Novel room-temperature perylene liquid crystals: synthesis of 1,7-dibrominated cholesterol–perylene bisimides with different ester-bridging chains and their mesomorphic properties

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ABSTRACT
Three novel 1,7-dibrominated cholesterol–perylene liquid crystals 6a, 6b and 6c with different ester-bridging chains were designed and synthesised in yields of 30–40\%. Their structures were characterised by FT-IR, \textsuperscript{1}H NMR and HR-MS spectra. Their mesomorphic behaviours were studied by differential scanning calorimetry (DSC), polarising optical microscopy (POM) and X-ray diffraction (XRD). Compounds 6a, 6b and 6c exhibit hexagonal columnar liquid crystalline phase at room temperature. Their mesomorphic temperature ranges are as wide as 140–162°C. Their fluorescence spectra suggested that they possess good fluorescence properties in solution. The soft ester-bridging chains are more favourable for room-temperature mesophase and high fluorescence than the rigid ester-bridging chain.

1. Introduction
In recent years, perylene bisimides (PBIs) were used as versatile building blocks to construct well-defined supramolecular structures due to their unique π–π stacking [1–3]. In order to obtain the high-ordering PBI materials with good exciton diffusion length and charge carrier mobility [4,5], PBI liquid crystals (LCs) or organogels were paid much attention because they

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possessed excellent π–π stacking action and improved the supramolecular self-assembling processes [6]. By modifying imide groups with siloxane [7,8], polyoxyethylene chain [9], alkyl esters [10], organosilica [11], dendritic peptides [12], phenoxo substituents [13,14], alkoxy or alkyl groups [15,16] and fluoreponenyl groups [17], the perylene LCs were synthesised conveniently and exhibited interesting mesomorphic properties. The survey of these literatures suggested that perylene LCs showed wide temperature range of mesophase but the LC temperatures (usually >100°C) were far higher than room temperature [18]. However, mesophase temperature near room temperature is important for keeping the self-assembling property for a long time after thermal processing [19,20]. In general, the decrease of the rigidity of perylene core or the increase of the numbers and bulk of soft alkyl chains are the key methods to decline the mesophase temperature. For example, by introducing tri-(dodecyl-oxy)phenyl groups [21], tridodecylphenyl groups [22] or tri-alkyl-gallic groups [23] onto imides of perylene, the obtained perylene LCs exhibited mesophase at room temperature or near room temperature. On the other hand, it is well known that cholesterol was seen as good synthetic platform to construct various liquid crystalline materials [24–31]. Its long and big alkyl unit was favourable for efficient self-assembly and decreasing the LC temperature. Lately, several cholesterol–perylene derivatives were prepared and exhibited excellent supramolecular self-assemble properties to form all kinds of organogels [32–34], but the mesomorphic property of cholesterol–perylene derivative was not investigated up to now. In this paper, 1,7-dibrominated perylene imides was used as LC core and two cholesterol units were introduced onto imides by different ester-bridging chains. The obtained 1,7-dibrominated cholesterol–PBI possess good mesomoprhic properties at room temperature. Their LC phase transition temperature and fluorescence properties are influenced by the different structures of ester-bridging chains.

2. Results and discussion
2.1. Synthesis and characterisation

Previous research had proved that the bay-substituents of perylene could produce steric hindrance to twist the plane of rigid perylene core and enhanced the dissolubility remarkably in all kinds of solvents [35], but the large substituents destroyed the π–π stacking dramatically and were not favourable for mesophase. Thus, in this paper, 1,7-dibrominated perylene imides, with two moderate bulky Br groups on bay-positions, was used as synthetic platform to prepare cholesterol–perylene LCs. On the other hand, for the sake of decreasing LC temperature and avoiding the influence of hydrogen bond, the different long alkyl chains with two ester groups were designed as spacers between perylene core and cholesterol unit, although the normal amide groups were usually used for bridging chains [33,34]. Therefore, the synthetic routes of novel cholesterol–perylene derivatives were designed as Scheme 1. Indeed, we had also tried to synthesise the similar derivative with no bay-substituent on perylene core. But the dissolvability of corresponding perylene imides with no bay-substituent (analogue of compound 5) was very poor in CH2Cl2 and the esterifying reaction in next step was unsuccessful. These designed perylene–cholesterol trimers were expected to possess excellent liquid crystalline behaviours in comparison with the similar trimers or oligomers in literatures [36,37].

