Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Synthesis, mesomorphic and photophysical properties of novel triads and pentads of perylene liquid crystals with cholesterol units on bay-position

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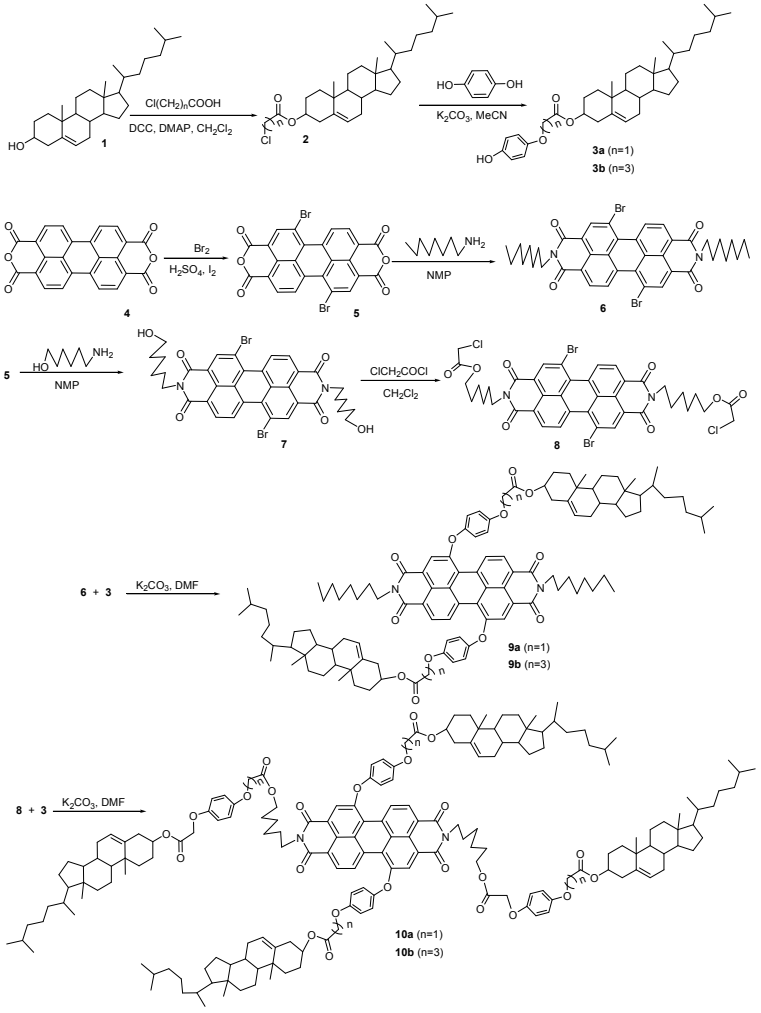
The synthetic process of target compounds and their characteristic spectra.

Compounds **2a** and **2b** were synthesized by the reported procedures in our previous paper (Tetrahedron Letters, 2015, 56(6), 866-870). Compound **5** was prepared according to the published literature (J Org Chem, 2004, 69, 7933-7939.)



Scheme S1 The synthetic routes of novel perylene liquid crystals **9a**, **9b**, **10a** and **10b**

1. The synthetic procedure of compounds **3a** and **3b**. Under N_2 atmosphere, the mixture of compound **2a** or **2b** (1 mmol), hydroquinone (0.55g, 5 mmol) and K_2CO_3 (0.69g, 5 mmol) were stirred in DMF (50 mL) at 110°C for 20h. TLC detection suggested the disappearance of compound **2**. After cooling, 50 mL of HCl solution (1M) was added slowly in the reaction system, and the white precipitates appeared. Then the precipitates were filtered and purified by recrystallization with (CH_2Cl_2/ CH_3OH (1/1, v/v)) for three times. The compound **3a** and **3b** were obtained as white solid in the yields of 63% and 67%, respectively. Compound **3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δppm: 0.68~2.35 (m, 43H of cholesterol), 4.55 (s, 2H, OCH_2), 4.76 (bs, 1H, OCH on cholesterol), 5.40 (s, 1H, CH=C on cholesterol), 6.77 (d, *J*=8.0Hz, 2H, ArH), 6.82 (d, *J*=8.0Hz, 2H, ArH), 6.86 (s, 1H, OH). Compound **3b**: ^{1}H NMR (400 MHz, $CDCl_3$) δppm: 0.68~2.35 (m, 45H of cholesterol), 2.50 (t, 2H, *J*=7.6Hz, CH_2CO), 3.51 (t, 2H, *J*=7.6Hz, OCH_2), 3.96 (bs, 1H, OCH on cholesterol), 4.60 (bs, 1H, OH), 5.38 (s, 1H, CH=C on cholesterol), 6.76 (d, *J*=8.0Hz, 2H, ArH), 6.78 (d, *J*=8.0Hz, 2H, ArH).

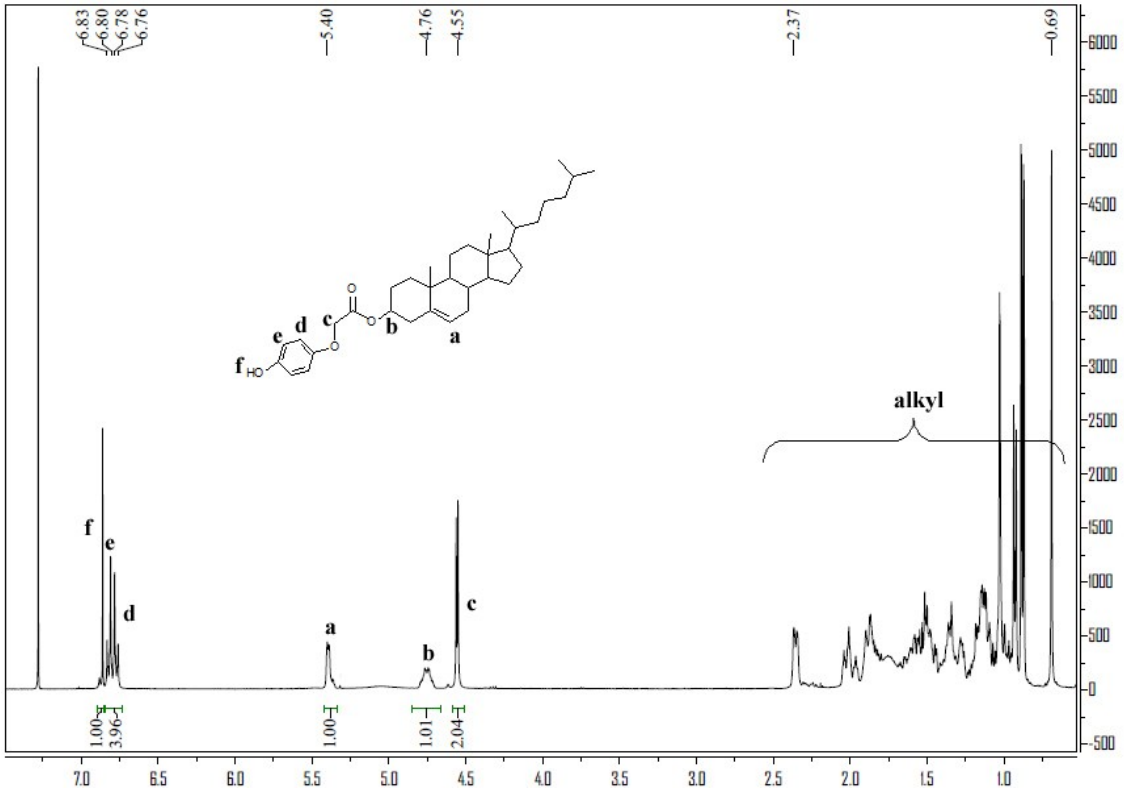


Figure S1. ^{1}H NMR spectrum of compound **3a**

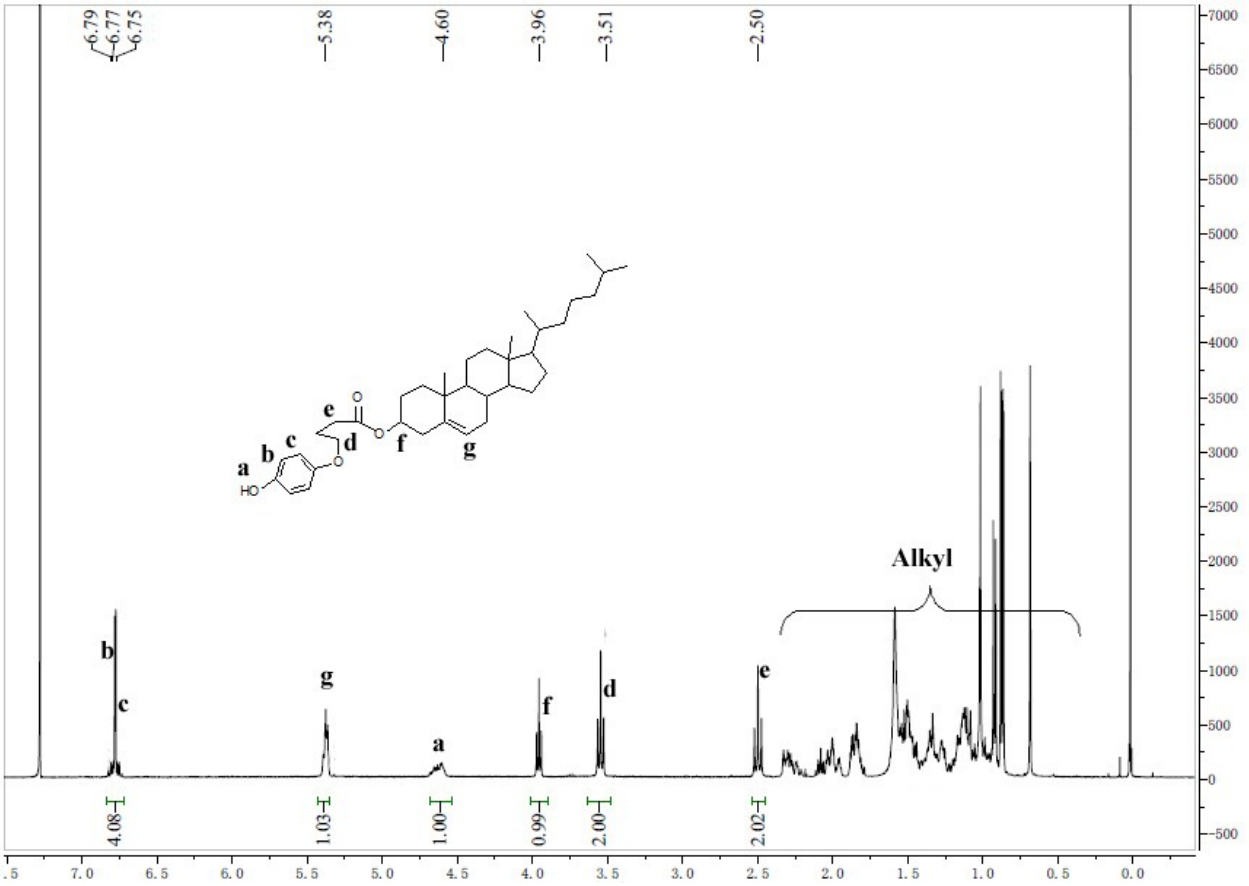


Figure S2. ^{1}H NMR spectrum of compound **3b**

3 The synthetic procedure of compound **6**. The mixture of 1,7-dibromoperylene tetracarboxylic anhydride **5** (0.55g, 1 mmol) and octylamine (0.27g, 2.1 mmol) were stirred in NMP (50 mL) under N_2 atmosphere at 80 ^{o}C for 10 h. After cooling, 50 mL of distilled water was poured in the reaction mixture, and the red precipitates were appeared. Then the red precipitates were filtered and washed by methanol. The crude product was purified by column chromatography (CH_2Cl_2/ ethyl acetate(5/1, v/v)). The compound **6** were obtained as red solid in the yield of 86%. Compound **6**: ^{1}H NMR (400 MHz, $CDCl_3$) δppm: 9.34(d, J = 8.0 Hz, 2H, ArH), 8.78(s, 2H, ArH), 8.57(d, J = 8.0 Hz, 2H, ArH), 4.16(t, J = 8.0 Hz, 4H, NCH_2), 1.73(bs, 4H, CH_2), 1.22-1.50 (m, 20H, CH_2), 0.88 (t, J = 8.0Hz, 6H, CH_3); MALDI-TOF-MS ($C_{40}H_{40}Br_2N_2O_4$) $[M]^+$: Calcd.: 772.1. found:771.6.

