Tetraphenylethene-Triphenylene Oligomers with an Aggregation-Induced Emission Effect and Discotic Columnar Mesophase

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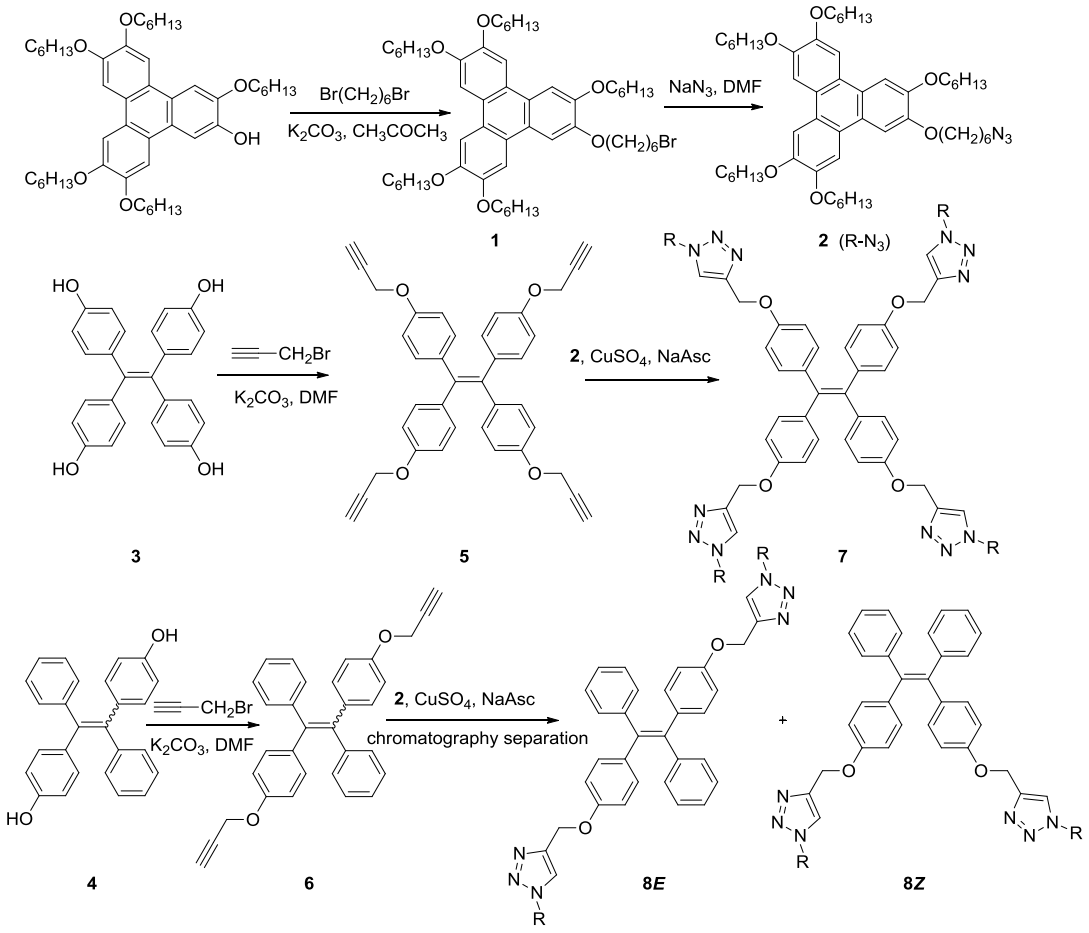
Supporting Information



Synthesis of tetraphenylethene-triphenylene oligomers.

Instruments and Reagents

^{1}H NMR and ^{13}C NMR were recorded by using a Varian INOVA 400 MHz spectrometer or a Bruker-Advance-600 NMR spectrometer in $CDCl_3$ at using TMS as the internal standard. The high resolution mass spectra were measured with a Varian 7.0T FTICR-MS instrument. IR spectra were recorded on a Bruker VERTEX70 spectrometer. Elemental analysis was measured with Carlo

Erba 110b micro elementary analysis instrument. UV-vis absorption spectra were recorded using a UV-4802S spectrophotometer. The fluorescent emission spectra were measured using a Perkin Elmer LS55 spectrofluorophotometer. Scanning electron microscopy (SEM) images were observed using FET quanta-250 SEM instruments at accelerating voltages of 30 kV. Mesomorphic textures were observed and recorded by using a polarizing optical microscope (POM, Olympus, BH-2), with a hot stage (Mettler, FP80HT) and controller (Mettler, FP80HT). Phase transition temperatures and enthalpies of discogens were investigated using a TA-DSC Q100 calorimeter under N_2 atmosphere with heating and cooling rate 10 ^oC/min. Thermal gravimetric analysis was carried out using a TA Q-500 instrument with heating rate as 30 ^oC/min under N_2 atmosphere. XRD experiments were performed on Philips X′Pert Pro MPD DY1291 X-ray diffractometer, with a flat plate camera using nickel-filtered Cu Kα radiation λ = 0.1542 nm.

Unless otherwise noted, reagents and solvents were commercial products and used without further purification.

Synthesis and Characterization

Synthesis of **1**

2-hydroxyl-3,6,7,10,11-pentakishexyloxytriphenylene (1.42 g, 1.6 mmol) and potassium carbonate (0.37 g, 2.68 mol) was added to acetone 150 mL. Then 1,6-dibromohexane (652 mg, 2.68 mmol) was added, and the solution was refluxed 24 h. The mixture was poured into water and extracted with dichloromethane. The organic layer was dried with magnesium sulfate, and the organic solvent was removed under vacuum. The crude compound was purified by column chromatography *V*(CH_2Cl_2) : *V*(petroleum ether) = 2 : 1 with silica gel afforded **1** white solid (1.1 g, 86%, mp: 60^oC).

Synthesis of **2**

A mixture of **1** (1.05 g, 1.15 mmol) and NaN_3 (749 mg, 11.5 mmol) in DMF was stirred at 80 ^oC for 24 h. After added 20 mL water, the reaction mixture was extracted with dichloromethane. The organic layer was dried with magnesium sulfate, and the organic solvent was removed under vacuum. The crude compound was purified by column chromatography *V*(CH_2Cl_2) : *V*(petroleum ether) = 1 : 2 with silica gel. Resulting solid was recrystallization from ethanol afforded product as **2** white solid (0.9 g, 90%, mp: 54^oC) .

Synthesis of **3**

Under a nitrogen atmosphere, a 3-necked flask equipped with a magnetic stirrer was charged with Zn powder (1.10 g, 16.9 mmol) and THF (40 mL). The mixture was cooled to 0 °C, and $TiCl_4$ (1 mL, 2.0 mmol) was added slowly by syringe with the temperature maintained under 10 °C. The suspended mixture was warmed to room temperature and stirred for 0.5 h, then heated to reflux for 2.5 h. The mixture was again cooled to 0 °C, charged with pyridine (0.5 mL, 6 mmol), and stirred for 10 min. The soln of two diaryl ketones (2.0 g, 7.9 mmol) in THF (20 mL) was added slowly. When the addition was complete, the mixture was heated to reflux until the carbonyl compounds were consumed (monitored by TLC). The reaction was quenched by addition of 10% 50 mL aq K_2CO_3 and extracted with ethyl acetate. The organic layer was dried with magnesium sulfate, and the organic solvent was removed under vacuum. The crude compound was purified by column

chromatography *V*(CH_2Cl_2) : *V*(petroleum ether) = 1 : 1 with silica gel. Resulting solid was recrystallized from methanol afforded product as 1,1,2,2-tetrakis(4-methoxyphenyl)ethene as a white solid (1.3 g, 69.4%).

Under an nitrogen atmosphere, into a flask were added (1.0 g, 2.2 mmol) of 1,1,2,2-tetrakis(4-methoxyphenyl)ethene and 12 mL of acetic acid (AcOH). Hydrobromic acid (7.2 g, 35.4 mmol) was added carefully to the mixture under stirring. The resultant suspension was refluxed for 24 h. After cooling to room temperature, the reaction mixture was poured into 200 mL of ice-water, then the resulting precipitate was filtered. The crude product was dried under vacuum. Resulting solid was purified by column chromatography *V*(ethyl acetate) : *V*(petroleum ether) = 6 : 1 with silica gel to give compound **3** as a pale yellow solid powder (850 mg, 93.7%).

