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LETTER

Novel room-temperature thermotropic liquid crystals: Synthesis and mesomorphism of gallic-perylene-gallic trimers

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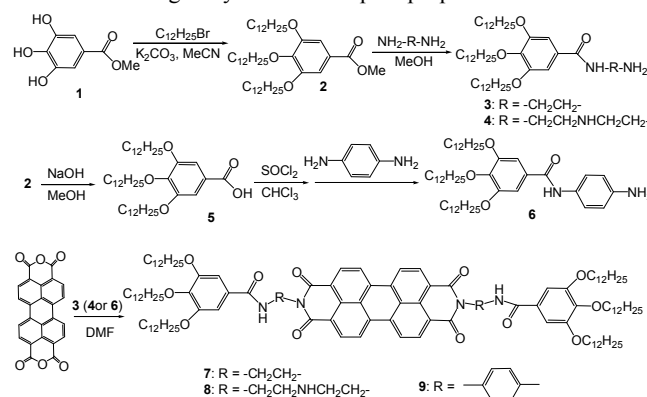
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Three novel gallic-perylene-gallic trimers **7**, **8** and **9** were synthesized by reacting gallic amino derivatives **3**, **4** or **6** with perylene tetracarboxylic anhydride in yields of 75%, 78% and 80%, respectively. Compounds **7** and **8** with soft bridging chains exhibit columnar mesophase at room temperature but compound **9** with rigid bridging chain has no mesophase.

Discotic liquid crystals (LC), with readily self-assemble structure to construct ordered columnar phase that can in turn lead to efficient, directional charge migration, are outstanding candidates for use in organic photoelectric devices, photovoltaic devices, thin film transistors and organic light emitting diodes, etc.¹⁻² Up to now, some discotic liquid crystals, such as triphenylene-based liquid crystals³⁻⁶, and phthalocyanine-based liquid crystals⁷⁻⁹, were investigated extensively.

Perylene derivatives with aromatic imide groups are usually planar, rigid, polar and thermostable. These structural characteristics are favorable for using them as rigid components in organic discotic liquid crystal materials.¹⁰ Moreover, perylenes have been paid particular attentions due to their excellent absorption and emission properties in both solution and solid state. For example, a perylene bisimide derivative exhibits outstanding photovoltaic performance in conjunction with hexabenzocoronene discotic materials.¹¹ Additionally, perylene diimide derivatives possess compact and electron deficient cores, demonstrating a great potential as *n*-type (electron-transporting) semiconductors in comparison to the more common *p*-type counterpart in organic semiconductors.^{12,13} Due to these excellent photoelectric properties, all kinds of perylene derivatives, including perylene liquid crystals, have been reported so far. Generally, perylene liquid crystals were obtained by attaching multiple long aliphatic chains at the imide positions.¹⁴ The first perylene liquid crystals with polyoxyethylene chains were described by Cormier and Gregg.¹⁵ Several perylene-triphenylene derivatives were synthesized as good liquid crystal materials.¹⁶⁻¹⁸ Perylene bisimide discotic liquid crystal were also prepared by modifying imide groups with siloxane¹⁹, alkyl esters²⁰, organosilica²¹, dendritic peptides²², fluoro-pentenyl groups²³, respectively. It was found in these literatures that LC properties were strongly influenced by the nature of the substituents. Most of these perylene liquid crystals possess wide temperature ranges of liquid crystalline phases. They usually display mesophase

beyond the room temperature.²⁴ However, room-temperature liquid crystal is an important property to retain the self-assemble over long periods of time after thermal processing.^{22,25} Up to now, only several room-temperature perylene liquid crystals were reported by introducing alkoxy or alkyl groups^{26,27}, tri-(dodecyloxy)phenyl groups²⁸, phenoxy substituents^{29,30}, and tridodecylphenyl groups³¹ onto imide or perylene core. Lately, Percec group also synthesized several perylene bisimides containing six long alkyl chains with interesting self-repairing complex helical columns near room temperature.³²⁻³⁴ Inspired by the findings described above, in this paper, we designed and synthesized three novel perylene bisimides derivatives containing two gallic acid amides units. The separating procedures were simple with recrystallization and the yields were as high as 75~80%. Moreover, the mesomorphic properties of these novel gallic-perylene-gallic trimers were studied by differential scanning calorimetry (DSC), polarized optical microscopy (POM) and X-ray diffraction (XRD) analysis. The results indicated that compounds **7** and **8** with soft bridging chains exhibit columnar mesophase at room temperature. The scopes of phase transfer temperatures are as wide as 133.9°C and 140.7°C, respectively. But compound **9** with rigid bridging chain has no mesophase. This paper described two unusual room-temperature perylene liquid crystals and gave a good example on how the bridging chains influence greatly on mesomorphic properties.