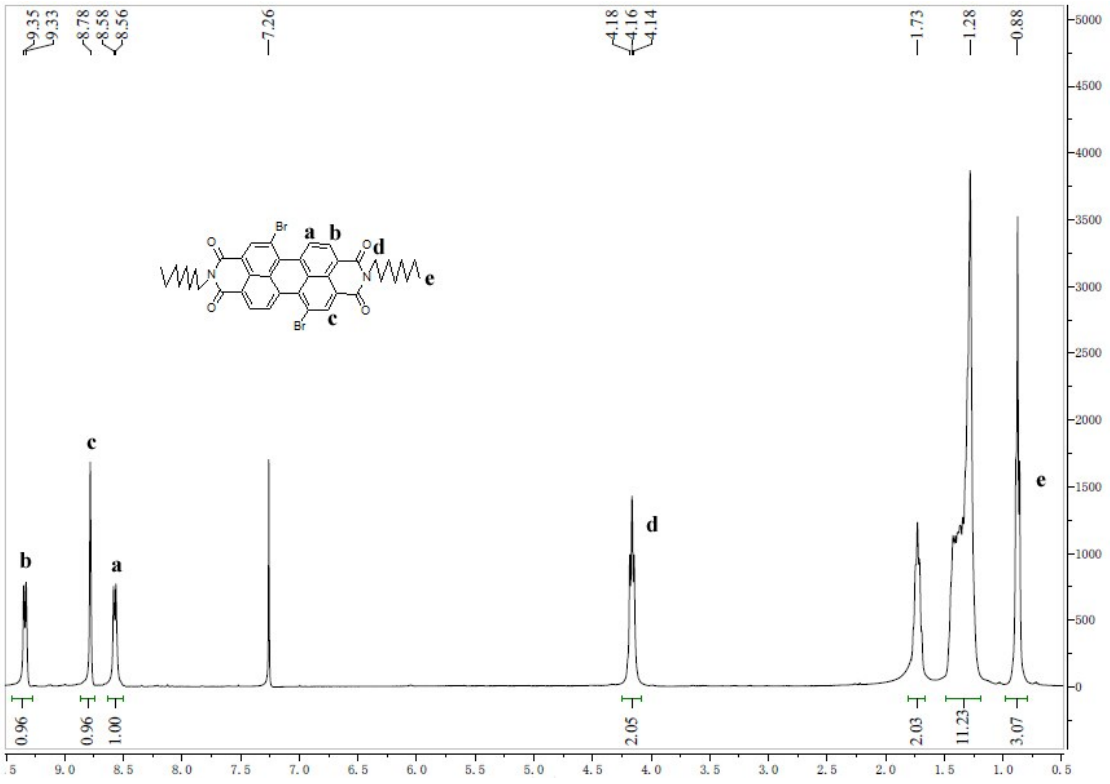


Figure S3. ^{1}H NMR spectrum of compound **6**

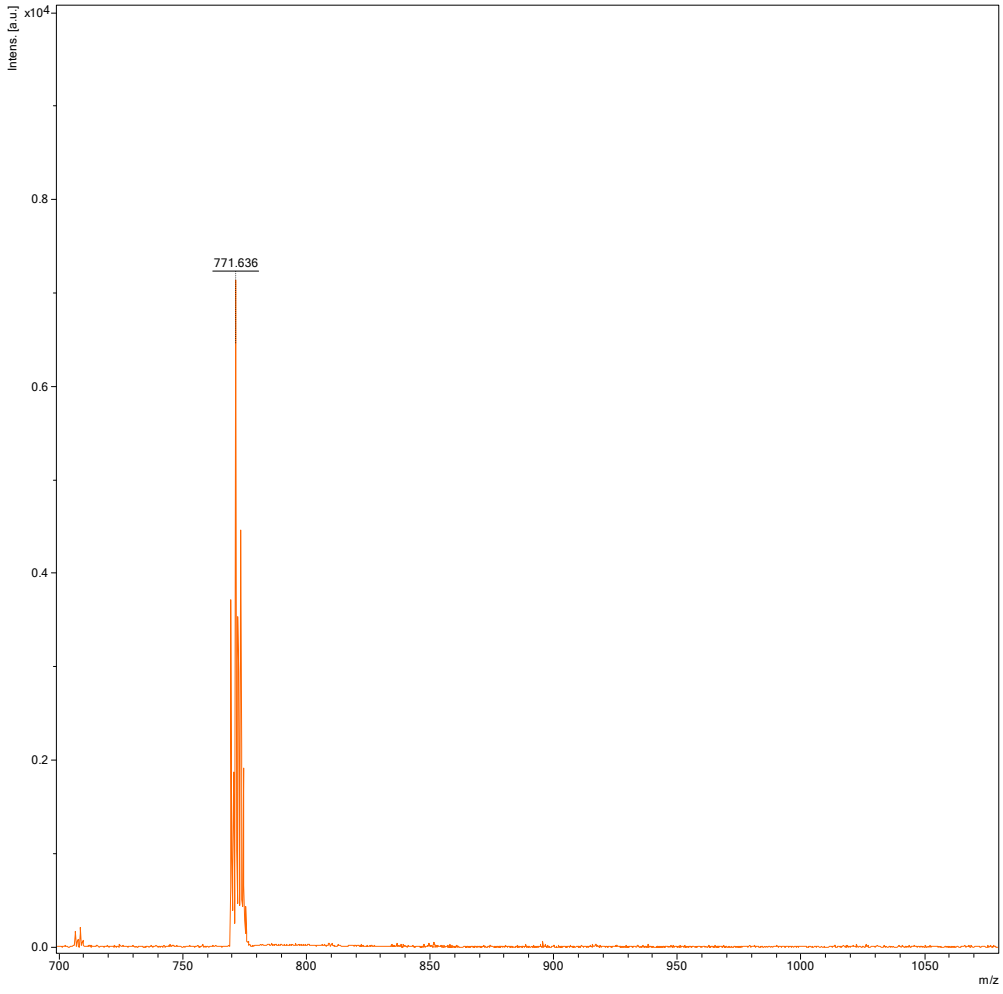


Figure S4. MALDI-TOF-MS spectrum of compound **6**

4 The synthetic procedure of compound **7**. 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 N_2 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 **7**: FT-IR(KBr), v/cm^{-1}: 3392, 2937, 1698, 1658, 1591, 1435, 1337, 1241, 1052, 808, 746. MALDI-TOF-MS: calculated for $C_{36}H_{32}Br_2N_2O_6$ 771.0503[M+Na]$^+$; found 771.0525.