Synthesis of **4**

Under a nitrogen atmosphere, a 3-necked flask equipped with a magnetic stirrer was charged with Zn powder (2.62 g, 40.37 mmol) and THF (60 mL). The mixture was cooled to 0 °C, and $TiCl_4$ (2.22 mL, 20.21 mmol) was added slowly by syringe with the temperature maintained under 10 °C. The suspended mixture was warmed to r.t. and stirred for 0.5 h, then heated to reflux for 2.5 h. The mixture was again cooled to 0 °C, charged with pyridine (0.5 mL, 6 mmol), and stirred for 10 min. The soln of two diaryl ketones (4.0 g, 10.20 mmol) in THF (50 mL) was added slowly. When the addition was complete, the mixture was heated to reflux until the carbonyl compounds were consumed (monitored by TLC). The reaction was quenched by addition of 10% 100 mL aq K_2CO_3 and extracted with ethyl acetate. The organic layer was dried with magnesium sulfate, and the organic solvent was removed under vacuum. The crude compound was purified by column chromatography *V*(CH_2Cl_2) : *V*(petroleum ether) = 1 : 1 with silica gel. Resulting solid was recrystallization from methanol afforded product as 1,2-bis(4-methoxyphenyl)-1,2-diphenylethene white solid (3.0 g, 81.1%).

Under an nitrogen atmosphere, into a flask were added (1.0 g, 2.55 mmol) of 1,2-bis(4-methoxyphenyl)-1,2-diphenylethene and 12 mL of acetic acid (AcOH). hydrobromic acid (4.1 g, 20.4 mmol) was added carefully to the mixture under stirring. The resultant suspension was refluxed for 24 h. After cooling to room temperature, the reaction mixture was poured into 200 mL of ice-water, then the resulting precipitate was filtered. The crude product was dried under vacuum. Resulting solid was purified by column chromatography *V*(ethyl acetate) : *V*(petroleum ether) = 2 : 1 with silica gel to give compound **4** as a pale white solid powder (890 mg, 96%).

Synthesis of **5, 6**

A mixture of compound **3** (100 mg, 0.25 mmol) and potassium carbonate (278 mg, 2.01 mmol) was added to DMF (10 mL). Then the 3-bromoprop-1-yne (126 mg, 1.06 mmol) was added, and the solution was stirred over 12 h at 70 ^{o}C under a nitrogen atmosphere. After removing the solvent, the residue was washed with water and extracted with dichloromethane. The organic layer was dried with magnesium sulfate, and the organic solvent was removed under vacuum. The crude compound was purified by column chromatography *V*(CH_2Cl_2) : *V*(petroleum ether) = 1 : 1 with silica gel to afford the product as a yellow solid **5** (110 mg, 79.7%). ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ: 6.93 (d, *J* = 8.4, 8H, Ar**H**), 6.69 (d, *J* = 8.4, 8H, Ar**H**), 4.61 (d, *J* = 1.8, 8H, 4×C**H**$_2$), 6.93 (d, *J* = 8.4, 8H, C**H**≡C-).

To the mixture of **4** (182 mg, 0.5 mmol) and potassium carbonate (138 mg, 1 mmol) in DMF

(10 mL), 3-bromoprop-1-yne (150 mg, 1.26 mmol) was added, and the solution was stirred over 12 h at 70 °C under a nitrogen atmosphere. After removing the solvent, the residue was washed with water and extracted with dichloromethane. The organic layer was dried with magnesium sulfate, and the organic solvent was removed under vacuum. The crude compound was purified by column chromatography *V*(CH_2Cl_2) : *V*(petroleum ether) = 1 : 1 with silica gel to afford the product as a pale white solid powder **6** (180 mg, 87.4%). ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ: 7.12 ~ 7.06 (m, 6H, Ar**H**), 7.04 ~ 7.00 (m, 4H, Ar**H**), 6.95 ~ 6.91 (m, 4H, Ar**H**), 6.72 ~ 6.68 (m, 4H, Ar**H**), 4.62 ~ 4.60 (m, 4H, OC**H**$_2$), 2.50 ~ 2.48 (m, 2H, C**H**≡C-).

Synthesis of **7**

To the mixture of **2** (229 mg, 0.263 mmol) and **5** (35 mg, 0.064 mmol) in 10 mL of THF-H_2O (*V*/*V* = 2 : 1), $CuSO_4$ • $5H_2O$ (8 mg, 0.032 mmol) and sodium-L-ascorbate (13 mg, 0.065 mmol) were added. The mixture was stirred at room temperature for 12 h. The reaction was monitored by TLC. After completion of the reaction, the solvent was evaporated under reduced pressure. The resulting residue was extracted with ethyl acetate, washed with water, and brine, respectively. The combined organic phase was dried with anhydrous sodium sulfate, concentrated, and purified by column chromatography *V*(CH_2Cl_2) : *V* (petroleum ether) : *V* (ethyl acetate) = 1 : 1 : 1 with silica gel yielding a pale white solid **7** (200 mg, 77.8 %, m.p. 112 °C). ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ: 7.83 (s, 24H, Ar**H**), 7.59 (s, 4H, =C**H**), 6.93 (d, *J* = 8.4 Hz, 8H, Ar**H**), 6.72 (d, *J* = 8.4 Hz, 8H, Ar**H**), 5.10 (s, 8H, OC**H**$_2$), 4.38 (t, *J* = 7.8 Hz 8H, NC**H**$_2$), 4.23 ~ 4.20 (m, 48H, OC**H**$_2$CH$_2$), 1.99~1.91 (m, 62H, C**H**$_2$), 1.64 ~ 1.58 (m, 48H. C**H**$_2$), 1.40 ~ 1.38 (m, 82H. C**H**$_2$), 0.94 ~ 0.91 (m, 60H, C**H**$_3$). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ: 156.7, 149.0, 148.99, 148.9, 148.8, 144.1, 138.6, 137.2, 132.6, 123.7, 123.6, 123.5, 122.4, 113.9, 107.4, 107.38, 107.34, 107.2, 69.8, 69.74, 69.7, 69.6, 69.3, 62.0, 50.3, 31.7, 30.3, 29.4, 26.4, 25.9, 22.7, 14.1. IR (KBr), ν (cm^{-1}): 3066 (=C-H stretching), 2928 (CH_2 asymmetrical stretching), 2855 (CH_2 symmetrical stretching), 1617 (C=C and N=N stretching), 1514, 1466, 1436 (Ar stretching). HRMS m/z (ESI): Calcd for $C_{254}H_{360}N_{12}O_{28}Na^+$ 4051.7073, Found: 4051.7047. Anal, calcd for $C_{253}H_{358}N_{12}O_{28}$: C 75.67, H 8.99, N 4.19; found: C 75.07, H 9.01, N 4.08 %.

Synthesis of **8**

To the mixture of **2** (430 mg, 0.494 mmol) and **6** (100 mg, 0.243 mmol) in 10 mL of THF-H_2O (*V*/*V* = 2 : 1), $CuSO_4$ • $5H_2O$ (15 mg, 0.06 mmol) and sodium ascorbate (124 mg, 0.121 mmol) were added. The mixture was stirred at room temperature for 12 h. The reaction was monitored by TLC. After completion of the reaction, the solvent was evaporated under reduced pressure. The resulting residue was extracted with ethyl acetate, washed with water, and brine, respectively. The combined organic phase was dried with anhydrous sodium sulfate, concentrated, and purified by column chromatography *V*(petroleum ether) : *V* (CH_2Cl_2) : *V* (ethyl acetate) = 3 : 1 : 1 with silica gel yielding a pale white solid **8*E*** (160 mg, 37 %, m.p. 150 °C) and colorless solid **8*Z*** (270 mg, 62.5%, m.p. 92 °C).

8*E*: ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ: ^{1}H NMR ($CDCl_3$, TMS, 600MHz) δ: 7.83 (s, 12H, Ar**H**), 7.58 (d, *J* = 16.8 Hz, 2H, C=C**H**), 7.12 ~ 7.06 (m, 6H, Ar**H**), 7.03 ~ 6.99 (m, 4H, Ar**H**), 6.94 ~ 6.90 (m, 4H, Ar**H**), 6.73 ~ 6.68 (m, 4H, Ar**H**), 5.12 (d, *J* = 15 Hz, 4H, OC**H**$_2$), 4.39 (t, *J* = 6.6 Hz, 4H, NC**H**$_2$), 4.23 (t, *J* = 6 Hz, 24H, OC**H**$_2$CH$_2$), 2.01 ~ 1.92 (m, 32H, C**H**$_2$), 1,67 ~ 1.38 (m, 68H. C**H**$_2$), 0.94 (t, *J* = 7.2 Hz, 30H, C**H**$_3$). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ: 156.7,

149.0, 148.98, 148.9, 148.7, 144.2, 144.1, 139.7, 136.9, 132.5, 131.3, 127.7, 126.2, 123.6, 123.7, 122.4, 113.8, 107.5, 107.4, 107.3, 107.1, 69.8, 69.7, 69.69, 69.5, 69.3, 62.0, 50.3, 31.7, 31.66, 30.3, 29.45, 29.43, 29.4, 29.3, 26.3, 25.9, 25.6, 22.7, 14.1. IR (KBr), *v* (cm^{-1}): 3066 (=C-H stretching), 2928 (CH_2 asymmetrical stretching), 2855 (CH_2 symmetrical stretching), 1617 (C=C and N=N stretching), 1514, 1466, 1436 (Ar stretching). HRMS m/z (ESI): Calcd for $C_{140}H_{190}N_6O_{14}Na^+$ 2203.4265, Found: 2203.4261. Anal, calcd for $C_{140}H_{184}N_6O_{14}$: C 77.10, H 8.78, N 3.85; found: C 77.16, H 8.70, N 3.79 %.