According to the literature method [38], by reacting cholesterol with succinic anhydride, maleic anhydride or glutaric anhydride, the cholesterol derivatives with terminal carboxyl 2a, 2b and 2c were prepared in high yields of 80–90%, respectively. On the other hand, the 1,7-dibrominated perylene bisanhydrides 4 were obtained according to the published procedures [35]. Synthesis of PBI 5 was accomplished by the ammonolysis reaction of compound 4 with 6-amino-1-hexanol in NMP solution at 95°C for 6 h. The yield of compound 5 was as high as 85%. Due to the poor dissolubility [35], compounds 4 and 5 were difficult to be purified and used for next step directly. By treating compound 5 and compounds 2a–2c in dry CH2Cl2 with DCC and DMAP as condensating catalyst, cholesterol–perylene derivatives 6a–6c were obtained after column chromatography in yields of 30–40%. In these condensation reactions, some other by-products, such as the complicated isomers in bromination reaction, were separated out but their structures were difficult to be deduced. The novel perylene derivatives 6a, 6b and 6c were characterised by FT-IR, NMR, and high-resolution MS analysis. The mass spectrometry spectra exhibited corresponding molecular ion peaks at 1707.7776, 1703.7420 and 1735.8039, respectively. In the 1H NMR spectra, all signals of protons agreed well with the structures of compounds 6a–6c in Scheme 1. Especially, the ArH of perylene core showed two symmetrical doublets and one singlet, indicating the 1,7-bis-substituents on the perylene skeleton (Figure 1 illustrated the representative 1H NMR spectrum of compound 6b). The 13C NMR
also supported the 1,7-bis-substituents structures. All these characteristic data were in accordance with the structures of compounds 6a-6c. The results implied that the isomers of brominated products (such as 1,6-dibrominated isomers) were removed completely by column chromatography, although compounds 4 and 5 were not purified before reaction. The obtained cholesterol–perylene derivatives 6a-6c can dissolve well in organic solvents such as CHCl₃, toluene, THF and DMF.

### 2.2. Mesomorphic studies

The mesomorphic properties of compounds 6a, 6b and 6c were preliminarily studied by differential scanning calorimetry (DSC). Figure 2 and Table 1 presented the DSC traces and the data of phase transition. It can be seen that compounds 6a, 6b and 6c possessed two phase transition behaviours upon second heating and cooling. For compound 6a with succinic spacers, two exothermic peaks on heating at 34.9°C and 197.7°C, and two endothermic peaks on cooling at 32.6°C and...
180.8°C were clearly detected. Compound 6b with maleic spacers exhibited two exothermic peaks at 50.3°C and 190.4°C for heating and two endothermic peaks at 44.9°C and 172.6°C for cooling. Compound 6c with glutaric spacers also showed two exothermic peaks for heating at 26.2°C and 174.5°C and two endothermic peaks for cooling at 24.9°C and 168.2°C. These DSC data implied that compounds 6a, 6b and 6c have the reversible phase transition of solid state–mesophase and mesophase–isotropic phase on cooling and heating. The slightly hysteresis phenomena could be ascribed to supercooling, which was usually observed for such viscous materials. Based on these DSC data, it could be deduced that compounds 6a-6c possessed liquid crystalline behaviours on heating and cooling, which were further supported by polarising optical microscopy (POM) images. Moreover, compounds 6a-6c showed low solid state–mesophase temperatures. Especially, the solid state–mesophase temperatures of compounds 6a and 6c were as low as 25–35°C. Comparing perylene LCs with normal alkyl chains on imides [7–17], the low phase transition temperatures could be attributed to the favourable influences of big cholesterol unit and Br-substituents on bay-positions. The solid state–mesophase temperature (50.3°C) of compound 6b was higher obviously than that of compounds 6a and 6c, which could be ascribed to the influence of rigid maleic unit. On the other hand, the mesophase temperature ranges of compounds 6a, 6b and 6c after calculation were as wide as 162.8°C, 140.1°C and 148.3°C, respectively. These results suggested that novel 1,7-dibrominated cholesterol–perylene LCs possess not only the wide mesophase temperature ranges but also the room-temperature mesophase.

