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Synthesis, Photophysics, and Electroluminescence of Poly(dibenzofluorene)s

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Measurement and Characterization. ^1H NMR, ^{13}C NMR, and 2D-NMR spectra were recorded by Varian Mercury plus 400 spectrometers, and chemical shifts were reported in ppm units with tetramethylsilane as an internal standard. Chloroform ($CDCl_3$) was mainly used as the solvent for recording NMR spectra. Infrared spectra were measured KBr pellets on a Shimadzu IR Prestige-21 spectrometer, where the percentage of transmittance versus the wavenumber (in cm^{-1}) was plotted. Molecular weights and polydispersities of polymers were determined by gel permeation chromatography (GPC) analysis with polystyrene as the standard. The mobile phase was THF flowing at 1.0 mL/min. Elemental analyses were performed on a Vario EL Elemental Analysis Instrument (Elementar Co.). The UV-visible absorption spectra were obtained in chloroform on a Shimadzu UV-3150 spectrophotometer. The photoluminescence spectra were recorded on a Shimadzu RF-5301 PC fluorometer at room temperature. A Shimadzu DTG-60H thermal analyzer was used to record thermogravimetric analysis (TGA) under a heating rate of 10 °C/min and a nitrogen flow rate of 20 mL/min. Cyclic voltammetry was carried out on a T30/FRA2 electrochemical workstation with platinum at a scan rate of 50 mV/s against a $Ag/AgNO_3$ reference electrode with nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, $TBAPF_6$) in acetonitrile (CH_3CN). To measure the PL quantum yields (Φ_e), polymer solutions in spectral grade THF were prepared. The concentration (10^{-5} M) was adjusted so that the absorbance of the solution would be lower than 0.1. A 10^{-5} M solution of 9,10-diphenylanthracene in toluene ($\Phi_e = 0.93$) was used as a standard.[15]

Matrixassisted laser desorption/ionization (MALDI) mass spectrometry experiments were carried out using a Shimadzu AXIMA- CFR™ *plus* time-of-flight mass spectrometer (Kratos Analytical, Manchester, UK). The mass scale was calibrated externally, using the peptides angiotensin II, bradykinin fragmenti VII, and PxivR (Sigma, St. Louis, MO) as mass standards. Those MALDI analyses of the polymers with matrix and salt utilized the following compound as matrix: dithranol (DI; Aldrich) and silver trifluoroacetate (TFAAg, Aldrich) as cationization salt. The solvent, inhibitor-free tetrahydrofuran (THF; Fluka), stored in a Sure/Seal bottle, was used as received. For MALDI tests, the polymer solutions (5 mg/mL) were prepared in THF. The matrix, 1,8-dihydroxy-9[10*H*]-anthracenone (dithranol), was also dissolved in THF (20 mg/mL). A 2 μL portion of the polymer solution was mixed with 20 μL of the matrix solution. A silver trifluoroacetate solution (2 μL of a solution at 5 mg/mL in THF) was finally added to favor ionization by cation attachment. A 2 μL portion of the final solution was deposited onto the sample target and allowed to dry in air at room temperature.

Fabricating Light-Emitting Devices. Polymer LED devices were fabricated having the configuration of ITO/poly-(styrenesulfonate)(PSS)-doped poly (3,4-ethylenedioxythiophene) (PEDOT) (35 nm)/light-emitting layer (50-70 nm)/ Ba(100 nm)/Al(100 nm). To improve hole injection and substrate smoothness, the PEDOT was spin-coated directly onto the ITO glass and dried at 80 °C for 12 h under vacuum. The light-emitting layer was spin-coated on top of the PEDOT layer using toluene as the solvent and then dried for 3 h at 60 °C under vacuum. Prior to film casting, the polymer solution was filtered through a Teflon filter (0.45 μm). The cathode Ba was deposited onto the polymer layer by evaporation, followed by an additional layer of Al (100 nm) deposited onto the alloy as a protection layer.