8*Z*: ^{1}H NMR ($CDCl_3$, TMS, 600 MHz) δ: 7.83 (s, 12H, Ar**H**), 7.58 (d, *J* = 16.2 Hz, 2H, C=C**H**), 7.11 ~ 7.06 (m, 6H, Ar**H**), 7.03 ~ 6.99 (m, 4H, Ar**H**), 6.93 ~ 6.90 (m, 4H, Ar**H**), 6.73 ~ 6.68 (m, 4H, Ar**H**), 5.12 (d, *J* = 14.4 Hz, 4H, OC**H**$_2$), 4.41 ~ 4.37 (m, 4H, NC**H**$_2$), 4.23 (t, *J* = 6 Hz, 24H, OC**H**$_2$CH$_2$), 2.01 ~ 1.92 (m, 32H, C**H**$_2$), 1,67 ~ 1.39 (m, 68H. C**H**$_2$), 0.94 (t, *J* = 7.2 Hz, 30H, C**H**$_3$). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ: 156.8, 156.75, 149.0, 148.98, 148.9, 148.7, 144.1, 144.0, 139.8, 139.7, 139.6, 136.9, 136.8, 132.6, 132.5, 131.34, 131.32, 127.7, 127.6, 126.2, 123.7, 123.65, 122.5, 122.46, 122.4, 113.9, 113.8, 107.4, 107.37, 107.1, 69.8, 69.7, 69.69, 69.5, 69.3, 62.0, 50.3, 31.7, 31.66, 30.3, 29.7, 29.44, 29.4, 29.3, 26.3, 25.9, 25.6, 22.7, 14.1. IR (KBr), *v* (cm^{-1}): 3066 (=C-H stretching), 2928 (CH_2 asymmetrical stretching), 2855 (CH_2 symmetrical stretching), 1617 (C=C and N=N stretching), 1514, 1466, 1436 (Ar stretching). HRMS m/z (ESI): Calcd for $C_{140}H_{190}N_6O_{14}Na^+$ 2203.4265, Found: 2203.4258. Anal, calcd for $C_{140}H_{184}N_6O_{14}$: C 77.10, H 8.78, N 3.85; found: C 77.31, H 8.69, N 3.77 %.

