Electronic Supplementary Material (ESI) for ChemComm.

Aggregated-induced emission of [3]cumulenes functionalized with heptagon-containing polyphenylenes

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- Electronic Supplementary Information -

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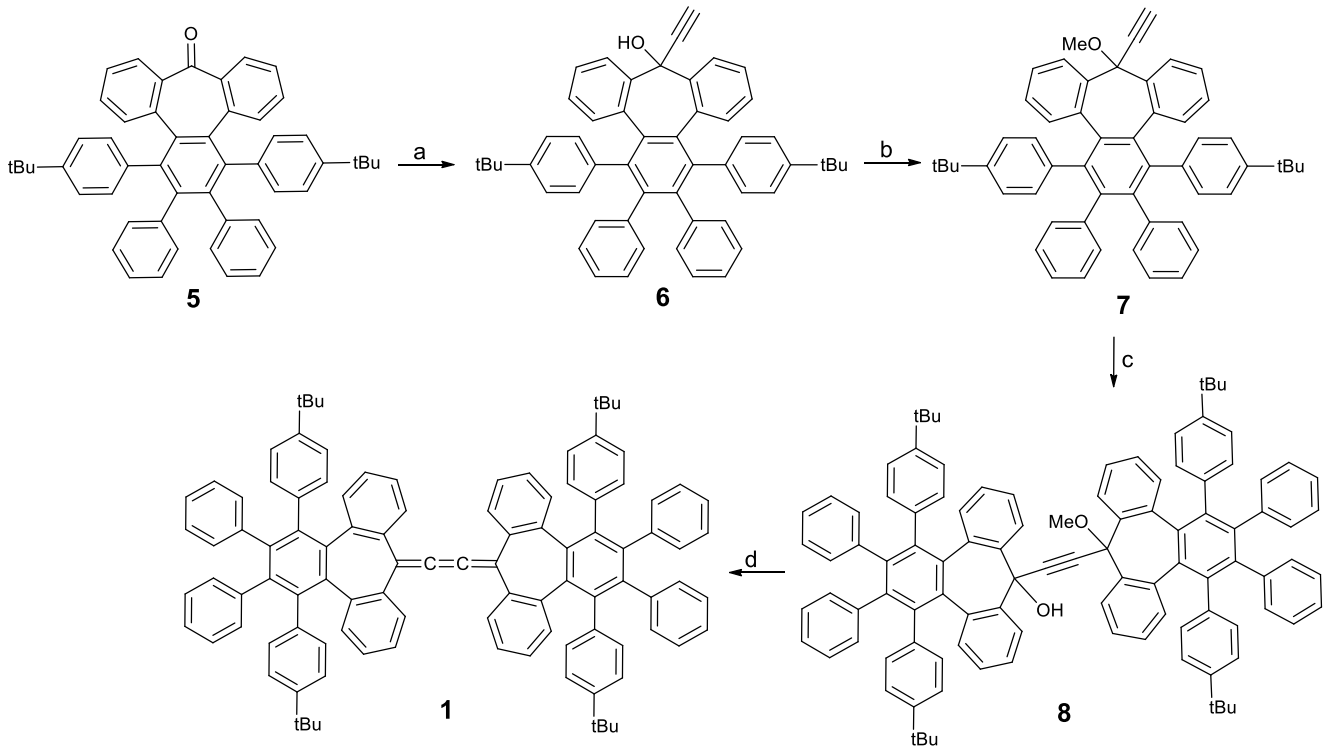
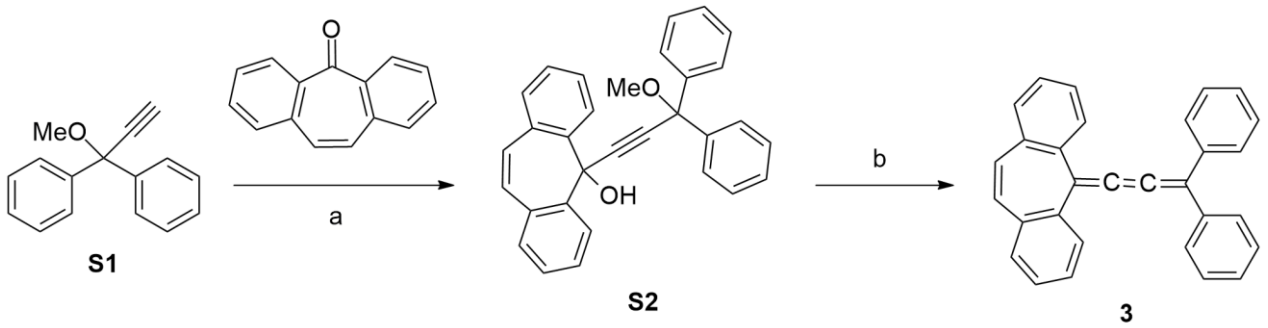
General Details

Unless otherwise stated, all reagents and solvents (CH_2Cl_2, EtOAc, hexane, Et_3N) were purchased from commercial sources and used without further purification. Compounds TPBT[S1], **S1**[S1], **2**[S2], **S3**[S2] and **5**[S3], were prepared according to literature procedures. Dry THF was freshly distilled over Na/benzophenone. Dry CH_2Cl_2 was purchased from Sigma-Aldrich. Flash column chromatography was carried out using Silica gel 60 (230-400 mesh, Scharlab, Spain) as the stationary phase. Analytical TLC was performed on aluminium sheets coated with silica gel with fluorescent indicator UV_{254} (Alugram SIL G/UV_{254}, Mackerey-Nagel, Germany) and observed under UV light (254 nm) and/or stained with phosphomolybdic acid (10% ethanol solution). Preparative TLC plates were purchased from ANALTECH, Silica gel G, (20×20cm, 500 micron). ^1H and ^{13}C NMR spectra were recorded on Varian 300, 400, 500 or 600 MHz spectrometers, at a constant temperature of 298 K. Chemical shifts are reported in ppm and referenced to residual solvent, 7.26 ppm for $CDCl_3$ and 5.30 ppm for CD_2Cl_2. Coupling constants (*J*) are reported in Hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: m = multiplet, quint. = quintet, q = quartet, t = triplet, d = doublet, s = singlet, tt = triple triplet, td = triple doublet, dd = double doublet, b = broad. Assignment of the ^{13}C NMR multiplicities was accomplished using DEPT techniques. MALDI-TOF mass spectra were recorded on a Bruker Ultraflex III mass spectrometer. IR-ATR spectra were recorded on a Perkin Elmer Spectrum Two IR Spectrometer.

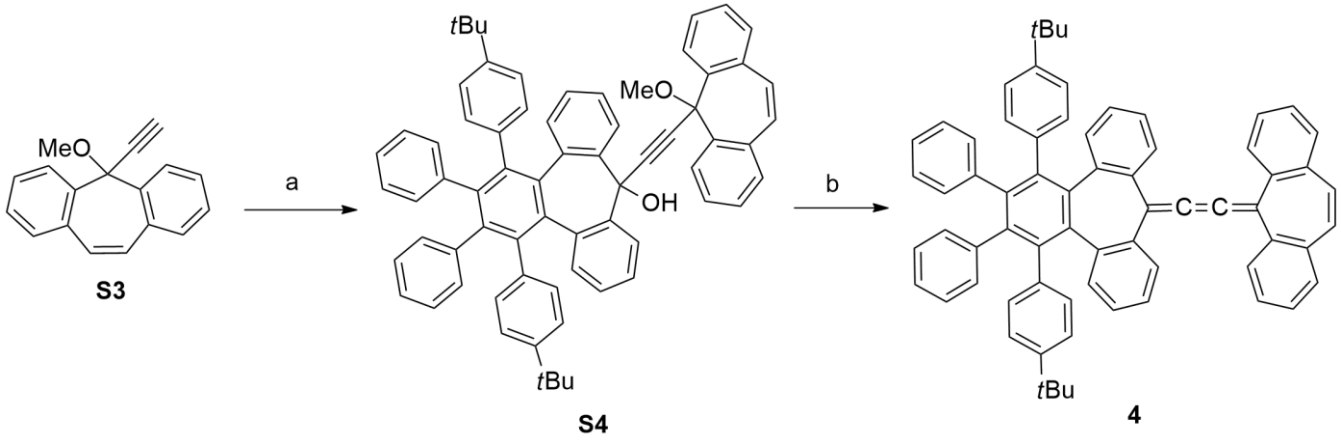
Synthesis



Scheme S1. Synthesis of compound **1**. a) Ethynylmagnesium bromide, THF, –40 °C to rt , 16 h, 79%; b) NaH, DMF, 0 °C, 30 min; then MeI, DMF, rt, 1 h, 99%; c) *n*BuLi, THF, –78 °C, 30 min; then **5**, THF, –78 °C to rt, 16 h, 13%; d) $SnCl_2 \cdot 2H_2O$, HCl, Et_2O, 1 h, rt, 45%.



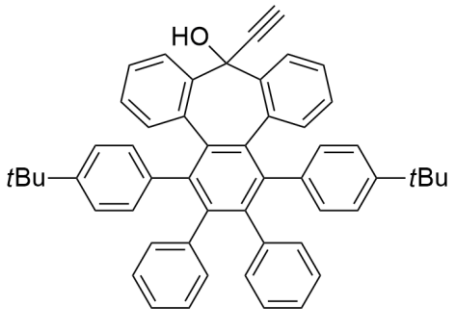
Scheme S2. Synthesis of compound **3**. a) *n*BuLi, THF, –78 °C, 1 h; then dibenzosuberenone, THF, –78°C to rt, 16 h, 85%; b) $SnCl_2 \cdot 2H_2O$, HCl, Et_2O, 2 h, rt, 50%.



Scheme S3. Synthesis of compound **4**. a) *n*BuLi, THF , –78 °C, 30 min; then **5**, THF, –78 °C to rt, 16 h, 14%; b) $SnCl_2 \cdot 2H_2O$, HCl, Et_2O, 2 h, rt, 50%.

