Supporting Information

Multichromophoric Polyphenylene Dendrimers – Toward Brilliant Light Emitters with Increased Number of Fluorophores

Ingo Oesterling and Klaus Müllen*

Max-Planck-Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany

Experimental Section

General: Unless stated otherwise, all reagents were obtained from commercially sources and were used without further purification. **7**[1], **8**[2], **10**[3], **12**[4], **14**[5], **22**[6], **24**[2], **26**[7], were produced according to the literature. The solvents were used in HPLC grade purity as purchased. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AMX250, AC300, AMX500, and AMX700 NMR spectrometers. Field desorption (FD) mass spectra were recorded on a VG-Instruments ZAB 2-SE-FDP using 8 kV accelerating voltage. MALDI-TOF mass spectra were measured using a Bruker Reflex II spectrometer, using dithranol as matrix. UV/Vis absorbance spectra were obtained on a Perkin-Elmer Lambda 15, and fluorescence spectra were measured on a SPEX Fluorolog 2 spectrometer. Elemental analyses were performed by the Micoanalytical Laboratory of Johannes Gutenberg University of Mainz (Germany). Melting points were measured using a Büchi Melting Point Apparatus B545. Size exclusion chromatography (SEC) was performed in THF at room temperature using 515 pump (Waters), 717plus injector (Waters), 10 μm guard column, and SDV GPC columns with 500 Å, 10^4 , and 10^6 Å porosities (PSS, Mainz), UV S-3702 (SOMA) (at 254 nm) and RI ERC 7512 refractive index (ERMA Inc.) detectors.

2,5-Bis(4-bromophenyl)-3,4-(4-tri*iso*propylsilylethynylphenyl)cyclopenta-2,4-dien-1-one (9)

A mixture of 4,4´-bis(triisopropylsilylethynyl)benzil **(7)** (3.10 g, 5.43 mmol) and 1,3-bis(4-bromophenyl)acetone **(8)** (2.00 g, 5.43 mmol) in ethanol (24 mL) was flushed with argon and heated to 80 °C. A solution of KOH (0.274 g, 4.88 mmol) in ethanol (4 mL) was added and the mixture was stirred for 20 min under argon atmosphere at 80 °C. After cooling to room temperature the brown precipitate was collected by filtration, washed with ethanol and dried under vacuum. Column chromatography on silica gel (petroleum ether/CH_2Cl_2 (3:1)) gave **9** (3.41 g, 70%) as a brown-violet solid.
^{1}H NMR (250 MHz, $C_2D_2Cl_4$, 298 K): δ = 7.34 (d, ^3J = 8.5 Hz, 4 H), 7.26 (d, ^3J = 8.2 Hz, 4 H), 6.98 (d, ^3J = 8.5 Hz, 4 H), 6.77 (d, ^3J = 8.2 Hz, 4 H), 1.04 ppm (s, 42 H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 306 K): δ = 199.36 (q), 154.16 (q), 132.31 (t), 132.28 (q), 131.94 (t), 131.79 (t), 129.51 (q), 129.41 (t), 125.23 (q), 124.45 (q), 122.45 (q), 106.78 (q), 93.22 (q), 19.02 (t), 11.59 ppm (t); IR (KBr pellet, cm^{-1}): v = 3035, 2943, 2864, 2154, 1712, 1602, 1487, 1462, 827, 667; UV/Vis (CH_3Cl): λ_{max} (ε) = 384 nm (15470), 282 nm (46505 M^{-1}cm^{-1}); MS (FD, 8 kV): *m/z* (%): 900.9 (100%) [M$^+$].

Compound 13

Compound **12** (600 mg, 0.988 mmol) and **9** (357 mg, 0.395 mmol) were dissolved in toluene (35 mL) and ethanol (3 mL). A solution of K_2CO_3 (1.09 g, 7.90 mmol) in water (4 mL) was added and the mixture was flushed with argon. $Pd(PPh_3)_4$ catalyst (45.6 mg, 0.0395 mmol) was added and the reaction mixture stirred under argon in the dark for 16 h at 80 °C. The reaction mixture was cooled to room temperature, and washed three times with distilled water and dichloromethane. The organic phase was separated, dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The crude material was purified by column chromatography on silica gel (CH_2Cl_2). A final column

chromatography on silica gel (toluene/ethyl acetate (50/3)) gave **13** (320 mg, 47%) as a red solid.

^{1}H NMR (250 MHz, $C_2D_2Cl_4$, 298 K): δ = 8.56 – 8.53 (m, 4 H), 8.46 – 8.39 (m, 8 H), 8.07 (d, ^{3}J = 8.5 Hz. 2 H). 7.62 – 7.55 (m. 4 H), 7.49 (d. ^{3}J = 8.5 Hz, 4 H), 7.43 – 7.36 (m, 10 H), 7.26 (d, ^{3}J = 7.5 Hz, 4 H), 6.97 (d, ^{3}J = 8.5 Hz, 4 H), 2.66 (sept., ^{3}J = 6.8 Hz, 4 H), 1.10 – 1.06 ppm (m, 66 H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 298 K): δ = 200.58 (q), 164.14 (q), 154.44 (q), 145.89 (q), 143.12 (q), 139.33 (q), 138.05 (q), 137.83 (q), 132.78 (q), 132.58 (q), 132.36 (t), 132.29 (t), 131.50 (q), 130.72 (q), 130.60 (t), 130.42 (q), 130.31 (t), 129.74 (t), 129.62 (t), 129.58 (q), 129.42 (t), 128.79 (q), 128.75 (t), 128.61 (q), 127.53 (t), 127.11 (q), 125.79 (q), 124.45 (t), 124.38 (q), 124.25 (t), 124.01 (t), 121.11 (q), 121.03 (q), 120.73 (t), 120.52 (t), 106.95 (q), 93.15 (q), 29.28 (t), 24.38 (t), 19.03 (t), 11.61 ppm (t); UV/Vis (CH_3Cl): λ_{max} (ε) = 513 (83216), 526 (82845 $M^{-1}cm^{-1}$); Fluorescence (CH_3Cl, excitation: 500 nm): λ_{max} = 569 nm; MS (FD, 8 kV): *m/z* (%):1704.4 (100%) [M^{+}], 852.5 (43%) [M^{2+}].