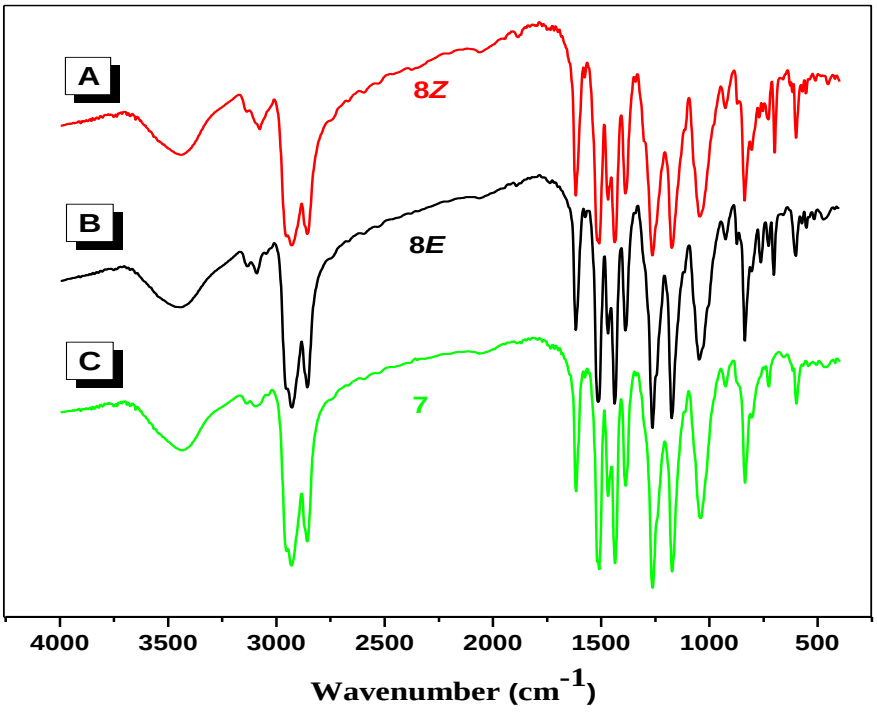


Fig. S1 IR spectra of oligomers (A) **8*Z***, (B) **8*E*** and (C) **7**

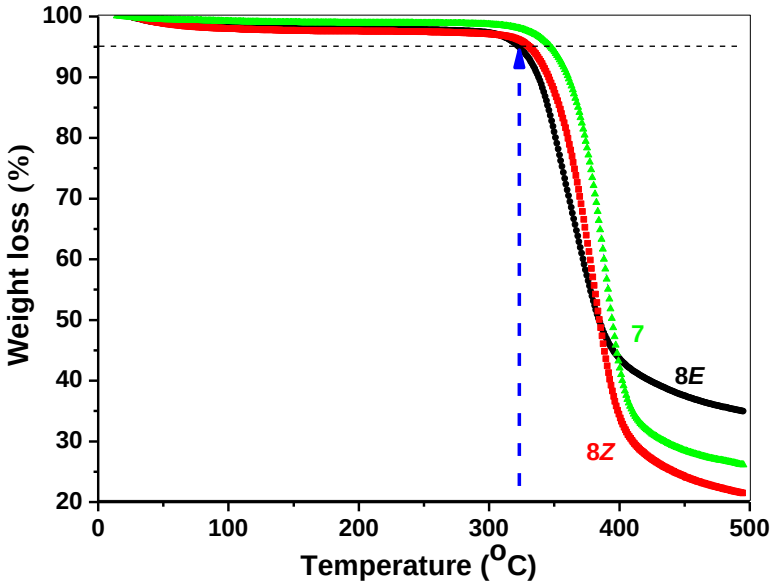


Fig. S2 TGA thermograms of oligomers

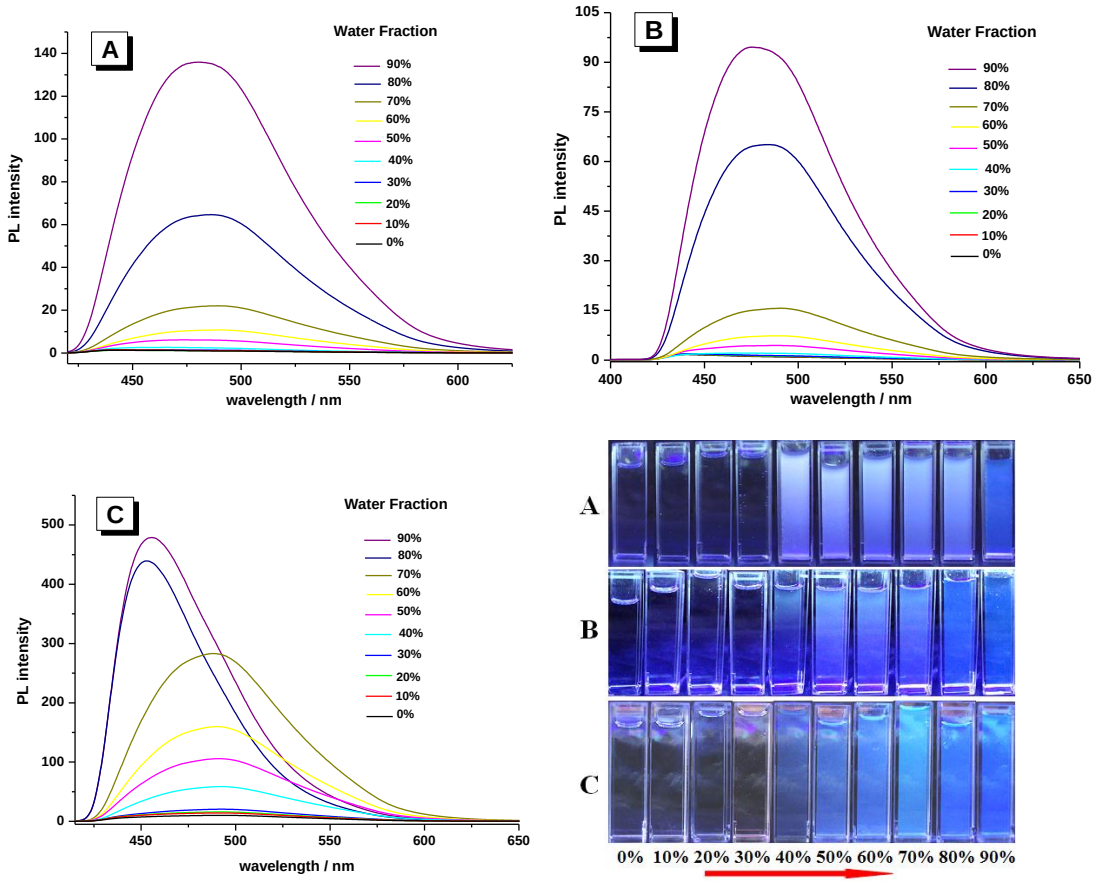


Fig. S3 Fluorescence spectra of **8*E***(A), **8*Z***(B), **7**(C) in water/THF mixtures (10^{-5} mol·L^{-1}) (percentages are volume fractions of water). peak intensities with the volume fractions of water insets are the fluorescence emission images of **8*E***(A), **8*Z***(B), **7**(C) in 0% to 90% volume fractions of water under UV light, excitation wavelength: 365 nm (10^{-5} mol. L^{-1}).

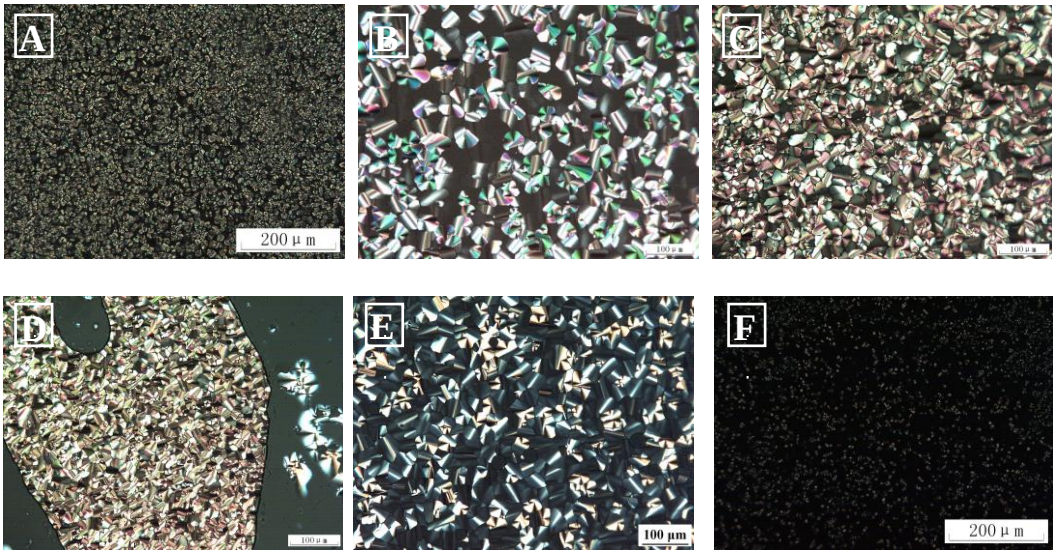


Fig. S4 Optical textures of the complex **7-TNF** (A) in a 2 : 1 mole ratio at 96 ^{o}C with crossed polarizers, (B) in a 1 : 1 mole ratio at 120 ^{o}C with crossed polarizers, (C) in a 1 : 2 mole ratio at 180 ^{o}C with crossed polarizers, (D) in a 1 : 3 mole ratio at 100 ^{o}C, crossed polarizers, (E) in a 1 : 4 mole ratio at 120 ^{o}C, crossed polarizers, (F) in a 1 : 5 mole ratio at 73^{o}C, crossed polarizers.