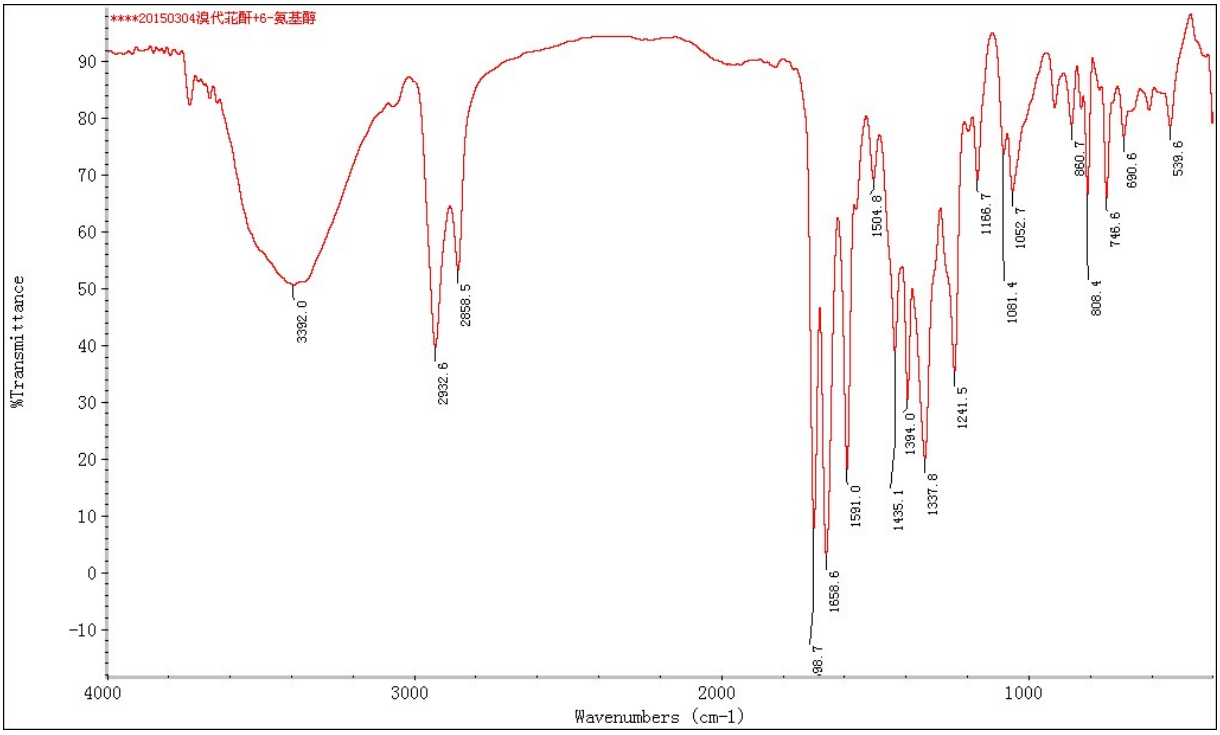


Figure S5. FT-IR spectrum of compound **7**

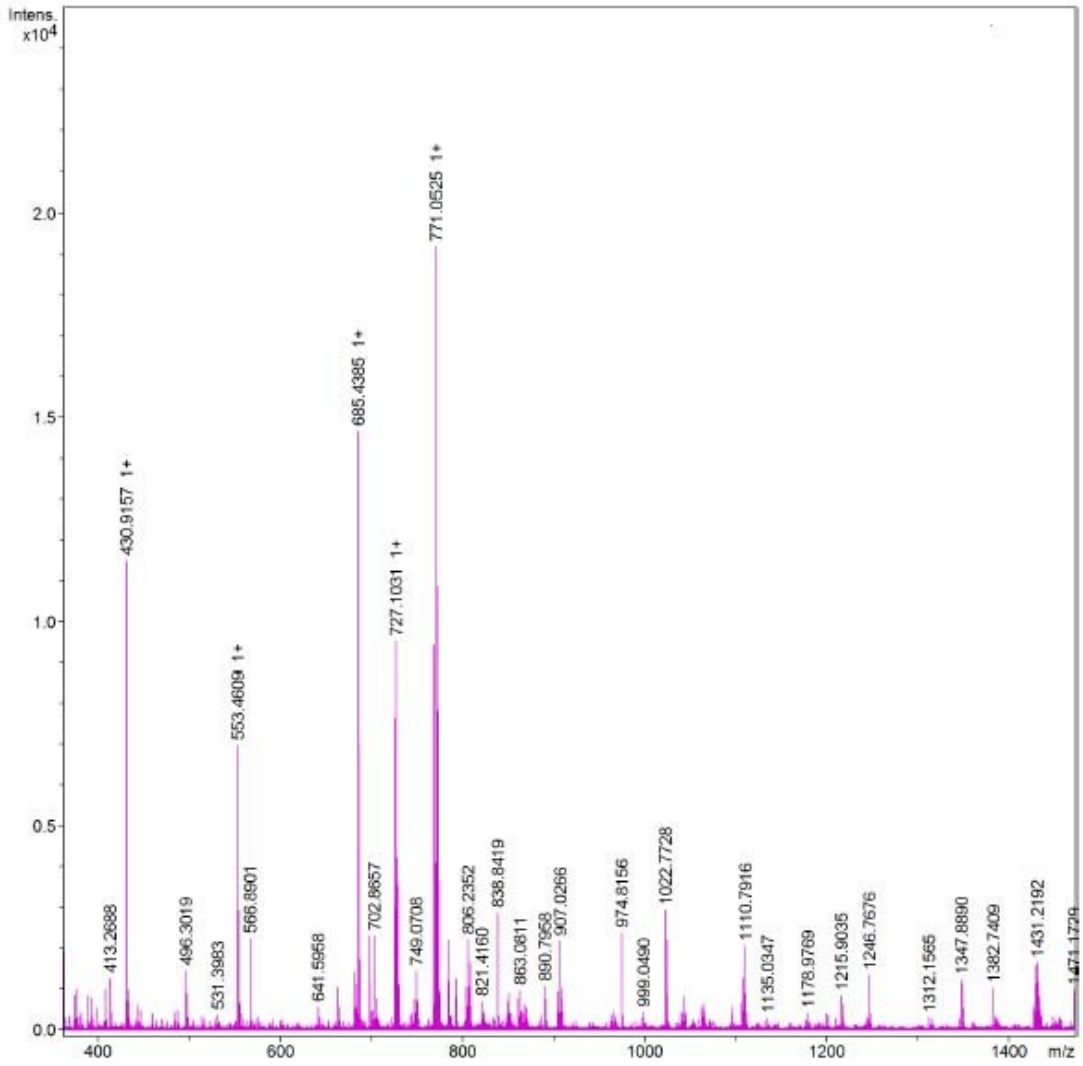


Figure S6. HR-MS(ESI) spectrum of compound **7**

The synthetic procedure of compound **8**. The mixture of compound **7** (0.38g, 0.05 mmol) and chloracetyl chloride (0.5 mL) were stirred in CH_2Cl_2 (10 mL) under N_2 atmosphere at 35°C for 6h. TLC detection implied the disappearance of reactant. Then, 10 mL of distilled water was added and the organic layer was seperated. The organic layer was washed with brine solution and dried over anhydrous $MgSO_4$. The solution was concentrated and 10 mL of MeOH was added in it. The red precipitate was collected and purified by column chromatography (CH_2Cl_2/ ethyl acetate(10/1, v/v)). The compound **8** were obtained as red solid in the yield of 75%. Compound **8**: ^{1}H NMR (400 MHz, $CDCl_3$) δppm: 9.44(d, J = 8.0 Hz, 2H, ArH), 8.87(s, 2H, ArH), 8.66(d, J = 8.0 Hz, 2H, ArH), 4.16-4.22(m, 8H, OCH_2 and NCH_2), 4.06 (s, 4H, $ClCH_2CO$), 1.40-1.80(m, 16H, CH_2); MALDI-TOF-MS ($C_{40}H_{34}Br_2Cl_2N_2O_8$) $[M]^+$: Calcd.: 900.0. found:899.5.