Scheme 1 The synthetic routes of compounds **7**, **8** and **9**

The synthetic routes of the novel gallic-perylene-gallic trimers were shown in Scheme 1. According to the literature methods³⁵, by reacting methyl gallate **1** with bromodecane in $K_2CO_3/MeCN$,

gallic derivative **2** with three long alkyl chains was obtained in yield of 80%. Subsequently, the ammonolysis derivatives **3** and **4** were prepared by reacting compound **2** with excess ethylenediamine or diethylenetriamine in yields of 86% and 80%, respectively. Also, by the hydrolysis of compound **2**, subsequently converting to acyl chloride and then reacting with *p*-phenylene diamine, the gallic derivative **6** was synthesized in yield of 70% smoothly. Finally, by treating compound **3** (**4** or **6**) with perylene tetracarboxylic anhydride in formdimethylamide (DMF) at 110°C overnight, the target compounds **7**, **8** and **9** were obtained in yields of 75%, 78% and 80%, respectively. The separating procedures were simple with recrystallization. It is worthy of noting that this reaction was carried out efficiently in DMF solution without catalyst, instead of the usual reaction condition of quinoline as solvent and zinc acetate as catalyst.^{10,36}

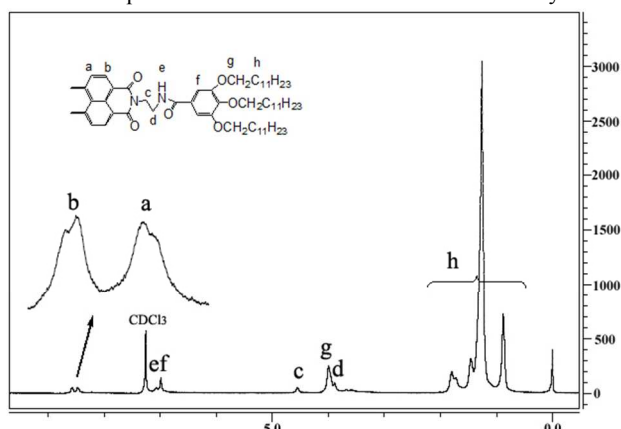


Figure 1 The ^1H NMR spectrum of compound **7**

The structures of novel perylene derivatives were confirmed by the changes of fourier transform infrared spectroscopy spectra of perylene tetracarboxylic anhydride and compounds **7**, **8** and **9**. The disappearance of the anhydride C=O vibration bands at 1770 cm^{-1} and the appearance of imide C=O vibration bands at 1696 cm^{-1} indicate that the anhydride groups are substituted by amide groups completely. Also, the mass spectrometry (MS) spectra of compounds **7**, **8** and **9** showed corresponding molecular ion peaks at 1789.4, 1875.8 and 1885.6, respectively. In the ^1H nuclear magnetic resonance (NMR) spectra of compounds **7**, **8** and **9**, all signals of protons were assigned well for the structures of target molecules. Especially, the ArH of perylene skeleton exhibit two symmetrical doublets at 8.48ppm and 8.60ppm (the ^1H NMR spectrum of compound **7** was illustrated in Figure 1). These ^1H NMR spectra suggested compounds **7**, **8** and **9** possess symmetrical structures which were also supported by the ^{13}C NMR. Elemental analyses were in agreement with the calculated contents of carbon, nitrogen and hydrogen in these compounds. All these characteristic data are in accordance with the structures of compounds **7**, **8** and **9**.