Fig. S5 ^{1}H NMR spectrum of **3**

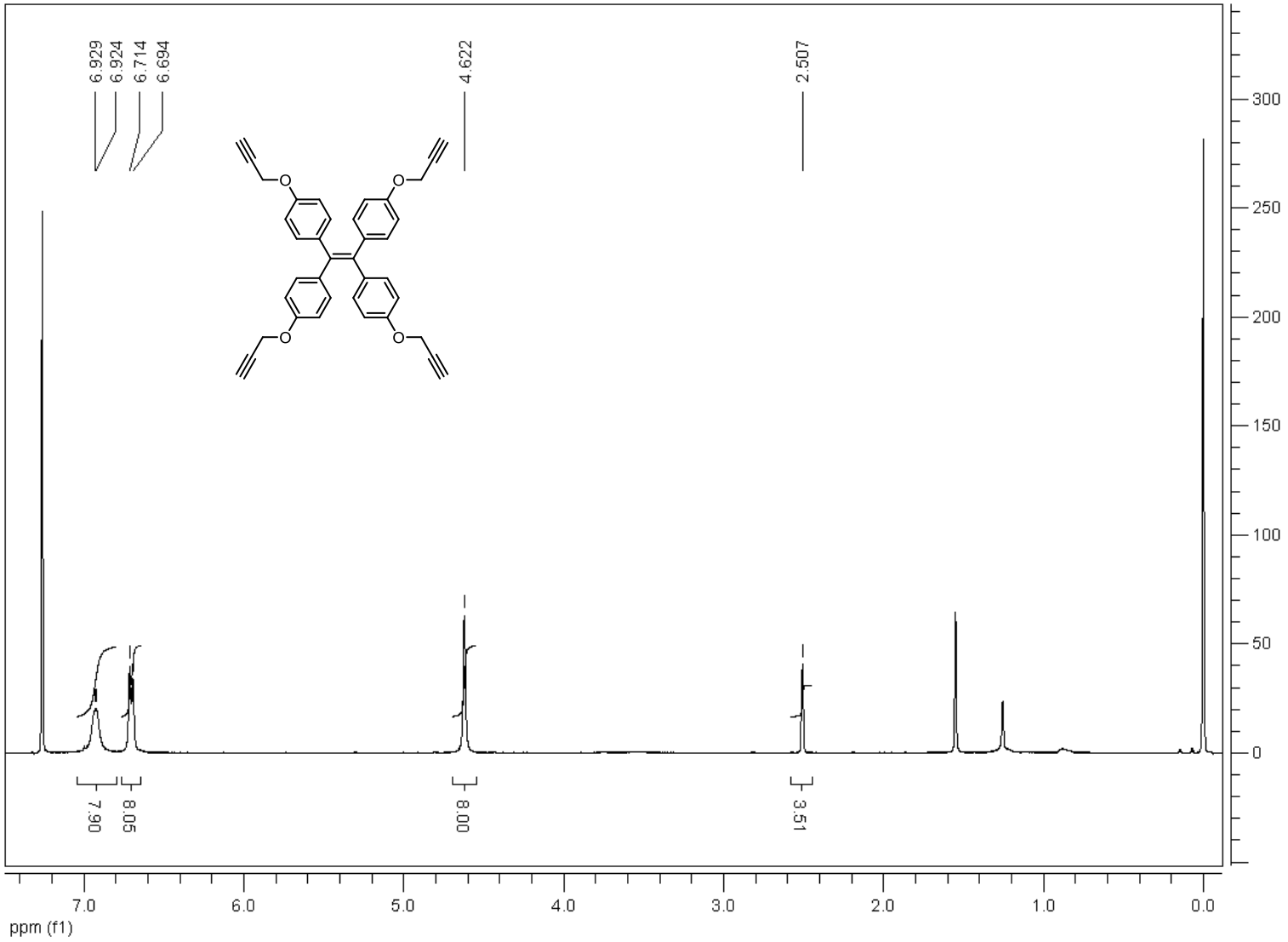


Fig. S6 ^{1}H NMR spectrum of **4**

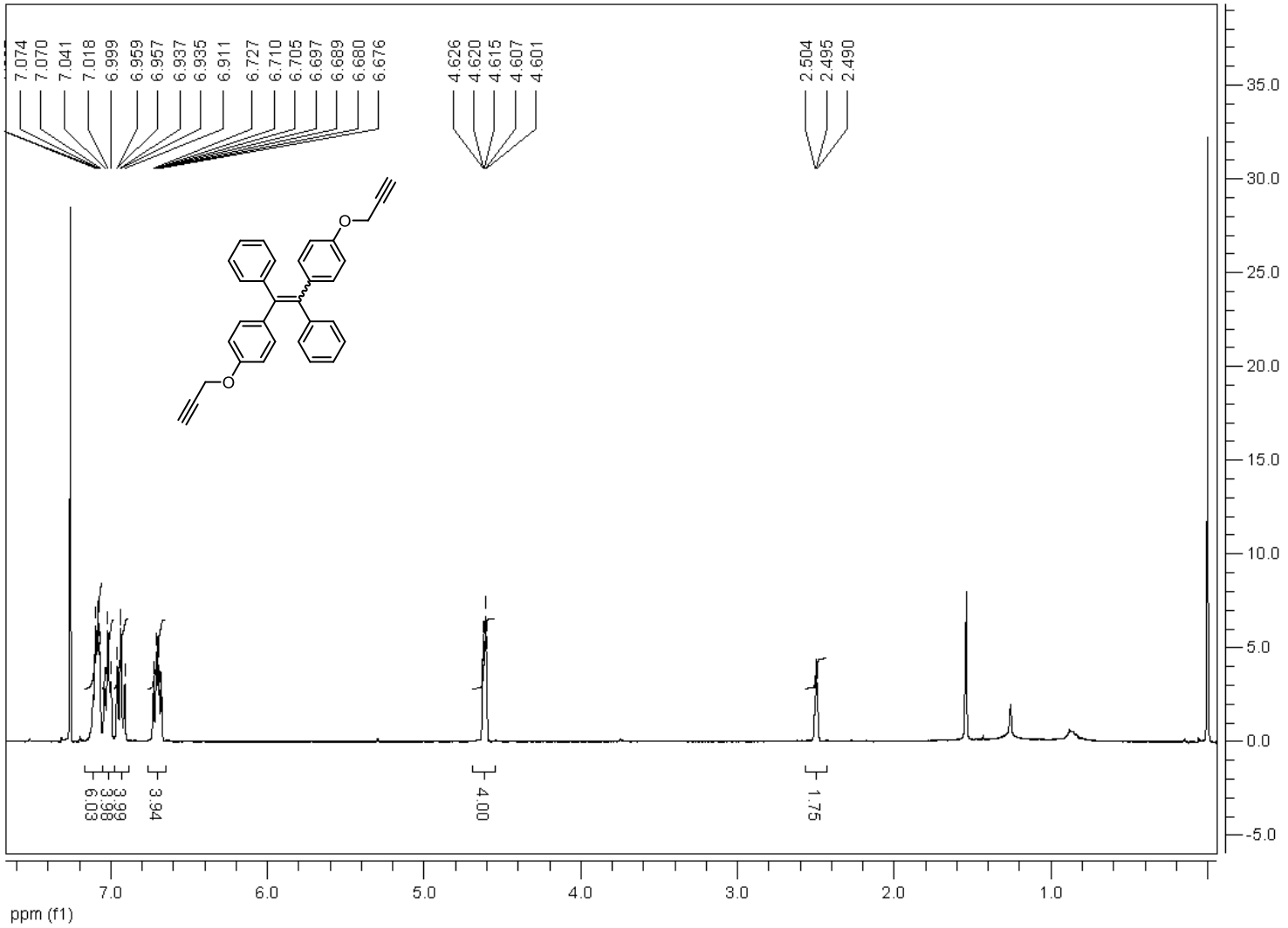


Fig. S7 ^{1}H NMR spectrum of **7**