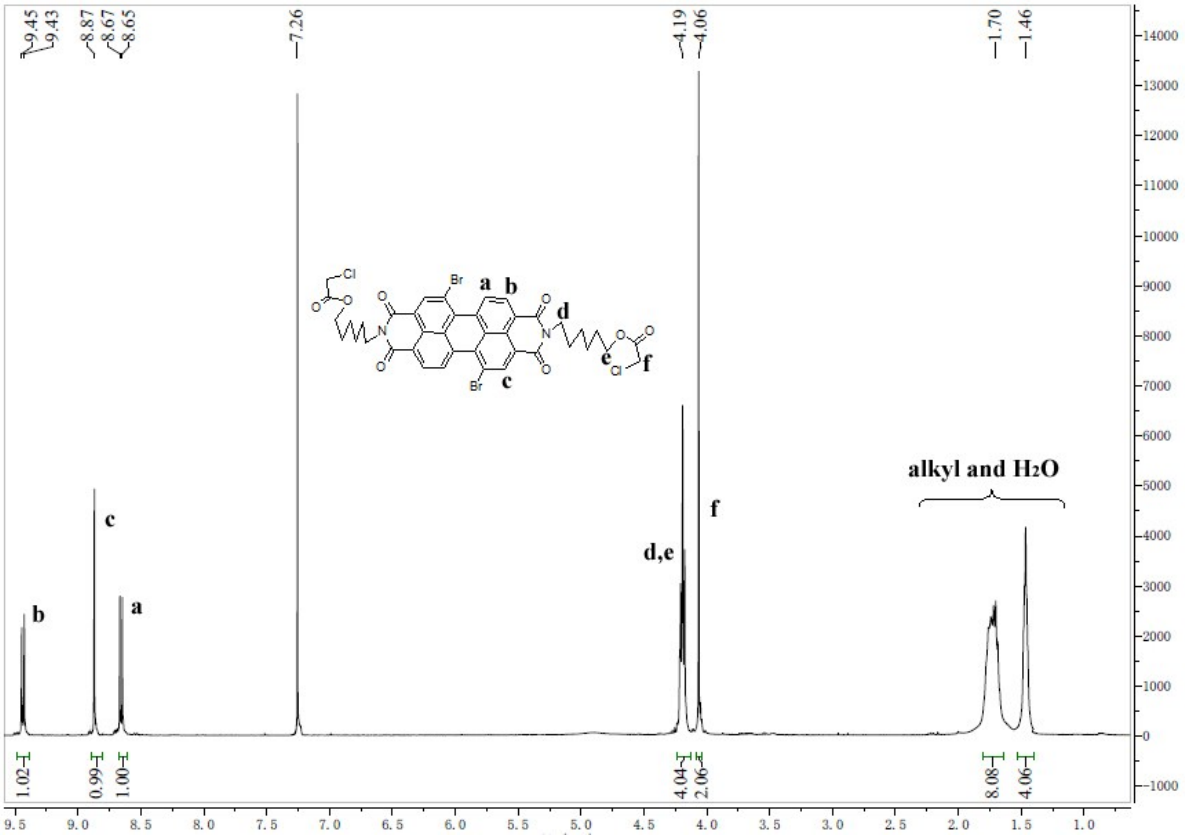


Figure S7. ^{1}H NMR spectrum of compound **8**

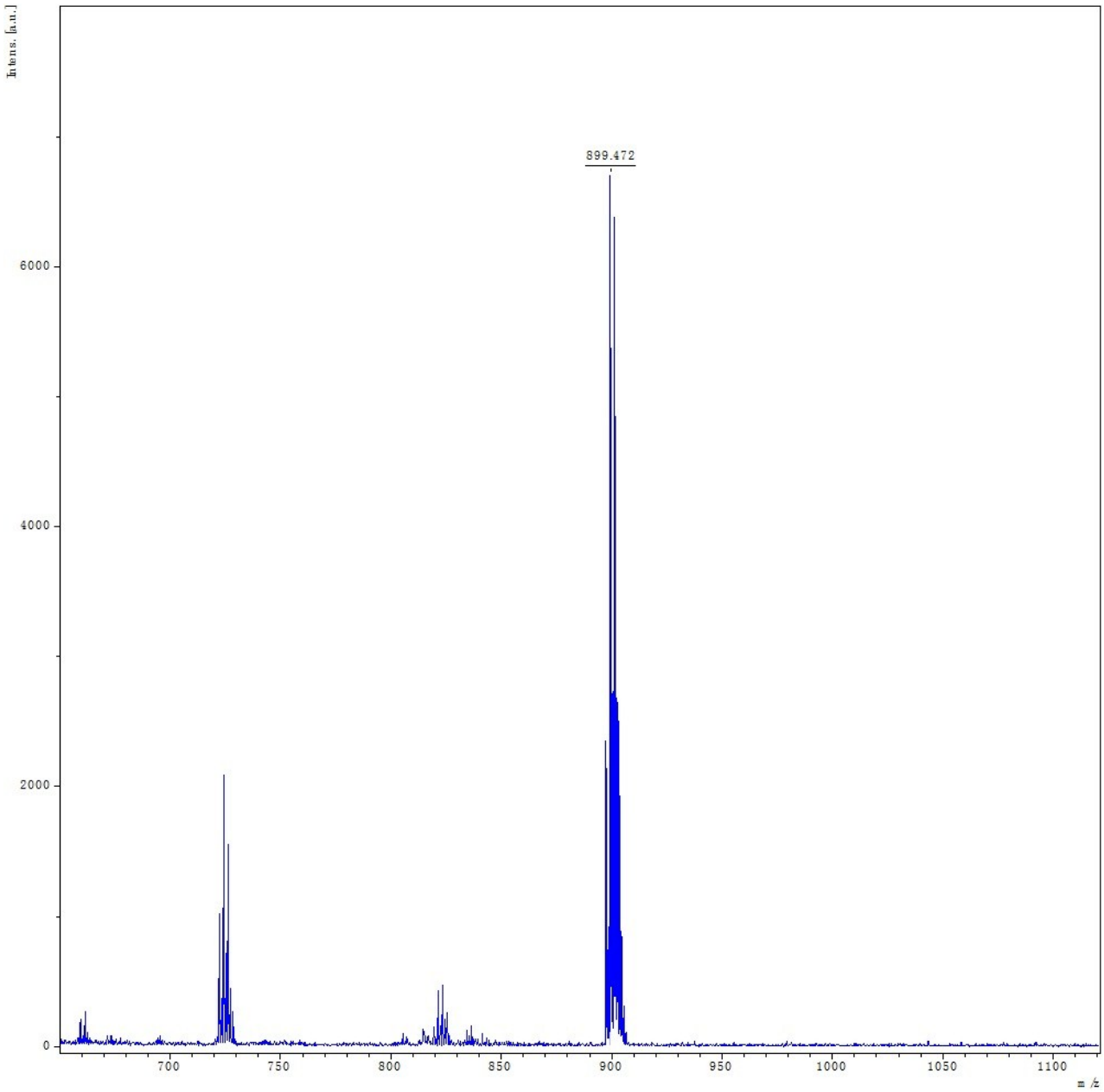


Figure S8. MALDI-TOF-MS spectrum of compound **8**

5. The synthetic procedure of compound**s 9a** and **9b**. The mixture of compound **6** (0.39g, 0.5 mmol), compound **3a** or **3b** (1.3mmol), anhydrous K_2CO_3 (0.18g, 1.3mmol) were stirred in DMF (30 mL) under N_2 atmosphere at 95^{o}C for 10 h. TLC detection implied the disappearance of compound **6**. After cooling, 50 mL of HCl solution (1M) was added and the solution was extracted with 40 mL of $CHCl_3$. The organic layer was washed with brine solution and dried over anhydrous $MgSO_4$. After filtration, the solution was concentrated and purified by column chromatography (CH_2Cl_2/ ethyl acetate(6/1, v/v)). The compound **9a** and **9b** were obtained as red solid in the yield of 60% and 65%, respectively. Compound **9a**: ^{1}H NMR (400 MHz, $CDCl_3$) δppm: 9.60(d, *J*=8.0Hz, 2H, ArH), 8.61(d, *J*=8.0Hz, 2H, ArH), 8.29(s, 2H, ArH), 7.12(d, *J*=8.0Hz, 4H, ArH), 7.01(d, *J*=8.0Hz, 4H, ArH), 5.40 (bs, 2H, C=CH), 4.77 (bs, 2H, OCH), 4.63 (s, 4H, OCH_2CO), 4.13(t, 4H, *J*=8.0Hz, NCH_2), 0.64-2.41(m, 116H, CH, CH_2 and CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δppm: 168.14, 163.28, 162.86, 155.79, 155.38, 149.10, 139.25, 124.82,

123.70, 123.59, 123.33, 123.12, 123.04, 122.14, 121.04, 119.68, 116.73, 115.85, 75.41, 66.21, 56.68, 56.14, 50.01, 42.32, 39.72, 39.52, 36.59, 36.19, 35.80, 31.83, 29.23, 23.84, 22.57, 19.33, 18.72, 14.11, 11.87; MALDI-TOF-MS Calcd.for *m*/*z* = 1684.1, found: *m*/*z* = 1683.1 (M^-). HR-MS(ESI) ($C_{110}H_{142}N_2O_{12}$) $[M]^+$: Calcd.: 1684.0591. found:1684.0636. **9b**: ^{1}H NMR (400 MHz, $CDCl_3$) δppm: 9.63(d, *J*=8.0Hz, 2H, ArH), 8.61(d, *J*=8.0Hz, 2H, ArH), 8.29(s, 2H, ArH), 7.11(d, *J*=8.0Hz, 4H, ArH), 6.98(d, *J*=8.0Hz, 4H, ArH), 5.38 (bs, 2H, C=CH), 4.65 (bs, 2H, OCH), 4.14(t, 4H, *J*=7.2Hz, NCH_2), 4.05(t, 4H, *J*=7.2Hz, OCH_2), 0.64-2.57(m, 124H, CH, CH_2 and CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δppm: 172.57, 163.37, 162.99, 157.20, 156.42, 148.24, 139.72, 133.51, 130.03, 1224.74, 124.51, 123.61, 123.21, 122.98, 122.71, 121.26, 121.15, 116.31, 116.26, 74.23, 67.39, 56.59, 56.08, 50.03, 42.32, 40.63, 39.73, 39.42, 38.17, 36.92, 36.68, 36.19, 35.80, 32.63, 31.82, 31.04, 29.71, 28.23, 28.02, 27.11, 24.72, 24.29, 23.83, 22.57, 20.98, 19.27, 18.65, 14.10, 11.79; MALDI-TOF-MS Calcd.for *m*/*z* = 1740.1, found: *m*/*z* = 1740.8 (M^+). HR-MS(ESI) ($C_{114}H_{150}N_2O_{12}$) $[M]^+$: Calcd.: 1740.1217. found:1740.1227.

