



Synthesis and mesomorphic properties of novel columnar liquid crystals based on polytopic gallic ethers with multiple-hydrogen bonding cyanuric cores



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ABSTRACT

The gallic–cyanuric monomer **4**, gallic–cyanuric dimer **5**, gallic–cyanuric trimer **6** and gallic–cyanuric tetramer **7** containing multiple hydrogen bond were designed and synthesized in yields of 70–80%. Their symmetric structures were characterized by element analyses, FT-IR, ESI-MS, and NMR spectra. Their hexagonal columnar liquid crystalline phases were confirmed by DSC, POM, and XRD analyses. The scope of mesomorphic temperature of compounds **5**, **6**, and **7** is as wide as 45.7, 70.1, and 134.4 °C, respectively. The more gallic ether units are favorable for excellent mesophase.

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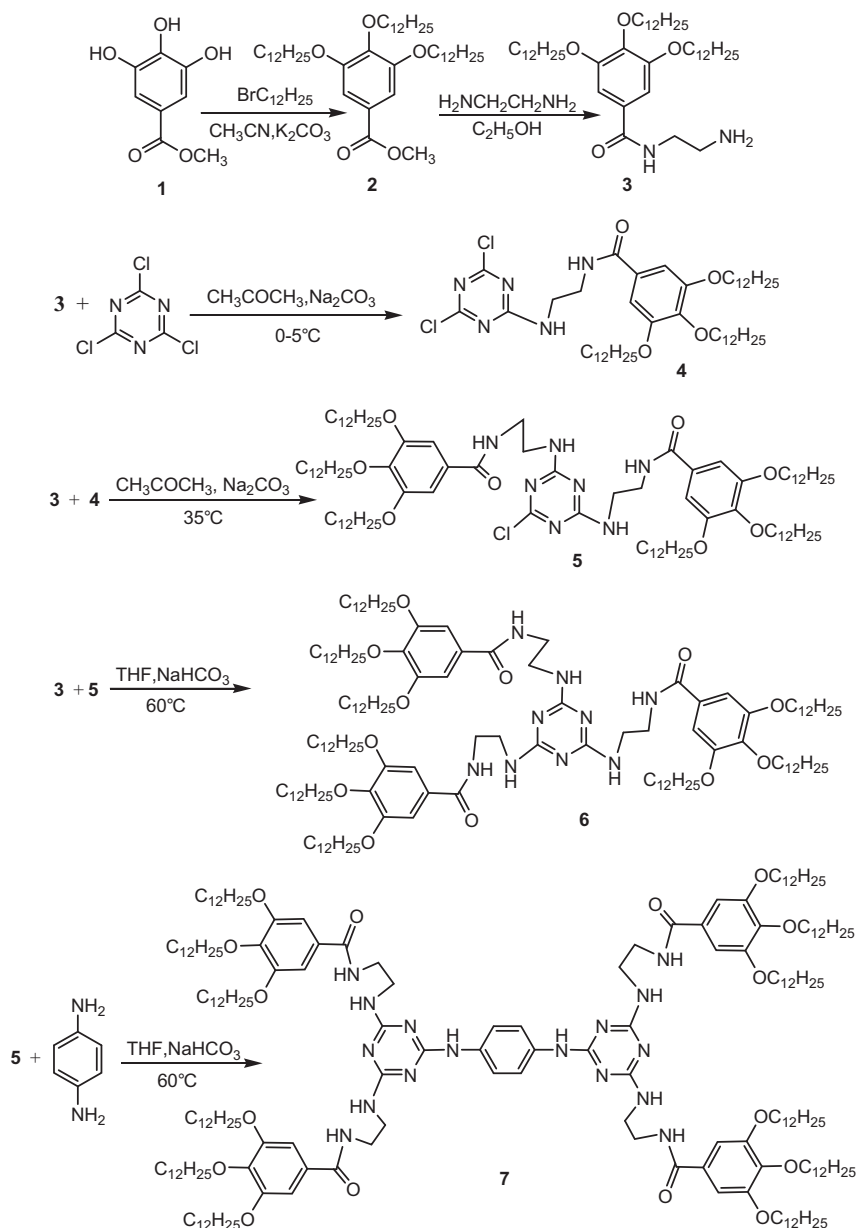
Columnar liquid crystals (LC) have attracted increasing research interest in recent years based on their 1D charge transport and self-healing properties, which make them unique promising candidates for use in organic photoelectric devices, organic field effect transistors, thin film transistors, organic light emitting diodes, etc.^{1–4} Usually, the columnar LCs were easily obtained by symmetric large conjugated aromatic core with several aliphatic side chains. For instance, the triphenylene, phthalocyanine, and hexabenzocoronene derivatives with three to six aliphatic chains were extensively studied as excellent columnar LCs materials.^{5–10} Lately, gallic ethers or their analogues with three long aliphatic chains on their phenolic groups were seen as good structural units to construct novel columnar LCs by connecting with a large conjugated aromatic core. For examples, Laschat described saddle-shaped tetraphenylenes with peripheral gallic esters displaying columnar mesophases.¹¹ Detert reported the synthesis and mesomorphic properties of some tris-triazolotriazine derivatives with 1,2-bis-substituted or 1,2,3-tri-substituted alkoxy side chains on phenyl groups.^{12,13} Our groups also presented novel room-temperature liquid crystals of gallic–perylene–gallic trimers.¹⁴ On the other hand, some research showed that the hydrogen bonding made great influences on the formation of liquid crystals when no large conjugated aromatic structure was introduced as core. Maeda