No special caution was required as all synthesized [3]cumulene derivatives were bench stable for months upon air and light exposure. All [3]cumulene derivatives are prepared under acid media ($SnCl_2$/HCl) using HCl (1M in Et_2O) in a considerable excess (up to 400 equiv.). We have also tested the stability of [3]cumulene **3** against base by adding 6 equiv. of NEt_3 to a solution of **3** in $CDCl_3$ at room temperature during 24 h. No decomposition was observed by ^{1}H-NMR. We have also studied the stability of **1** and **3** against heat, by heating solutions in $C_2D_2Cl_4$ and DMSO-D_6, respectively, showing no decomposition after heating 3 h at 100ºC

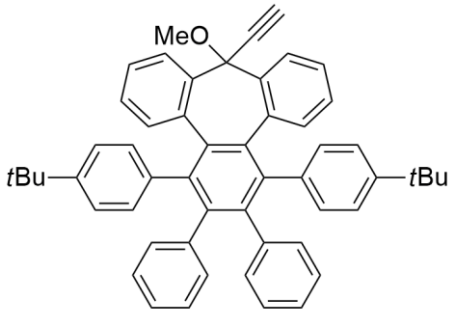
Compound 6



6

Compound **5**[S3] (217 mg, 0.32 mmol) was dissolved in freshly distilled THF (15 mL) under an Ar atmosphere. The resulting solution was cooled to –40 ºC and ethynylmagnesium bromide (0.5 M in THF, 1.9 mL, 0.96 mmol) was added dropwise via syringe. The reaction was allowed to warm to rt and stirred for 16 h. The mixture was diluted with EtOAc (40 mL) and washed with $NH_4Cl_{(aq)}$ (15 mL) and brine (15 mL), the organic layer was separated and dried with anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude was purified by column chromatography (SiO_2, Hexane/CH_2Cl_2 3:2) affording **6** (176 mg, 79%) as a white solid. M.p.: 314 – 316 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.08 – 6.96 (m, 6H), 6.93 (d, *J* = 7.9 Hz, 2H), 6.86 (d, *J* = 7.4 Hz, 2H), 6.83 – 6.74 (m, 4H), 6.71 – 6.58 (m, 6H), 6.36 (d, *J* = 7.8 Hz, 2H), 3.02 (s, 1H), 2.51 (s, 1H), 1.12 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 148.1(C), 145.8 (C), 142.4 (C), 140.8 (C), 139.3 (C), 138.0 (C), 137.8 (C), 133.8 (C), 133.3 (CH), 131.9 (CH), 131.7 (CH), 130.8 (CH), 129.8 (CH), 126.6 (CH), 126.3 (CH), 125.9 (CH), 125.3 (CH), 125.1 (CH), 123.6 (CH), 123.0 (CH), 119.0 (CH), 84.6 (C), 72.2 (CH), 70.1 (C), 34.1 (C), 31.2 (CH_3); HR-MS (MALDI DCTB+PEGNa600): *m/z* calcd. for $C_{53}H_{46}O$ $[M]^+$: 698.3543; found: 698.3536; IR (ATR): 3537, 3297, 2956, 1192, 698 cm^{-1}.

Compound 7

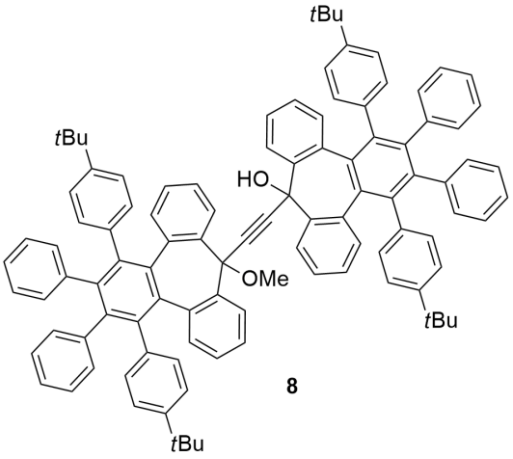


7

Compound **6** (176 mg, 0.25 mmol) was dissolved in anhydrous DMF (10 mL) under an Ar atmosphere and cooled to 0 ºC. Then, NaH (60% in mineral oil, 25.5 mg, 0.63 mmol) was added to the alcohol solution and stirred for 30 min at 0 ºC. Then, MeI (20 µL, 0.38 mmol) was added, the cooling bath was removed and the reaction was stirred at room temperature for 1 h. The mixture was quenched by addition of ice, extracted with EtOAc (60 mL) and washed with water (15 mL) and brine (15 mL). The organic layer was separated and dried with anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude was purified by column chromatography (SiO_2, Hexane/CH_2Cl_2 85:15) affording **7** (177 mg, 99%) as a white solid. M.p.: 320 – 322 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 7.7 Hz, 2H), 7.01 – 7.07 (m, 4H), 6.98 (t, *J* = 7.6 Hz, 2H), 6.93 (d, *J* = 7.7 Hz, 2H), 6.84 (d, *J* = 7.1 Hz, 2H), 6.74 – 6.82 (m, 4H), 6.71 (d, *J* = 7.9 Hz, 2H), 6.65 (t, *J* = 7.4 Hz, 2H), 6.60 (t, *J* = 7.5 Hz, 2H), 6.37 (d, *J* = 7.7 Hz, 2H), 3.93 (s, 3H), 2.55 (s, 1H), 1.12 (s,

18H); ^{13}C NMR (101 MHz, $CDCl_3$): δ =148.2 (C), 145.0 (C), 142.6 (C), 141.1 (C), 139.2 (C), 138.3 (C), 138.2 (C), 134.4 (C), 133.6 (CH), 132.1 (CH), 132.0 (CH), 131.0 (CH), 130.0 (CH), 126.8 (CH), 126.5 (CH), 126.1 (CH), 125.3 (CH), 125.2 (CH), 123.8 (CH), 123.2 (CH), 119.9 (CH), 80.4 (C), 76.7 (C), 75.0 (CH), 53.9 (CH_3), 34.3 (C), 31.3 (CH_3); HR-MS (MALDI DCTB+PPG790+NaI): *m/z* calcd. for $C_{54}H_{48}NaO$ $[M+Na]^+$: 737.3597; found: 735.3590; IR (ATR): 3275, 2953, 1391, 1073, 697 cm^{-1}.

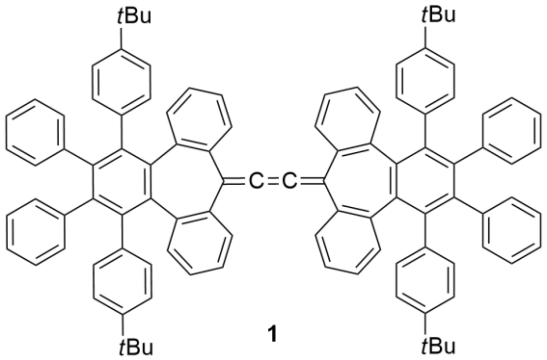
Compound 8



8

7 (105 mg, 0.15 mmol) was dissolved in freshly distilled THF (5 mL) under an Ar atmosphere and cooled to –78 ºC. Then, *n*-butyllithium (2.5 M in hexanes, 50 µL, 0.18 mmol) was added and stirred for 30 min at the same temperature. After this time, a solution of compound **5** (80 mg, 0.12 mmol) in distilled THF (5 mL) was added dropwise to the mixture and the reaction was allowed to warm to rt and stirred for 16 h. The mixture was diluted with EtOAc (40 mL) and washed with water (15 mL) and brine (15 mL), the organic layer was separated and dried with anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude was purified by column chromatography (SiO_2, Hexane/CH_2Cl_2 8:2) affording **8** (21 mg, 13%) as a white solid. M.p.: 342 – 346 ºC; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.7 Hz, 2H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 4H), 7.10 – 6.93 (m, 16H), 6.84 (d, *J* = 7.6 Hz, 2H), 6.80 (d, *J* = 7.8 Hz, 2H), 6.74 – 6.64 (m, 8H), 6.60 (t, *J* = 7.2 Hz, 2H), 6.55 (d, *J* = 7.8 Hz, 2H), 6.47 (t, *J* = 7.6 Hz, 2H), 6.37 (d, *J* = 7.8 Hz, 2H), 6.34 – 6.25 (m, 6H), 6.16 (d, *J* = 8.0 Hz, 2H), 4.22 (s, 3H), 2.10 (s, 1H), 1.12 (s, 18H), 1.02 (s, 18H); HR-MS (MALDI DCTB+PPGNa1000+PPGNa2000+NaI): *m/z* calcd. for $C_{105}H_{92}Na_1O_2$ $[M+Na]^+$: 1407.6990; found:1407.6979; IR (ATR): 3563, 2924, 1731, 1267, 699 cm^{-1}.

Compound 1

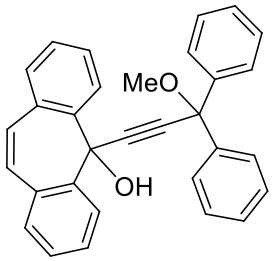


1

To a suspension of $SnCl_2{\cdot}2H_2O$ (28 mg, 0.15 mmol) in a solution of $HCl_{(g)}$ (1 M in Et_2O, 6 mL), under an Ar atmosphere, a solution of **7** (21 mg, 15×10^{-3} mmol) in anhydrous Et_2O (4 mL) was added. Immediately, the white solution turned light yellow and was stirred at room temperature for 1 h. The mixture was diluted with EtOAc (40

mL) and quenched with $NaHCO_{3(sat)}$ (10 mL). The organic phase was collected and washed with $NaHCO_{3(sat)}$ (15 mL) and brine (15 mL), the organic layer was separated and dried with anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude was purified by column chromatography (SiO_2, Hexane/CH_2Cl_2 85:15) and by preparative TLC (Hexane/CH_2Cl_2 8:2), affording **1** (9 mg, 45%) as a green/yellow solid. M.p.: >350 ºC; ^{1}H NMR (600 MHz, CD_2Cl_2): δ = 7.58 (d, *J* = 6.9 Hz, 4H), 7.39 (d, *J* = 7.7 Hz, 4H), 7.12 (td, *J* = 7.5, 1.3 Hz, 4H), 7.08 (dd, *J* = 8.2, 2.0 Hz, 4H), 7.02 (td, *J* = 7.6, 1.3 Hz, 4H), 6.98 (dd, *J* = 8.1, 2.2 Hz, 4H), 6.91 (dd, *J* = 7.9, 1.3 Hz, 4H), 6.83 (dd, *J* = 8.1, 2.1 Hz, 4H), 6.77 (tt, J = 7.4, 1.2 Hz, 4H), 6.68 (td, J = 7.6, 1.4 Hz, 4H), 6.57 (td, *J* = 7.6, 1.3 Hz, 4H), 6.47 (d, *J* = 7.8 Hz, 8H), 1.14 (s, 36H); ^{13}C NMR (151 MHz, CD_2Cl_2): δ = 153.1 (C) , 148.2 (C), 145.9 (C), 142.0 (C), 140.8 (C), 140.8 (C) , 137.9 (C), 137.2 (C), 135.3 (C), 133.1 (CH), 132.6 (CH), 132.0 (CH), 130.5 (CH), 130.2 (CH), 126.7 (CH), 126.5 (CH), 126.3 (CH), 125.8 (CH), 125.7 (CH), 125.1 (CH), 123.8 (CH), 123.5 (C), 123.1 (CH), 34.0 (C), 31.9 (CH_3); HR-MS (MALDI DCTB+PPG790): *m/z* calcd. for $C_{104}H_{88}$ $[M]^+$: 1336.6881; found: 1336.6858; IR (ATR): 2922, 1739, 1365, 1092 cm^{-1}.