The mesomorphic behaviours of compounds **7**, **8** and **9** were investigated by DSC as shown in Figure 2. The enthalpies of phase transitions were listed in Table 1. Their similar phase transitions temperatures and enthalpies suggested they possess good reversible phase transitions on

heating and cooling. The enthalpies changes of Cr-LC were smaller a little than that of LC-Iso, which might indicated their crystalline phase were mixed with some amorphous phase. Compound **7** shows two phase transfer temperatures at -1.5°C and 132.4°C in the second heating and two reverse processes at 122.8°C and -7.9°C in the cooling. Similarly, compound **8** exhibits two phase transfer temperatures at 15.3°C and 135.9°C for the second heating scan and two reverse processes at 130.3°C and 9.3°C upon cooling. However, compound **9** shows only one peak at second heating or cooling at 158°C . These DSC data suggest that the crystal phase-mesophase-isotropic phase exists on the heating and cooling process for compounds **7** and **8**, but no mesophase phase occurred for compound **9**. Comparing with the structures of compounds **7**, **8** and **9**, these DSC results could be explained by that the soft bridging chains between gallic unit and perylene unit in compounds **7** and **8** are favourable for mesophase. But rigid bridging chain in compound **9** is an obstacle for mesophase due to the core of planar rigid π -conjugate system is too large to produce liquid crystal. Moreover, these DSC data indicate that compounds **7** and **8** present the mesomorphic properties at room temperature, which were seldom observed for perylene liquid crystals.²⁴ Also, from these DSC data, the scopes of phase transfer temperatures are calculated as wide as 133.9°C and 140.7°C for compounds **7** and **8**, respectively. These scopes of phase transfer temperatures are wider than that of most reported perylene liquid crystals.²⁴

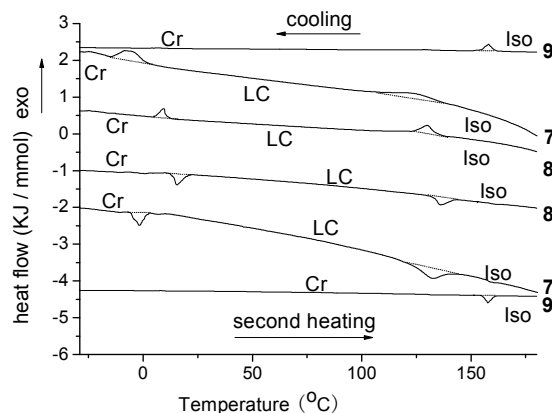


Figure 2 The DSC traces of compounds **7**, **8** and **9** on second heating and cooling (scan rate $10^\circ\text{C min}^{-1}$)

Table 1 Transition temperatures ($^\circ\text{C}$) and enthalpy changes (kJ/mol) of compound **7**, **8** and **9**

compound	Phase transition ^[a]	Heating scan T(ΔH)	Cooling scan T(ΔH)
7	Cr-LC	$-1.5(11.46)$	$-7.9(13.28)$
	LC-Iso	$132.4(12.25)$	$122.8(10.67)$
8	Cr-LC	$15.3(9.77)$	$9.3(8.28)$
	LC-Iso	$135.9(10.86)$	$130.3(11.69)$
9	Cr-Iso	$158.4(7.22)$	$157.8(7.03)$

[a] Cr=crystalline, LC=liquid crystal, Iso=isotropic

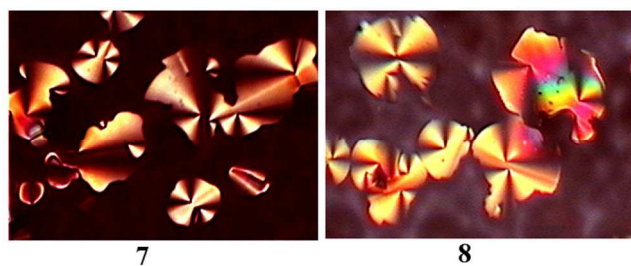


Figure 3 The textures of **7** and **8** obtained with polarized optical microscopy on cooling at 90°C ($\times 400$)

Based on the DSC results, POM was used to study the mesomorphic textures of compounds **7** and **8**. Figure 3 showed their LC textures at the corresponding temperatures. It can be seen that the pseudo-confocal conic textures were observed for compounds **7** and **8**. These textures are typical for columnar mesomorphism, although it is difficult to speculate the specific columnar phase (such as hexagonal or rectangular). Some researchers also reported the similar results that the mesogens typically stack to form columns (not necessarily simple one-molecule-wide columns), but there is no positional order among the columns.^{10, 19, 24, 36}