showed several liquid crystals based on hydrogen bonding supramolecular assemblies by combination with π -conjugated anion receptors.¹⁵ Saigo presented columnar liquid crystals of 3,4,5-tris(11-acryloyloxyundecyloxy)benzoic acid with 2-amino-1-propanol based on hydrogen bonding.¹⁶ Shin also exhibited C₃-symmetric hexa-alkylated liquid crystals with interesting transformation from smectogen to discogen via hydrogen bonding.¹⁷ Moreover, Laschat synthesized wedge-shaped 1,2-diamidobenzenes forming columnar mesophases via hydrogen bonding,¹⁸ but the similar wedge-shaped molecules without hydrogen bonding were difficult to show the similar columnar liquid crystals.¹⁹ Nonetheless, the columnar liquid crystal of symmetric polytopic gallic derivatives without a large conjugated aromatic core was not concerned so far. Inspired by these successful cases of columnar liquid crystal based on hydrogen bonding, in this Letter, we designed and synthesized several symmetric polytopic gallic ethers with triazine cyanuric cores containing multiple amino groups, which could produce multiple hydrogen bonding. The mesomorphic studies showed that although these cyanuric cores were not large conjugated aromatic ones, the columnar liquid crystals were observed for these compounds unambiguously due to the intermolecular action of hydrogen bonding of multiple amino groups.

The synthetic routes for gallic–cyanuric monomer **4**, gallic–cyanuric dimer **5**, gallic–cyanuric trimer **6**, and gallic–cyanuric tetramer **7** are illustrated in Scheme 1. Firstly, according to the

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Scheme 1. The synthetic routes of title compounds **4**, **5**, **6**, and **7**.

literature methods,²⁰ by reacting methyl gallate **1** with bromodecane in $\text{K}_2\text{CO}_3/\text{MeCN}$, gallic derivative **2** with three long alkyl chains was conveniently prepared in yield of 80%. Then the ammonolysis derivatives **3** was obtained by reacting compound **2** with excess ethylenediamine in yield of 86%. On the other hand, it was well known that the three Cl groups of cyanuric chloride could be selectively substituted by changing the reaction temperatures. Thus, the gallic-cyanuric monomer **4** was easily synthesized by the nucleophilic substitution of gallic amide derivative **3** with cyanuric chloride in Na_2CO_3 /acetone system under the temperature of 0–5 °C in yield of 80%. Subsequently, reacting compound **3** with gallic-cyanuric monomer **4** afforded gallic-cyanuric dimer **5** in same reaction system at 35 °C in yield of 76%. Furthermore, gallic-cyanuric trimer **6** was obtained by condensation of compounds **5** with **3** in NaHCO_3 /THF system at 60 °C in yield of 70%. Also, by refluxing gallic-cyanuric dimer **5** with *p*-phenylene diamine in NaHCO_3 /THF system at 60 °C, gallic-cyanuric tetramer **7** was separated in yield of 72% after column

chromatography. It was worthy of noting that all these polytopic gallic ethers with multiple-azo cyanuric cores **4**, **5**, **6**, and **7** were prepared in simple separating procedures of recrystallization or flash column chromatography in yields of 70–80%.

The structures of all new compounds **4**, **5**, **6**, and **7** were confirmed by element analyses, FT-IR, ESI-MS, and NMR spectra. In their ESI-MS spectra, all of them showed corresponding molecular ion peaks (M^+ , MH^+ or MK^+) at 865.2, 1584.6, 2226.1, and 3127.8 which suggested the condensation of mono-, di-, tri-, and tetra-substituted gallic-cyanuric derivatives was successfully accomplished as expected. In their ^1H NMR spectra, the corresponding proton signals were well assigned to their structures. Moreover, their ^{13}C NMR spectra also exhibited corresponding peaks, for examples the peaks for C=O and OCH_2 at approximately 165 and 74 ppm, respectively. All these characteristic data supported certainly the structures of compounds **4**, **5**, **6**, and **7** in Scheme 1.

The differential scanning calorimetry (DSC) was preliminarily used to investigate the mesomorphic behaviors of compounds **4**,

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