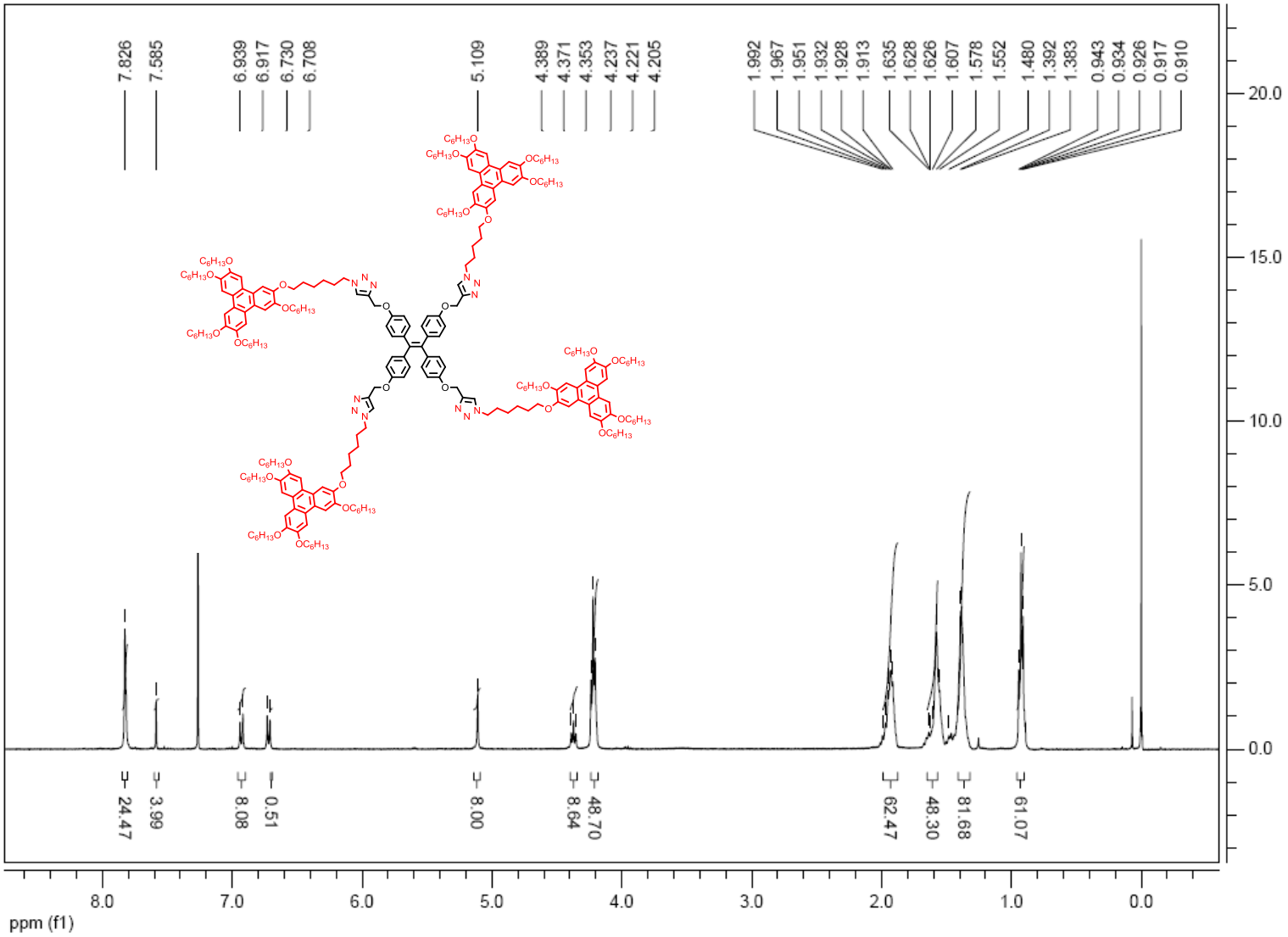


Fig. S8 ^{13}C NMR spectrum of **7**

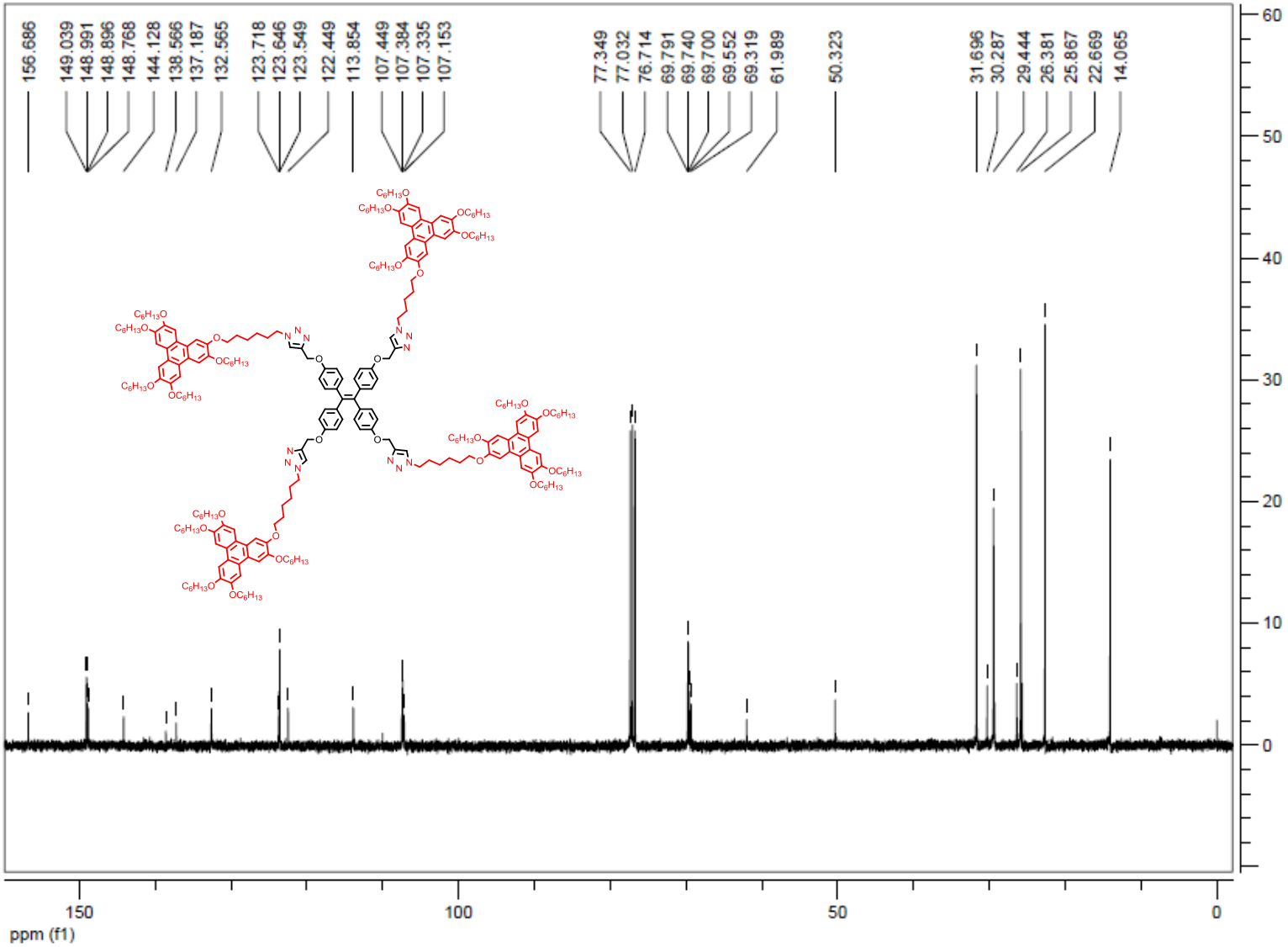


Fig. S9 MS spectrum of 7

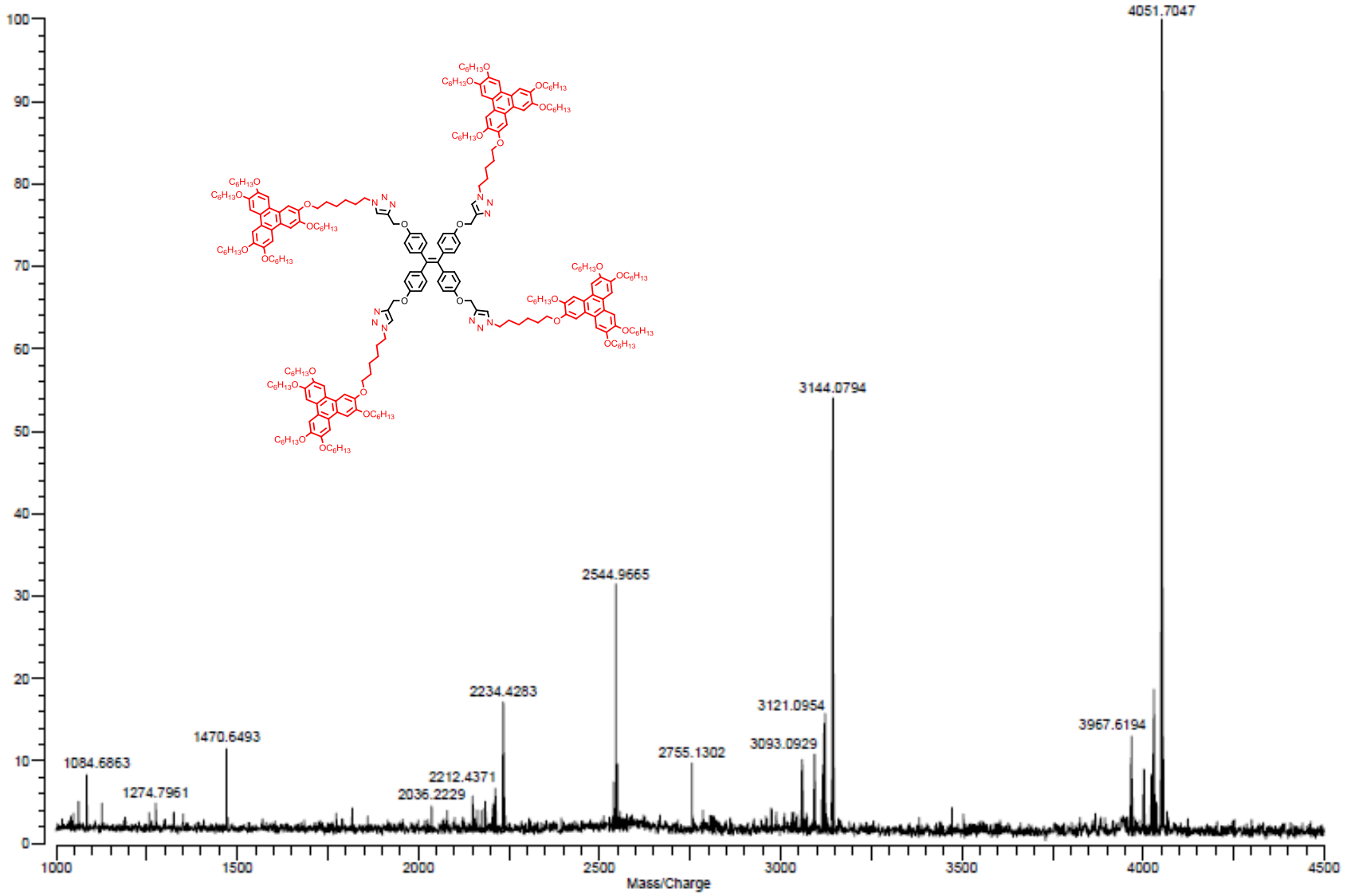