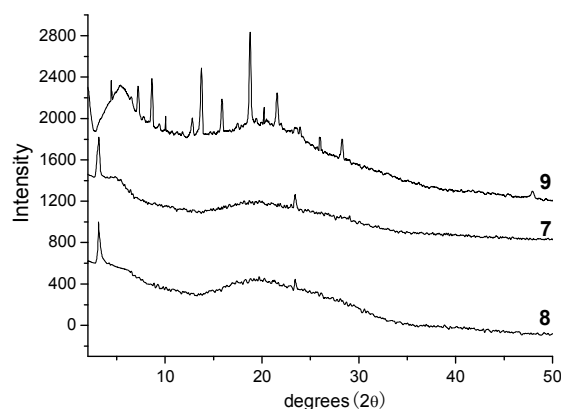


Figure 4. XRD traces of compounds **7**, **8** and **9** measured at 90°C

In order to investigate further the molecular stacking behaviours of mesophase, compounds **7**, **8** and **9** were investigated by XRD at corresponding temperatures (Figure 4). In Figure 4, the complicated peaks of compound **9** were observed for crystalline phase. Also, the XRD of compound **9** over 158°C should no obvious peaks because it was at isotropic phase. However, typical peaks of columnar phase of perylene liquid crystals were observed for compounds **7** and **8**. The reflections at about $2\theta = 3.1^\circ$ correspond to the distances of 28.5Å, which agree reasonably with the molecular length of the perylene diimide group. The broad halos at $2\theta = 15\sim 25^\circ$ are assigned to the average distances of the molten alkyl chains. The reflections at 23.5° indicate the spacing of approximately 3.7Å, which is the typical characteristic of intracolumnar order of discotic liquid crystals with π - π interactions. Although no other obvious XRD reflection is observed to support further the columnar phase, it is reasonable to deduce their columnar liquid crystals based on

these XRD data and the above POM results. These deductions were also in accordance with the similar perylene bisimides containing six long alkyl chains possessing complex helical columns reported by Percec group lately.³²⁻³⁴ However, it is difficult to deduce the specific phase structures of compounds **7** and **8**, such as hexagonal or rectangular liquid crystal phase, due to the absence of characteristic peaks on XRD traces. These XRD results might imply no positional order among the columns, which are in accordance with the analysis of POM results and other columnar perylene liquid crystals with no positional order.^{10, 19, 24, 36}

Combining all the mesomorphic experimental results of DSC, POM and XRD data, it could be concluded that compounds **7** and **8** exhibit columnar mesophases at room temperature and possess wide scopes of phase transfer temperatures, although it is difficult to speculate the specific phase structures.

In conclusion, three novel gallic-perylene-gallic trimers were synthesized conveniently in yields of 75~80% and possess symmetrical structures. Their mesomorphic properties were studied by the DSC, POM and XRD analyses. Compounds **7** and **8** with soft bridging chains show mesophase at room temperature with wide scopes of phase transfer temperature (133.9°C and 140.7°C, respectively) but compound **9** with rigid bridging chain has no mesophase. The POM and XRD results indicate compounds **7** and **8** possess columnar mesophase. These gallic-perylene-gallic trimers are the first liquid crystal of perylene bisimides with amide and amine groups, and their unusual mesomorphic properties were seldom observed for perylene derivatives. This paper also gave a good example on how the bridging chains influence greatly on mesomorphic properties. Based on these research results, the other gallic-perylene-gallic trimers with various bridging chains, which are expected to have unique mesomorphic properties, are being investigated in the following work.

Experimental

General

All chemical reagents were obtained from commercial suppliers. The other organic solvents and inorganic reagents were purified according to standard anhydrous methods before use. NMR spectra were recorded in CDCl_3 on a Bruker-ARX 400 instrument at 30°C. MS spectra were obtained from DECAX-30000 LCQ Deca XP mass spectrometer. Elemental analyses were performed at Vario EL III Elemental Analyzer. POM (Leica DMRX) was used along with a hot stage (Linkam THMSE 600) to examine phase transitions. Thermal analysis of the materials was carried out using DSC (Thermal Analysis Q100) at a scanning rate of 10°C/min under N_2 atmosphere. XRD experiments were performed on SEIFERT-FPM (XRD7), using Cu K α 1.5406 Å as the radiation source with 40 kV, 30 mA power.