Di-a-naphthylcarbino1(2).[16] The preparation of this carbinol according to the directions given in the literature. A solution of bromonaphthalene (23 g, 0.11 mol) in 60 mL THF was added slowly with stirring to a mixture of magnesium turnings (2.4 g, 0.1 mol), 7 mL of THF and a crystal of iodine under nitrogen. After 20 h at room temperature, freshly distilled ethyl formate (3.1 g, 0.035 mol) was added, a few drops at a time. The white carbinol, in the form of its magnesium bromide addition product, precipitated almost completely. After twenty-four hours the THF was decanted and the precipitate decomposed with ice and the calculated amount of dilute hydrochloric acid. The crystalline product was washed with a small amount of dilute hydrochloric acid, dried and then triturated with a small quantity of ether several times. The yield of pure product **2** was 5.0 g (76%). Three recrystallizations (cyclohexane) gave small needles which incorporated cyclohexane: mp 125-127 ºC; ^{1}H NMR δ, 2.40 (d, *J* = 4.7 Hz, 1 H, OH), 7.31 (d, *J* = 4.7 Hz, 1 H collapses to singlet when exchanged with D_2O, C*H*OH), 7.36-7.53 (m, 8 H), 7.81-7.93 (m, 4 H), 8.03-8.08 (m, 2 H); ^{13}C NMR δ, 69.1, 123.1, 124.4, 124.9, 125.1, 125.9, 128.0, 128.3, 130.5, 133.4, 137.9. Anal. Calcd for $C_{21}H_{16}O$ (284.35): C, 88.70; H, 5.67. Found: C, 88.92; H, 6.23.

13*H*-Dibenzo[*a, i*]fluorene (3).[17] This reaction was performed as follows. A 0.50 g (1.76 mmol) portion of the carbinol **2** and 1.5 g of crystalline H_3PO_4 were ground together. The paste was transferred to a round-bottomed flask, which was evacuated at 1-2 mbar. The flask was placed in an oil bath at 160 °C for 1 h. The resulting solid was crushed to a powder, washed with distilled H_2O, and taken up in benzene. The organic phase was washed with H_2O until the water washings were neutral. The benzene phase was dried with anhydrous $MgSO_4$ and then concentrated to give 0.40 g of crude reaction mixture. Column chromatography (petroleum ether-dichloromethane 10:1, changed gradually to 1:1) afforded **3** as the second fraction: 0.15 g (32%) of as white platelets, R_f = 0.32; mp 233-235 °C; ^{1}H NMR *δ* 8.11 (d, *J* = 8.3 Hz, 2H, $H_{1,12}$), 7.97 (d, *J* = 8.4, 2H, $H_{6,7}$), 7.90-7.94 (m, 4H, $H_{4,5,8,9}$), 7.58 (ddd, *J* =7.1, 8.1, 1.0, 2H, $H_{2,11}$), 7.47 (ddd, *J* = 8.0, 7.0, 1.0, 2H, $H_{3,10}$) 4.47 (s, 2H, $H_{13,13'}$) (assignments are based on 2D); ^{13}C NMR *δ* 140.1, 139.9, 133.5, 131.7, 129.2, 127.8, 125.5, 125.0, 124.3, 118.6, 35.6; GC-MS retention time 23.6 min.

13, 13'-Dioctyl-dibenzo[*a,i*]fluorene (4) To a solution of 26.6g (100 mmol) of **3** in THF (300 mL) at -78 °C was added dropwise, 130 mL (210 mmol) of n-butyllithium (1.6 M in hexane; Aldrich). The mixture was stirred at -78 °C for 45 min, and 45.40 g (235 mmol) of octyl bromide (Aldrich) in THF (50 mL) was added dropwise to the mixture. The solution was allowed to warm to room temperature and was stirred for 3 h. The mixture was poured into water and extracted with ether. The organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure. The excess of octyl bromide was removed by distillation (44 °C/0.3 mmHg) to give **4**. R_f = 0.87 (silica TLC in hexane). ^{1}H NMR *δ* 8.11 (d, *J* = 8.3 Hz, 2H, $H_{1,12}$), 7.97 (d, *J* = 8.4, 2H, $H_{6,7}$), 7.90-7.94 (m, 4H, $H_{4,5,8,9}$), 7.58 (ddd, *J* =

7.1, 8.1, 1.0, 2H, $H_{2,11}$), 7.47 (ddd, *J* = 8.0, 7.0, 1.0, 2H, $H_{3,10}$) 1.92 (m, 4H, *J* = 3.8 Hz), 1.25-1.04 (m, 20H), 0.86 (t, 6H, *J* = 5.1 Hz), 0.69 (m, 4H, *J* = 3.8 Hz). ^{13}C NMR δ 141.2, 139.7, 134.5, 133.2, 129.2, 128.7, 125.6, 126.0, 123.4, 119.7, 60.4, 40.3, 31.8, 29.8, 29.0, 23.9, 22.7, 14.2. HRMS. Calcd for $C_{37}H_{46}$: C, 90.55; H, 9.45. Found: C, 90.52; H, 9.48.