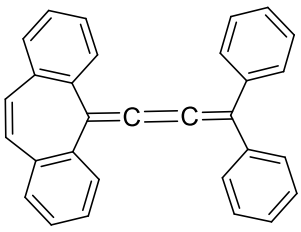
Compound S2



S2

Compound **S1**[S1] (384 mg, 1.74 mmol) was dissolved in freshly distilled THF (10 mL) under an Ar atmosphere and cooled to –78 ºC. Then, *n*-butyllithium (2.5 M in hexanes, 0.7 mL, 1.74 mmol) was added, the solution turned yellow/orange and it was stirred at the same temperature for 1 h. Then, a solution of dibenzosuberenone (358 mg, 1.74 mmol) in distilled THF (6 mL) was added dropwise to the mixture and the reaction was allowed to warm to rt and stirred for 16 h. The mixture was diluted with EtOAc (80 mL) and washed with water (25 mL) and brine (25 mL), the organic layer was separated and dried with anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude was purified by column chromatography (SiO_2, Hexane/CH_2Cl_2 3:2) affording **S2** (631 mg, 85%) as a white solid. M.p.: 130 – 132 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): 8.09 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 7.3 HZ, 4H), 7.43 – 7.49 (m, 4H), 7.26 – 7.40 (m, 8H), 7.20 (s, 2H), 3.35 (s, 3H), 3.25 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 143.1 (C), 140.3 (C), 132.8 (C), 131.6 (CH), 129.2 (CH), 128.6 (CH), 128.2 (CH), 127.7 (CH), 127.3 (CH), 126.8 (CH), 123.5 (CH), 91.3 (C), 81.0 (C), 52.8 (CH_3); HR-MS (ESI+MeOH+NaI): *m/z* calcd. for $C_{31}H_{24}O_2Na$ $[M+Na]^+$: 451.1668; found: 451.1663; IR (ATR): 3461, 3065, 1062, 766 cm^{-1}.

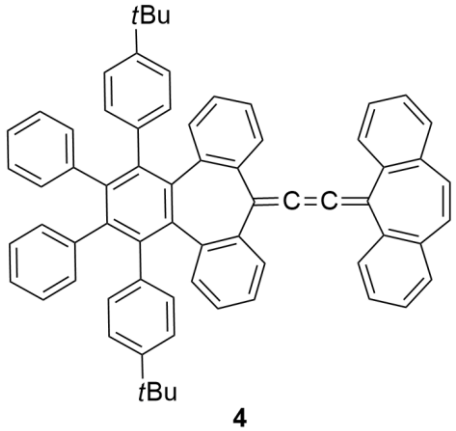
Compound 3



3

Compound **S2** (327 mg, 0.77 mmol) and $SnCl_2 \cdot 2H_2O$ (200 mg, 1.06 mmol) were dissolved in anhydrous Et_2O (12 mL) under an Ar atmosphere. To this mixture, a solution of $HCl_{(g)}$ (1 M in Et_2O, 0.8 mL, 0.77 mmol) was added. Immediately, the white solution turned orange and it was stirred at room temperature for 2 h. The mixture was diluted with EtOAc (80 mL) and quenched with $NaHCO_{3(sat)}$ (30 mL). The organic phase was collected and washed with $NaHCO_{3(sat)}$ (2 × 30 mL) and brine (30 mL), the organic layer was separated and dried with anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude was purified by column chromatography (SiO_2, Hexane/CH_2Cl_2 9:1) affording **3** (146 mg, 50%) as a crystalline orange solid. M.p.: 197 – 199 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 7.6 Hz, 2H), 7.56 (d, *J* = 7.1 Hz, 4H), 7.28-7.39 (m, 10H), 7.25 (td, *J* = 7.3, 1.3 Hz, 2H), 6.72 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 156.9 (C), 150.6 (C), 139.6 (C), 138.9 (C), 135.1 (C), 131.9 (CH), 130.5 (CH), 130.3 (CH), 129.4 (CH), 129.0 (CH), 128.5 (CH), 128.1 (CH), 128.0 (CH), 123.6 (C), 122.8 (C); HR-MS (TOF MS EI+): *m/z* calcd. for $C_{30}H_{20}$ $[M]^+$: 380.1564; found: 380.1555; IR (ATR): 2956, 1722, 1447, 1069 cm^{-1}.

Compound 4



4

Compound **S3**[S2] (441 mg, 1.81 mmol) was dissolved in freshly distilled THF (20 mL) under an Ar atmosphere and cooled to –78 ºC. Then, *n*-butyllithium (2.5 M in hexane, 0.9 mL, 2.17 mmol) was added, the solution turned yellow and stirred at the same temperature for 1 h. After this time, a solution of **5** (970 mg, 1.45 mmol) in distilled THF (13 mL) was added dropwise to the mixture and the reaction was allowed to warm to rt and stirred for 16 h. The mixture was diluted with EtOAc (100 mL) and washed with water (25 mL) and brine (25 mL), the organic layer was separated and dried with anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude was purified by column chromatography (SiO_2, Hexane/CH_2Cl_2 7:3) affording **S4** (188 mg, 14%) as a white solid directly used in the next step without further characterization. To a suspension of $SnCl_2 \cdot 2H_2O$ (58 mg, 0.3 mmol) in a solution of $HCl_{(g)}$ (1 M in Et_2O, 5 mL), under an Ar atmosphere, a solution of **S4** (30 mg, 0.03 mmol) in anhydrous Et_2O (3 mL) was added. Immediately, the white solution turned yellow, and it was stirred at room temperature for 2 h. The mixture was diluted with EtOAc (40 mL) and quenched with $NaHCO_{3(sat)}$ (10 mL). The organic phase was collected and washed with $NaHCO_{3(sat)}$ (15 mL) and brine (15 mL), the organic layer was separated and dried with anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude was purified by column chromatography (SiO_2, Hexane/CH_2Cl_2 8:2) affording **4** (13 mg, 50%) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 7.7 Hz, 2H), 7.39 (dd, *J* = 14.6, 7.5 Hz, 4H), 7.25 – 7.35 (m, 6H), 7.02 (t, *J* = 7.7 Hz, 4H), 6.92 (dd, *J* = 14.0, 7.1 Hz, 4H), 6.88 (d, *J* = 7.7 Hz, 2H), 6.80 (s, 2H), 6.77 (dd, *J* = 15.8, 8.1 Hz, 4H), 6.65 (t, *J* = 7.5 Hz, 2H), 6.57 (t, *J* = 7.6 Hz, 2H), 6.48 (d, *J* = 7.8 Hz, 2H), 6.42 (d, *J* = 7.9 Hz, 2H), 1.14 (s, 18H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 158.9 (C), 151.0 (C), 148.0 (C), 146.3 (C), 142.0 (C), 141.0 (C), 140.9 (C), 139.5 (C), 138.1 (C), 137.7 (C), 135.6 (C), 135.1 (C), 133.4 (CH), 132.4 (CH), 132.0 (CH), 131.9 (CH), 130.7 (CH), 130.6 (CH), 130.5 (CH), 130.2 (CH), 129.1 (CH), 128.1 (CH), 126.9 (CH), 126.6 (CH), 126.4 (CH), 125.9 (CH), 125.7 (CH), 125.3 (CH), 124.3 (C), 123.9 (CH), 123.2 (CH), 122.8 (C), 34.3 (C), 31.4 (CH_3); HR-MS (MALDI DCTB+PEGNa600+PEGNa1000): *m/z* calcd. for $C_{68}H_{54}$ $[M]^+$: 870.4220; found: 870.4233; IR (ATR): 2923, 1738, 1365, 1217 cm^{-1}.

