Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Support Information

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

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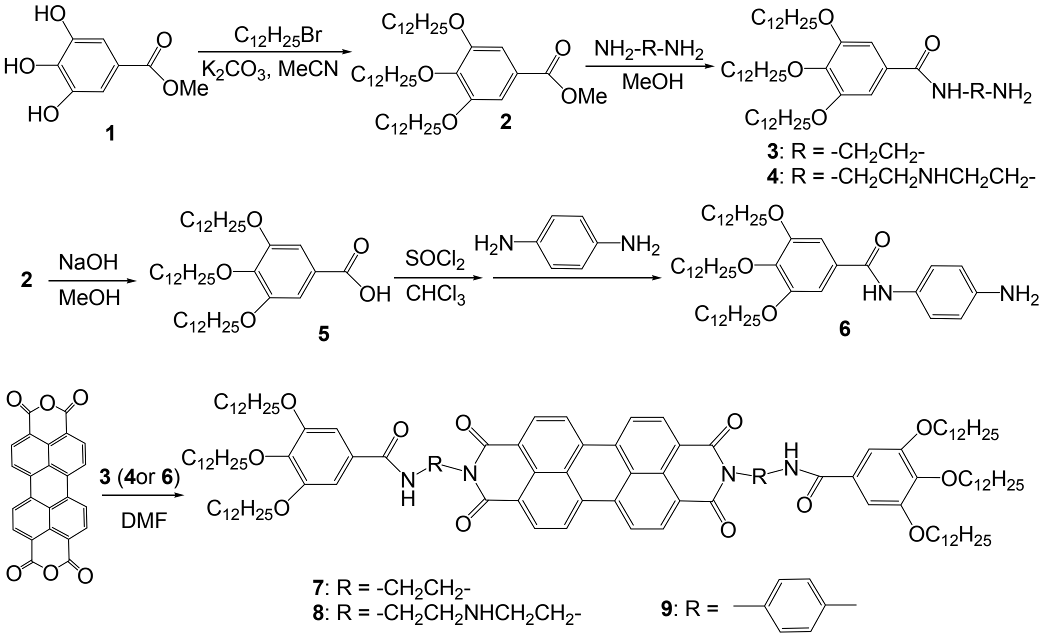
1. General

All chemical reagents were obtained from commercial suppliers and used without further purification. The other organic solvents and inorganic reagents were purified according to standard anhydrous methods before use. TLC analysis was performed using pre-coated glass plates. NMR spectra were recorded in $CDCl_3$ 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 DECAX-30000 LCQ Deca XP mass spectrometer. Elemental analyses were performed at Vario EL III Elemental Analyzer. A polarized 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 a differential scanning calorimeter (DSC) (Thermal Analysis Q100) at a scanning rate of 10°C/min under N_2 atmosphere. X-ray diffraction (XRD) experiments were performed on SEIFERT-FPM (XRD7), using Cu Kα 1.5406 A ° as the radiation source with 40 kV, 30 mA power.

Gallic derivative **2** with three long alkyl chains was prepared according to the literature method (V. S. K. Balagurusamy, G. Ungar, V. Percec and G. Johansson, *J. Am. Chem. Soc.* 1997, **119**, 1539.).



Scheme 1 Synthetic route of title compounds

2. The synthetic procedure of compound 2

According to the published method [*J. Am. Chem. Soc.* 1997, **119**, 1539], the mixture of methyl gallate **1** (0.37g, 2 mmol), 1-bromododecane (1.75g, 7mmol) and anhydrous K_2CO_3 (1.38g, 10 mmol) was stirred and refluxed in MeCN (50mL) for 24 h. The TLC detection indicated the disappearance of the methyl gallate. Then the mixture was cooled to room temperature and 100 mL of water was added in it. The resulting precipitation was filtered and washed by water (20mL) for three times. The crude product was recrystallized with little $CHCl_3$ and methanol to give white compound **2** in yield of 80%. The characteristic data were in accordance with literature [*J. Am. Chem. Soc*. 1997, **119**, 1539].