Fig. S10 ^{1}H NMR spectrum of 8*E*

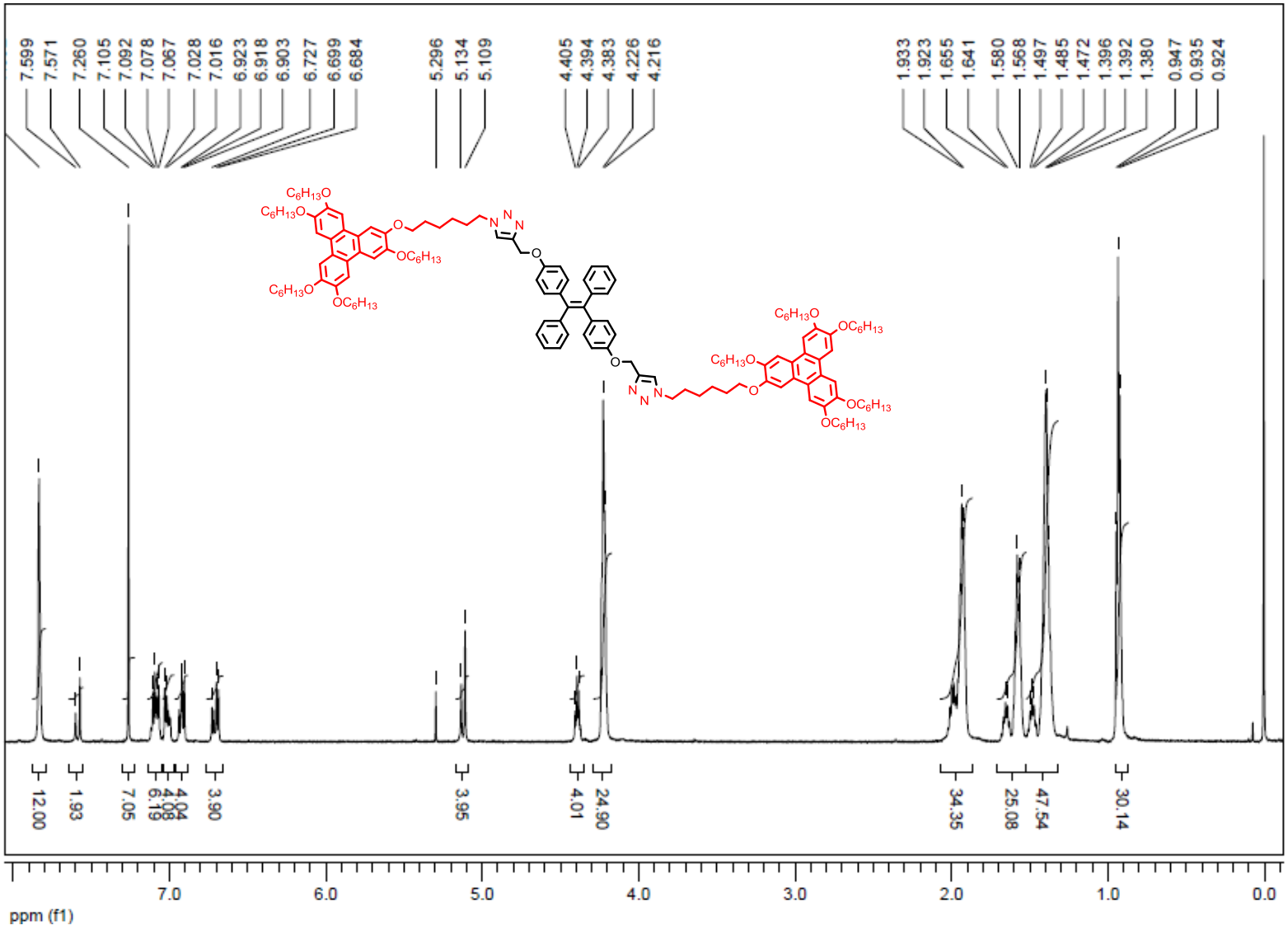


Fig. S11 ^{13}C NMR spectrum of 8*E*

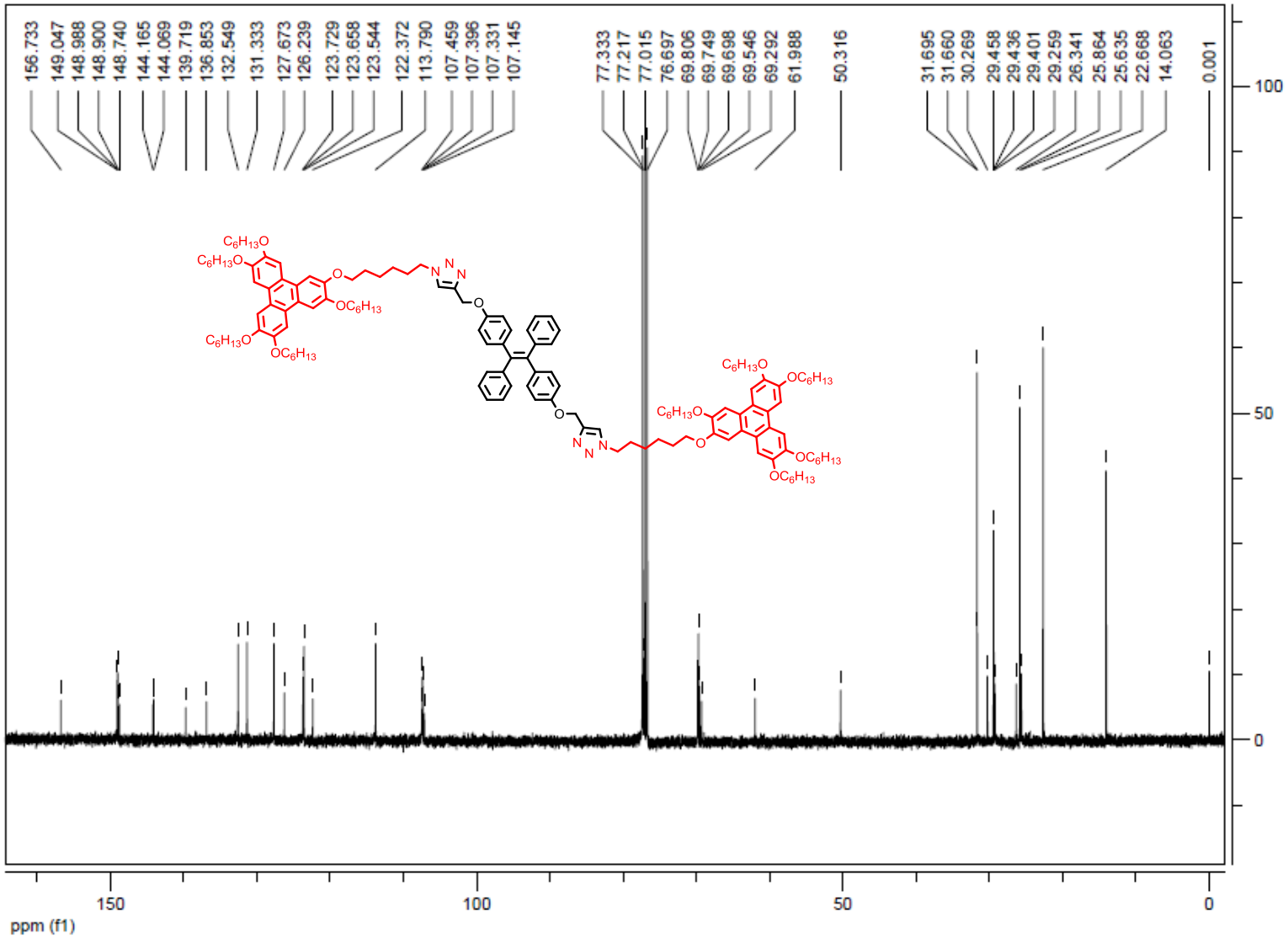


Fig. S12 MS spectrum of 8*E*

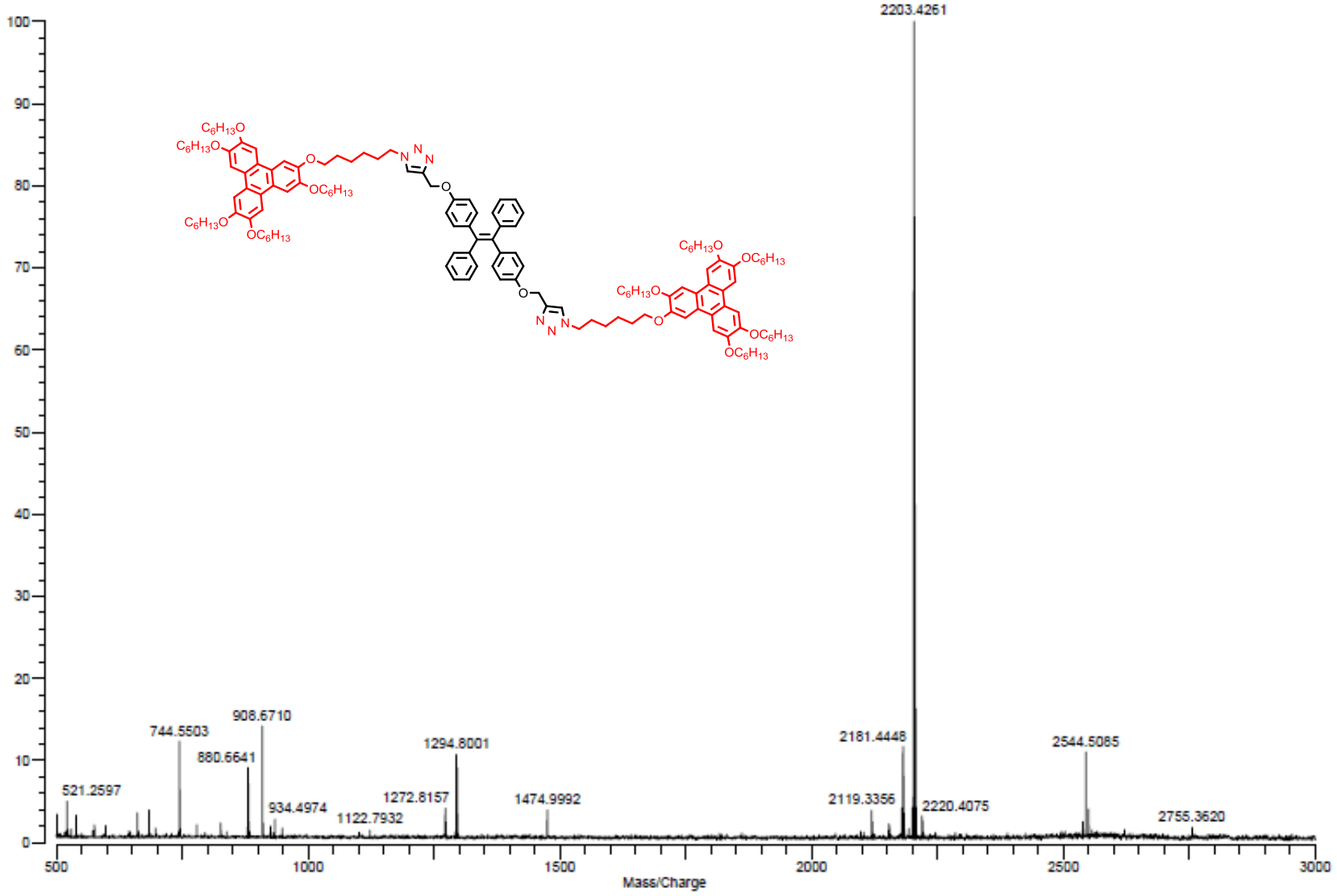