^{1}H and ^{13}C NMR spectra of new compounds

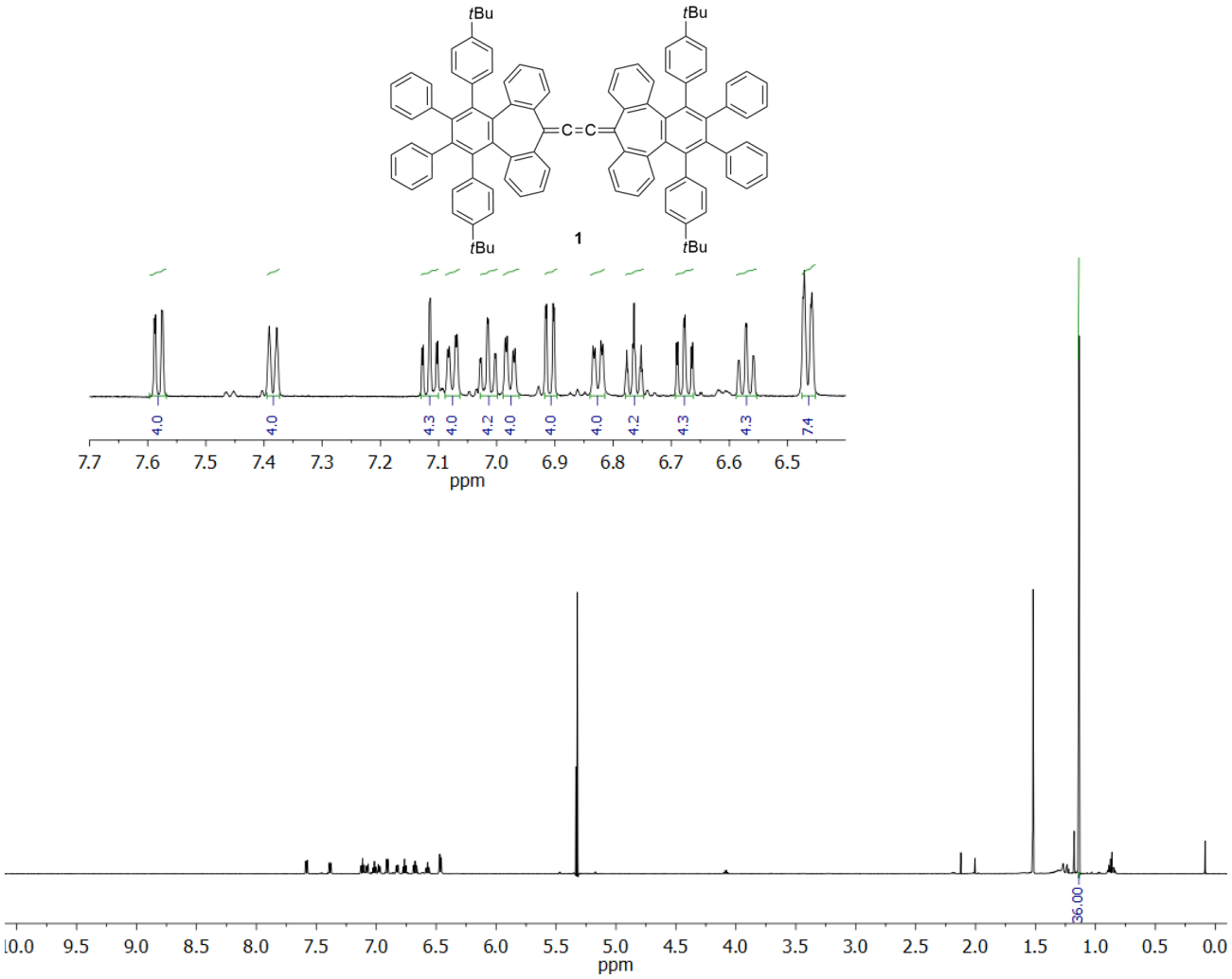


Figure S1. ^{1}H NMR (600 MHz, CD_2Cl_2) spectrum of compound **1**.

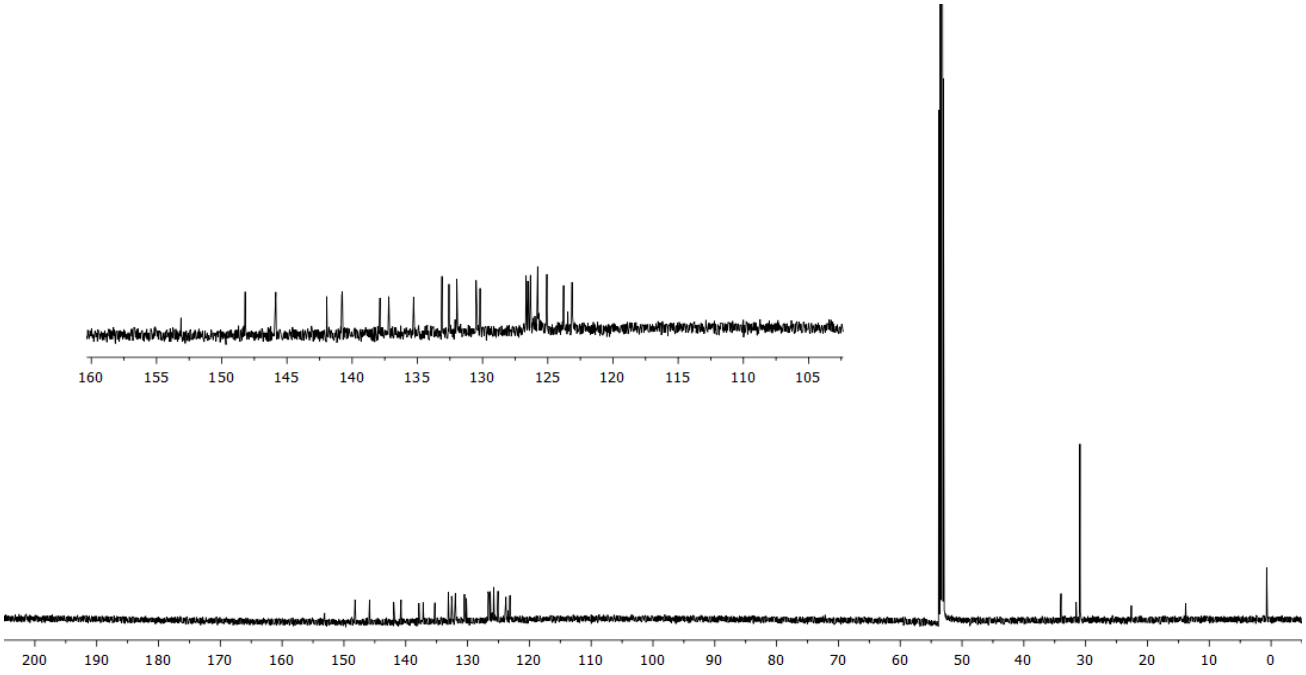


Figure S2. ^{13}C NMR (151 MHz, CD_2Cl_2) spectrum of compound **1**.

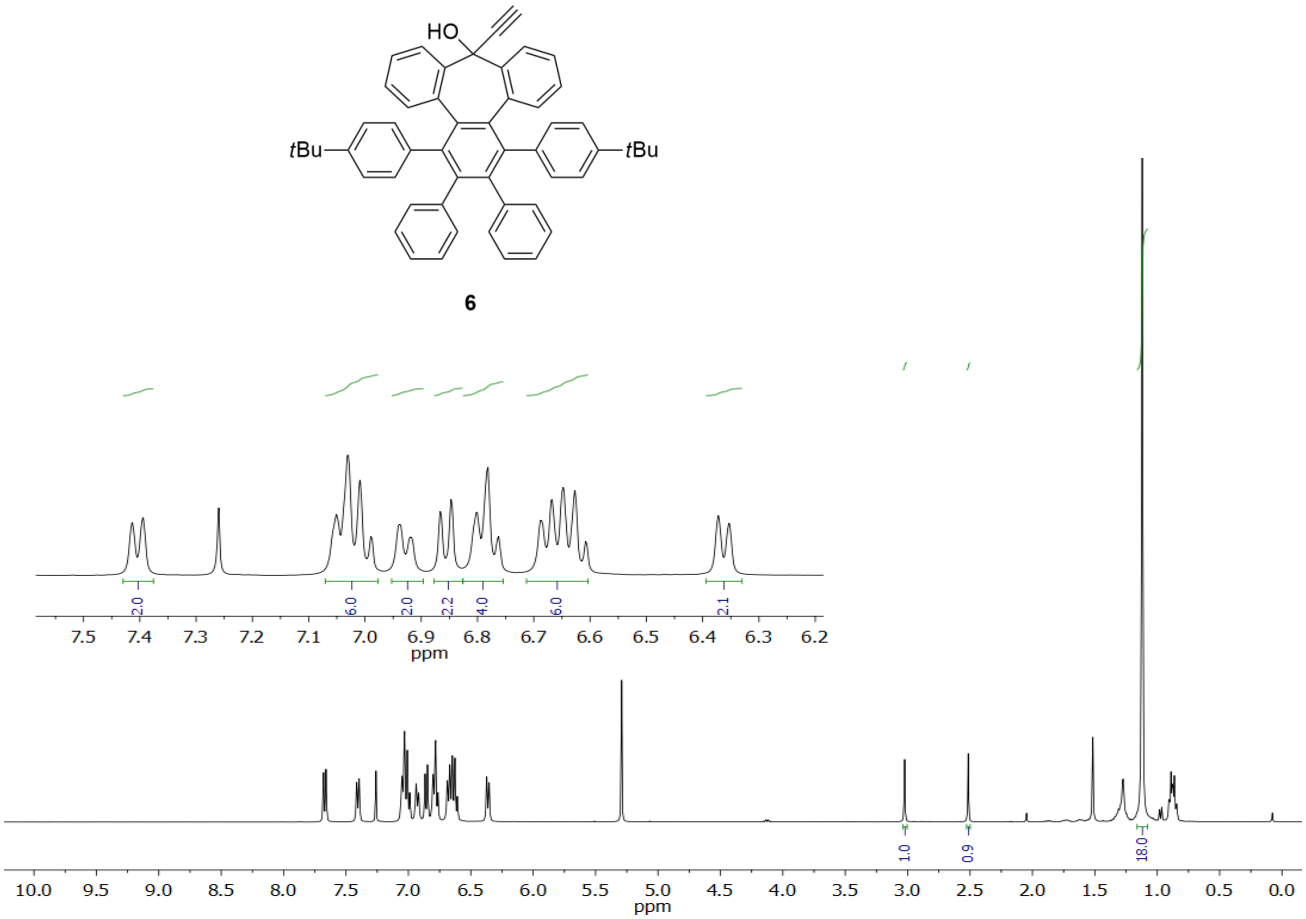


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6**.

