectric columns have been achieved in the self-organised supramolecular systems with hydrogen bonding, and switchable ferroelectric columns have been observed in several bowlic LCs. The genuine columnar ferroelectrics with the polarisation along the z axis (Ising type) in these bowlic LCs could lead to new types of LCD with very fast response times and open a brand-new door for the development of ferroelectric or antiferroelectric soft materials with great potential applications in ultrahigh-density memory devices and beyond.

It is anticipated that bowlic LCs could play an increasingly important role in the prosperous area of nanoscience and nanotechnology, and such a promising research field would also give rise to meaningful multidisciplinary cooperation of scientists and engineers from different backgrounds. However, since most of the related research endeavour in this burgeoning field remains in the preliminary stage, we may still have much chances to find new bowlic LCs. Moreover, stimuli-responsive bowlic LCs could be developed by incorporating the bowlic cores with different responsive moieties, and chiral bowlic LCs could be fabricated by introducing chiral centre in bowlic molecules or doping chiral dopants into achiral bowlics as we do in rodic and discotic systems [130–136]. For device applications, many problems and questions need to be further addressed. For example, the response speed of switchable ferroelectric columns in current systems is very slow. Much efforts should be devoted to the alignment control with suitable molecular orientations in the viscous columnar phases of bowlic LCs by applying different external stimuli such as electric field, magnetic field, light and thermal treatment [137–139]. The relationships between molecular orientation and device performance should be investigated. Furthermore, bowlic LC nanocomposites and their promising properties can be explored in the future. Bowlics could be used as templates to direct the self-assembly of colloidal particles or polymers. The dispersion of 1D and 2D nanostructures such as nanorods, nanotubes and graphene derivatives in bowlic columnar nanostructures should enable the fabrication of even more complex 3D colloidal nanostructures for applications in micro/nanophotonics and other distinct areas, which would also be an ideal platform to control, explore and understand the organisation properties of different nanomaterials from the nanometre to micrometre scales in a controllable and programmable technique [140–146]. Since the ground work done so far is encouraging, one can expect that the future breakthroughs in such promising topics would not only broaden our knowledge of soft matter but also promote their diverse applications as intelligent advanced functional materials.

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