3. The synthetic procedure of compound 3

Compound **2** (0.69g, 1 mmol) was refluxed with 1 mL of ethylenediamine in 15 mL of methanol for 8 h. TLC detection suggested the disappearance of compound **2**. Then the solvent was evaporated under reduced pressure and the residue was recrystallized in $MeOH/CHCl_3$. Compound **3** was obtained as white soft solid in yield of 86%. Compound **3**: ^1H NMR (400 MHz, $CDCl_3$) δppm: 0.89(bs, 9H, CH_3), 1.26-1.79(m, 60H, CH_2), 2.15(s, 2H, NH_2), 3.12 (bs, 2H, CH_2), 3.44(bs, 2H, CH_2), 3.95(bs, 6H, CH_2), 7.04(s, 2H, ArH), 7.21(bs, 1H, NH); MS *m/z* (%): 717.2 (M^+, 100). Anal. calcd for $C_{45}H_{84}N_2O_4$: C 75.36, H 11.81, N 3.91; found C 75.41, H 11.86, N 3.87%.

4. The synthetic procedure of compound 4

Compound **2** (0.69g, 1 mmol) was refluxed with 1 mL of diethylenetriamine in 15 mL of methanol for 8 h. TLC detection suggested the disappearance of compound **2**. Then the solvent was evaporated under reduced pressure and the residue was recrystallized in $MeOH/CHCl_3$. Compound **4** was obtained as white soft solid in yields of 80%. Compound **4**: ^1H NMR (400 MHz, $CDCl_3$) δppm: 0.89(bs, 9H, CH_3), 1.25-1.78(m, 60H, CH_2), 2.12(bs, 3H, NH and NH_2), 2.83-3.42 (m, 8H, CH_2), 3.98(bs, 6H, CH_2), 7.05(s, 2H, ArH), 7.17(bs, 1H, NH); MS *m/z* (%): 760.6 (M^+, 100). Anal. calcd for $C_{47}H_{89}N_3O_4$: C 74.25, H 11.80, N 5.53; found C 74.21, H 11.84, N 5.49%.

5. The synthetic procedure of compound 6

Compound **2** (0.69g, 1 mmol) was refluxed with 10 mL of 20% NaOH aqueous solution in 20 mL of MeOH for 6 h. TLC detection suggested the disappearance of compound **2**. After cooling, the solvent was treated with 10% HCl to pH =7 and then the most of MeOH in solution was evaporated under reduced pressure and the precipitation (compound **5**) was appeared. The precipitation was filtered, dried and then refluxed in 15 mL of $CHCl_3$ with excess $SOCl_2$ (3 mmol) for 5 h. Then the solution and excess $SOCl_2$ were evaporated under reduced pressure. The 15 mL of $CHCl_3$ containing *p*-phenylene diamine (5 mmol) was added and refluxed for 4 h. After reaction, the solvent was evaporated under reduced pressure and the residue was recrystallized in $MeOH/CHCl_3$ for three times to remove the excess *p*-phenylene diamine. Compound **6** was obtained as white solid in yields of 70%. Compound **6**: ^1H NMR (400 MHz, $CDCl_3$) δppm: 0.89(bs, 9H, CH_3), 1.25-1.80(m, 60H, CH_2), 3.97(bs, 6H, CH_2), 4.01(bs, 2H, NH_2), 6.64(d, $J = 8.0$ Hz, 2H, ArH), 7.05(s, 2H, ArH), 7.41(d, $J = 8.0$ Hz, 2H, ArH), 7.81(bs, 1H, NH); MS *m/z* (%): 764.6 (M^+, 100). Anal. calcd for $C_{49}H_{84}N_2O_4$: C 76.91, H 11.06, N 3.66; found C 76.84, H 11.01, N 3.55%.

6. The synthetic procedure of target compound 7

Perylene tetracarboxylic anhydride (0.196g, 0.5 mmol) and compound **3** (0.72g, 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 $CHCl_3/MeOH$. The red soft solids were obtained in the yields of 75%. Compound **7**: ^{1}H NMR (400 MHz, $CDCl_3$) δppm: 0.88(bs, 18H, CH_3), 1.24-1.80(m, 120H, CH_2), 3.89 (bs, 4H, CH_2), 3.99(bs, 12H, CH_2), 4.55(bs, 4H, CH_2), 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); ^{13}C NMR (150 MHz, $CDCl_3$) 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 $C_{114}H_{172}N_4O_{12}$: C 76.47, H 9.68, N 3.13; found C 76.41, H 9.73, N 3.07%.