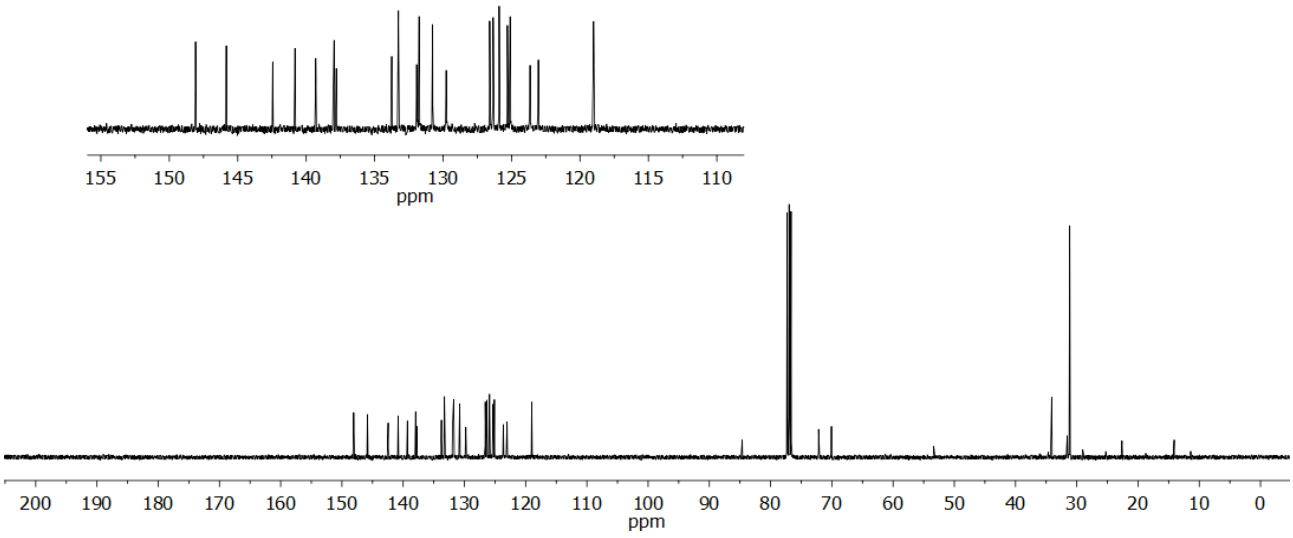


Figure S4. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **6**.

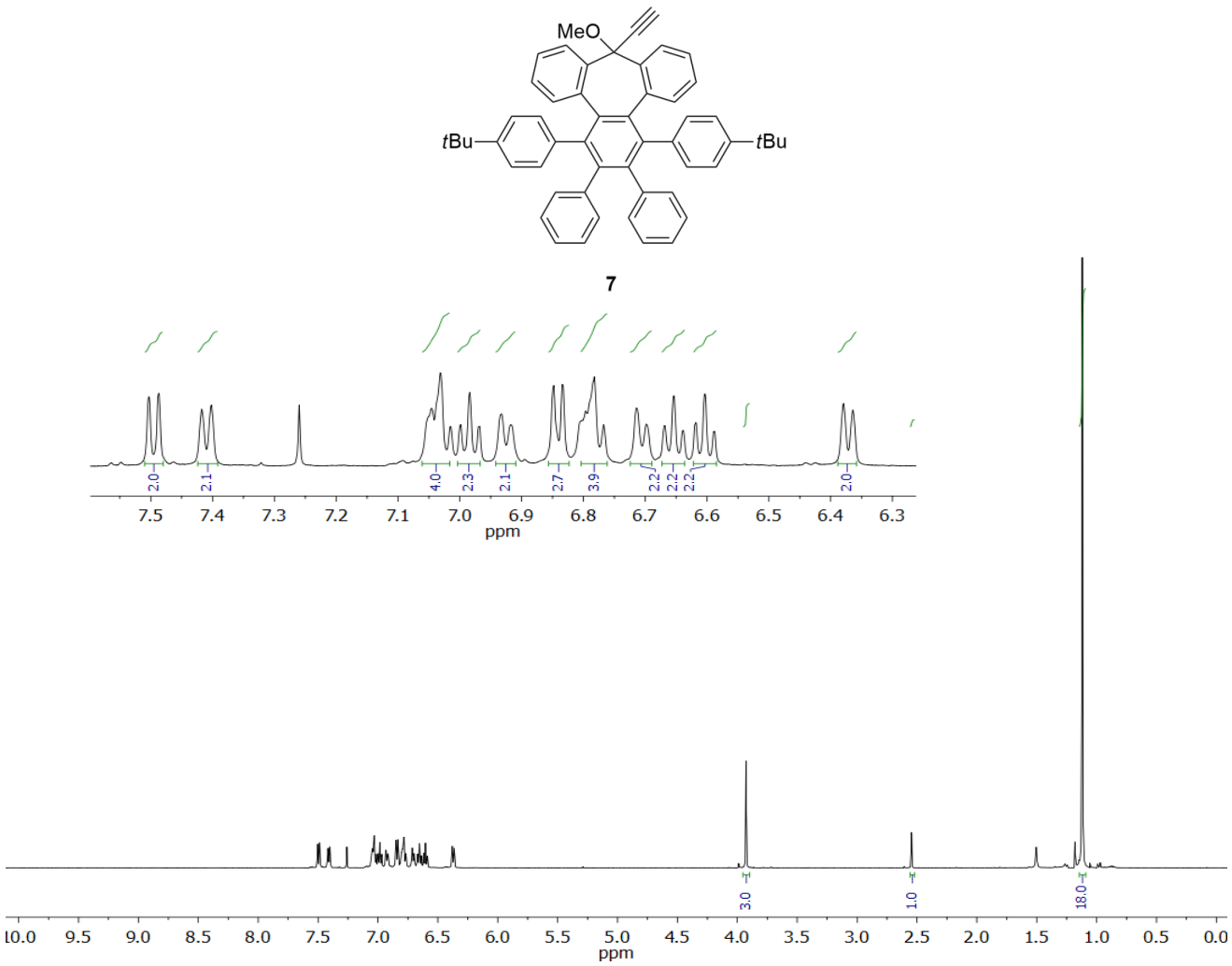


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **7**.

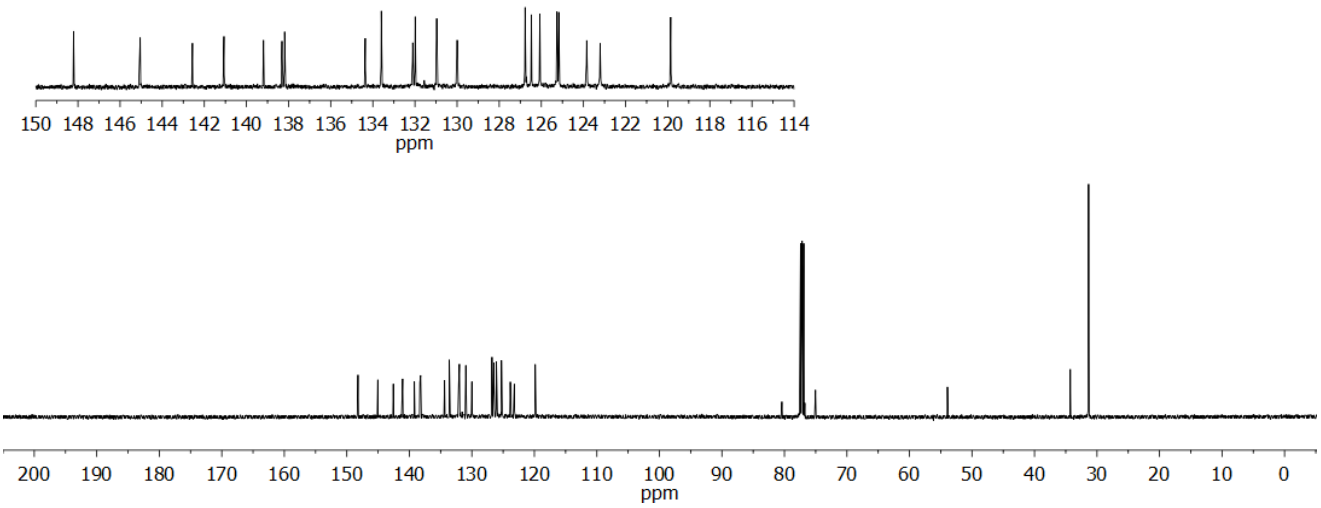


Figure S6. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **7**.

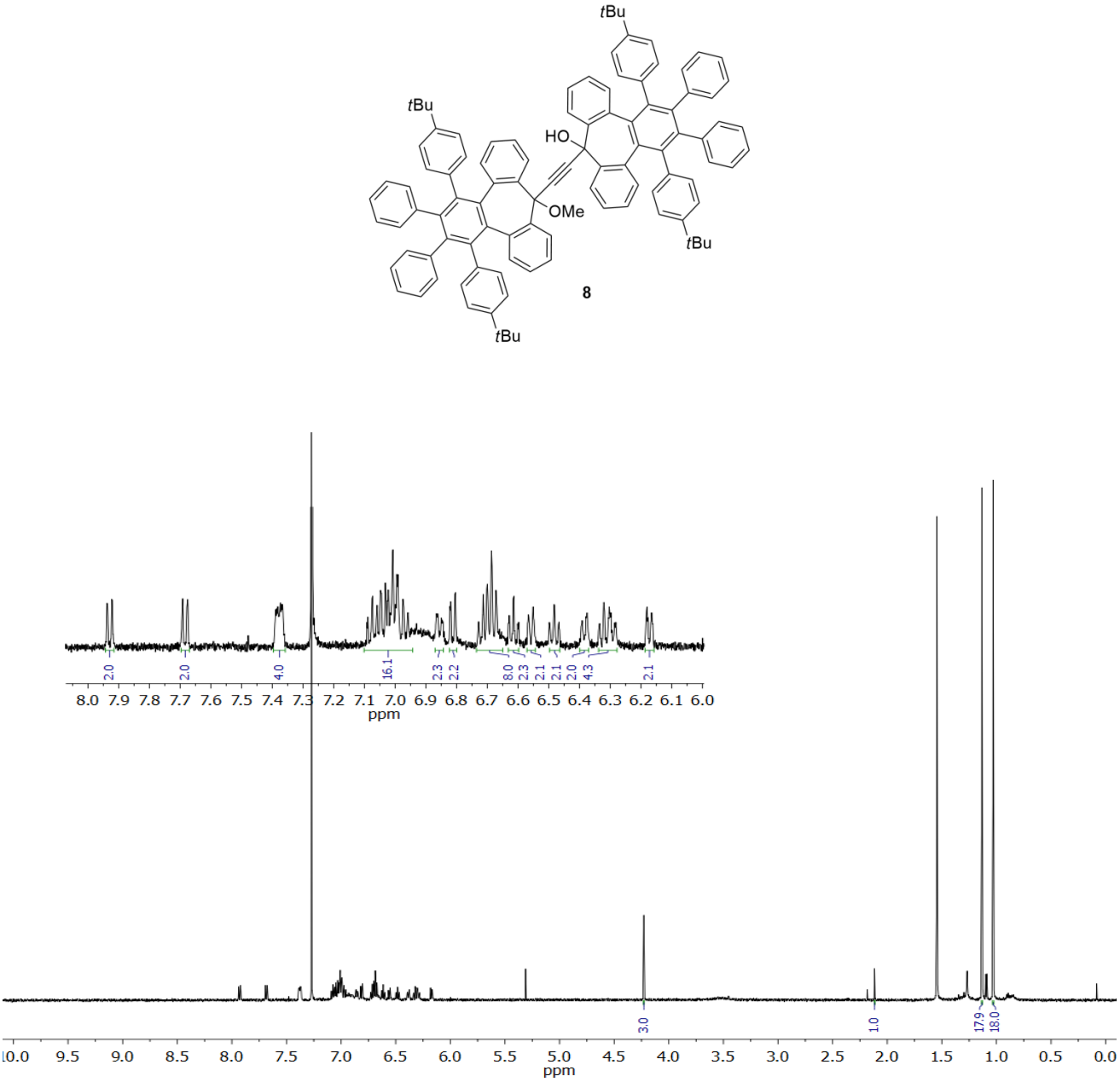


Figure S7. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **8**.