5,8-Dibromo-13, 13'-dioctyl-dibenzo[*a,i*]fluorene (5)

To a solution of 9,9-dioctylfluorene (4) (15.01 g, 38.42 mmol) in $CHCl_3$ (58 mL) at 0 °C were added 96 mg (0.59 mmol) of ferric chloride and 4.14 mL (80.52 mmol) of bromine. It is important that the reaction proceeds in the dark to avoid any bromination of the aliphatic part of the molecule. The solution was warmed to room temperature and was stirred for 3 h. The resulting slurry was poured into water and washed with sodium thiosulfate until the red color disappeared. The aqueous layer was extracted with $CHCl_3$ (two times), and the combined organic layers were dried over magnesium sulfate to afford 21.07 g (>99%) of the title product as a pale-brown solid. R_f = 0.85 (silica TLC in hexane). ^{1}H NMR δ 8.48 (d, *J* = 8.1 Hz, 2H, $H_{4,9}$), 8.18 (s, 2H, $H_{6,7}$), 8.14 (d, *J* = 8.7 Hz, 2H, $H_{1,12}$), 7.74 (ddd, *J* =8.1, 7.1, 1.0, 2H, $H_{3,10}$), 7.68 (ddd, *J* = 8.0, 7.0, 1.0, 2H, $H_{2,11}$), 1.86 (m, 4H, *J* = 3.7 Hz), 1.26-1.05 (m, 20H), 0.83 (t, 6H, *J* = 3.6 Hz), 0.58 (m, 4H, *J* = 3.5 Hz). ^{13}C NMR δ 146.3, 145.6, 140.3, 135.3, 132.8, 131.7, 128.2, 126.0, 124.4, 119.7, 60.1, 41.5, 32.6, 30.9, 28.7, 22.9, 22.5, 14.1. HRMS. Calcd for $C_{37}H_{44}Br_2$: C, 68.52; H, 6.84. Found: C, 68.50; H, 6.88. MALDI-TOF: *m/z* 648.2, 646.2 ($M[^{79}Br]^+$, $M[^{81}Br]^+$ 100%, 100%), 570.2, 568.2 ($[M-^{79}Br]^+$, $[M-^{81}Br]^+$ 70%, 70%), 490.4 ($[M-2Br]^+$, 35%). The 2D NMR spectrum is shown in the Supporting Information.

13*H*-Dibenzo[*a,g*]fluorene (7).[18] Reaction of **6** with 2-(bromomethyl)naphthalene by the usual method (24-h reaction time) furnished the corresponding alkylated ketone (76%), mp 67-68.0 °C. Cyclodehydration of this ketone (9.0 g) with methanesulfonic acid for 1 h at room temperature afforded a dihydro product. This compound (4.03 g, 15 mmol) and DDQ (3.75 g, 16.5 mmol) in 190 mL of dry benzene was heated at reflux for 5 min under N_2. The hydroquinone that separated on cooling was removed by filtration, and the solution was evaporated to dryness. The residue was dissolved in hexane-benzene (2:l) and filtered through a short column of Florisil. Evaporation of the solvent left **7** (85%), mp 175-175.5 °C (benzene); NMR δ 8.80 (d, 1, H_7, J = 8.52 Hz), 8.50 (d, 1, H_6, J = 8.65 Hz), 8.06 (d, 1, H_1, J = 8.11 Hz), 7.95 (m, 3, Ar), 7.79 (d, 1, Ar, J = 8.26 Hz), 7.77 (d, 1, Ar, J = 8.16 Hz), 7.28-7.62 (m, 4, Ar), 4.22 (s, 2, CH_2). ^{13}C NMR δ 145.7, 145.1, 143.9, 140.2, 139.4, 137.6, 135.6, 134.1, 129.7, 129.5, 128.4,127.3, 126.8, 125.1, 124.8, 124.0, 122.9, 122.6, 122.4, 119.6, 36.7.

13, 13'-Dioctyl-dibenzo[*a,g*]fluorene (8)

The preparation was similarly to the procedure of **4**. ^{1}H NMR δ 8.77 (d, 1, H_7, J = 8.57 Hz), 8.52 (d, 1, H_6, J = 8.56 Hz), 8.12 (d, 1, H_1, J = 8.15 Hz), 7.88 (m, 3, Ar), 7.78 (d, 1, Ar, J = 8.23 Hz), 7.71 (d, 1, Ar, J = 8.46 Hz), 7.23-7.60 (m, 4, Ar), 1.82 (m, 4H, J = 3.8 Hz), 1.22-0.99 (m, 20H), 0.88 (t, 6H, J = 5.1 Hz), 0.55 (m, 4H, J = 3.8 Hz). ^{13}C NMR δ 146.9, 145.9, 142.1, 140.2, 139.0, 138.5, 138.0, 137.6, 136.2, 135.6, 135.0, 134.2, 132.4, 130.5, 129.5, 127.5, 126.8, 125.1, 122.4, 119.6, 36.7, 58.5, 40.5, 33.6, 29.7, 28.5, 21.9, 20.5, 14.0. HRMS. Calcd for $C_{37}H_{46}$: C, 90.55; H, 9.45. Found: C, 90.44; H, 9.56.