Synthetic procedures of compounds **7**, **8** and **9**

Perylene tetracarboxylic anhydride (0.196g, 0.5 mmol) and compound **3** (**4** or **6**) (1 mmol) were stirred and heated in

DMF (30 mL) at 110°C overnight. TLC detection indicated the disappearance of materials. Then distilled water was added in the reaction mixture, and the produced red precipitates were filtered. The red precipitates were washed with methanol. The crude products were purified by recrystallization with CHCl₃/MeOH. The red soft solids were obtained in the yields of 75%, 78% and 80%, respectively. Compound 7: ¹H NMR (400 MHz, CDCl₃) δppm: 0.88(bs, 18H, CH₃), 1.24-1.80(m, 120H, CH₂), 3.89 (bs, 4H, CH₂), 3.99(bs, 12H, CH₂), 4.55(bs, 4H, CH₂), 6.99(s, 4H, ArH), 7.07(s, 2H, NH), 8.48 (d, *J* = 7.6 Hz, 4H, ArH), 8.60 (d, *J* = 7.6 Hz, 4H, ArH); ¹³C NMR (150 MHz, CDCl₃) δppm: 14.049, 22.628, 26.036, 26.110, 29.170, 29.311, 29.411, 29.545, 29.636, 30.281, 31.862, 39.747, 69.096, 73.401, 105.474, 122.750, 123.072, 125.797, 125.867, 129.050, 131.257, 134.220, 140.792, 152.894, 163.690, 167.557; MS *m/z* (%): 1789.4 (M⁺, 100). Anal. calcd for C₁₁₄H₁₇₂N₄O₁₂: C 76.47, H 9.68, N 3.13; found C 76.41, H 9.73, N 3.07%. Compound 8: ¹H NMR (400 MHz, CDCl₃) δppm: 0.89(bs, 18H, CH₃), 1.25-1.79(m, 120H, CH₂), 3.25(bs, 2H, NH), 3.51-4.61(m, 28H, OCH₂ and NCH₂), 6.98(s, 4H, ArH), 7.08(s, 2H, NH), 8.46 (d, *J* = 7.6 Hz, 4H, ArH), 8.58 (d, *J* = 7.6 Hz, 4H, ArH); MS *m/z* (%): 1875.8 (M⁺, 100). Anal. calcd for C₁₁₈H₁₈₂N₆O₁₂: C 75.52, H 9.77, N 4.48; found C 75.47, H 9.72, N 4.44%. Compound 9: ¹H NMR (400 MHz, CDCl₃) δppm: 0.88(bs, 18H, CH₃), 1.23-1.81(m, 120H, CH₂), 3.97(bs, 12H, CH₂), 6.99(bs, 4H, ArH), 7.03 (s, 2H, NH), 8.49 (d, *J* = 6.8 Hz, 4H, ArH), 8.54 (s, 8H, ArH), 8.56 (d, *J* = 6.8 Hz, 4H, ArH); MS *m/z* (%): 1885.6 (M⁺, 100). Anal. calcd for C₁₂₂H₁₇₂N₄O₁₂: C 76.67, H 9.19, N 2.97; found C 76.61, H 9.25, N 3.03%.

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Notes and references

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† Electronic Supplementary Information (ESI) available: The experimental procedures in details were presented in supplementary information. See DOI: 10.1039/b000000x/

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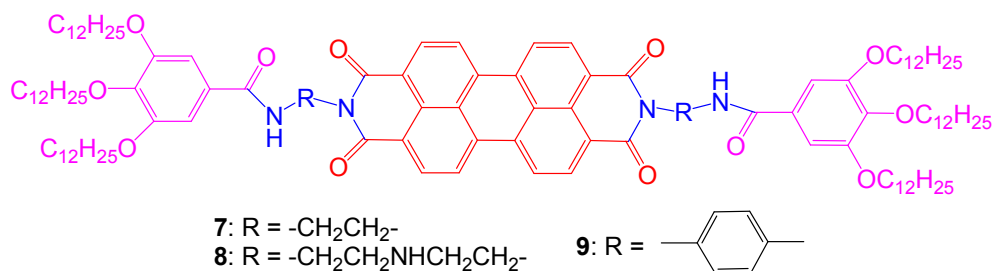
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Novel room-temperature thermotropic liquid crystals: Synthesis and mesomorphism of gallic-perylene-gallic trimers

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