Compound 4

Branching unit **13** (130 mg, 0.0763 mmol) and tetraphenylmethane core **24** (5.29 mg, 0.0127 mol) were dissolved in diphenylether (5 mL). The reaction mixture was flushed with argon and stirred under argon in the dark at 180 °C for 2 d. After the mixture had been allowed to cool, the crude product was precipitated in methanol (300 mL). The precipitate was filtered, dried, and purified by column chromatography on silica gel (toluene/ethyl acetate (50/3)). A final preparative TLC (CH_2Cl_2) gave **4** (62.7 mg, 69%) as a red solid.

M.p. >350 °C; ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 8.54 - 8.48 (m, 8 H), 8.26 - 8.06 (m, 24 H), 7.88 (d, ^{3}J = 7.4 Hz, 4 H), 7.73 - 7.08 (m, 128 H), 6.92 (d, ^{3}J = 7.9 Hz, 16 H), 2.86 – 2.66 (m, 16 H), 1.21 (d, ^{3}J = 5.7 Hz, 48 H), 1.13 – 1,08 ppm (m, 216 H); ^{13}C NMR (75 MHz, CD_2Cl_2, 300 K): δ = 164.29 (q), 164.25 (q), 164.03 (q), 163.86 (q), 146.53 (q),

146.35 (q), 145.61 (q), 143.01 (q), 142.61 (q), 141.64 (q), 141.37 (q), 141.32 (q), 140.81 (q), 140.76 (q), 140.20 (q), 140.16 (q), 139.40 (q), 139.22 (q), 139.15 (q), 138.17 (q), 137.95 (q), 137.69 (q), 137.42 (q), 137.04 (q), 136.80 (q), 132.49 (q), 132.25 (t), 132.21 (t), 132.10 (t), 132.02 (q), 131.96 (t), 131.87 (q), 131.82 (t), 131.37 (t), 131.08 (t), 130.70 (q), 130.17 (t), 130.04 (q), 129.98 (t), 129.69 (t), 129.61 (t), 129.37 (q), 129.32 (t), 129.16 (q), 129.11 (t), 128.57 (q), 128.41 (q), 128.28 (q), 128.19 (q), 128.03 (t), 127.20 (t), 127.09 (t), 126.99 (q), 126.41 (q), 124.41 (t), 124.12 (t), 123.92 (t), 123.54 (t), 121.80 (q), 121.48 (q), 121.29 (q), 121.16 (q), 120.88 (q), 120.76 (q), 120.47 (t), 120.44 (t), 120.37 (t), 119.73 (t), 119.67 (t), 119.64 (t), 107.27 (q), 91.37 (q), 91.31 (q), 64.54 (q) , 29.60 (q), 24.20 (q), 24.13 (q), 18.85 (q), 18.82 (q), 11.75 (q), 11.73 ppm (q); UV/Vis (CH_3Cl): λ_{max} (ε) = 503 (282856), 524 (279813 M^{-1} cm^{-1}); Fluorescence (CH_3Cl, excitation: 500 nm): λ_{max} = 582 nm; MALDI-TOF-MS: *m/z* calcd: 7121.78; found: 7122 [M^+]

***N,N´*-Bis(4-bromo-2,6-dimethylphenyl)-1,6,7,12-tetrachloroperylene-3,4:9,10-tetracarboxdiimide (16)**

1,6,7,12-Tetrachloroperylene-3,4,9,10-tetracarboxdianhydride **(14)** (3.00 g, 5.66 mmol), 2,6-dimethyl-4-bromoaniline **(15)** (11.3 g, 56.6 mmol) and propanoic acid (30 mL) were stirred at 160 °C for 16 h. After cooling to room temperature water was added and the precipitate was filtered and washed with a mixture of methanol/water (1:1) to give an orange solid. The product was purified by column chromatography on silica gel (CH_2Cl_2) to give **16** (3.59g, 52%) as an orange solid.

M.p. >350 °C; ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 298 K): δ = 8.67 (s, 4 H), 7.39 (s, 4 H), 2.08 ppm (s, 12 H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 298 K): δ = 161.69, 138.41, 136.04, 133.82, 132.57, 131.97, 131.84, 129.37, 124.10, 123.44, 123.11, 18.15 ppm; IR (KBr pellet, cm^{-1}): ν = 3068, 2922 1714, 1677, 1589, 1382, 1241, 856, 806, 684; UV/Vis (CH_3Cl): λ_{max} (ε) = 522 (42946), 488 (29832), 427 nm (11392 $M^{-1}cm^{-1}$); Fluorescence (CH_3Cl, excitation: 488 nm): λ_{max} = 552 nm; MS (FD, 8 kV): *m/z* (%): 894,2 (100%)

[M^+], 447.3 (22%) [M^{2+}]; elemental analysis calcd (%) for $C_{40}H_{20}Cl_4N_2O_4$: C 53.73, H 2.25, N 3.13; found C 53.71, H 2.26, N 3.09.

_N_,_N_´-Bis(4-bromo-2,6-dimethylphenyl)-1,6,7,12-tetrakis[4´-(1´´,1´´,3´´,3´´-tetramethylbutyl)phenoxy]perylene-3,4:9,10-tetracarboxdiimide (18)

A solution of **16** (1.50 g, 1.68 mmol), 4-(1,1,3,3-tetramethylbutyl)-phenol **(17)** (3.46 g, 16.8 mmol) and K_2CO_3 (1.16 g, 8.39 mmol) in NMP (50 mL) was stirred at 90 °C under argon atmosphere for 16 h. After cooling to room temperature the reaction mixture was precipitated from a half-concentrated HCl solution. Vacuum filtration and column chromatography on silica gel (petroleum ether/CH_2Cl_2 (3/2)) gave **18** (2.11 g, 80%) as a red solid.

M.p. 342 °C; ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 298 K): δ = 8.09 (s, 4 H), 7.29 (s, 4 H), 7.21 (d, ^3J = 8,5 Hz, 8 H), 6.84 (d, ^3J = 8,5 Hz, 8 H), 2.01 (s, 12 H), 1.64 (s, 8 H), 1.27 (s, 24 H), 0.68 ppm (s, 36 H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 300 K): δ = 162.75 (q), 156.61 (q), 152.41 (q), 147.32 (q), 138.29 (q), 133.30 (q), 133.27 (q), 131.67 (t), 127.99 (t), 122.84 (q), 122.35 (q), 120.76 (q), 119.97 (q), 119.95 (t), 119.76 (t), 57.21 (q), 38.57 (q), 32.60 (q), 32.15 (t), 31.86 (t), 18.15 ppm (t); UV/Vis (CH_3Cl): λ_{max} (ε) = 592 nm (59959), 549 nm (34765), 453 nm (20476 $M^{-1}cm^{-1}$); Fluorescence (CH_3Cl, excitation: 540 nm): λ_{max} = 623 nm; MS (FD, 8 kV): *m/z* (%): 1574.5 (100%) [M^+]; elemental analysis calcd (%) for $C_{96}H_{104}Br_2N_2O_8$: C 76.72, H 7.52, N 1.67; found C 76.84, H 7.49, N 1.59.