2,8-Dibromo-13, 13'-dioctyl-dibenzo[*a,g*]fluorene (9)

The preparation was similarly to the procedure of **5**. ^{1}H NMR δ 8.88 (d, J = 8.2 Hz, 1H, H_3), 8.57 (d, J = 8.7 Hz,1H, H_9), 8.43 (d, J = 8.8 Hz, 1H, H_{12}), 8.15 (s, 1H, H_7), 8.13 (d, J = 8.8 Hz, 1H, H_6), 7.93 (s, 1H, H_1), 7.88 (d, 1H, J = 8.7 Hz, H_{10}), 7.73 (ddd, J = 8.4, 8.2, 1.4, 1H, H_4), 7.63-7.68 (ddd, 2H, $H_{5,11}$), 1.82 (m, 4H, J = 3.6 Hz), 1.26-1.05 (m, 20H), 0.83 (t, 6H, J = 3.6 Hz), 0.58 (m, 4H, J = 3.5 Hz). ^{13}C NMR δ 151.6, 145.7, 140.2, 135.7, 134.1, 131.8, 131.5, 130.3, 129.8, 128.7, 128.5, 127.8, 127.5, 126.6, 125.4, 124.8, 124.3, 122.9, 122.6, 119.3, 57.5, 40.1, 31.9, 29.9, 29.2, 23.4, 22.7, 14.2. HRMS. Calcd for $C_{37}H_{44}Br_2$: C, 68.52; H, 6.84. Found: C, 68.66; H, 6.78. MALDI-TOF: *m/z* 648.2, 646.2 ($M[^{79}Br]^+$, $M[^{81}Br]^+$ 100%, 100%), 571.3, 568.3 ($[M-^{79}Br]^+$, $[M-^{81}Br]^+$ 30%, 30%), 490.5 ($[M-2Br]^+$, 10%). The 2D NMR spectrum is shown in the Supporting Information

7*H*-Dibenzo[*c,g*]fluorene (11).[18] Reaction of **10** with 2-(bromomethyl)naphthalene by the usual method (24-h reaction time) furnished the corresponding alkylated ketone (79%), mp 56.5-58.0 °C: NMR δ 7.00-8.25 (m, 11, Ar), 3.55 (m, 1, methine), 2.52-3.00 (m, 4, benzylic), 1.45-2.25 (m, 2, aliphatic). Cyclodehydration of this ketone (8.0 g) in anhydrous HF for 72 h at room temperature afforded 8,9-dihydro-**7** (92% based on 5.0 g of unrecovered starting material), mp 133-134 °C. A solution of the dihydro compound (4.03 g, 15 mmol) and DDQ (3.75 g, 16.5 mmol) in 190 mL of dry benzene was heated at reflux for 5 min under N_2. The hydroquinone that separated on cooling was removed by filtration, and the solution was evaporated to dryness. The residue was dissolved in hexane-benzene (2:l) and filtered through a short column of Florisil. Evaporation of the solvent left 3.40 g (85%) of **11**, mp 142.5-143 °C (hexane-benzene); ^{1}H-NMR δ 8.71 (d, 2, $H_{1,12}$, J = 8.33 Hz), 7.94 (d, 2, $H_{4,10}$, J = 7.98 Hz), 7.83 (d, 2, $H_{5,8}$, J = 8.12 Hz), 7.69 (d, 2, $H_{6,8}$, J = 8.08 Hz), 7.50 (m, 4, $H_{2,3,11,12}$), 4.08 (s, 2, CH_2). ^{13}C NMR δ 144.8, 140.1, 139.6, 136.3, 134.1, 129.7, 128.5, 126.3, 124.1, 119.6, 37.9.