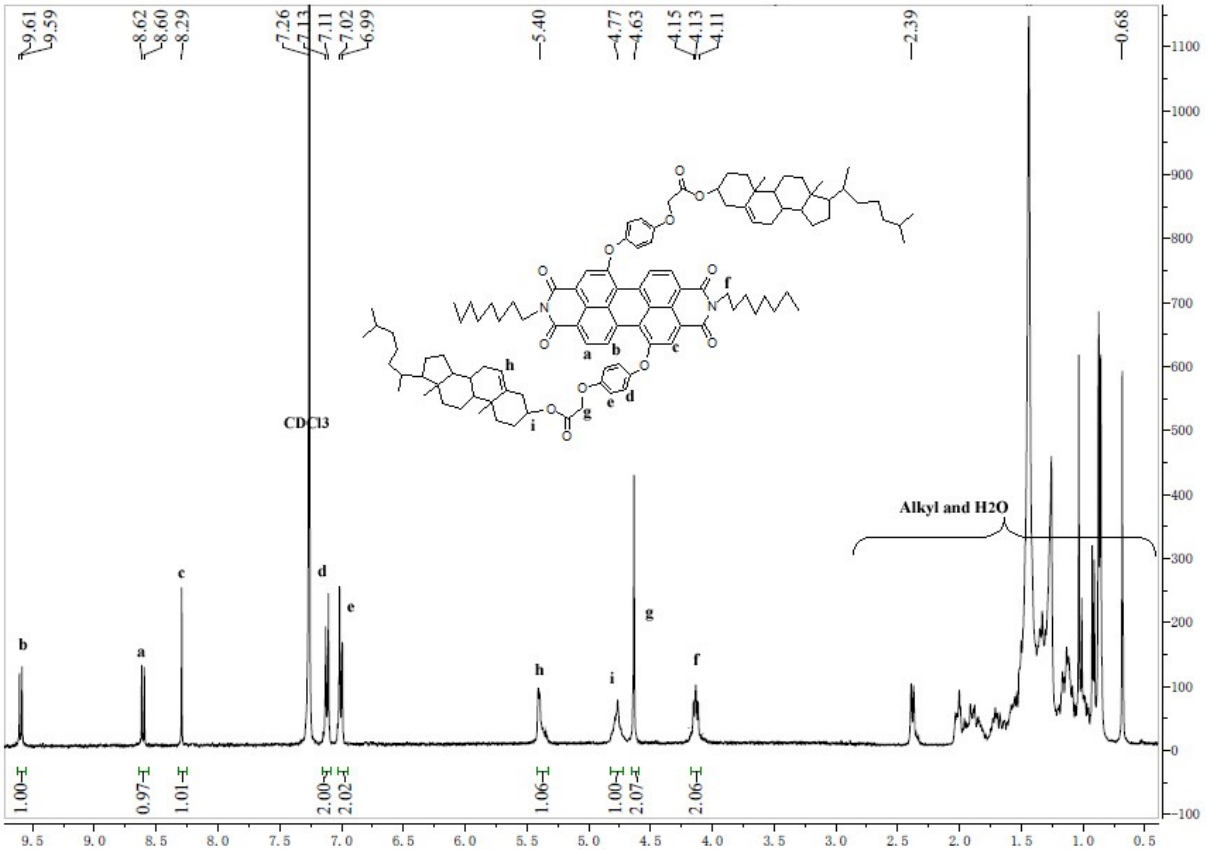


Figure S9. ^{1}H NMR spectrum of compound **9a**

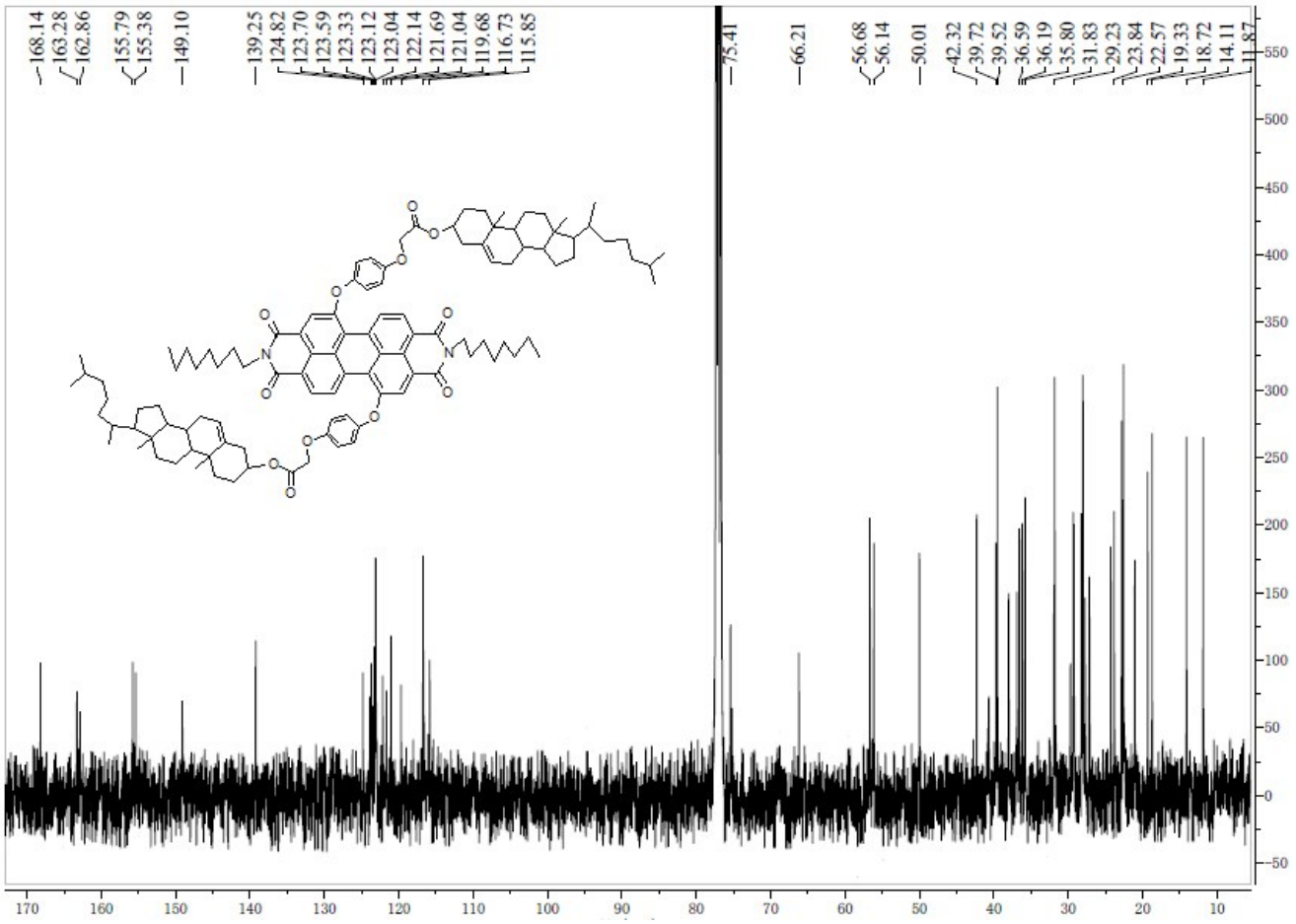


Figure S10. ^{13}C NMR spectrum of compound **9a**

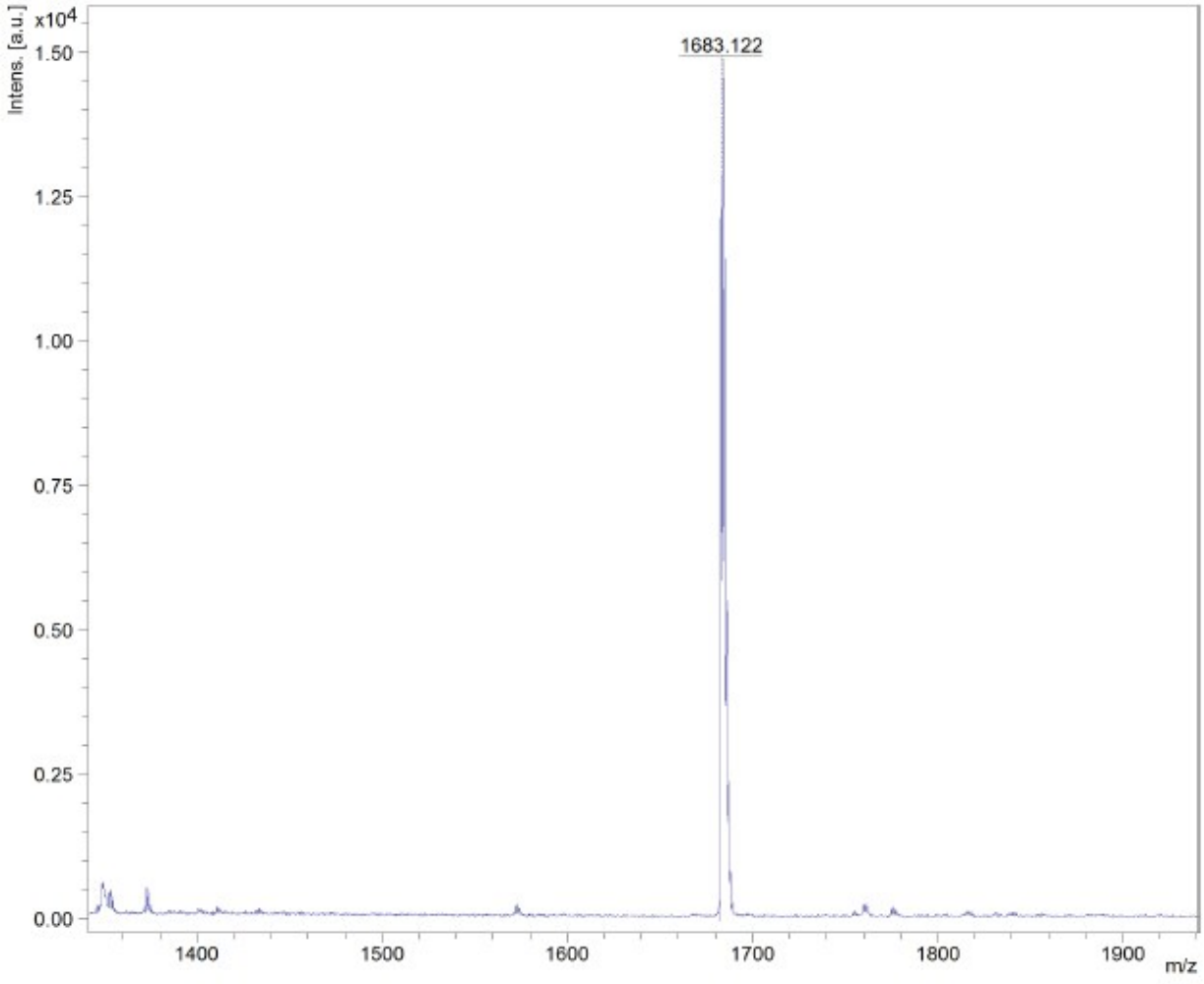


Figure S11. MALDI-TOF-MS spectrum of compound **9a**

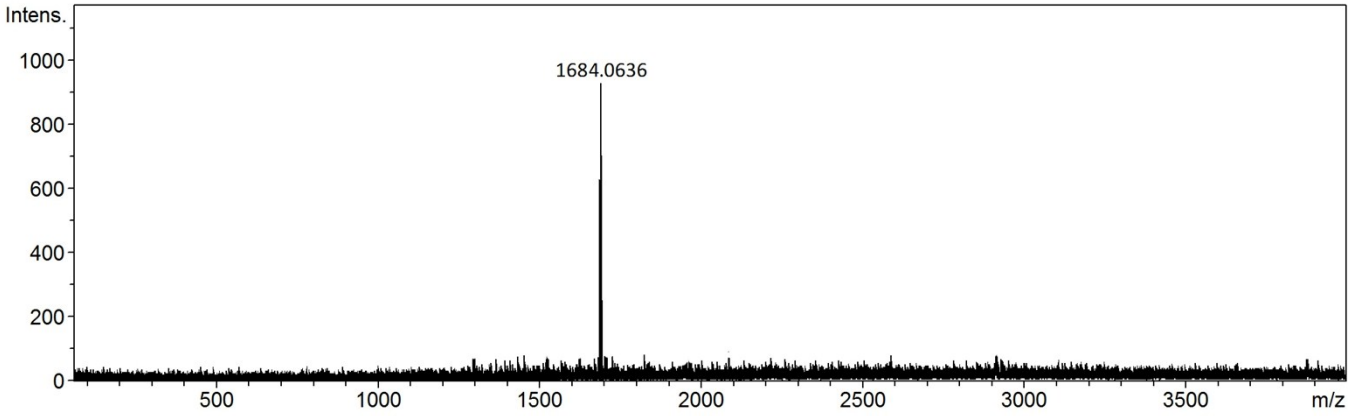


Figure S12. HR-MS(ESI) spectrum of compound **9a**

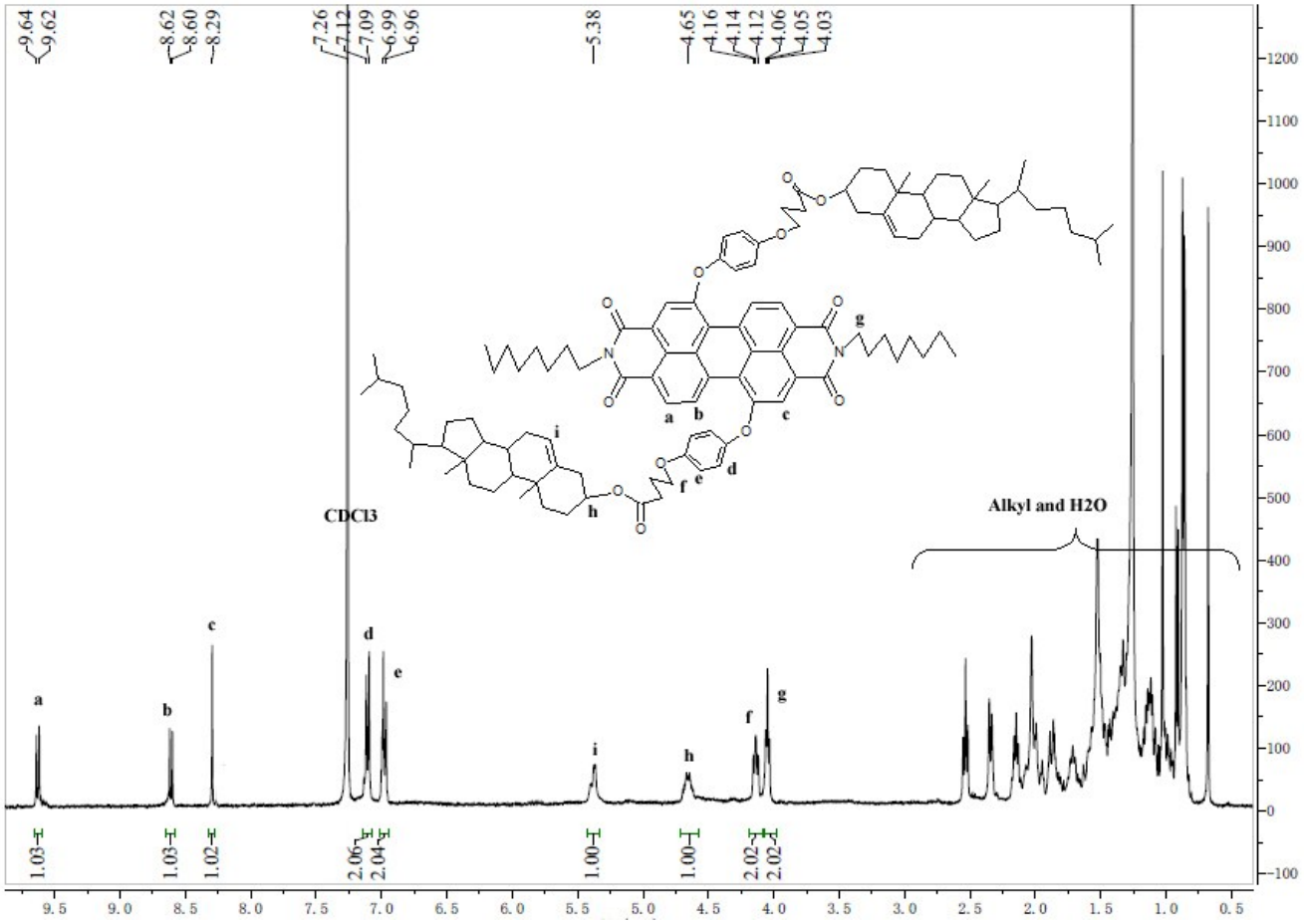


Figure S13. ^{1}H NMR spectrum of compound **9b**

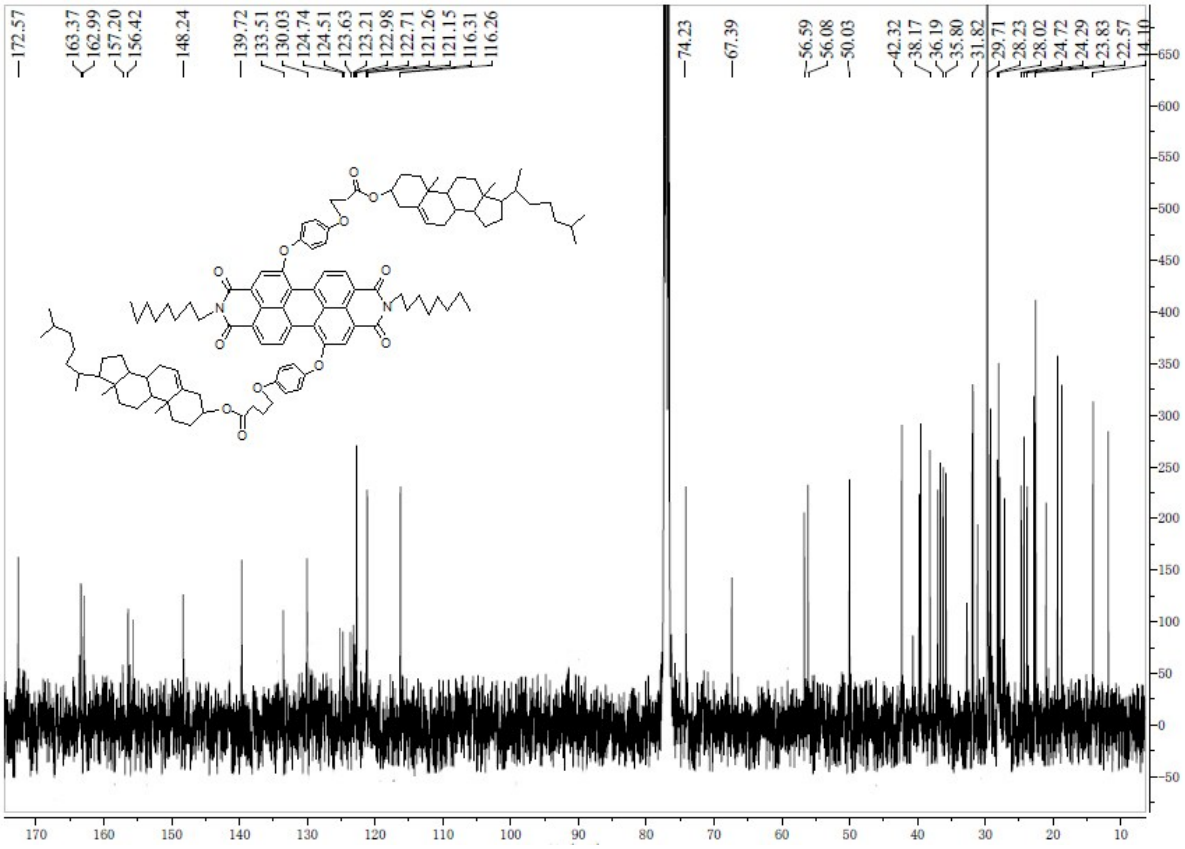


Figure S14. ^{13}C NMR spectrum of compound **9b**

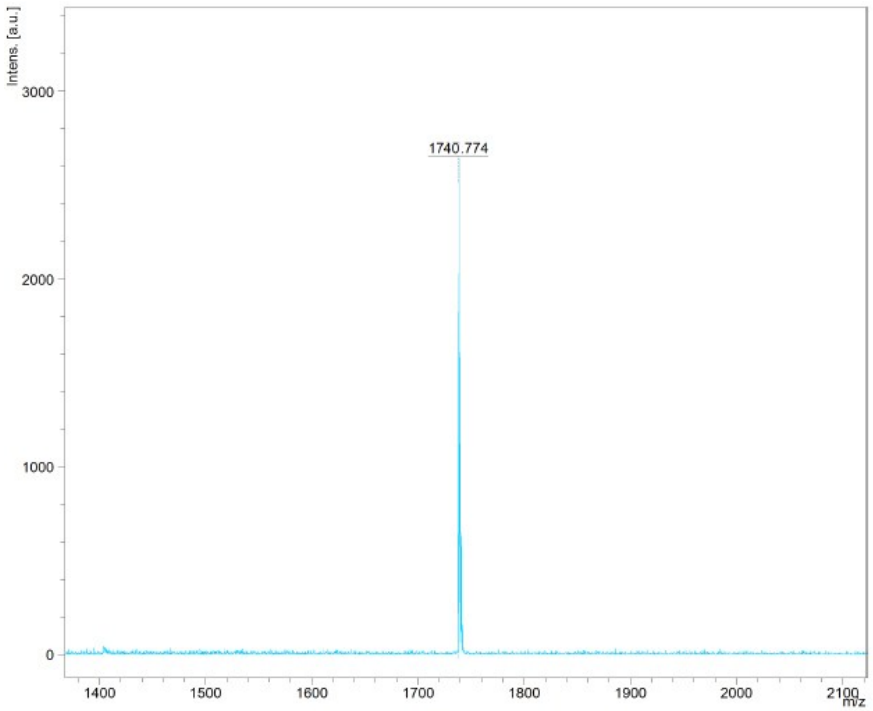


Figure S15. MALDI-TOF-MS spectrum of compound **9b**

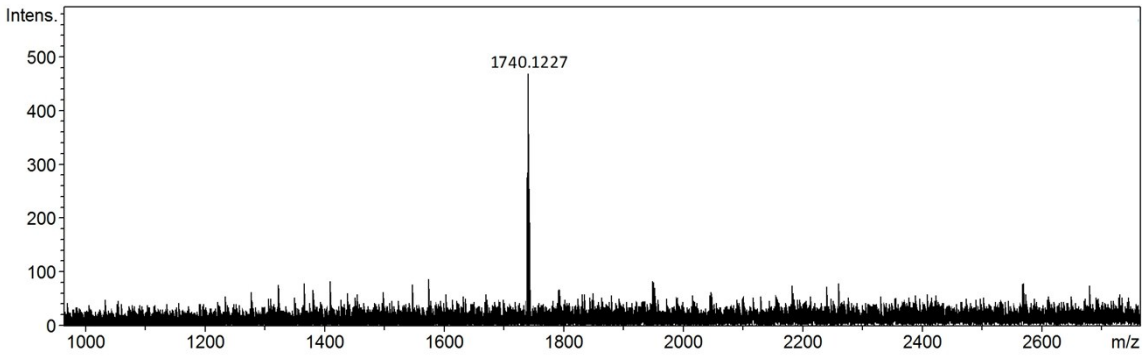


Figure S16. HR-MS(ESI) spectrum of compound **9b**

6. The synthetic procedure of compound**s 10a** and **10b**. The mixture of compound **8** (0.27g, 0.3 mmol), compound **3a** or **3b** (1mmol), anhydrous K_2CO_3 (0.21g, 1.5mmol) were stirred in DMF (30 mL) under N_2 atmosphere at 105°C for 20 h. TLC detection implied the disappearance of compound **8**. After cooling, 50 mL of HCl solution (1M) was added and the solution was extracted with 40 mL of $CHCl_3$. The organic layer was washed with brine solution and dried over anhydrous $MgSO_4$. After filtration, the solution was concentrated and purified by column chromatography (CH_2Cl_2/ ethyl acetate(8/1, v/v)). The compound **10a** and **10b** were obtained as red solid in the yield of 55% and 58%, respectively. Compound **10a**: ^{1}H NMR (400 MHz, $CDCl_3$) δppm: 9.55(d, *J*=8.0Hz, 2H, ArH), 8.55(d, *J*=8.0Hz, 2H, ArH), 8.23(s, 2H, ArH), 7.09(d, *J*=8.0Hz, 4H, ArH), 6.98(d, *J*=8.0Hz, 4H, ArH), 6.80(s, 8H, ArH), 5.39 (bs, 2H, C=CH), 5.34 (bs, 2H, C=CH), 4.83 (bs, 4H, OCH), 4.63(s, 4H, OCH_2CO), 4.55(s, 