_N_-(4-Triisopropylsilylethynyl-2,6-dimethylphenyl)-_N_´-(4-bromo-2,6-dimethylphenyl)-1,6,7,12-tetrakis[4´-(1´´,1´´,3´´,3´´-tetramethylbutyl)phenoxy]perylene-3,4:9,10-tetracarboxdiimide (20)

A solution of **18** (4.54 g, 2.88 mmol), CuI (54.9 mg, 0,288 mmol), triphenylphosphane (75.7 mg, 0.288 mmol) and $Pd(PPh_3)_2Cl_2$ (101 mg, 0.114 mmol) in THF (70 mL) and triethylamine (140 mL) was heated to 80 °C. Under argon atmosphere a solution of triisopropylsilylacetylene **(19)** (684 mg, 3.75 mmol) in THF (4 mL) was added via a syringe over a period of 5 h. The reaction mixture was stirred in the dark at 80 °C for another 10 h under argon atmosphere.

After cooling to room temperature CH_2Cl_2 was added and the organic phase was washed with water, hydrochloric acid (2 N), a saturated solution of ammonium chloride, and water again. The organic phases were combined, dried with $MgSO_4$ and concentrated in *vacuo*. Column chromatography on silica gel (petroleum ether/CH_2Cl_2 (3:2)) gave **20** (1.53 g, 32%) as a red solid.

M.p. 202 °C; ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 298 K): δ = 8.10, 8.09 (2s, 4 H), 7.29 (s, 2 H), 7.25 (s, 2 H), 7.21 (d, ^3J = 8.8 Hz, 8 H), 6.84 (d, ^3J = 8.8 Hz, 8 H), 2.01, 2.00 (2s, 12 H), 1.64 (s, 8 H), 1.27 (s, 24 H), 1.05 (s, 21 H), 0.68 ppm (s, 36 H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 298 K): δ = 162.77 (q), 162.74 (q), 156.61 (q), 156.53 (q), 152.44 (q), 147.24 (q), 138.29 (q), 136.26 (q), 134.23 (q),133.28 (q), 132.30 (t), 131.68 (t), 127.98 (t), 124.40 (q), 122.84 (q), 122.50 (q), 122.27 (q), 120.84 (q), 120.64 (q), 120.00 (q), 119.93 (t), 119.80 (t), 106.65 (q), 91.63 (q), 57.20 (q), 38.55 (q), 32.60 (q), 32.14 (t), 31.83 (t), 19.03 (t), 18.16 (t), 18.12 (t), 11.57 ppm (t); IR (KBr pellet, cm^{-1}): ν = 3039, 2954, 2863, 2150, 1709, 1675, 1587, 1502, 1473, 1405, 1338, 1286, 1209, 1172, 1014, 881, 835, 683; UV/Vis (CH_3Cl): λ_{max} (ε) = 591 nm (45970), 549 nm (26810), 453 nm (15494 $M^{-1}cm^{-1}$); Fluorescence (CH_3Cl, excitation: 575 nm): λ_{max} = 627 nm; MS (FD, 8 kV): *m/z* (%): 1675.7 (100%) [M^+]; elemental analysis calcd (%) for $C_{107}H_{125}BrN_2O_8Si$: C 76.72, H 7.52, N 1.67; found C 76.67, H 7.55, N 1.60.

3,4-Bis(4-(4,4,5,5-tetramethyl-1,3-dioxaborolan-2-yl) phenyl)-2,5-diphenylcyclopenta-2,4-dien-1-one (23)

Compound **22** (1.00 g, 1.84 mmol), bis(pinacolato)diboron **(11)** (1.12 g, 4.43 mmol) and dry potassium acetate (1.09 g, 11.1 mmol) were dissolved in dry dioxane (200 mL) and the mixture was flushed with argon. Pd(dppf) catalyst (0.151 g, 0.184 mmol) was added and the reaction mixture was stirred under argon in the dark for 16 h at 75 °C. After cooling to room temperature CH_2Cl_2 was added and the organic phase was washed with water, dried with $MgSO_4$ and concentrated in *vacuo*. The resulting brown solid was used without further purification in the next step.
The purification for characteristically data was done by column chromatography on silica gel (CH_2Cl_2).

^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 7.56 (d, ^3J = 8.3 Hz, 4 H), 7.29 (m, 10 H), 6.94 (d, ^3J = 8.3 Hz, 4 H), 1.32 ppm (s, 24 H); ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ = 200.52 (q), 154.95 (q), 136.28 (q), 134.49 (t), 131.26 (q), 130.52 (t), 128.84 (t), 128.37 (t), 127.92 (t), 126.20 (q), 84.35 (q), 25.09 ppm (t); IR (KBr pellet, cm^{-1}): ν = 3051, 2979, 2931, 1709, 1609, 1475, 1360, 1274, 1143, 1093, 1018, 962, 858, 655; MS (FD, 8 kV): *m/z* (%): 637.1 (100%) [M^+].

Compound 3

Compound **20** (370 mg, 0.221 mmol) and **23** (35.0 mg, 0.00552 mmol) were dissolved in toluene (8 mL) and ethanol (3 mL). A solution of K_2CO_3 (1.41 g, 2.21 mmol) in water (6.5 mL) was added and the mixture was flushed with argon. $Pd(PPh_3)_4$ catalyst (51.0 mg, 4.42×10^{-5} mol) was added, and the reaction mixture stirred under argon in the dark for 16 h at 80 °C. The reaction mixture was cooled to room temperature, and washed three times with distilled water and dichloromethane. The organic phase was separated, dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The crude material was purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 (3:2 → 2:3)) to give **3** (86.0 mg, 44%) as a violet solid.