7, 7'-Dioctyl-dibenzo[*c*,*g*]fluorene (12)

The preparation was similarly to the procedure of **4**. ^{1}H-NMR δ 8.72 (d, 2, $H_{1,12}$, J = 8.33 Hz), 7.94 (d, 2, $H_{4,10}$, J = 7.98 Hz), 7.83 (d, 2, $H_{5,8}$, J = 8.12 Hz), 7.69 (d, 2, $H_{6,8}$, J = 8.08 Hz), 7.50 (m, 4, $H_{2,3,11,12}$), 4.08 (s, 2, CH_2),1.86 (m, 4H, J = 3.7 Hz), 1.26-1.05 (m, 20H), 0.83 (t, 6H, J = 3.6 Hz), 0.58 (m, 4H, J = 3.5 Hz). ^{13}C NMR δ 144.8, 140.1, 139.6, 136.3, 134.1, 129.7, 128.5, 126.3, 124.1, 119.6, 58.9, 41.5, 32.8, 30.1, 28.3, 24.2, 23.5, 14.3.

5,9-Dibromo-7, 7'-Dioctyl- dibenzo[*c*,*g*]fluorene (13)

The preparation was similarly to the procedure of **5**. ^{1}H NMR δ 8.90 (d, J = 8.4 Hz, 2H, $H_{4,9}$), 8.30 (s, 2H, $H_{6,7}$), 8.24 (d, J = 8.7 Hz, 2H, $H_{1,12}$), 7.72 (ddd, J = 7.1, 8.1, 1.0, 2H, $H_{3,10}$), 7.67 (ddd, J = 8.0, 7.0, 1.0, 2H, $H_{2,11}$), 1.86 (m, 4H, J = 3.7 Hz), 1.26-1.05 (m, 20H), 0.83 (t, 6H, J = 3.6 Hz), 0.58 (m, 4H, J = 3.5 Hz). ^{13}C NMR δ 148.8, 146.5, 143.6, 140.3, 138.7, 135.6, 128.7, 125.3, 124.4, 118.9, 58.8, 40.5, 31.7, 29.7, 27.8, 23.2, 22.8, 14.2. HRMS. Calcd for $C_{37}H_{44}Br_2$: C, 68.52; H, 6.84. Found: C, 68.50; H, 6.88. MALDI-TOF: *m/z* 648.3, 646.3 ($M[^{79}Br]^+$, $M[^{81}Br]^+$ 100%, 100%), 570.4, 568.4 ($[M-^{79}Br]^+$, $[M-^{81}Br]^+$ 100%, 100%), 490.5 ($[M-2Br]^+$, 70%).