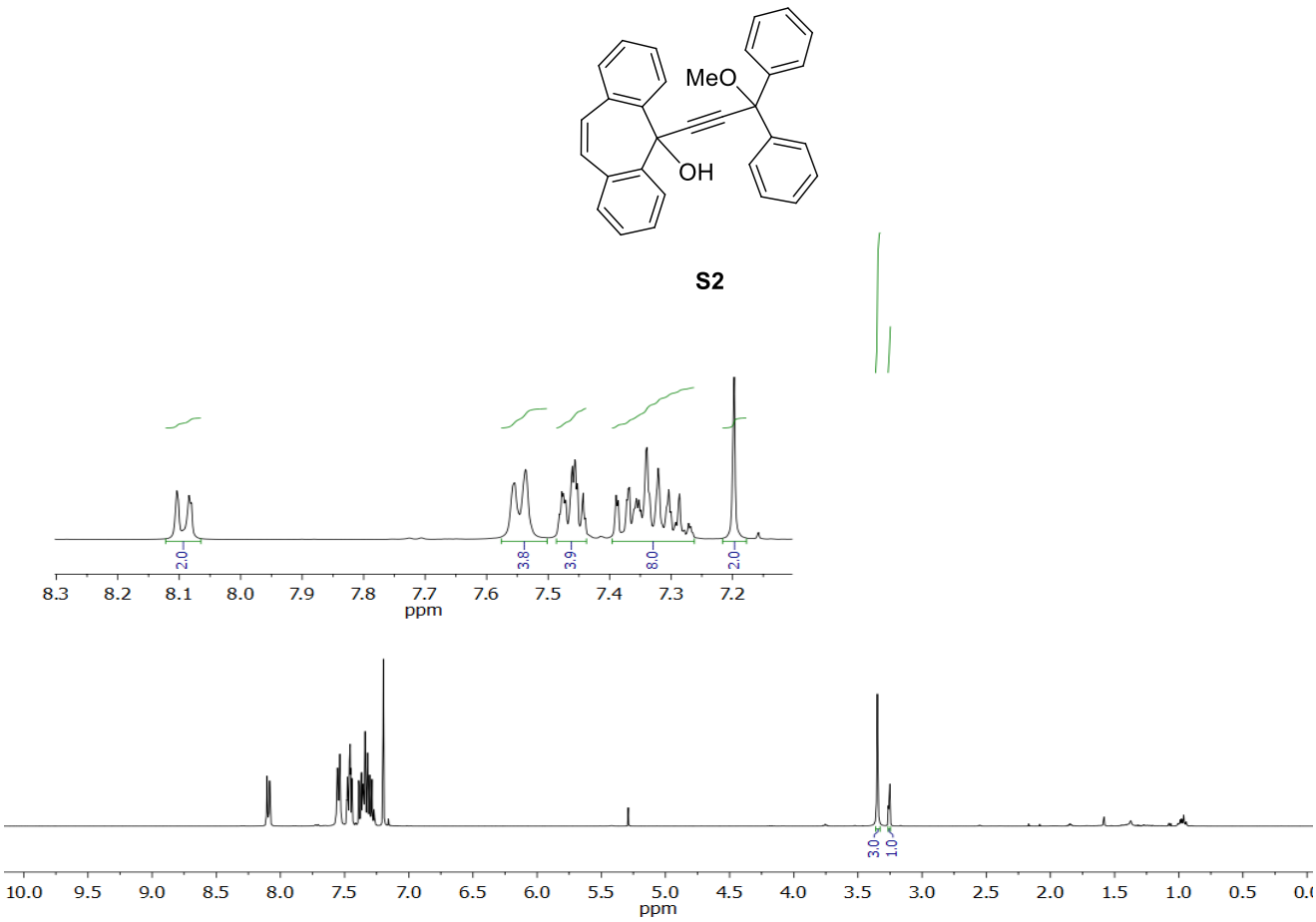


Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **S2**.

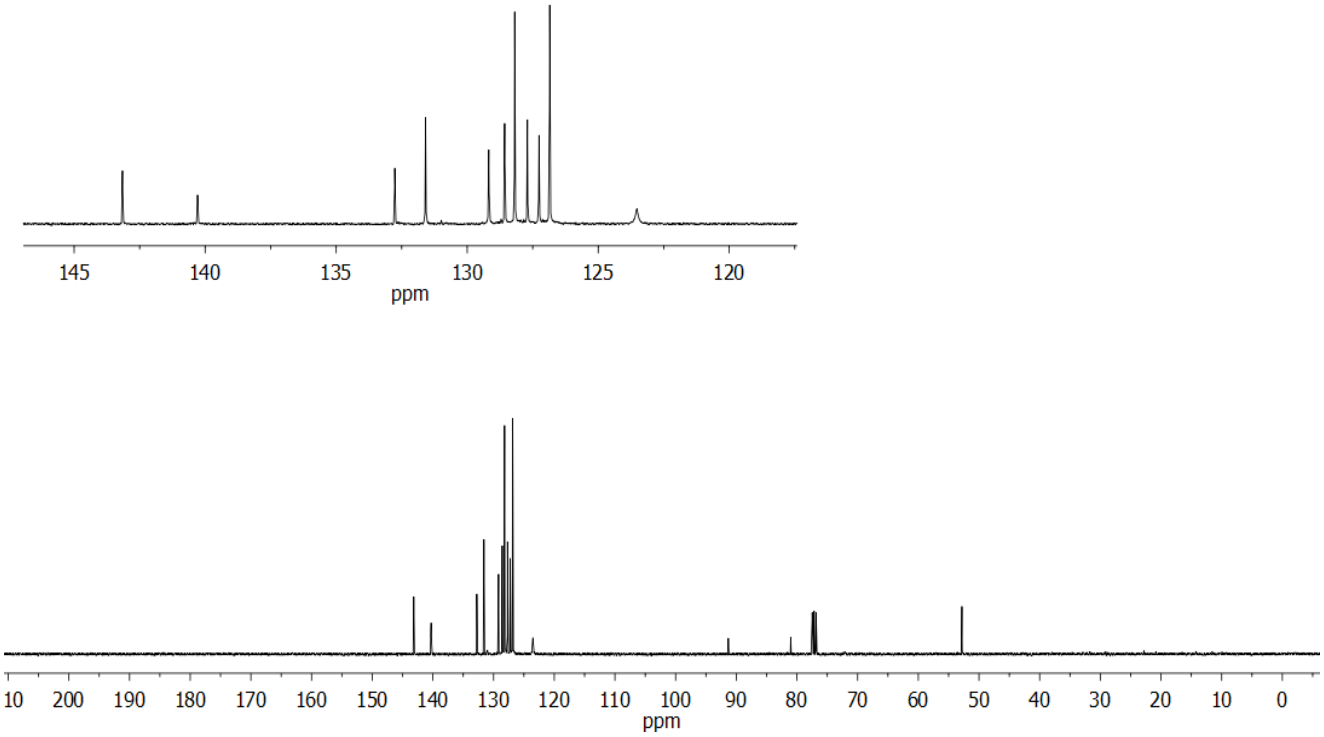


Figure S9. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **S2**.