M.p. > 300 °C; ^{1}H NMR (700 MHz, $C_2D_2Cl_4$, 298 K): δ = 8.12 (s, 8 H), 7.43 (d, ^{3}J = 7.3 Hz, 4 H), 7.36 (s, 4 H), 7.25 – 7.22 (m, 30 H), 6.97 (d, ^{3}J = 7.7 Hz, 4 H), 6.86 (d, ^{3}J = 7.7 Hz, 16 H), 2.08 (s, 12 H), 2.01 (s, 12 H), 1.64 (2s, 16 H), 1.28 (2s, 42 H), 1.06 (s, 48 H), 0.68 ppm (s, 72 H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 298 K): δ = 162.94 (q), 162.76 (q), 156.54 (q), 155.39 (q), 152.48 (q), 147.19 (q), 141.40 (q), 140.84 (q), 139.94 (q), 139.23 (q), 136.49 (q), 136.26 (q), 134.24 (q),133.43 (q), 133.28 (q), 132.30 (t), 131.04 (t), 130.56 (t), 130.28 (t), 129.63 (t), 128.39 (t), 127.96 (t), 127.47 (t), 127.18 (t), 124.40 (q), 122.45 (q), 120.73 (q), 120.01 (q), 119.89 (t), 119.81 (t), 106.66 (q), 91.63 (q), 57.21 (q), 38.54 (q), 32.59 (q), 32.13 (t), 31.85 (t), 19.03 (t), 18.42 (t), 18.12 (t), 11.57 ppm (t); UV/Vis (CH_3Cl): λ_{max} (ε) = 591 nm (96419), 545 nm (59341), 454 nm (34627) (M^{-1} cm^{-1}); Fluorescence (CH_3Cl, excitation: 540 nm): λ_{max} = 627 nm; MALDI-TOF-MS: *m/z* calcd: 3572.92; found: 3574 $[M+H]^{+}$.

Compound 5

Branching unit **3** (86.0 mg, 0.0241 mmol) and tetraphenylmethane core **24** (1.00 mg, 0.00241 mmol) were dissolved in *m*-xylene (3 mL). The reaction mixture was flushed with argon and refluxed under argon in the dark for 5 d. The reaction mixture was concentrated under reduced pressure and purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 (1:1)) to give **4** (30.0 mg, 86%) as a red solid.

M.p. > 350 °C; ^{1}H NMR (250 MHz, $C_2D_2Cl_4$, 298 K): δ = 8.12 - 8.10 (m, 32 H), 7.62 (s, 4 H), 7.33 – 7.20 (m, 136 H), 7.00 – 6.90 (m, 104 H), 6.71 (d, ^{3}J = 8.2 Hz, 8 H), 2.05 (s, 96 H), 1.73 (bm, 64 H), 1.35 (bm, 192 H), 1.13 (s, 168 H), 0.75 – 0.71 ppm (m, 288 H); ^{13}C NMR (175 MHz, $C_2D_2Cl_4$, 298 K): δ = 162.88 (q), 162.81 (q), 156.74 (q), 156.67 (q), 153.07 (q), 147.36 (q), 147.31 (q), 142.28 (q), 141.61 (q), 141.41 (q), 141.32 (q), 140.20 (q), 140.00 (q), 139.88 (q), 139.30 (q), 138.09 (q), 137.83 (q), 136.55 (q), 136.39 (q), 136.36 (q), 134.88 (q), 133.55 (q), 133.52 (q), 132.47 (t), 132.42 (t), 132.33 (t), 132.12 (t), 132.09 (t), 130.43 (t), 129.15 (t), 128.97 (t), 128.77 (t), 128.59 (q), 128.41 (t), 128.21 (t), 128.01 (t), 127.45 (t), 127.25 (t), 126.63 (t), 126.02 (t), 125.78 (t), 124.26 (q), 123.16

(q), 122.91 (q), 120.95 (q), 120.72 (q), 120.37 (q), 119.98 (t), 119.94 (t), 107.07 (q), 91.40 (q), 57.39 (q), 38.70 (q), 32.67 (q), 31.99 (t), 31.76 (t), 18.84 (t), 18.03 (t), 17.79 (t), 11.78 ppm (t); UV/Vis (CH_3Cl): λ_{max} (ε) = 588 nm (245435), 547 nm (153944), 453 nm (91006 $M^{-1}cm^{-1}$); Fluorescence (CH_3Cl, excitation: 575 nm): λ_{max} = 628 nm; MALDI-TOF-MS: *m/z* calcd: 14596.13; found: 14619 $[M+ Na^+]^+$; elemental analysis calcd (%) for $C_{1001}H_{1092}N_{16}O_{64}Si_8$: C 82.73, H 7.54, N 1.54; found C 81.05, H 7.52, N 1.44.

Compound 25

Compound **5** (170 mg, 0.0116 mmol) was dissolved in dry THF (6 mL) and flushed with argon for 10 min. Then tetrabutylammonium fluoride trihydrate (29.4 mg, 0.00932 mmol) in THF (1 mL) was added by syringe and the reaction mixture was stirred at room temperature. After 1 h, distilled water was added. The crude product was extracted with CH_2Cl_2 and washed with water. The organic phases were dried over $MgSO_4$ and then the solvent was evaporated under reduced pressure. Column chromatography on silica gel with toluene and then with ethyl acetate gave **25** (140 mg, 90%) as a red solid.

M.p. > 350 °C; ^{1}H NMR (250 MHz, $C_2D_2Cl_4$, 298 K): δ = 8.12 - 8.10 (m, 32 H), 7.62 (s, 4 H), 7.33 – 7.20 (m, 136 H), 7.00 – 6.90 (m, 104 H), 6.71 (d, ^3J = 8.2 Hz, 8 H), 2.05 (s, 96 H), 1.73 (bm, 64 H), 1.35 (bm, 192 H), 0.75 – 0.71 ppm (m, 288 H); ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ = 162.87 (q), 162.86 (q), 162.78 (q), 156.73 (q), 156.63 (q), 153.02 (q), 147.34 (q), 147.32 (q), 147.28 (q), 144.93 (q), 142.23 (q), 141.58 (q), 141.37 (q), 141.32 (q), 141.29 (q), 140.46 (q), 140.17 (q), 139.97 (q), 139.85 (q), 139.27 (q), 138.04 (q), 137.77 (q), 136.74 (q), 136.36 (q), 136.33 (q), 135.35 (q), 133.52 (q), 133.47 (q), 132.46 (t), 132.42 (t), 132.39 (t), 132.31 (t), 132.11 (t), 130.40 (t), 129.14 (t), 129.10 (t), 128.82 (t), 128.20 (t), 128.06 (q), 127.29 (t), 127.24 (t), 126.67 (t), 126.01 (t), 125.75 (t), 123.13 (q), 122.78 (q), 120.95 (q), 120.68 (q), 120.65 (q), 120.33 (q), 119.97 (t), 119.87 (t), 83.39 (q), 77.69 (t), 57.35 (q), 38.67 (q), 32.66 (q), 31.97 (t), 31.76 (t), 18.02 (t), 17.97 (t), 17.87 (t), 17.81 ppm (t); UV/Vis (CH_3Cl): λ_{max} (ε) = 591 nm (263762), 549

nm (155914), 453 nm (78961 M^{-1} cm^{-1}); Fluorescence (CH_3Cl, excitation: 540 nm): λ_{max} = 623 nm; MALDI-TOF-MS: *m/z* calcd: 13345.41; found: 13381 $[M+ Na^+]^+$.