Based on the DSC results, the polarised optical microscopy was employed to investigate the mesophase textures of compounds 6a, 6b and 6c upon heating and cooling. All of them exhibited two phase transitions of solid state–mesophase and mesophase–isotropic phase on heating and cooling. The cloudy liquid between the two phase transition temperatures and clear liquid above mesophase–isotropic phase temperature were observed on heating. Moreover, the mesophase textures emerged slowly upon cooling. Figure 3 exhibited the textures of compounds 6a, 6b and 6c at corresponding temperatures under POM. One can see that they possessed the pseudo-confocal conic textures, which are typical textures for columnar mesophase.

Furthermore, the columnar stacking behaviours of compounds 6a, 6b and 6c were investigated by X-ray diffraction (XRD) analysis. Figure 4 illustrated the XRD traces of mesophase at 100°C. In the small angle regions, two peaks at 3.3–4.0° were observed obviously for compounds 6a, 6b and 6c. In wide angle regions, all of them exhibited similar broad halos at 16 ~ 30° and a reflection at 24° approximately. These data strongly supported that they possessed columnar mesophase. The d-spacing calculated by 3.3–4.0° were 25.97 and 22.46 Å for compound 6a, respectively. The d-spacings calculated from these angles were 25.97 and 22.46 Å for compound 6a.

**Table 1.** Transition temperatures (peak temperature/°C) and associated enthalpy changes (kJ/mol in parentheses) of compounds 6a, 6b and 6c.

| Compd.       | Phase[a] | ΔT(°C) | Phase | ΔH(kJ/mol) | Phase | ΔT(°C) | ΔH(kJ/mol) | Phase |
|--------------|----------|--------|-------|------------|-------|--------|------------|-------|
| 6a (second heating) | Cr 34.9(20.1) | LC 197.7(16.3) | Iso   |
| 6a (cooling)   | Cr 32.6(13.9) | LC 180.4(8.8) | Iso   |
| 6b (second heating) | Cr 50.3(12.6) | LC 190.4(16.8) | Iso   |
| 6b (cooling)   | Cr 44.9(15.1) | LC 172.6(15.3) | Iso   |
| 6c (second heating) | Cr 26.2(19.9) | LC 174.5(17.4) | Iso   |
| 6c (cooling)   | Cr 24.9(13.3) | LC 168.2(12.8) | Iso   |

[a] Heating is Cr: crystalline, LC: liquid crystalline, Iso: isotropic.

**Figure 3.** (Colour online) Textures of compounds 6a, 6b and 6c obtained with polarised optical microscopy (×400) on cooling at 100°C.
25.66 and 22.24 Å for compound 6b, 26.35 and 22.81 Å for compound 6c, respectively. These data were well in accordance with the ratios of $2/\sqrt{3}$, indicating the hexagonal columnar LC. On the other hand, the molecular lengths of compounds 6a, 6b and 6c were calculated as 42 Å according to the Corey-Pauling-Koltun (CPK) model (Figure 5(a)), which was far bigger than the inter-column spacings of XRD data. These results suggested that the alkyl chains on imides of perylene were not straight linear but curly shape in mesomorphic phases. The curly shape might be favourable for the hexagonal columnar LC. The possible driving force might be the core-packing interaction for this kind of hairpin-like trimers [39]. According to the XRD analysis, the proposed arrangement for the molecular stacking of hexagonal columns of compounds 6a, 6b and 6c were presented in Figure 5(b).