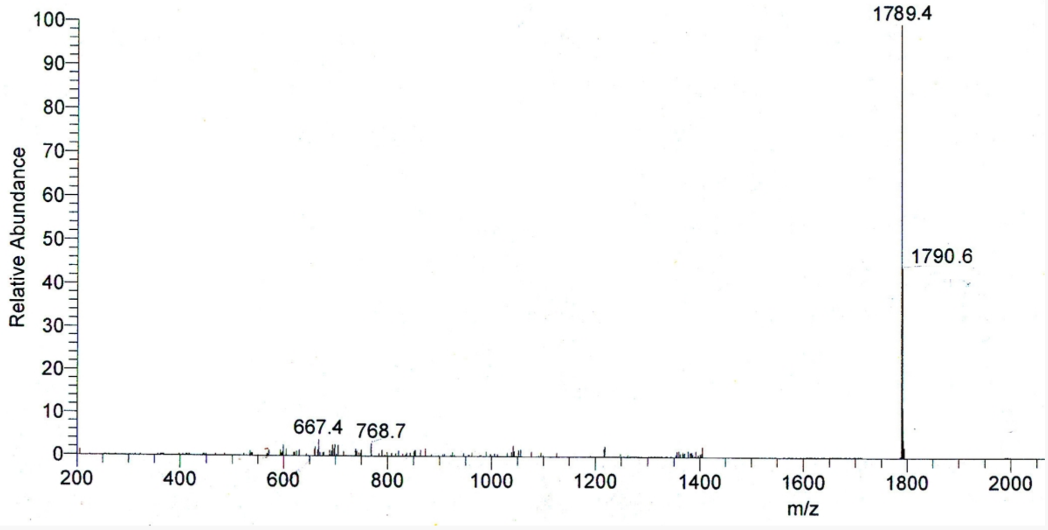


Figure 1 ESI-MS spectrum of compound **7**

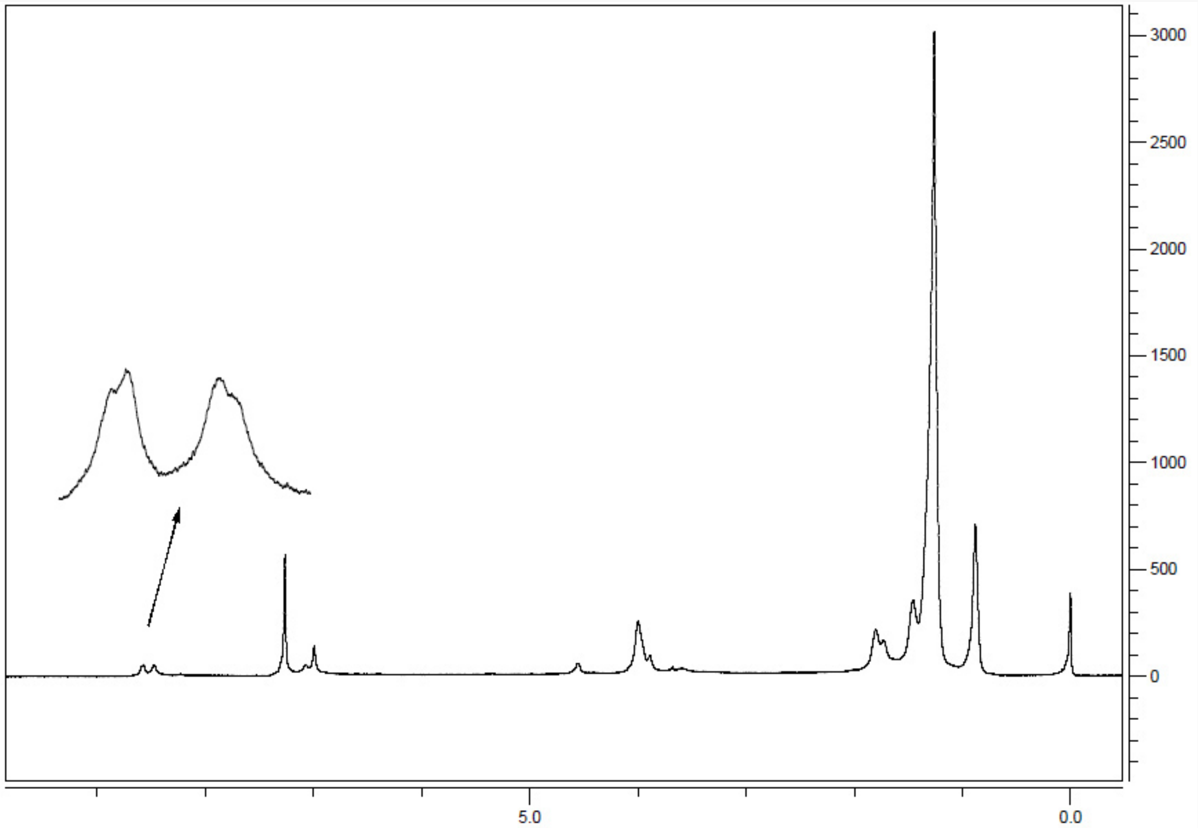


Figure 2 ^{1}H NMR spectrum of compound **7**

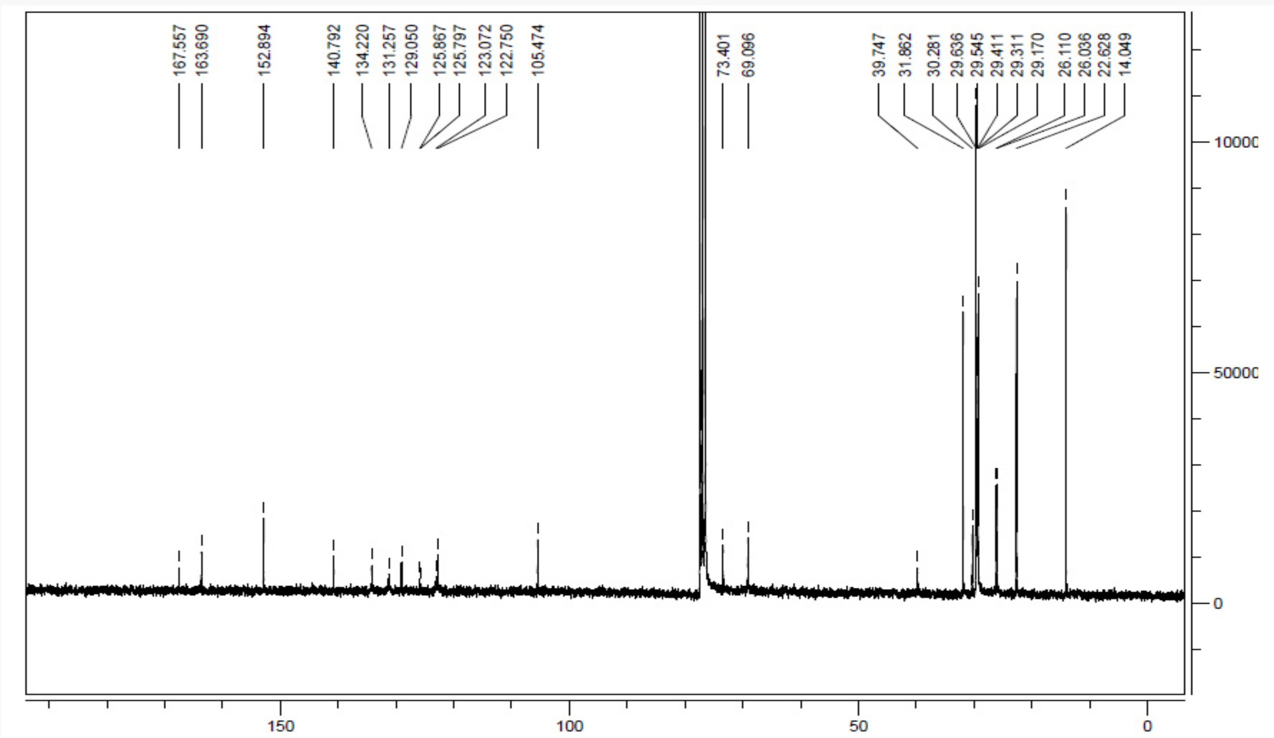


Figure 3 ^{13}C NMR spectrum of compound **7**

7. The synthetic procedure of target compound 8

Perylene tetracarboxylic anhydride (0.196g, 0.5 mmol) and compound **4** (0.76g, 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 $CHCl_3$/MeOH. The red soft solids were obtained in the yield of 78%. Compound **8**: ^1H NMR (400 MHz, $CDCl_3$) δppm: 0.89(bs, 18H, CH_3), 1.25-1.79(m, 120H, CH_2), 3.25(bs, 2H, NH), 3.51~4.61(m, 28H, OCH_2 and NCH_2), 6.98(s, 4H, ArH), 7.08(s, 2H, NH), 8.46 (d, J = 8.0 Hz, 4H, ArH), 8.58 (d, J =8.0 Hz, 4H, ArH); MS m/z (%): 1875.8 (M^+, 100). Anal. calcd for $C_{118}H_{182}N_6O_{12}$: C 75.52, H 9.77, N 4.48; found C 75.47, H 9.72, N4.44%.