Compound 6

Branching unit **3** (214 mg, 0.0599 mmol) and the first-generation dendrimer **25** (50.0 mg, 0.00599 mmol) were dissolved in diphenylether (10 mL). The reaction mixture was flushed with argon and stirred at 200 °C under argon in the dark until MALDI-TOF mass spectrum shows complete conversion. The reaction mixture was concentrated under reduced pressure, dissolved in THF, precipitated in methanol, and filtered. The final purification was performed by a size exclusion chromatography with THF as eluent, where the fraction corresponding to the first major peak is collected.

M.p. > 350 °C; ^{1}H NMR (700 MHz, CD_2Cl_2, 298 K): δ = 8.13 - 8.10 (m, 96 H), 7.68 (s, 8 H), 7.62 (s, 4 H), 7.33 – 7.16 (m, 408 H), 7.00 – 6.72 (m, 304 H), 2.06 (s, 288 H), 1.74 – 1.71 (m, 192 H), 1.36 – 1.33 (m, 576 H), 1.14 (s, 336 H), 0.75 – 0.73 (m, 864 H)
δ = 162.87 (q), 162.78 (q), 156.69 (q), 156.62 (q), 153.00 (q), 147.75 (q), 147.30 (q), 147.25 (q), 142.15 (q), 141.85 (t), 141.37 (q), 141.15 (t), 140.18 (q), 140.15 (q), 139.88 (q), 139.33 (q), 139.31 (q), 138.07 (q), 137.71 (q), 136.50 (q), 136.35 (q), 136.32 (q), 135.36 (q), 134.82 (q), 133.49 (q), 133.46 (q), 132.44 (t), 132.43 (t), 132.36 (t), 132.10 (t), 130.39 (t), 130.35 (t), 128.18 (t), 128.06 (t), 127.36 (t), 127.23 (t), 127.17 (t) 126.03 (t), 125.79 (t), 125.71 (t), 124.20 (q), 123.08 (q), 122.84 (q), 120.88 (q), 120.70 (q), 120.31 (q), 119.95 (t), 119.85 (t), 107.00 (q), 91.36 (q), 68.13 (q), 67.87 (q), 67.72 (q), 67.60 (q), 57.32 (q), 38.66 (q), 38.64 (q), 32.64 (q), 32.62 (q), 31.98 (t), 31.95 (t), 31.93 (t), 31.71 (t), 31.63 (t), 18.80 (t), 18.00 (t), 17.76 (t), 11.70 ppm (t); UV/Vis (CH_3Cl): λ_{max} (ε) = 590 nm (413484), 547 nm (276684), 452 nm (197836 M^{-1} cm^{-1}); Fluorescence (CH_3Cl, excitation: 540 nm): λ_{max} = 620 nm; MALDI-TOF-MS: *m/z* calcd: 41704.66; found: 41674 $[M]^+$.

Compound 27

Branching unit **3** (115 mg, 0.0322 mmol) and the ester-functionalized tetraphenylmethane core **26** (5.00 mg, 0.00538 mmol) were dissolved in diphenylether (3 mL). The reaction mixture was flushed with argon and stirred at 170 °C under argon in the dark for 5 d. The reaction mixture was precipitated in methanol, filtered, and purified by column chromatography on silica gel (petroleum ether/CH_2Cl_2 (1:1)) to give **27** (32.6 mg, 52%) as a red solid.

M.p. > 350 °C; ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 8.14 - 8.11 (m, 24 H), 7.62 (s, 3 H), 7.56 (s, 1 H), 7.46 – 7.17 (m, 114 H), 7.01 – 6.91 (m, 88 H), 6.72 – 6.70 (m, 8 H), 3.64, 3.63 (2s, 3 H), 2.34 – 2.25 (m, 4 H), 2.10 – 2.05 (s, 72 H), 1.74 – 1.64 (m, 52 H), 1.36 – 1.34 (m, 144 H), 1.14 (s, 126 H), 0.76 – 0.72 ppm (m, 216 H); ^{13}C NMR (175 MHz, $C_2D_2Cl_4$, 298 K): δ = 162.89 (q), 162.79 (q), 156.71 (q), 156.65 (q), 153.02 (q), 147.33 (q), 147.27 (q), 144.91 (q), 142.23 (q), 141.59 (q), 141.38 (q), 141.29 (q), 141.16 (q), 140.47 (q), 140.16 (q), 139.96 (q), 139.83 (q), 139.27 (q), 138.05 (q), 137.77 (q), 137.66 (q), 136.52 (q), 136.37 (q), 136.33 (q), 134.84 (q), 133.56 (q), 133.51 (q), 133.48 (q), 132.48 (t), 132.42 (t), 132.36 (t), 132.12 (t), 130.72 (t), 130.41 (t), 130.36 (t), 130.25 (t), 129.12 (t), 128.20 (t), 128.06 (t), 127.95 (t), 127.25 (t), 126.66 (t), 126.02 (t), 125.76 (t), 124.22 (q), 123.10 (q), 122.86 (q), 122.43 (t), 120.90 (q), 120.71 (q), 120.69 (q), 120.33 (q), 119.98 (t), 107.01 (q), 91.38 (q), 63.84 (q), 51.74 (t), 38.67 (q), 37.46 (q), 33.94 (q), 32.66 (q), 31.96 (t), 31.75 (t), 25.15 (q), 24.69 (q), 18.82 (t), 18.02 (t), 17.78 (t), 11.73 ppm (t); UV/Vis (CH_3Cl): λ_{max} (ε) 591 nm (201611), 549 nm (116409), 454 nm (56516 M^{-1} cm^{-1}); Fluorescence (CH_3Cl, excitation: 540 nm): λ_{max} = 623 nm; MALDI-TOF-MS: *m/z* calcd: 11564.85; found: 11609 $[M+ K^+]^+$.