The excellent fluorescence is the important property for perylene derivatives. The photophysical properties of compounds 6a, 6b and 6c were also studied by absorption spectra and fluorescence spectra. Figures 6 and 7 presented the representative absorption spectra and fluorescence spectra of compound 6a, respectively. In different organic solvents, the absorbency and fluorescence intensity changed dramatically, although the maximal absorption wavelength and emission wavelength shifted a little. The strongest emission in CHCl$_3$ solution was observed. Thus, the absorption spectra and fluorescence spectra of compounds 6a, 6b and 6c in CHCl$_3$ solution were studied in details and the results were shown in Figures 8 and 9. One can see that their maximal absorption spectra, maximal emission and Stokes shift (21 nm approximately) were almost same, suggesting the maximal absorption

**Figure 4.** XRD traces for compounds 6a, 6b and 6c on cooling at 100°C.

**Figure 5.** Schematic representation of columnar hexagonal packing parameters in liquid crystalline mesophases for compounds 6a, 6b and 6c.

**Figure 6.** (Colour online) Absorption spectra of 6a in different solvents ($10^{-5}$M).

**Figure 7.** (Colour online) Fluorescence spectra of 6a in different solvents ($10^{-5}$M). The excitation wavelength was 520 nm.
wavelength and emission wavelength were mainly decided by the structure of perylene core. However, they exhibited different absorbencies and fluorescence intensities, which could be attributed to the influences of alkyl chains on imides. The fluorescence intensity of compound 6b was lower obviously than that of compounds 6a and 6c. This result could be explained by that the maleic group is a rigid one, which is favourable for the orderly aggregates, resulting in the strong aggregation-caused quenching. The fluorescence of their solid state were also investigated but no fluorescence was detected, suggesting the strong aggregation-caused quenching in solid state. This phenomenon was normal for perylene derivatives. All these photophysical studies suggested that compounds 6a, 6b and 6c possess good fluorescence properties in solution. Compounds 6a and 6c with soft bridging chains exhibited stronger fluorescence than compound 6b with rigid bridging chain.

3. Conclusions

In conclusion, three novel cholesterol–perylene LCs with different ester-bridging chains 6a, 6b and 6c were designed and synthesised in yields of 30–40%. Their structures were characterised by FTIR, 1H NMR, MS spectra. Their mesomorphic behaviours were studied by DSC, POM and XRD. Their photophysical properties were also investigated by absorption spectra and fluorescence spectra. These mesomorphic results suggested that novel 1,7-dibrominated cholesterol–perylene derivatives are hexagonal columnar LCs at room temperature with wide mesophase temperature ranges. The photophysical results implied that they have good fluorescence properties in solution. Comparing with rigid ester-bridging chain, the soft ester-bridging chains were favourable for the room-temperature mesophase and excellent fluorescence.

4. Experimental

The organic solvents and inorganic reagents were purified according to standard anhydrous methods before use. All chemical reagents were obtained from Aladdin Co., Ltd. and used without further purification. Thin-layer chromatography (TLC) analysis was performed using pre-coated glass plates. Column chromatography was performed by using silica gel (200–300 mesh). IR spectra were recorded on a Perkin-Elmer PE-983 infrared spectrometer as KBr pellets with absorption in cm⁻¹. NMR spectra were recorded in CDCl₃ on a Bruker-ARX.
400 instrument at 30°C. Chemical shifts are reported in ppm, using tetramethylsilane (TMS) as internal standard. ESI-MS spectra were obtained from Bruker mass spectrometer. A polarised optical microscopy (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 N₂ atmosphere. XRD experiments were performed on SEIFFERT-FPM (XRD7), using Cu Ka 1.5406 Å as the radiation source with 40 kV, 30 mA power. Compounds 2a-2c and 4 were prepared by literature methods, respectively [35,38].