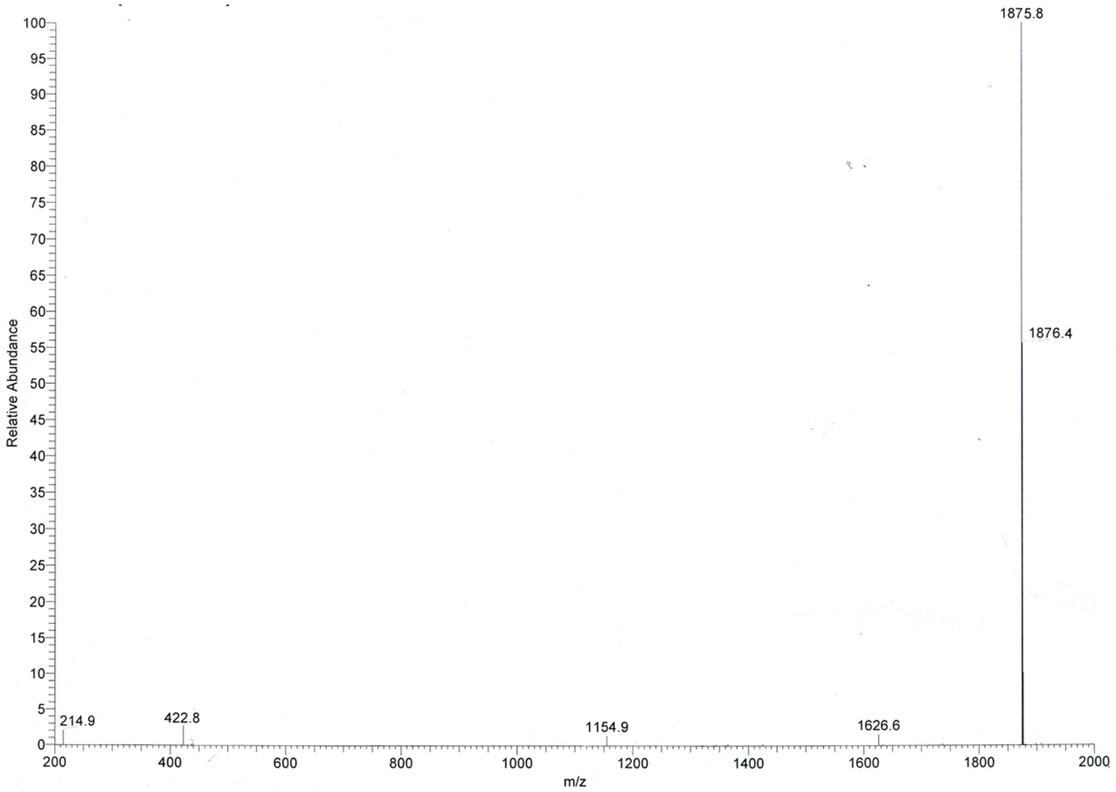


Figure 4 ESI-MS spectrum of compound **8**

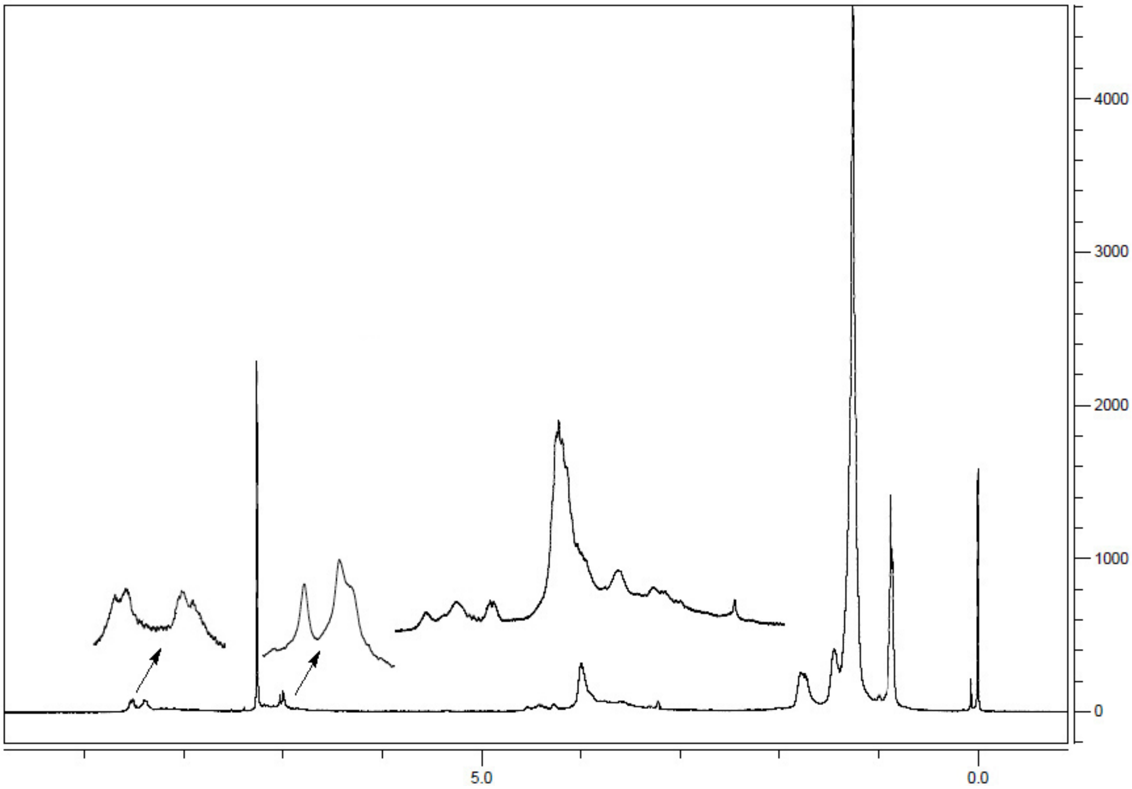


Figure 5 ^{1}H NMR spectrum of compound **8**

8. The synthetic procedure of target compound 9

Perylene tetracarboxylic anhydride (0.196g, 0.5 mmol) and compound **6** (0.77g, 1 mmol) were stirred and heated in DMF (30 mL) at 110^{o}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 $CHCl_3$/MeOH. The red soft solids were obtained in the yields of 80%, respectively. Compound **9**: ^{1}H NMR (400 MHz, $CDCl_3$) δppm: 0.88(bs, 18H, CH_3), 1.23-1.81(m, 120H, CH_2), 3.97(bs, 12H, CH_2), 6.99(bs, 4H, ArH), 7.03 (s, 2H, NH), 8.49 (d, *J* =6.8Hz, 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 $C_{122}H_{172}N_4O_{12}$: C 76.67, H 9.19, N 2.97; found C 76.61, H 9.25, N 3.03%.