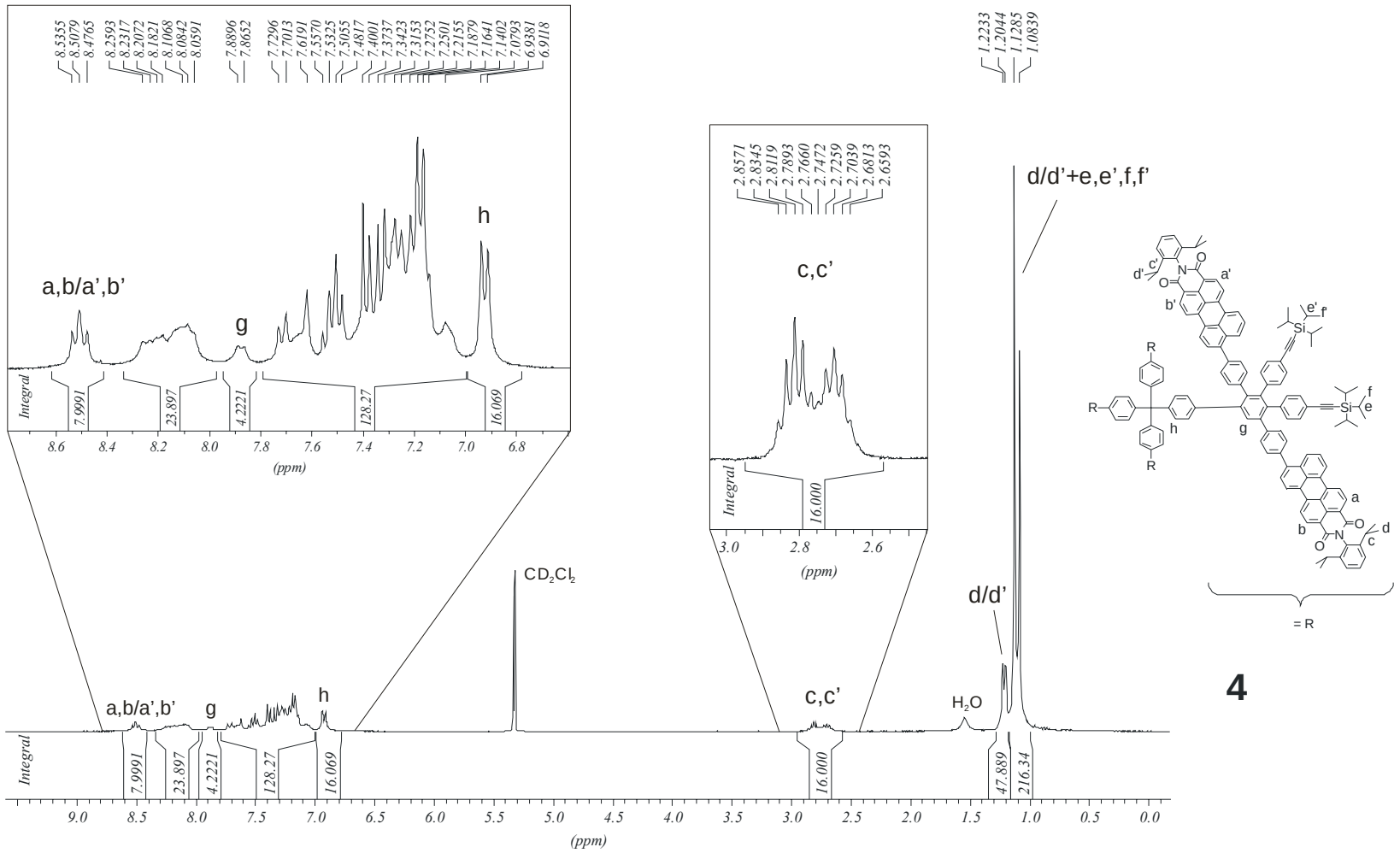

Figure 1. 300 MHz ^{1}H NMR spectrum of **4** in CD_2Cl_2 at 298 K.