4.1. Synthesis of perylene bisimides 5
The mixture of 1,7-dibromoperylene tetracarboxylic anhydride (0.5 g, 0.9 mmol) and 6-amino-1-hexanol (0.27 g, 2.3 mmol) were stirred in NMP (15 mL) under N₂ atmosphere at 95°C for 6 h. After cooling, 50 mL of distilled water was added in the reaction mixture, and the red precipitate was obtained. Then the red precipitate was filtered and washed with 30 mL of methanol. The crude product was obtained in yield of 85%. Due to the poor solubility of crude product, the NMR spectrum was not done. It was not further purified and used directly for the next step. Compound 5: FT-IR(KBr), v/cm⁻¹: 3392, 2937, 1698, 1658, 1591, 1435, 1337, 1241, 1052, 808, 746. HR-MS (ESI): m/z calculated for C₃₆H₃₂Br₂N₂O₆ 771.0503[M+Na]⁺; found 771.0525.

4.2. Synthesis of 1,7-dibrominated perylene–cholesterol derivative 6a
Under N₂ atmosphere, the mixture of compound 5 (0.22 g, 0.30 mmol) and compound 2a (0.36 g, 0.74 mmol) was stirred at room temperature in 50 mL of dry CH₂Cl₂ for 36 h by using DCC (0.2 g) and DMAP (0.1 g) as catalyst. TLC detection indicated the appearance of a new red dot. After reaction, the solution was washed by 3 × 60 mL of water. The organic layer was separated and dried by anhydrous MgSO₄. Then, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography (CH₂Cl₂/ethyl acetate (49/1, v/v)). Compound 6a was obtained as red solid in yield of 39%. Compound 6b: FT-IR(KBr), v/cm⁻¹: 2936, 2864, 1720,1703,1663, 1591, 1393, 1335, 1295, 1155, 809, 746.¹H-NMR(400 MHz, CDCl₃) δ (ppm): 9.51(d, J = 8.0 Hz, 2H, ArH), 8.93(s, 2H, ArH), 8.73(d, J = 8.0 Hz, 2H, ArH), 6.81(s, 4H, HC=CH), 5.38(bs, 2H, C=CH), 4.73 (bs, 2H, OCH), 4.19(m, 8H, NCH₂), 4.10(t, J = 9.6 Hz, 4H, OCH₂), 2.61(s, 8H, COCH₂), 0.62–2.30(m, 102H, CH₃, CH₂ and CH₃).¹³C-NMR(100 MHz, CDCl₃) δ (ppm): 172.41, 171.45, 162.82, 162.15, 139.61, 137.91, 132.90, 132.67, 129.14, 128.70, 128.40, 122.98, 122.64, 120.83, 74.09, 64.53, 56.51, 55.93, 49.82, 42.07, 40.45, 39.19, 37.80, 36.61, 36.41, 35.92, 35.73, 31.62, 29.10, 28.01, 27.54, 26.38, 25.63, 24.23, 23.84, 22.80, 20.71, 19.30, 11.51. HR-MS (ESI): m/z calculated for C₉₈H₁₂₃Br₂N₂O₁₂ 1707.7726 [M+Na]⁺; found 1707.7776.