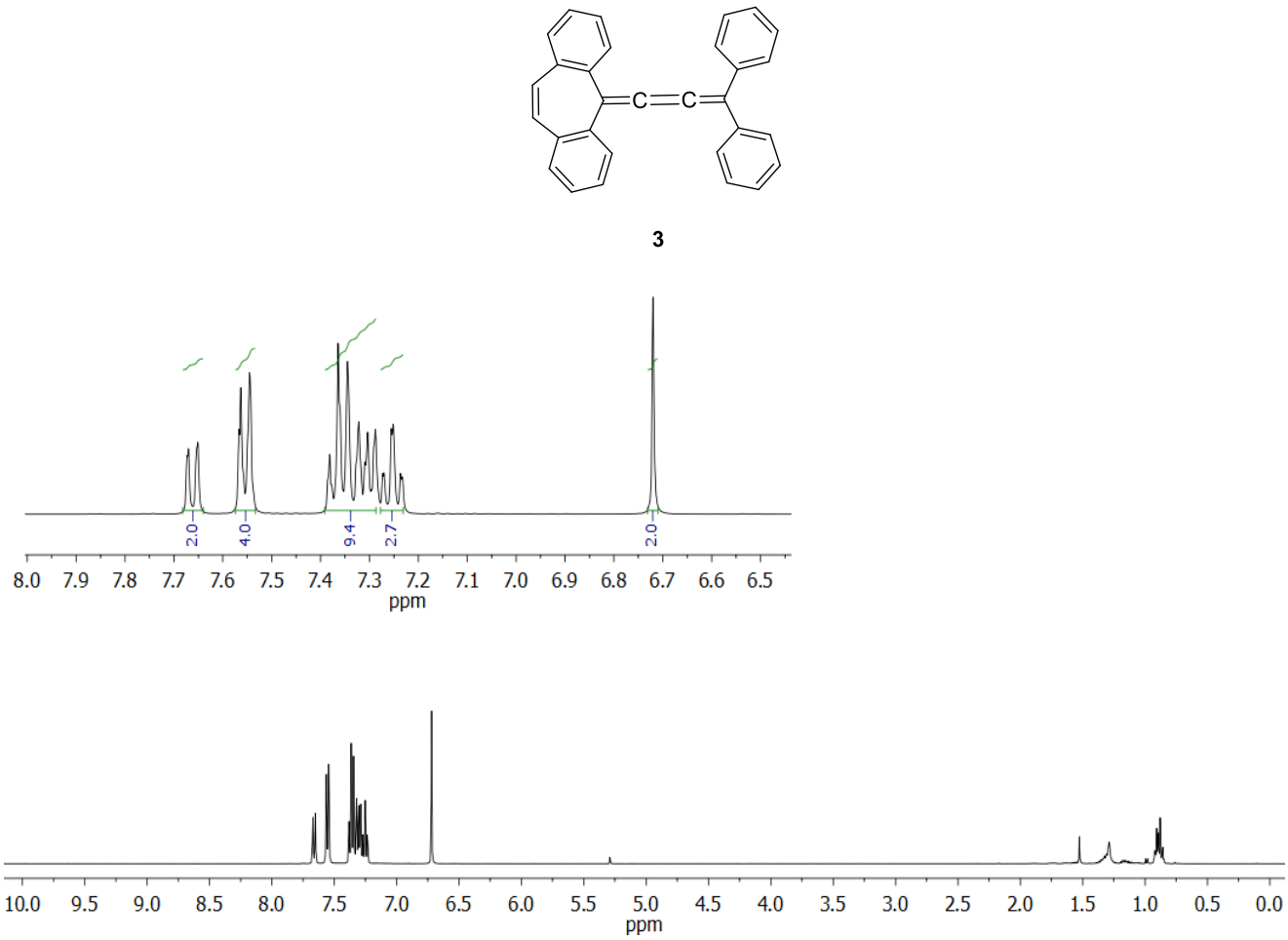


Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3**.

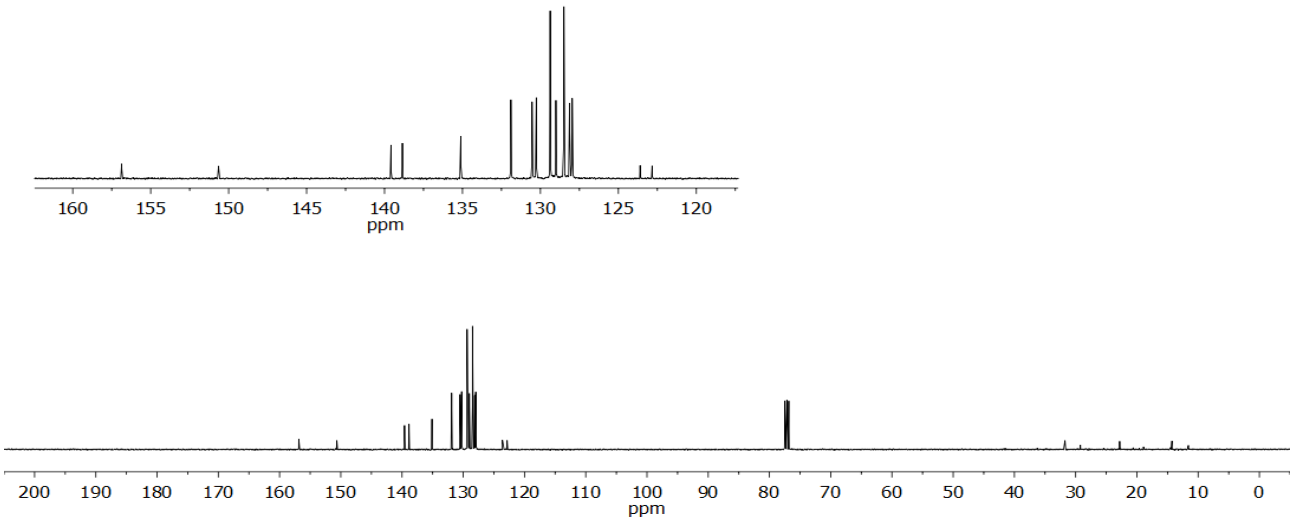


Figure S11. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **3**.

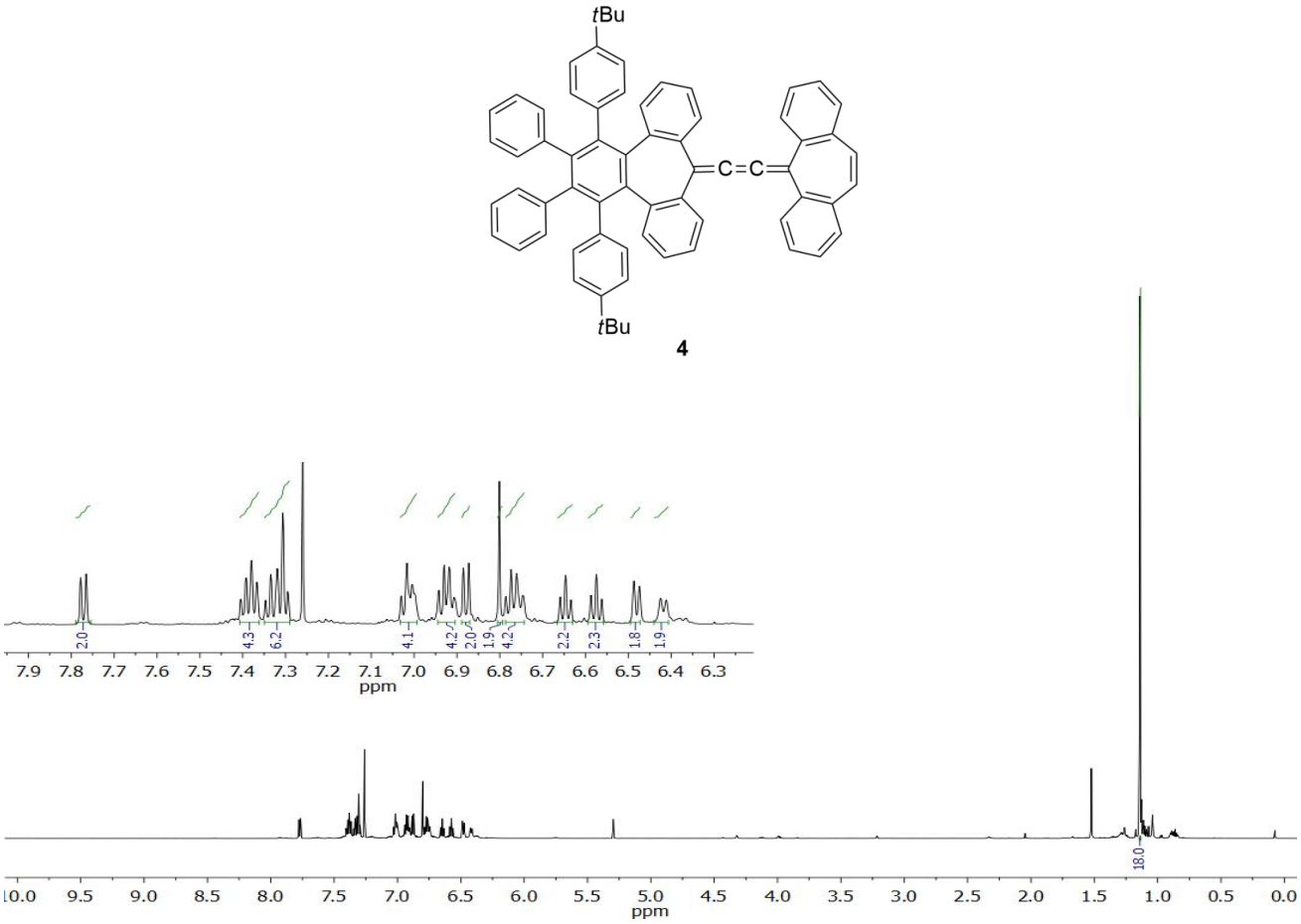


Figure S12. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound **4**.

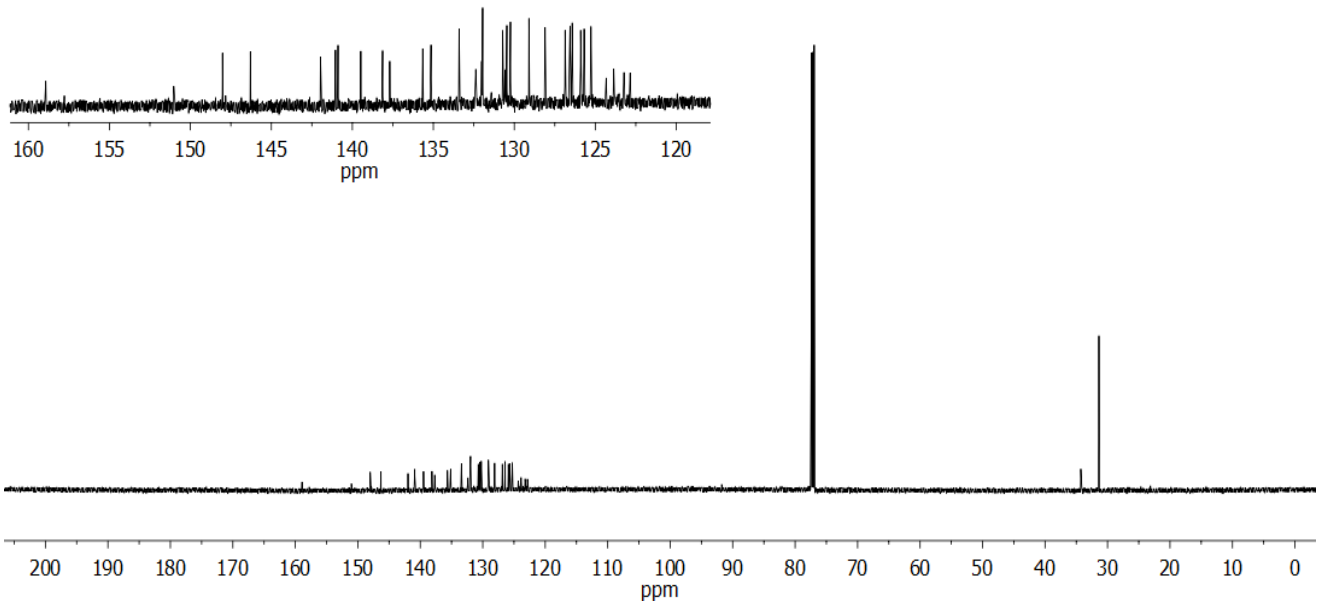


Figure S13. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound **4**.

