Supporting Information

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

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The synthetic process of target compounds and their characteristic spectra.

Compounds **2a-2c** and **4** were prepared by literature methods, respectively (J Org Chem. 2004;69:7933-7939 and J Appl Polym Sci. 1999;72:763-770)

Scheme S1. The synthetic routes of title compounds **6a-6c**

1. *Synthesis of perylene bisimides 5.*

The mixture of 1,7-dibromoperylene tetracarboxylic anhydride (0.5g, 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 precipitates were obtained. Then the red precipitates were filtered and washed with 30mL of methanol. The crude product was obtained in yield of 85%. Due to the poor solubility of crude product, the NMR spectra was not done. It was not further purified and used directly for the next step. Compound **5**: FT-IR(KBr), ν/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.

Scheme S2. FT-IR spectrum of compound **5**

Scheme S3. HR-MS(ESI) spectrum of compound **5**

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 CH₂Cl₂ by using DCC (0.2g) and DMAP (0.1g) as catalyst for 36 h. TLC detection indicated the appearance of a new red dot. After reaction, the solution was washed by 3×50 mL of water and 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 36%. Compound **6a**: FT-IR (KBr), ν/cm^{-1} : 2941, 2865, 1734, 1702, 1663, 1591, 1393, 1335, 1243, 1163, 808, 746. ¹H-NMR(400MHz, CDCl₃) δ (ppm): 9.51(d, J =8.0Hz, 2H, ArH), 8.93(s, 2H, ArH), 8.72(d, J =8.0Hz, 2H, ArH), 5.45(bs, 2H, C=CH), 4.59 (bs, 2H, OCH), 4.21(t, J =9.6Hz, 4H, NCH₂), 4.10(t, J =9.6Hz, 4H, OCH₂), 2.61(s, 8H, COCH₂), 0.62-2.30(m, 102H, CH, CH₂ and CH₃).

^{13}C -NMR(100MHz, CDCl_3) δ (ppm): 172.41, 171.45, 162.82, 162.15, 139.61, 137.91, 132.90, 132.67, 132.42, 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 $\text{C}_{98}\text{H}_{128}\text{Br}_2\text{N}_2\text{O}_{12}$ 1707.7726 $[\text{M}+\text{Na}]^+$; found 1707.7776.

Scheme S4. FT-IR spectrum of compound **6a**

Scheme S5. ^1H NMR spectrum of compound **6a**

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 by using DCC (0.2g) and DMAP (0.1g) as catalyst for 36 h. TLC detection indicated the appearance of a new red dot. After reaction, the solution was washed by 3×60 mL of water and 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(400MHz, CDCl₃) δ (ppm): 9.51(d, *J*=8.0Hz, 2H, ArH), 8.93(s, 2H, ArH), 8.73(d, *J*=8.0Hz, 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, CH, CH₂ and CH₃). ¹³C-NMR(100MHz, 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 C₉₈H₁₂₄Br₂N₂O₁₂ 1703.7413 [M+Na]⁺; found 1703.7420.

Scheme S8. FT-IR spectrum of compound **6b**

Scheme S9. ¹H NMR spectrum of compound **6b**

Scheme S10. ¹³C NMR spectrum of compound **6b**

Scheme S11. HR-MS(ESI) spectrum of compound **6b**

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 by using DCC (0.2g) and DMAP (0.1g) as catalyst for 36 h. TLC detection indicated the appearance of a new red dot. After reaction, the solution was washed by 3×60 mL of water and 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), ν/cm^{-1} : 2934, 2854, 1733, 1704, 1663, 1591, 1451, 1336, 1231, 1168, 808, 746. ¹H-NMR(400MHz, CDCl₃) δ (ppm): 9.51(d, $J=8.0\text{Hz}$, 2H, ArH), 8.94(s, 2H, ArH), 8.72(d, $J=8.0\text{Hz}$, 2H, ArH), 5.36(bs, 2H, C=CH), 4.50 (bs, 2H, OCH), 4.20(t, $J=9.6\text{Hz}$, 4H, NCH₂), 4.08(t, $J=9.6\text{Hz}$, 4H, OCH₂), 0.62-2.63(m, 114H, CH, CH₂ and CH₃). ¹³C-NMR(100MHz, 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, 30.97, 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.

Scheme S12. FT-IR spectrum of compound **6c**

Scheme S13. ¹H NMR spectrum of compound **6c**

Scheme S14. ¹³C NMR spectrum of compound **6c**

Scheme S15. HR-MS(ESI) spectrum of compound **6c**