



Novel gallic-calixarene liquid crystals: syntheses and conformation influences on mesomorphism



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ABSTRACT

Three novel gallic-calixarene derivatives **5**, **6** and **7** were prepared in yields of 57–76%. Their structures and conformations were confirmed by element analyses, IR, ESI-MS and NMR spectra. Compounds **5** and **6** with stable cone conformation show liquid crystalline behaviours but compound **7** with no stable conformation exhibits no mesophase. These results indicated that the stable cone conformation plays a crucial role for mesomorphic property.

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The design and synthesis of thermotropic liquid crystals (LCs) have attracted much research attentions due to their potential applications for use in various fields, such as organic light-emitting diodes, organic photovoltaic cells, organic field-effect transistors and gas sensors.^{1–5} Recently, the macrocycle-based liquid crystals containing both macrocyclic unit and liquid crystalline unit played active and important roles. The mesomorphic properties of this kind of molecules could be tuned by the structures and complexation behaviours of macrocyclic units. For example, the triphenylene dimers containing a shape-persistent conjugated macrocycle or crown ether macrocycle with interesting mesomorphic properties were reported by Cammidge group.^{6,7} Peng and Laschat, respectively, studied the syntheses and properties of similar triphenylene dimers containing conjugated macrocycle or crown ether macrocycle.^{8,9} The first cyclodextrin-triphenylene liquid crystal was also described by our group lately.¹⁰

Calixarenes were the important hosts after crown ether and cyclodextrin in the organic supramolecular chemistry.^{11,12} They were used as excellent synthetic platforms to construct all kinds of calixarene derivatives with various properties.^{11–14} Calixarene-based liquid crystals, as the significant part of macrocycle-based liquid crystals, were also investigated in some literature.¹⁵ For instance, the calixarene liquid crystals with long aliphatic chains were synthesized and exhibited interesting mesomorphic properties.^{16–23} Recently, our group studied the syntheses and mesophase

of series of triphenylene-based calixarene liquid crystals and cholesterol-based calix[4]arene liquid crystals.^{24–28} Nonetheless, the varieties and amounts of calixarene liquid crystals were far fewer than those of other normal liquid crystals.^{1,29,30} On the other hand, all the reported calixarene liquid crystals were synthesized by using calix[4]arene derivatives in stable cone conformation as synthetic platforms. Is the stable cone conformation necessary for calixarene derivatives bearing the mesophase? Also, how about the other calixarene skeletons, such as thiacalix[4]arene and calix[6]arene, used as platforms to construct calixarene liquid crystals? However, these issues were not involved in the literature up to now. In the present study, we designed and synthesized three novel calixarene liquid crystals by introducing the gallic units with three long alkyl chains onto different calixarene skeletons. Moreover, the influence of different conformations of calixarene skeleton on mesophase was investigated for the first time. The results implied that the conformations of calixarene skeletons play crucial roles for mesophase. The two gallic-calixarene derivatives in stable cone conformation possess columnar mesomorphic properties, but the gallic-calix[6]arene derivative with no stable conformation has no mesophase.

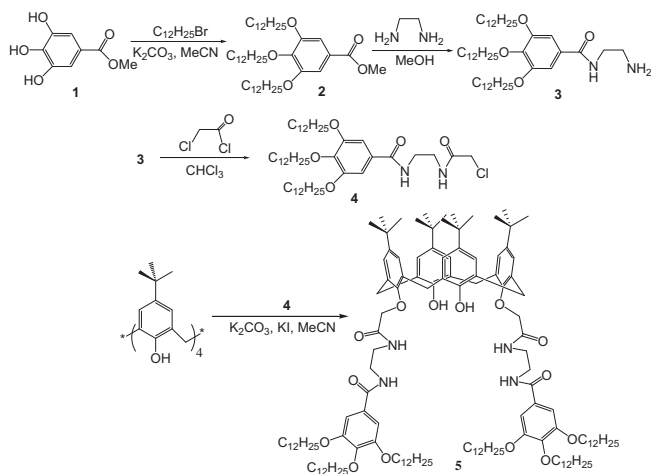
It was well-known that the gallic unit was reported as an excellent functional group for constructing liquid crystal by introducing three alkyl chains on the phenyl group.^{31–34} But it was not used to prepare the calixarene liquid crystal so far. On the other hand, it had been reported that the hydrogen bonding made great influence on the formation of columnar liquid crystal when no large conjugated aromatic structure was introduced as core.^{35–38} Due to the