4H, OCH_2CO), 4.50(s, 4H, OCH_2CO), 4.06-4.19(m, 8H, OCH_2 and NCH_2), 0.64-2.47(m, 188H, CH, CH_2 and CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δppm: 169.19, 168.45, 168.13, 162.94, 162.61, 159.08, 155.74, 154.52, 152.61, 139.24, 133.50, 133.32, 131.98, 130.47, 130.15, 128.87, 124.86, 124.76, 123.13, 123.00, 122.15, 121.74, 121.05, 116.73, 116.07, 115.87, 115.78, 75.40, 75.03, 71.88, 66.28, 66.19, 65.27, 56.54, 56.05, 49.86, 42.43, 39.66, 39.43, 37.95, 36.88, 36.54, 36.27, 35.86, 31.85, 29.71, 28.24, 27.93, 27.73, 26.56, 25.52, 24.17, 23.85, 22.77, 22.50, 20.90, 19.41, 18.72, 11.97; MALDI-TOF-MS Calcd.for *m*/*z* = 2812.7, found: *m*/*z* = 2812.3 (M^+). HR-MS(ESI) ($C_{180}H_{238}N_2O_{24}$) $[M]^+$: Calcd.: 2813.7526. found:2813.7513. Compound **10b**: ^{1}H NMR (400 MHz, $CDCl_3$) δppm: 9.64(d, *J*=8.0Hz, 2H, ArH), 8.61(d, *J*=8.0Hz, 2H, ArH), 8.29(s, 2H, ArH), 7.11(d, *J*=8.4Hz, 4H, ArH), 6.98(d, *J*=8.4Hz, 4H, ArH), 6.80(s, 8H, ArH), 5.37 (bs, 4H, C=CH), 4.64 (bs, 4H, OCH), 4.12-4.19(m, 8H, OCH_2CO and $ArOCH_2$), 4.02-4.08(m, 8H, OCH_2), 3.94(t, *J*=7.2Hz, 4H, NCH_2), 0.62-2.59(m, 204H, CH, CH_2 and CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δppm: 169.19, 168.53, 168.23, 163.26, 162.85, 159.03, 155.93, 154.58, 152.68, 139.28, 133.60, 132.02, 130.50, 128.92, 124.86, 123.71, 123.13, 123.00, 122.15, 121.74, 121.05, 116.73, 116.10, 115.87, 115.78, 75.53, 75.03, 71.76, 66.33, 66.03, 65.20, 56.54, 56.02, 49.99, 42.43, 40.40, 39.71, 39.58, 38.00, 36.91, 35.80, 31.91, 31.85, 29.71, 28.38, 28.24, 28.03, 27.73, 27.66, 26.69, 25.57, 24.29, 23.85,

22.84, 22.50, 21.05, 19.33, 18.72, 11.87; MALDI-TOF-MS Calcd.for *m*/*z* = 2926.0, found: *m*/*z* = 2925.0 (M^+). HR-MS(ESI) ($C_{188}H_{254}N_2O_{24}$) $[M]^+$: Calcd.: 2925.8778. found:2925.8809.