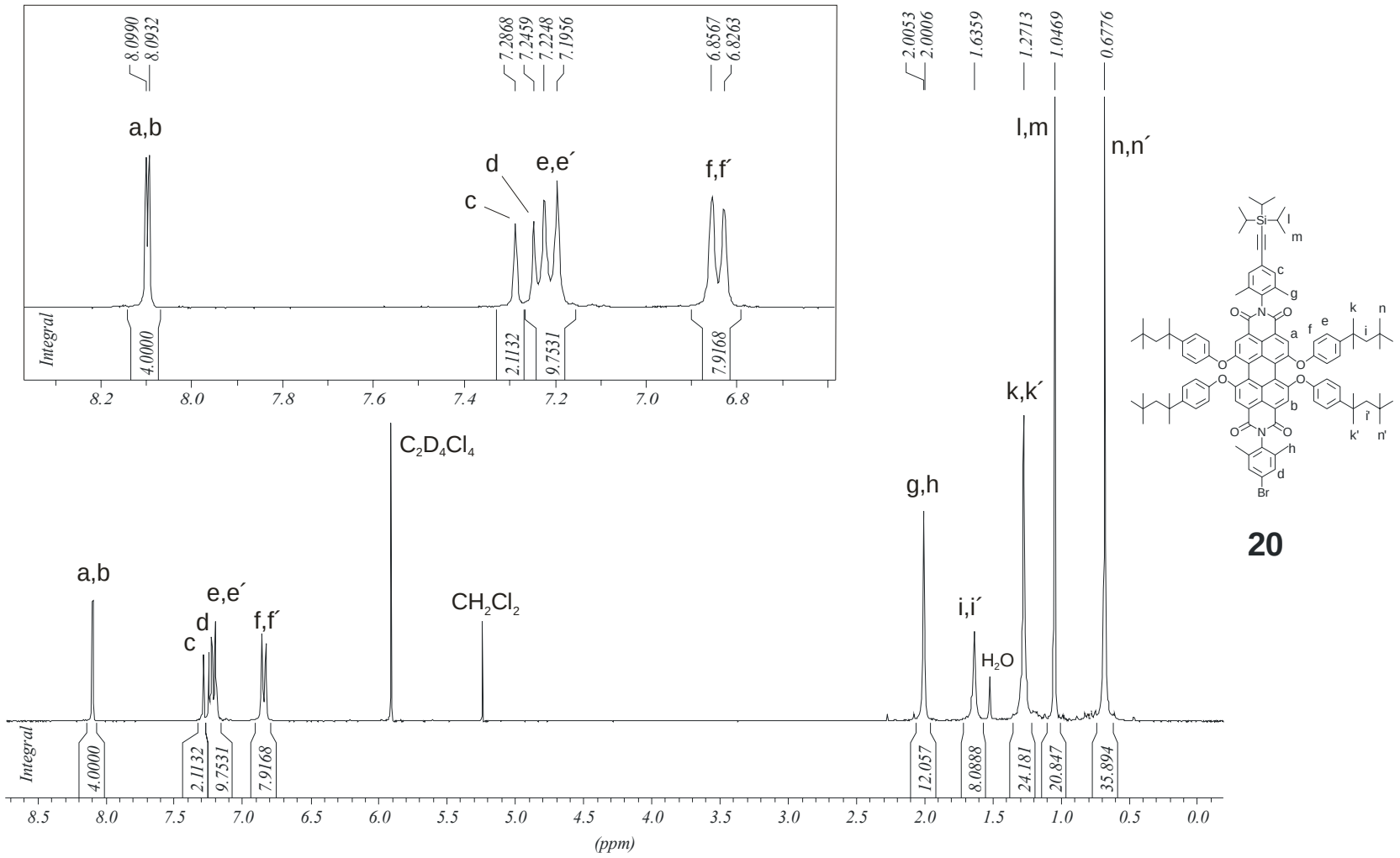

Figure 2. 300 MHz ^{1}H NMR spectrum of **20** in $C_2D_2Cl_4$ at 298 K.

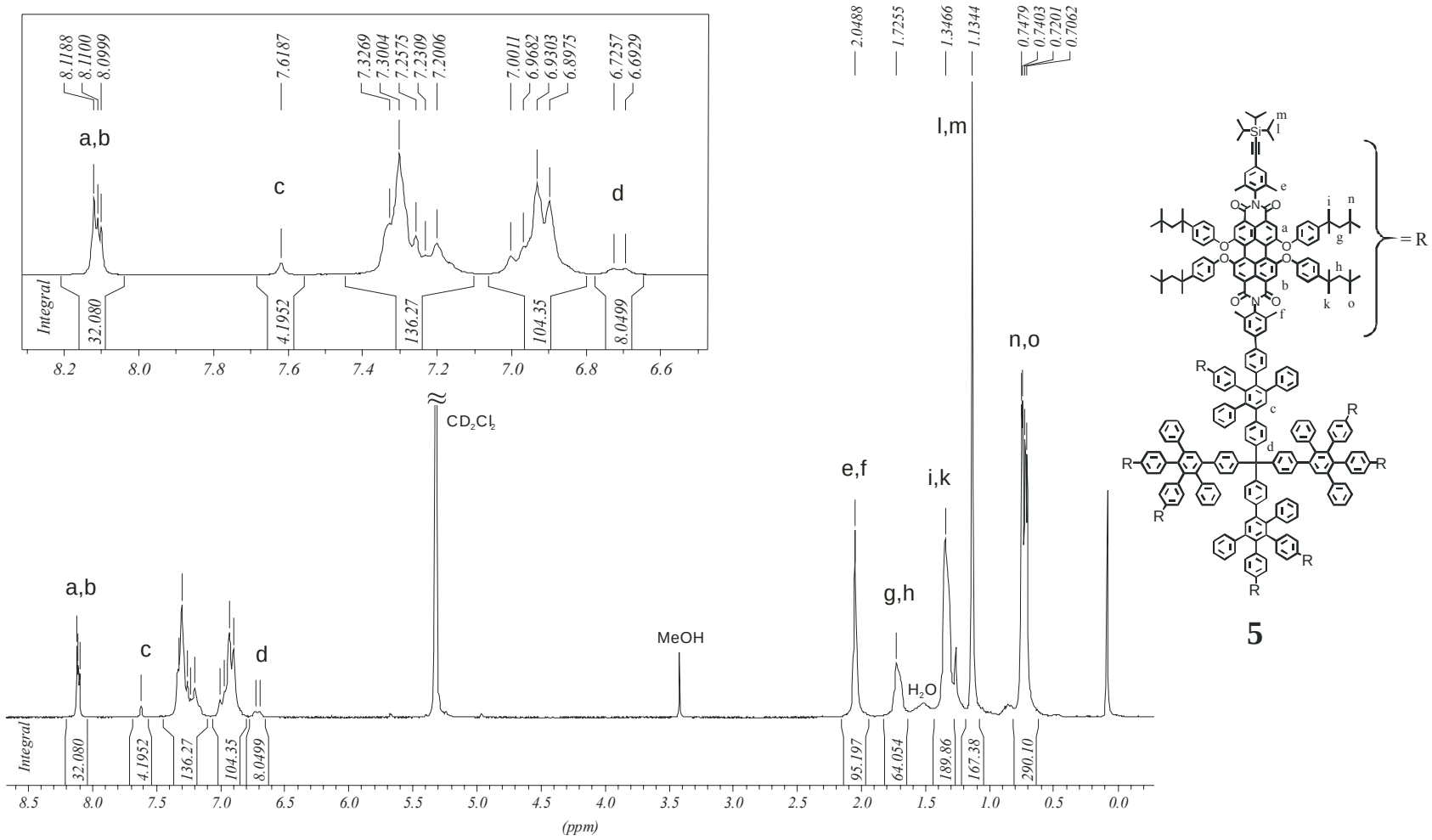

Figure 3. 250 MHz ^{1}H NMR spectrum of **5** in $C_2D_2Cl_4$ at 298 K.