4.3. Synthesis of 1,7-dibrominated perylene–cholesterol derivative 6b
Under N₂ atmosphere, the mixture of compound 5 (0.30 g, 0.40 mmol) and compound 2b (0.44 g, 0.90 mmol) was stirred at room temperature in 60 mL of CH₂Cl₂ for 36 h by using DCC (0.2 g) and DMAP (0.1 g) as catalyst. TLC detection indicated the appearance of a new red dot. After reaction, the solution was washed by 3 × 60 mL of water. The organic layer was separated and dried by anhydrous MgSO₄. Then, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography (CH₂Cl₂/ethyl acetate (49/1, v/v)). Compound 6b was obtained as red solid in yield of 39%. Compound 6b: FT-IR(KBr), v/cm⁻¹: 2936, 2864, 1720,1703,1663, 1591, 1393, 1335, 1295, 1155, 809, 746.¹H-NMR(400 MHz, CDCl₃) δ (ppm): 9.51(d, J = 8.0 Hz, 2H, ArH), 8.93(s, 2H, ArH), 8.73(d, J = 8.0 Hz, 2H, ArH), 6.81(s, 4H, HC=CH), 5.38(bs, 2H, C=CH), 4.73 (bs, 2H, OCH), 4.19(m, 8H, NCH₂ and OCH₂), 0.62–2.33(m, 102H, CH₃, CH₂ and CH₃).¹³C-NMR(100 MHz, CDCl₃) δ (ppm): 164.95, 164.27, 162.77, 162.31, 139.30, 137.93, 134.92, 134.0, 133.25, 132.96, 132.88, 129.95, 129.25, 128.53, 126.71, 123.01, 122.83, 122.57, 74.95, 65.09, 56.70, 56.11, 49.97, 42.05, 40.43, 39.58, 37.85, 36.78, 36.45, 35.78, 31.68, 28.20, 27.49, 26.45, 25.48, 24.12, 23.82, 22.82, 22.40, 19.26, 18.52, 11.87. HR-MS (ESI): m/z calculated for C₉₈H₁₂₃Br₂N₂O₁₂ 1707.7413 [M+Na]⁺; found 1703.7420.

4.4. Synthesis of 1,7-dibrominated perylene–cholesterol derivative 6c
Under N₂ atmosphere, the mixture of compound 5 (0.23 g, 0.31 mmol) and compound 2b (0.37 g, 0.74 mmol) was stirred at room temperature in 50 mL of CH₂Cl₂ for 36 h by using DCC (0.2 g) and DMAP (0.1 g) as catalyst. TLC detection indicated the appearance of a new red dot. After reaction, the solution was washed by 3 × 60 mL of water. The organic layer was separated and dried by
anhydrous MgSO₄. Then, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography (CH₂Cl₂/ethyl acetate (49/1, v/v)). Compound 6c was obtained as red solid in yield of 37%. Compound 6c: FT-IR(KBr), v/cm⁻¹: 2934, 2854, 1733, 1704, 1663, 1591, 1451, 1336, 1231, 1168, 808, 746. ¹H-NMR(400 MHz, CDCl₃) δ (ppm): 9.51(d, J = 8.0 Hz, 2H, ArH), 8.94(s, 2H, ArH), 8.72(d, J = 8.0 Hz, 2H, ArH), 5.36(bs, 2H, C=CH), 4.50 (bs, 2H, OCH), 4.20(t, J = 9.6 Hz, 4H, OCH₂), 0.62–2.63(m, 114H, CH, CH₂ and CH₃). ¹³C-NMR(100 MHz, CDCl₃) δ (ppm): 172.70, 171.26, 162.97, 162.36, 139.76, 139.40, 138.04, 132.99, 132.92, 129.16, 128.42, 127.03, 123.07, 122.64, 120.82, 74.01, 64.23, 56.68, 55.91, 49.95, 42.30, 39.57, 36.31, 35.80, 34.26, 33.21, 27.58, 26.04, 25.38, 24.57, 24.08, 23.56, 22.69, 22.33, 20.78, 19.98, 19.36, 18.73, 11.94. HR-MS (ESI): m/z calculated for C₁₀₀H₁₃₂Br₂N₂O₁₂ 1735.8040 [M+Na]⁺; found 1735.8039.

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Disclosure statement

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