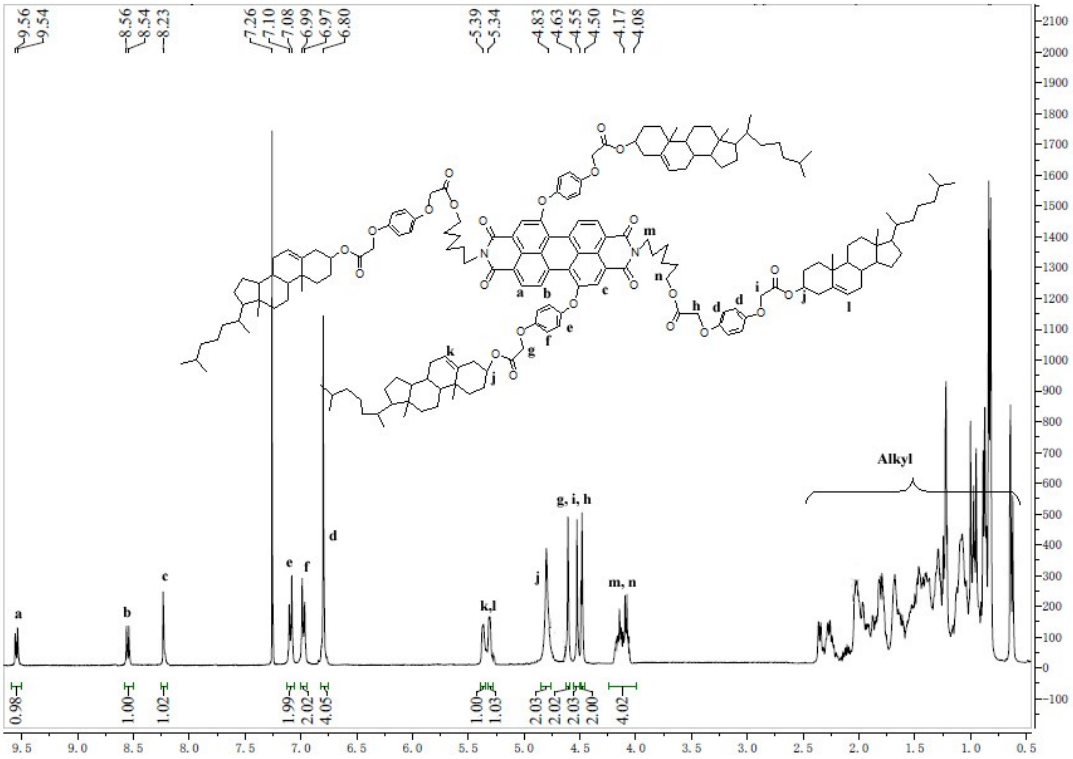


Figure S17. ^{1}H NMR spectrum of compound **10a**

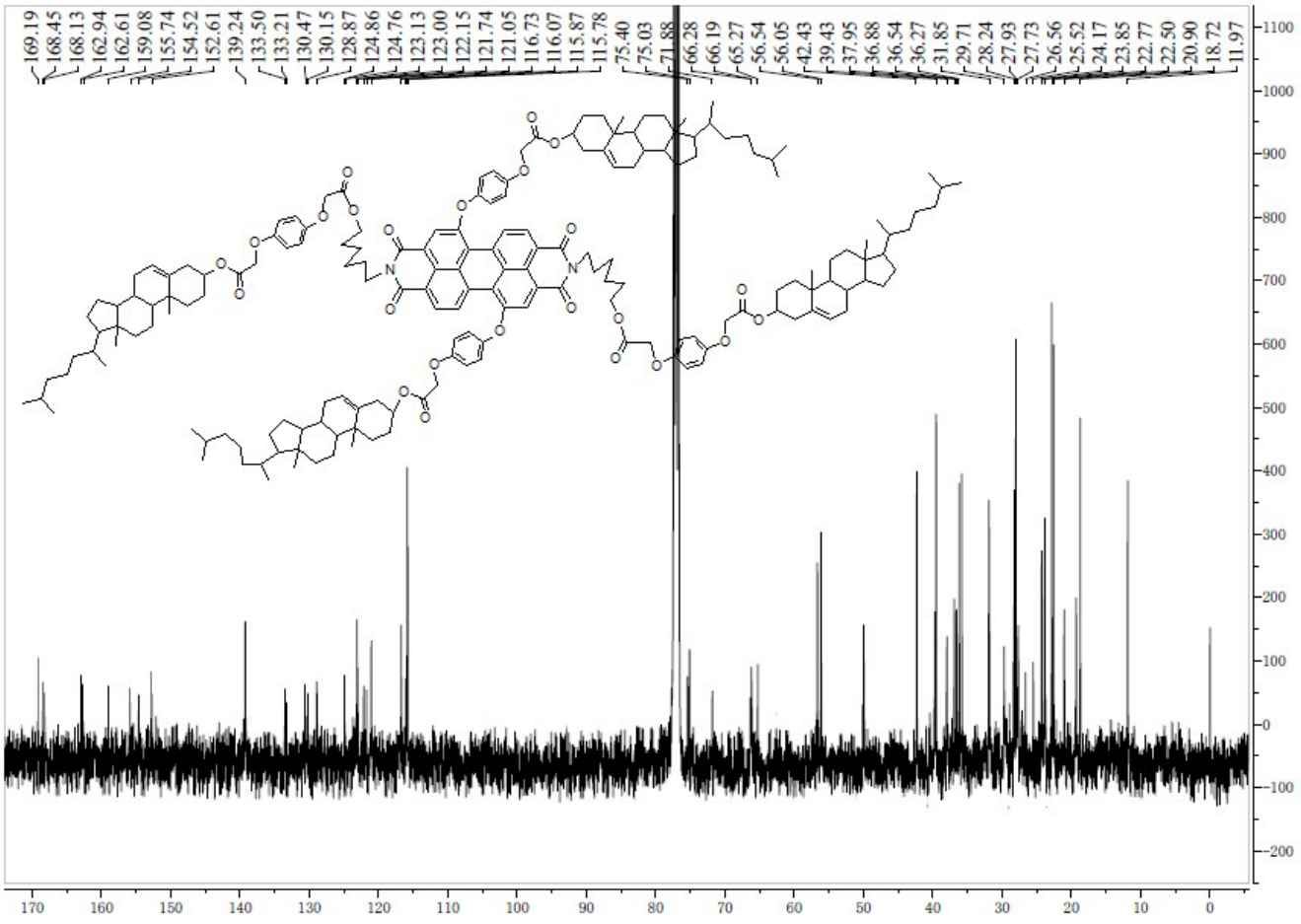


Figure S18. ^{13}C NMR spectrum of compound **10a**

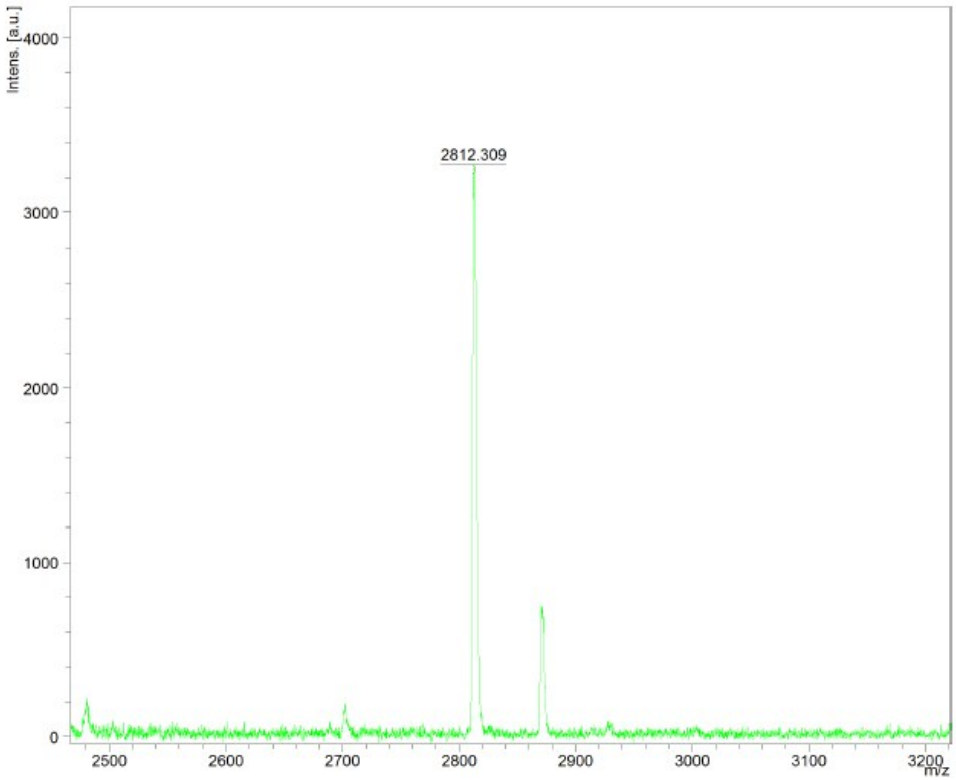


Figure S19. MALDI-TOF-MS spectrum of compound **10**

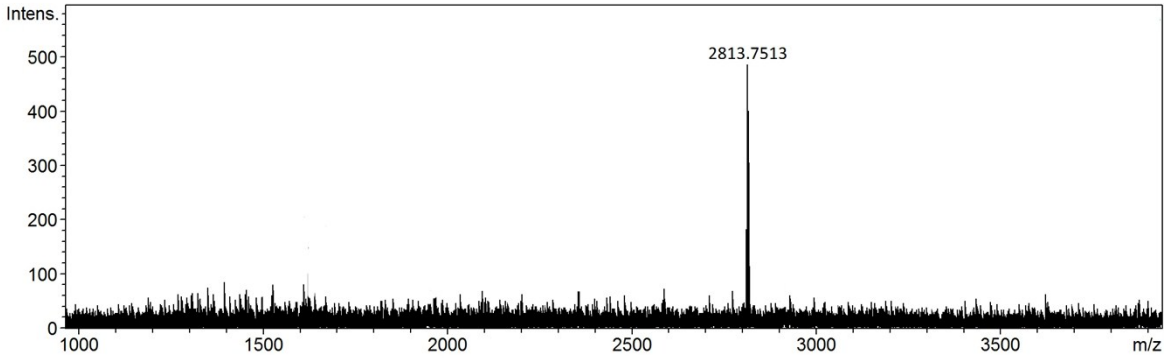


Figure S20. HR-MS(ESI) spectrum of compound **10a**

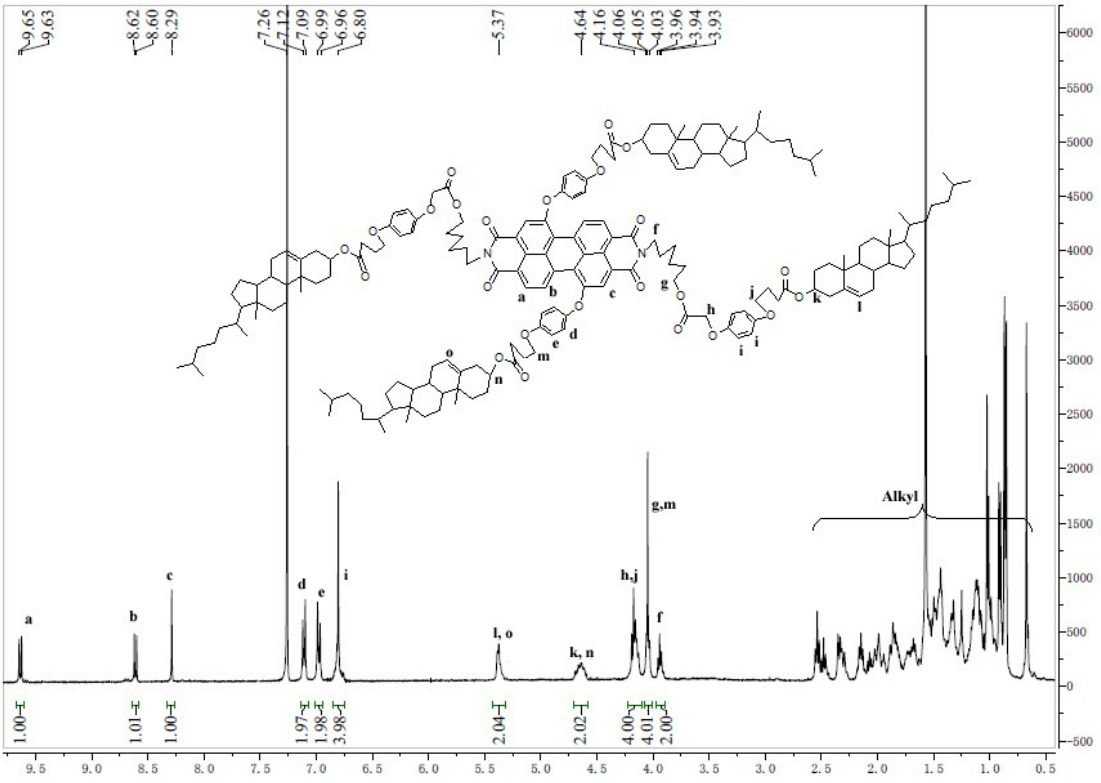


Figure S21. ^{1}H NMR spectrum of compound **10b**

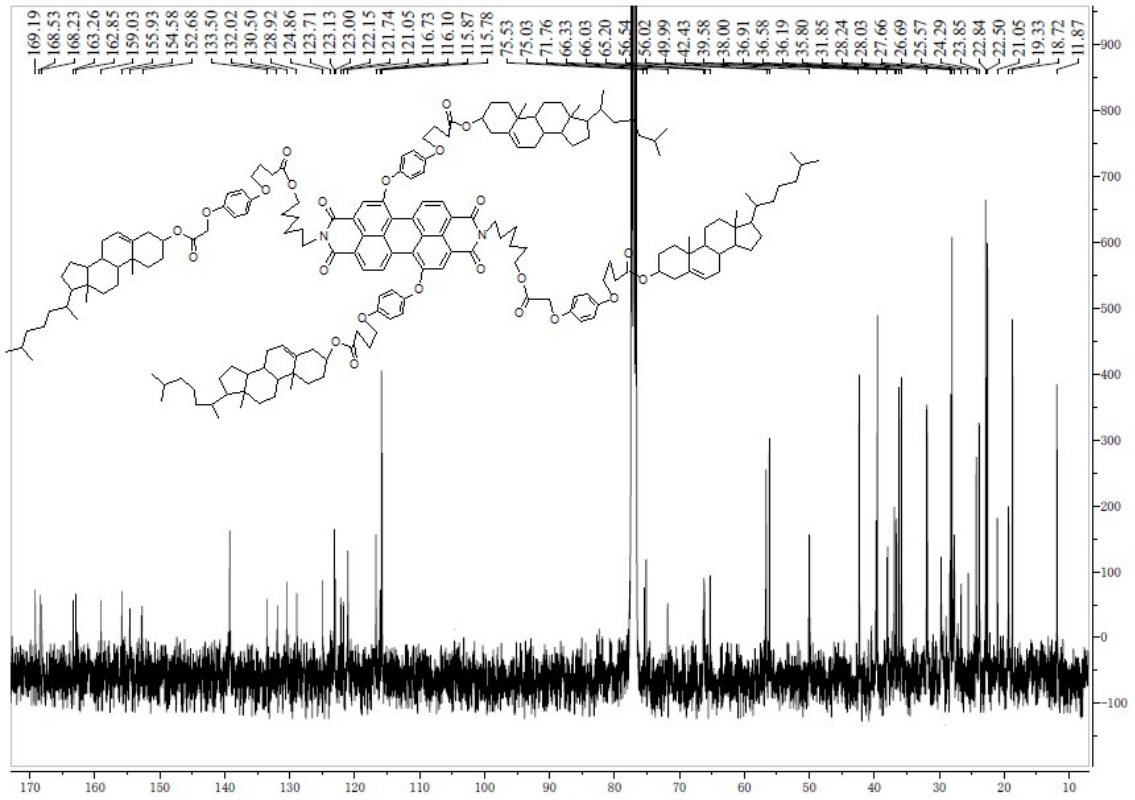