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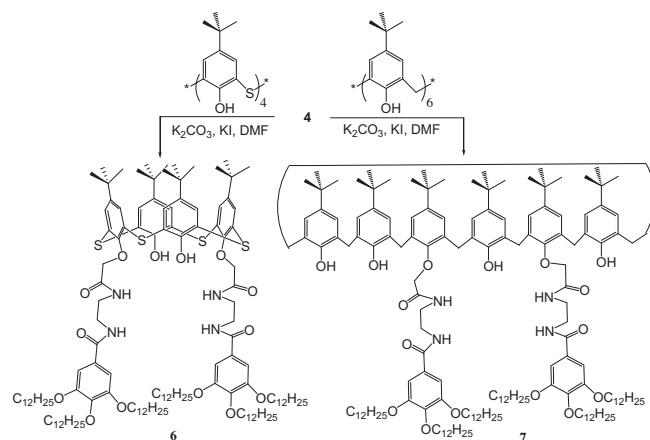
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calixarene unit which was not the conjugated aromatic structure, the amide bonds were introduced as bridges, which would be favourable for producing hydrogen bonding and then resulted in good columnar liquid crystalline behaviours. Thus, the synthetic route of the novel gallic-calix[4]arene derivative **5** was designed as shown in Scheme 1. According to the literature method,³⁹ gallic derivative **2** with three dodecyl on the phenyl group was prepared in yield of 80% by reacting methyl gallate **1** with bromodecane in K_2CO_3 /MeCN system. Furthermore, by reacting compound **2** with excess ethylenediamine in MeOH solution, the ammonolysis derivatives **3** were prepared in yield of 86% after recrystallization. The compound **3** was converted to gallic derivative **4** with terminal-chloride in yield of 85% by treating compound **3** with chloroacetyl chloride. Subsequently, by refluxing compound **4** with calix[4]arene in K_2CO_3 /MeCN system using KI as catalyst, the novel gallic-calix[4]arene derivative **5** was obtained in yield of 76% after column chromatography. The structure of target compound **5** was confirmed by element analysis, IR, ESI-MS and NMR spectra. The molecular ion peak (MNa^+) at 2186.1 in ESI-MS spectra suggested the accomplishment of bis-substituted structure. All the protons were assigned well in 1H NMR spectra. The two singlets (1:1) for *tert*-butyl groups, one pair of doublets (1:1) for the methylene bridges and two singlets (1:1) for ArH suggested compound **5** was in cone conformation or 1,3-alternate conformation. However, compound **5** possesses two phenolic hydroxyl groups which easily produce the hydrogen bonding to keep the cone conformation.^{40–43} Moreover, the difference values of two doublets of methylene bridges were 0.73 ppm, which was the characteristic of cone conformation (the methylene bridges in 1,3-alternate conformation showed overlapped signals or one pair of doublets (1:1), but the difference values of two doublets were smaller than 0.4 ppm).^{41–43} Thus, it could be deduced that compound **5** was in stable cone conformation.

In order to investigate the influence of conformation of calixarene skeleton on mesophase, thiacalix[4]arene and calix[6]arene were chosen as the synthetic platforms to prepare the analogous gallic-calixarene derivatives **6** and **7**. The synthetic routes are illustrated in Scheme 2. By treating compound **4** with thiacalix[4]arene or calix[6]arene in K_2CO_3 /DMF system using KI as a catalyst at 100 °C, the gallic-thiacalix[4]arene derivative **6** and gallic-calix[6]arene derivative **7** were prepared in yields of 62% and 57% after column chromatography, respectively. These reactions did not happen in K_2CO_3 /MeCN system and the yields of compounds **6** and **7** were lower than 20% in K_2CO_3 /DMF system when the reaction temperature was under 90 °C. The reason might be attributed to the steric hindrance of large bulk of compound **4**



Scheme 1. The synthetic route of gallic-calix[4]arene derivative **5**.



Scheme 2. The synthetic routes of compounds **6** and **7**.

and the low reaction activities of thiacalix[4]arene and calix[6]arene compared with calix[4]arene. Only 1,3-bis-substituted calixarene derivatives were separated out in these synthetic procedures of compounds **5**, **6** and **7** due to the intramolecular hydrogen-bonding influences of calixarene skeleton.^{11–14} The structures of compounds **6** and **7** were also studied by element analyses, IR, ESI-MS and NMR spectra. In their ESI-MS spectra, the molecular ion peaks (MH^+) at 2234.1 and 2485.6 strongly supported the bis-substituted pattern for compounds **6** and **7**, respectively. In the 1H NMR spectrum of compounds **6**, two singlets (1:1) for *tert*-butyl groups and two singlets (1:1) for ArH indicated that compound **6** was 1,3-bis-substituted pattern in cone or 1,3-alternate conformation. According to the similar analysis of compound **5**, the two phenolic hydroxyl groups were favourable for cone conformation by the hydrogen bonding action.^{44–47} Moreover, the difference values of two singlets of ArH were 0.39 ppm, which supported further the cone conformation (the 1,3-alternate conformation showed two singlets but the difference values of two singlets were smaller than 0.15 ppm).^{45–47} Based on these analyses, we deduced that compound **6** is also in stable cone conformation. As to compound **7**, its 1H NMR spectrum showed four singlets (1:2:2:1) for *tert*-butyl groups, indicating the 1,3-bis-substituted pattern for compound **7**. However, the overlapped signals for $ArCH_2Ar$ and ArH suggested that compound **7** possesses no stable conformation, which was in accordance with the reports of the large conformational freedom for calix[6]arene.^{48,49}

As compounds **5**, **6** and **7** had similar structures with different calixarene skeletons and various conformations, it was interesting to investigate their liquid crystalline properties and the influences of conformation on mesophase. The mesomorphic behaviours of compounds **5**, **6** and **7** were preliminarily studied by differential scanning calorimetry (DSC). The results are exhibited in Figure 1 and Table 1. One could see that compound **5** showed two phase transfer temperatures at 64.7 °C and 111.5 °C in the second heating and two reverse processes at 106.5 °C and 56.8 °C in the cooling. Compound **6** also exhibited similar changes at 63.8 °C and 80.6 °C for the second heating scan and two reverse processes at 76.2 °C and 57.4 °C upon cooling. However, only one peak at second heating or cooling was observed for compound **7** at 148 °C approximately. These DSC data suggested that compounds **5** and **6** have the crystal phase-mesophase-isotropic phase on the heating and cooling. Their similar phase transitions temperatures and enthalpies suggested they possess good reversible phase transitions on heating and cooling. The hysteresis phenomena observed for compounds **5** and **6** might be attributed to super-cooling, which was common for such viscous materials. Moreover, after calculation, the scope of mesomorphic temperature of compound **5** was

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