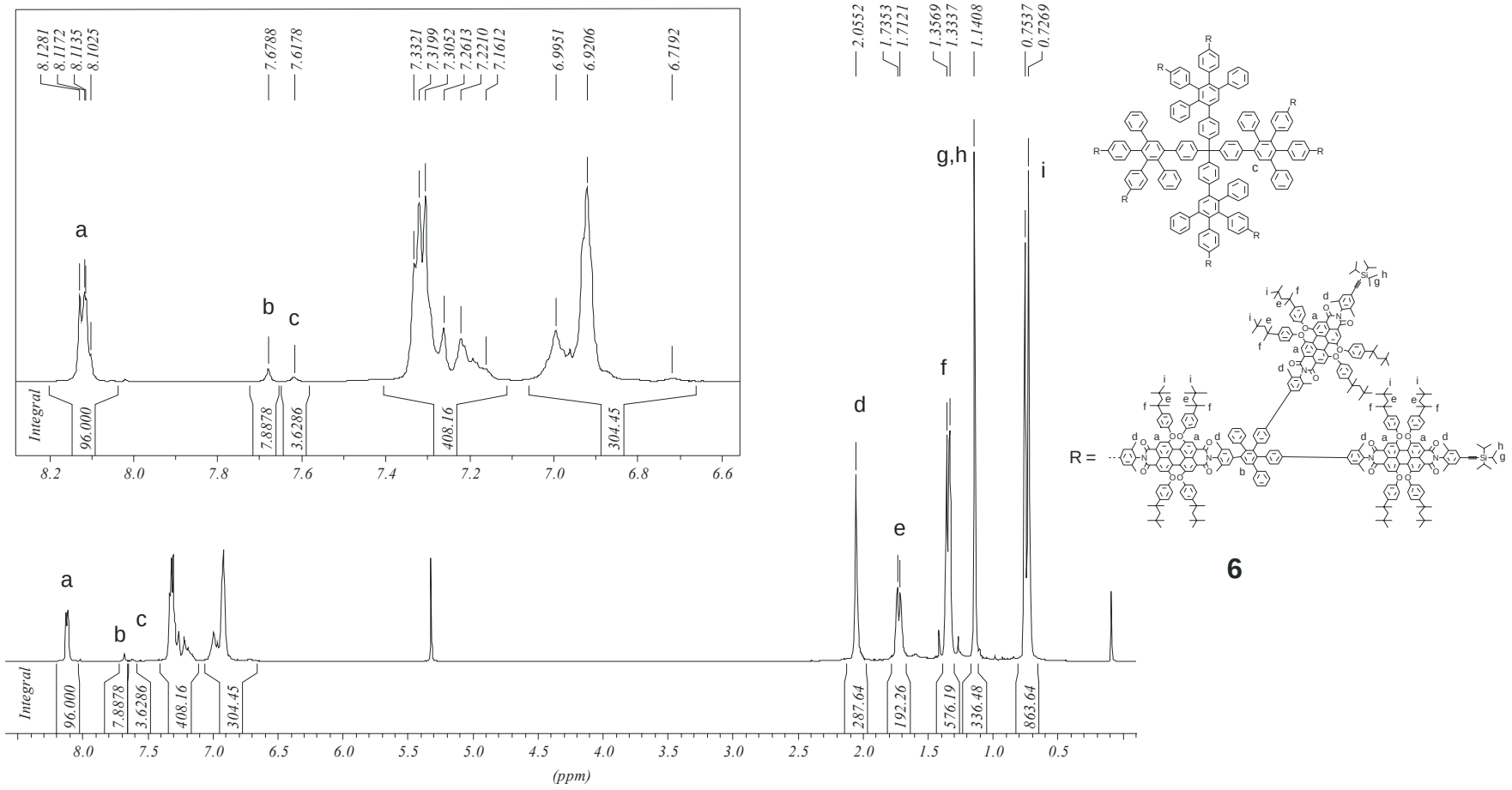

Figure 4. 700 MHz ^{1}H NMR spectrum of **6** in CD_2Cl_2 at 298 K.

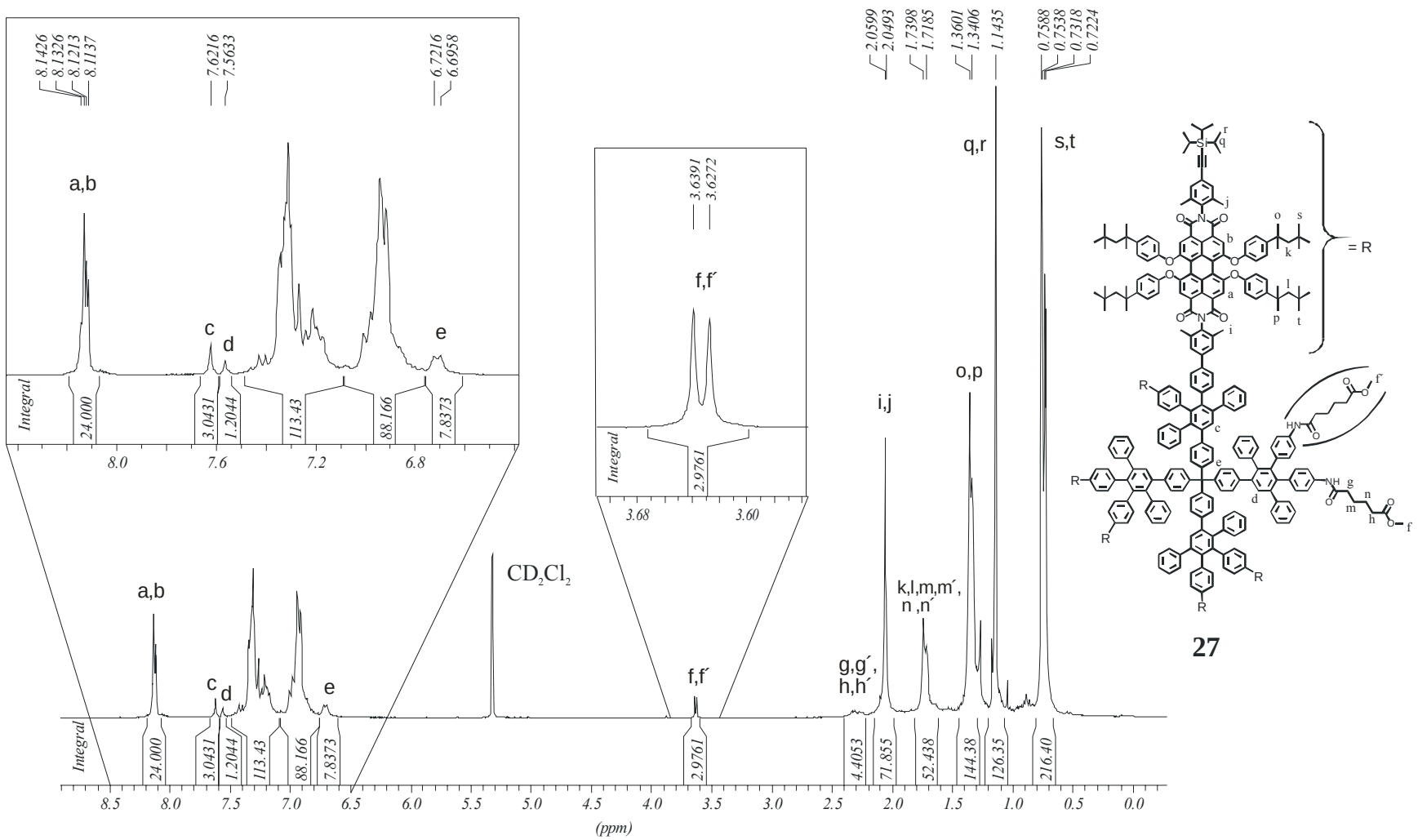

Figure 5. 300 MHz ^{1}H NMR spectrum of **27** in CD_2Cl_2 at 298 K.

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