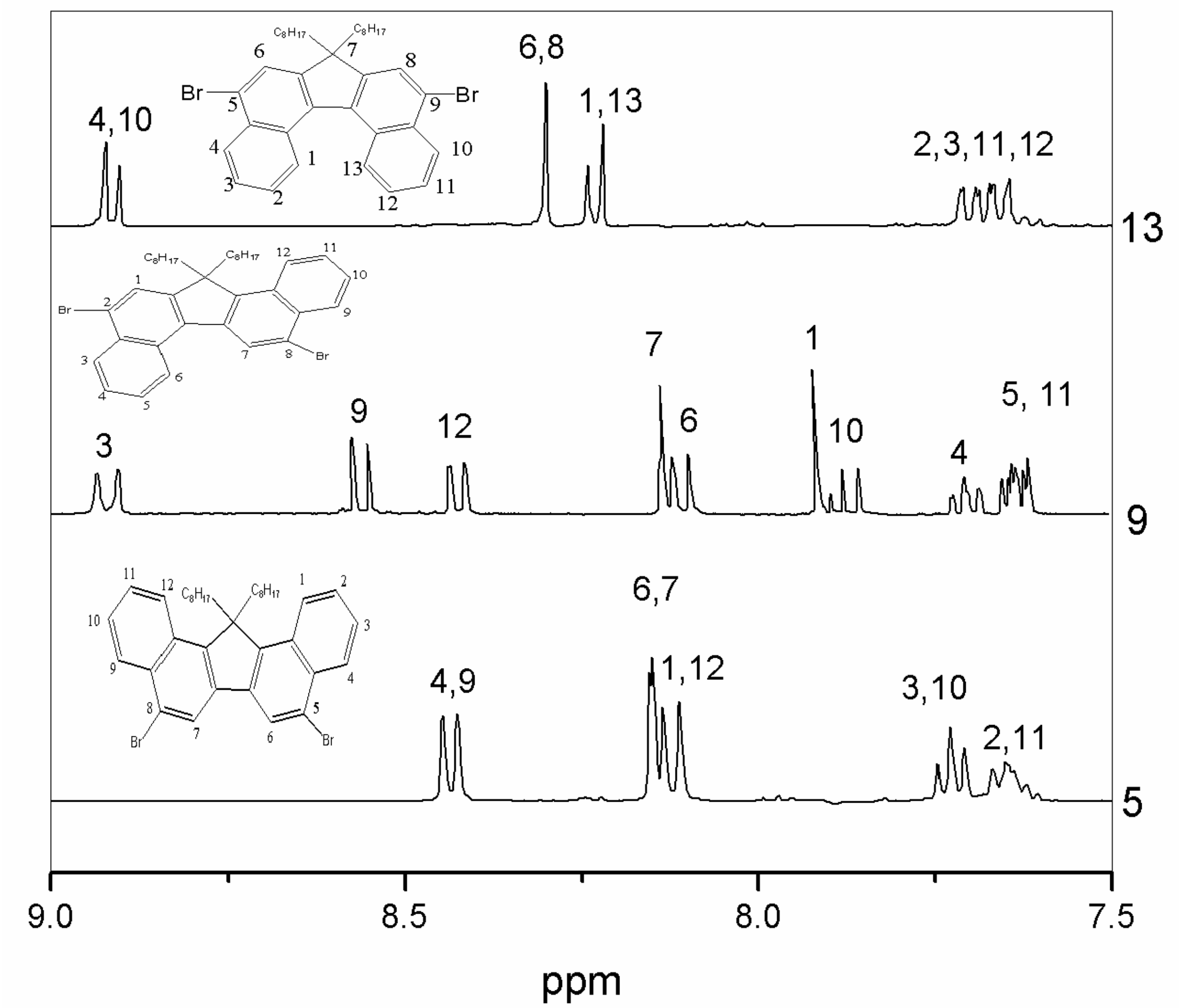

Figure S1. The ^{1}H-NMR spectra of the monomer of **5**, **9**, and **13**.