Fig. S13 ^{1}H NMR spectrum of 8*Z*

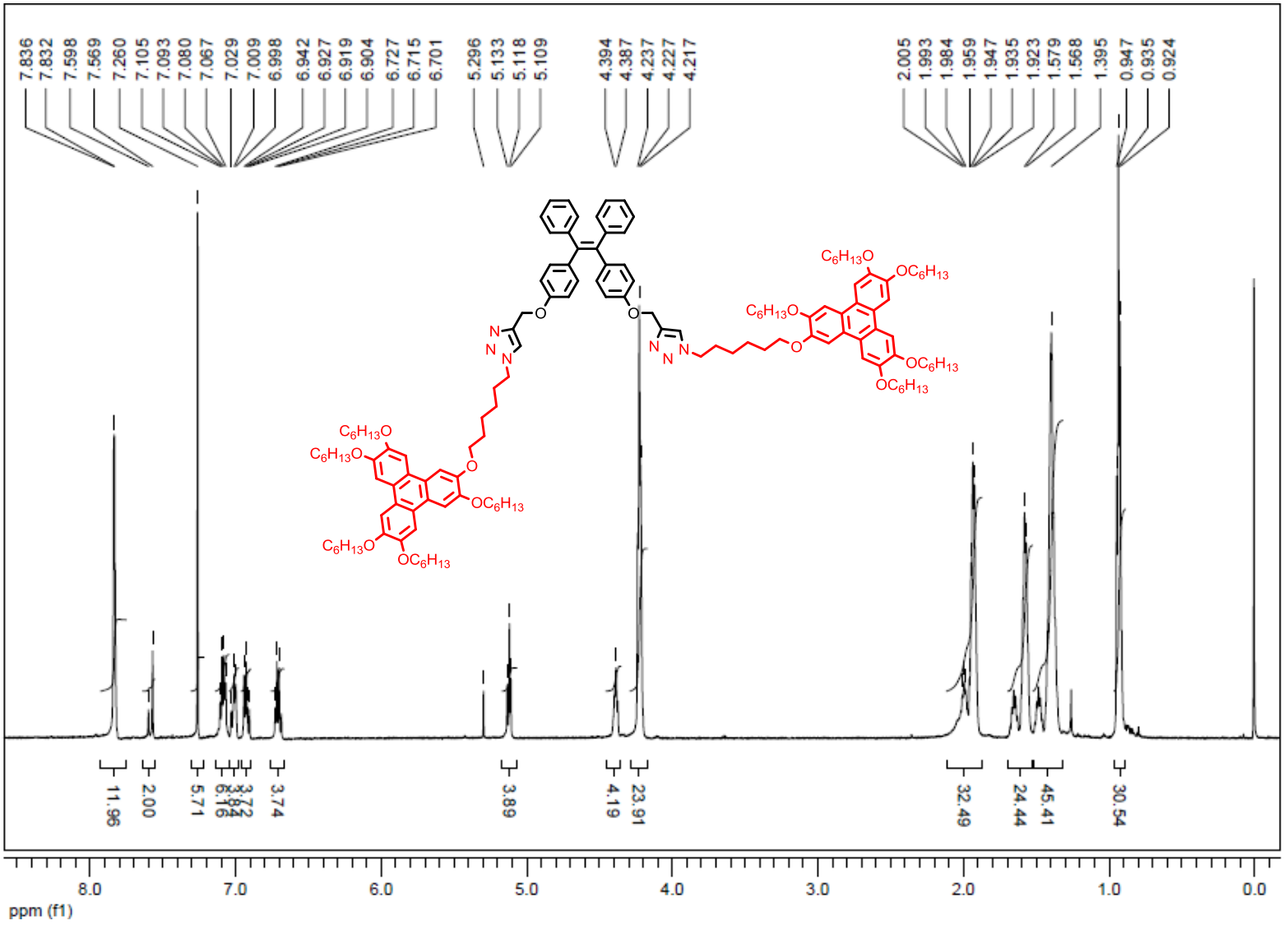


Fig. S14 ^{13}C NMR spectrum of 8*Z*

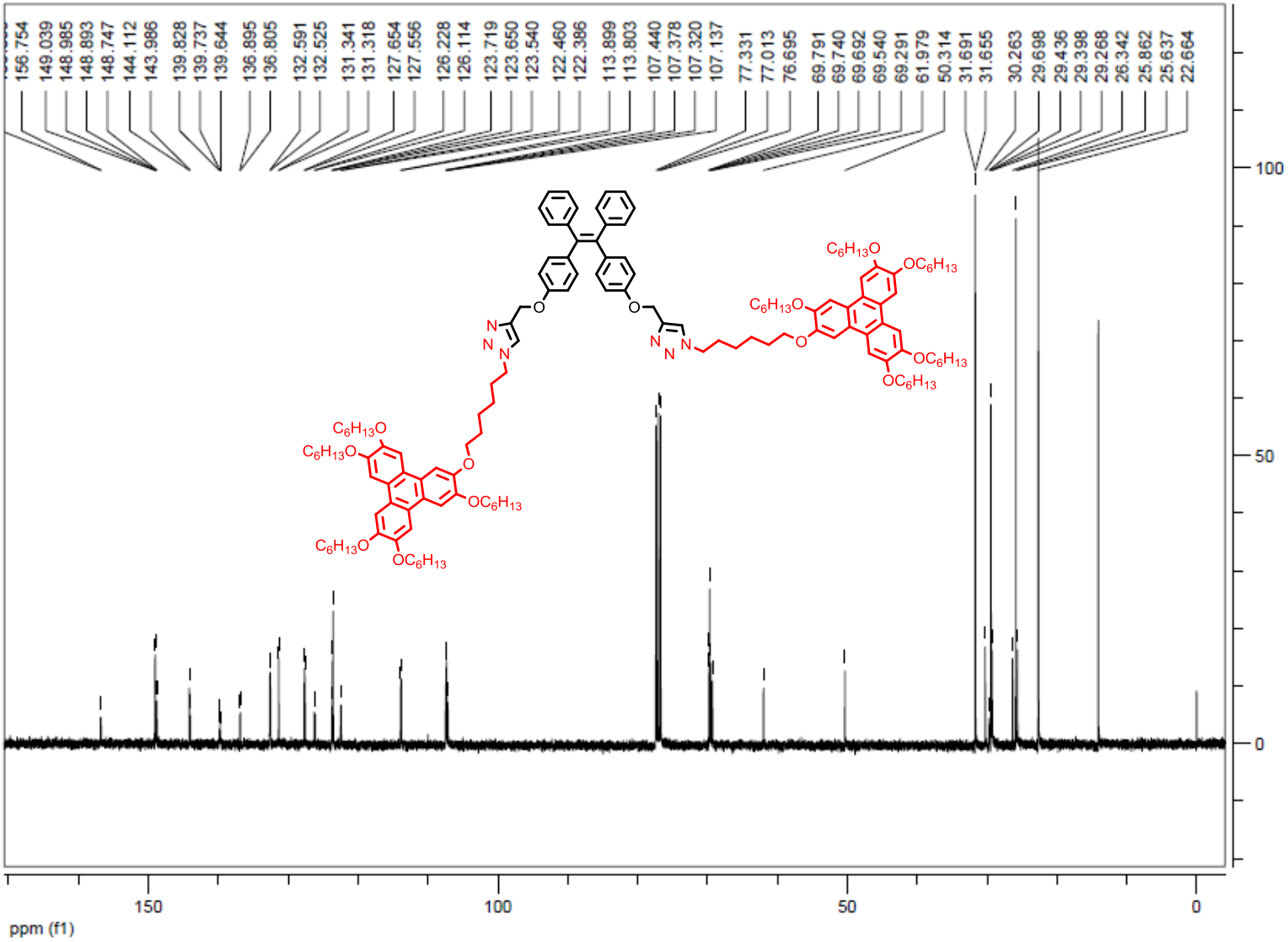


Fig. S15 MS spectrum of 8*Z*