Figure S22. ^{13}C NMR spectrum of compound **10b**

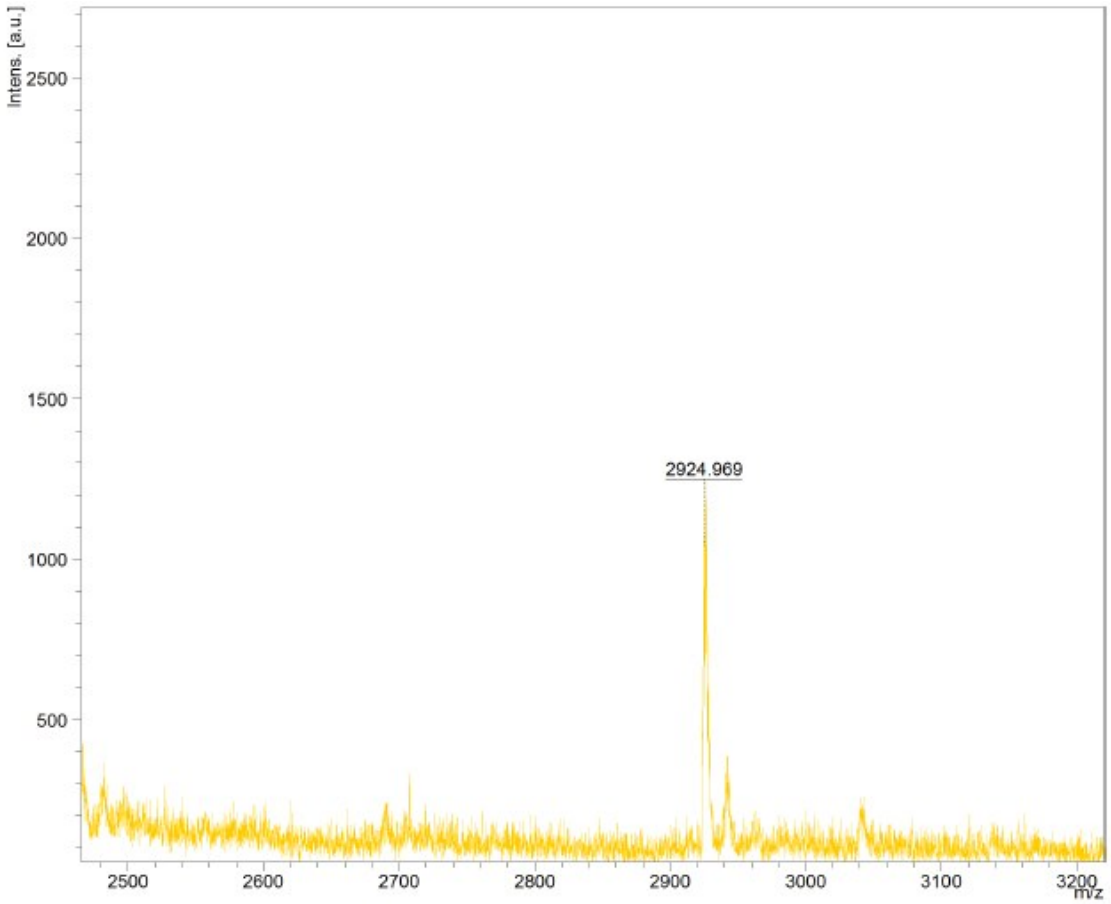


Figure S23. MALDI-TOF-MS spectrum of compound **10b**

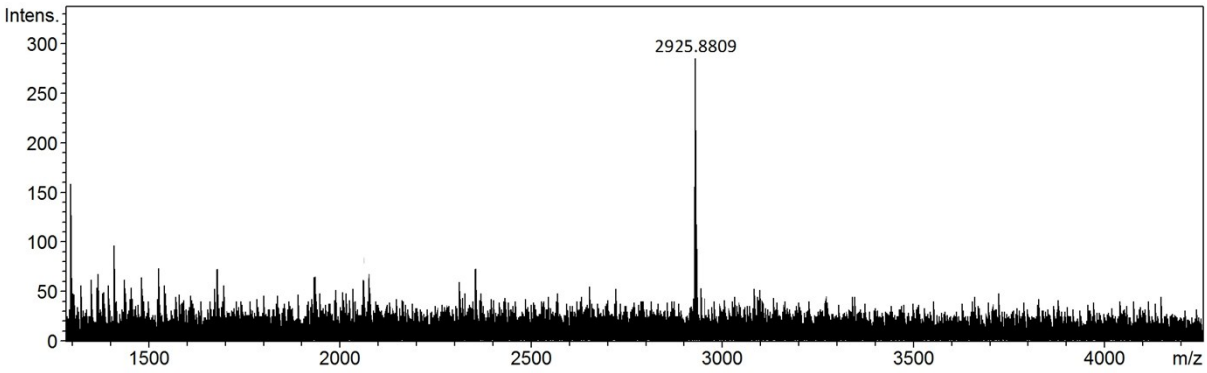


Figure S24. HR-MS(ESI) spectrum of compound **10b**

7.

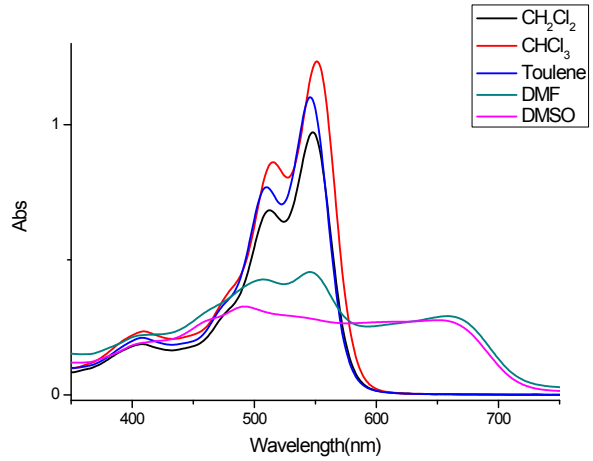


Figure S25 Absorption spectra of compound **12** in different solvents (10^{-5}M).

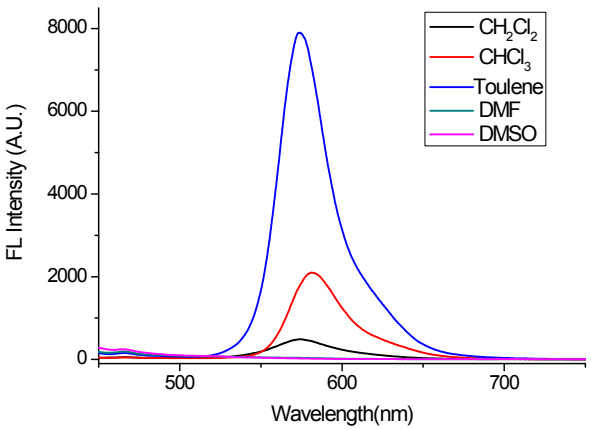


Figure S26 Fluorescence emission spectra of **12** in different solvents (10^{-5}M). The excitation wavelength was 518 nm.