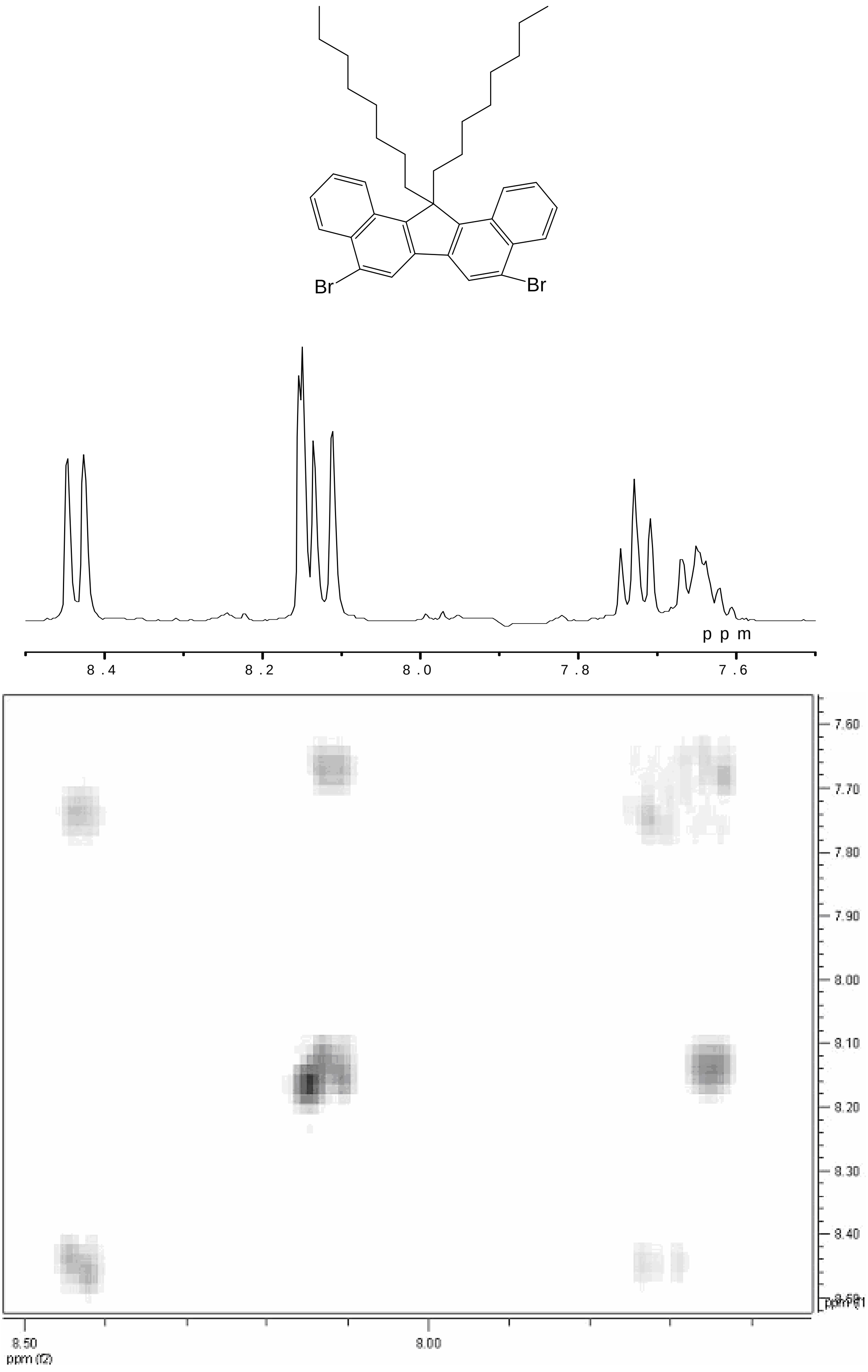

Figure S2. Partical ^1H-^1H DQF-COSY spectra of **5** in $CDCl_3$.

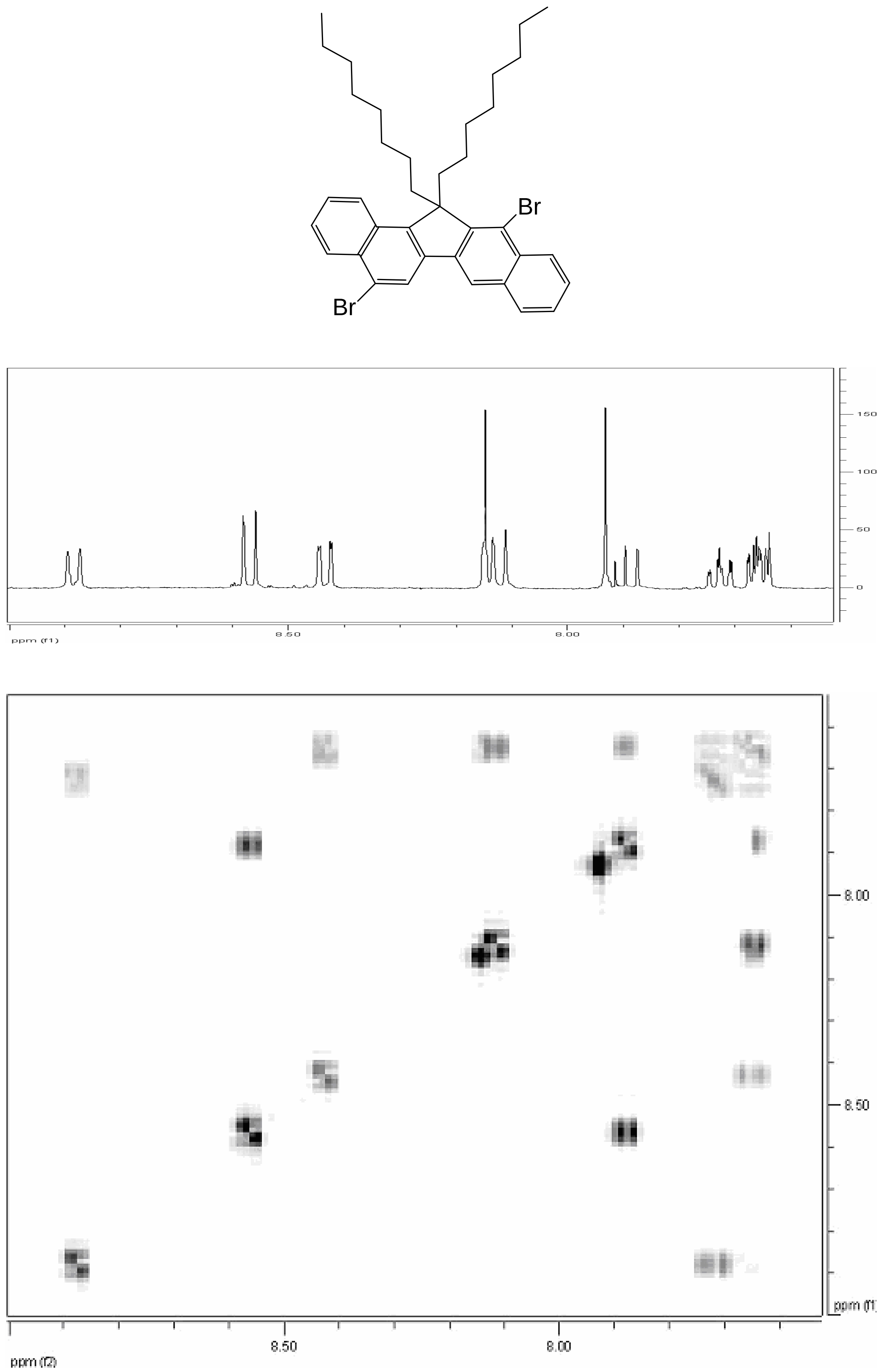

Figure S3. Partical ^{1}H-^{1}H DQF-COSY spectra of **9** in $CDCl_3$.