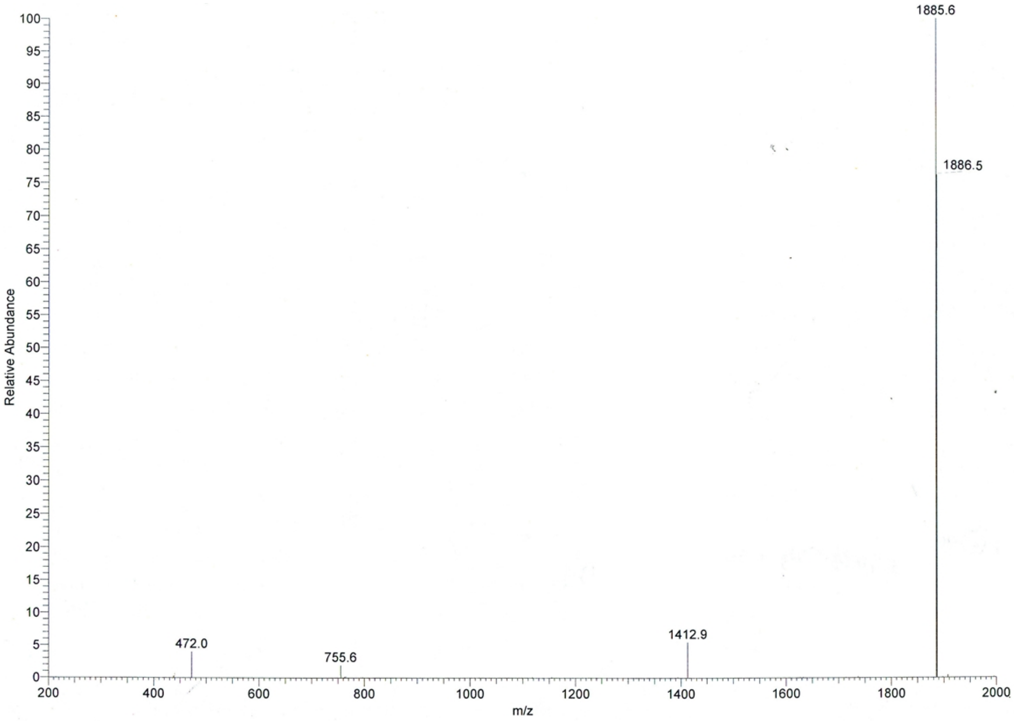


Figure 6 ESI-MS spectrum of compound 9

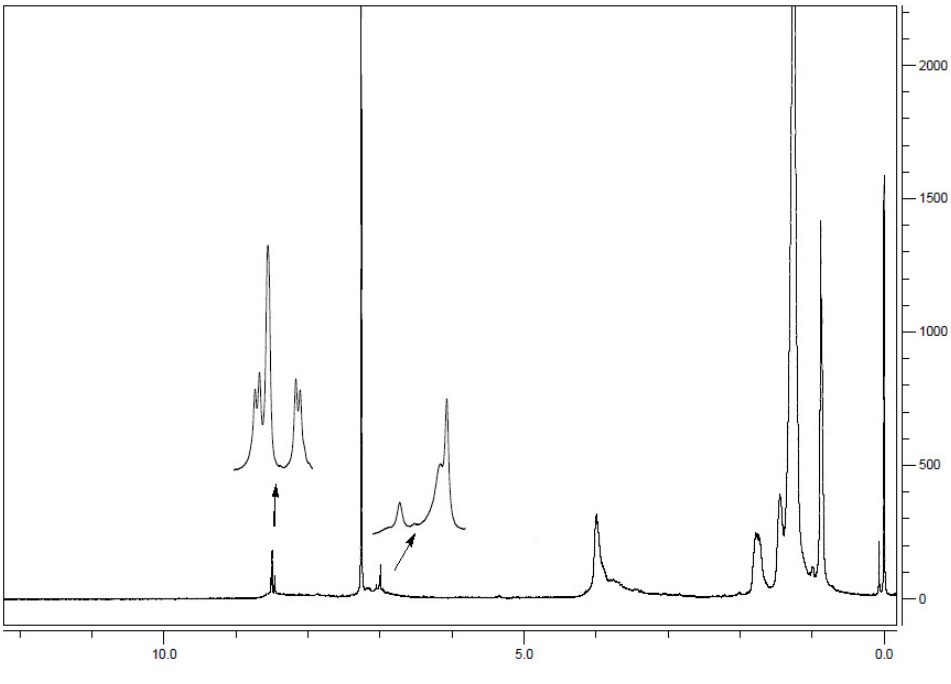


Figure 9 ^{1}H NMR spectrum of compound **9**