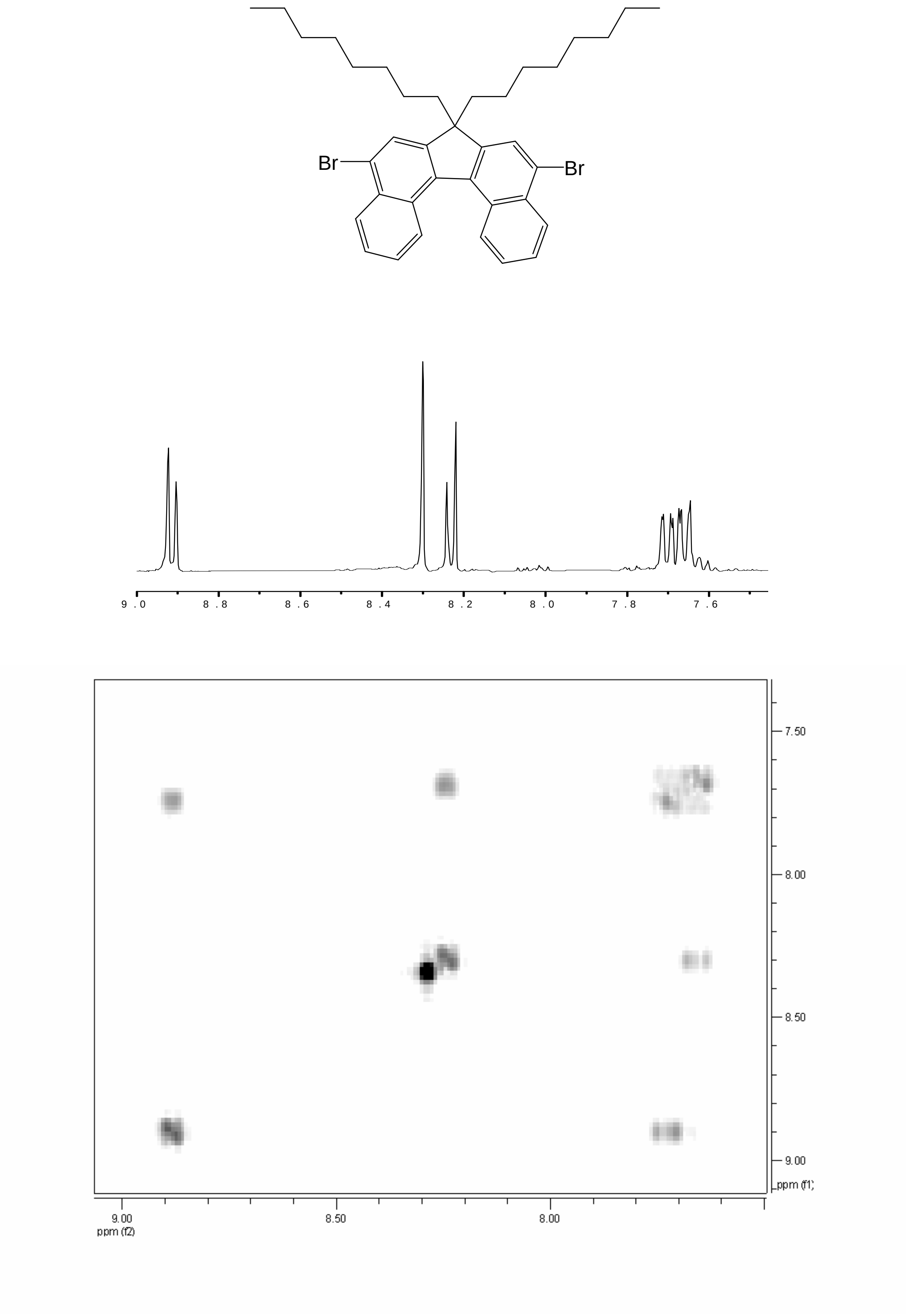

Figure S4. Partical ^{1}H-^{1}H DQF-COSY spectra of **13** in $CDCl_3$.