2D-NMR and MALDI-HRMS spectra of compound 1

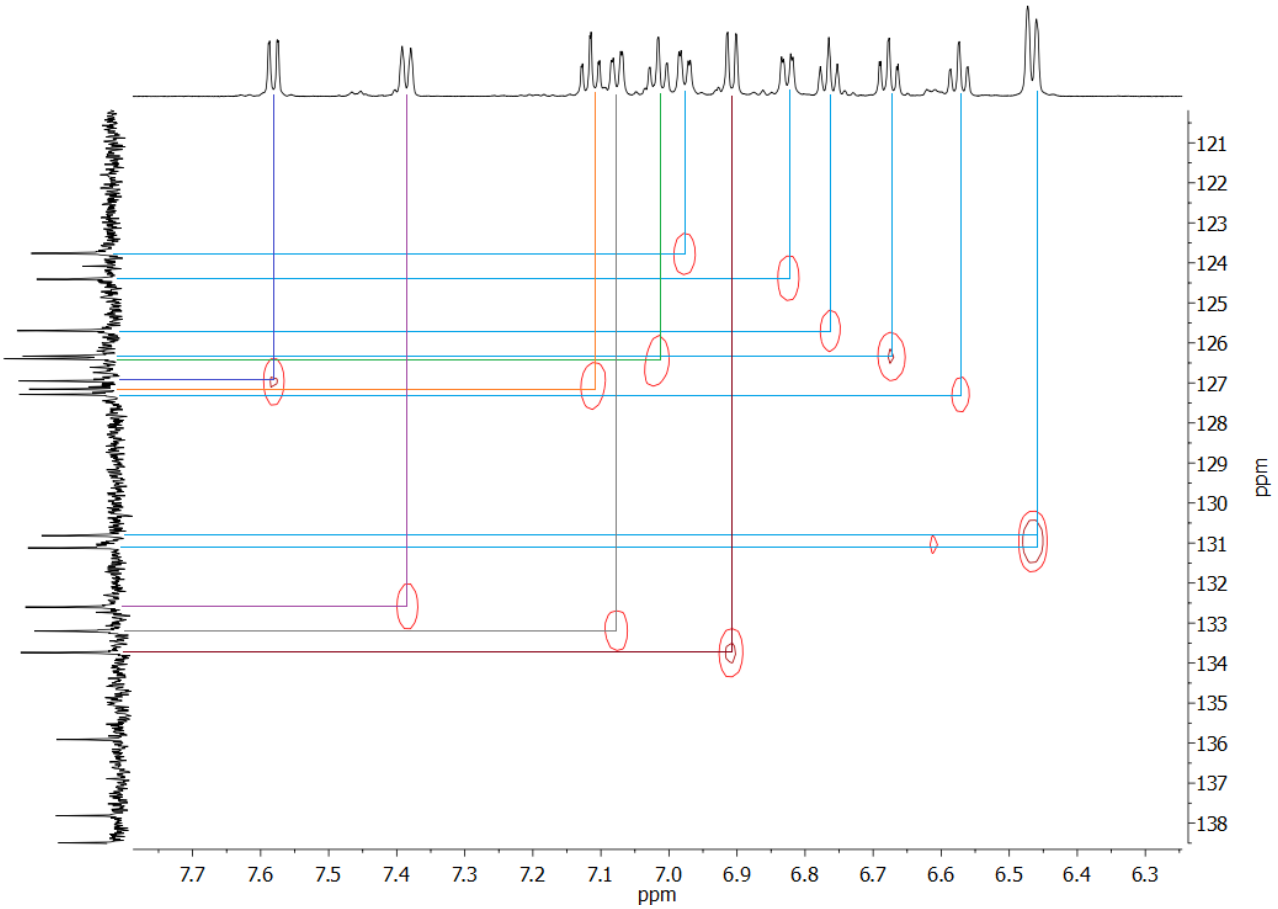


Figure S14. Partial HSQC (600 MHz and 151 MHz, CD_2Cl_2) spectrum of compound **1**.

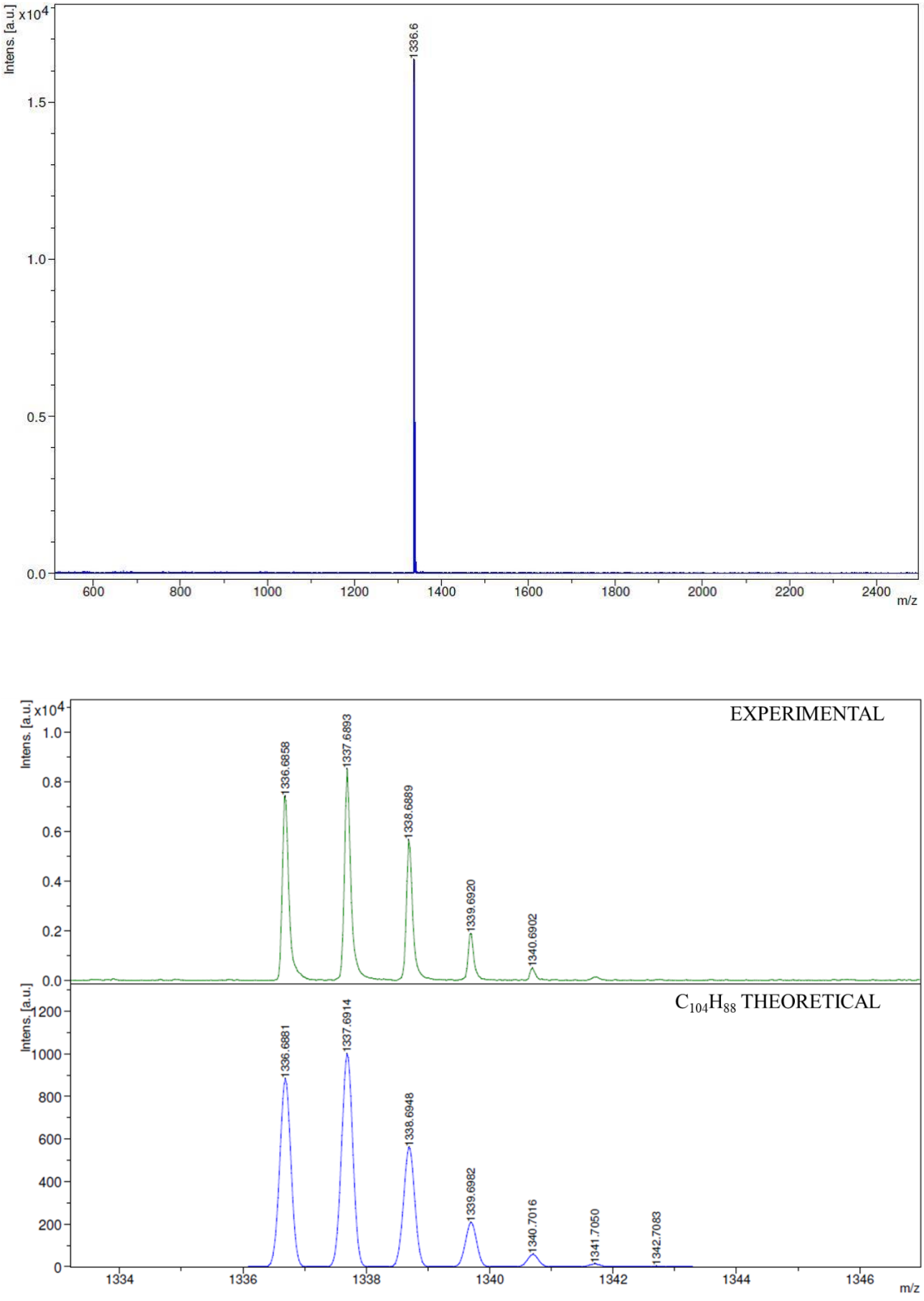


Figure S15. MS (MALDI-TOF) (top) and HR-MS (MALDI-TOF) (bottom) spectra of compound **1**.

Photophysical properties

The linear absorption spectra were recorded in a JASCO V-540 spectrophotometer. The fluorescence spectra were recorded using a Horiba Jobin Yvon Fluorlog 3-22 Spectrofluorimeter. The spectra were recorded at μM concentrations in different mixtures of THF (spectroscopic grade) and mili-Q water. The fluorescence quantum yields were determined using quinine sulfate in 0.5 M H_2SO_4 (ϕ = 0.546, λ_{em} = 400-500) as standard. The TPA spectra were measured by two-photon fluorescence (TPF) using Coumarin 153 in CCl_4 as standard to account for the collection efficiency and excitation pulse characteristics.[S4] The excitation source was a Ti:sapphire laser (Tsunami BB, Spectra-Physics, 710-990 nm, 1.7 W, 100 fs, 82 MHz). A modified setup that follows the one described by Xu and Webb was used to estimate the TPA cross-section in the 710-990 nm region.[S5] The two-photon absorption cross-section was calculated from the equation:

$$\sigma_2 = \left(\frac{F_2}{\phi C n}\right)_s \left(\frac{\phi C n \sigma_2}{F_2}\right)_{ref} \quad (1)$$

where F_2 stands for two-photon induced fluorescence intensity, ϕ is the one-photon excited fluorescence quantum yield, *n* refers to the refractive index in solution, *C* is the concentration and *s* and *ref* are relative to the sample and the TPA reference, respectively. The two-photon emission was measured within a narrow wavelength bandwidth selected by the H20Vis Jobin Yvon monochromator placed at the entrance of a PMC-100-4 photomultiplyer tube (Becker and Hickl GmbH). The integrated intensity over the entire emission band was extrapolated using the emission spectra corrected by the detector sensitivity. The fluorescence intensity was measured in a single photon count mode by integrating the number of emitted photon in a 10 ns time interval after the excitation pulse. The emission intensity dependence of the excitation power was checked to be quadratic. The lifetime was measured in a home-built setup using a linear excitation source operating at 330 nm with a 4MHz repetition rate (second harmonic of a Coherent Radiation Dye laser 700 series, 610-680 nm, 130 mW, 5 ps, 4MHz), an Hamamatsu R2809U-01 MCP-PMT (290−700 nm) as the detector and an SPC-160 photon counting board from Becker & Hickl GmbH.

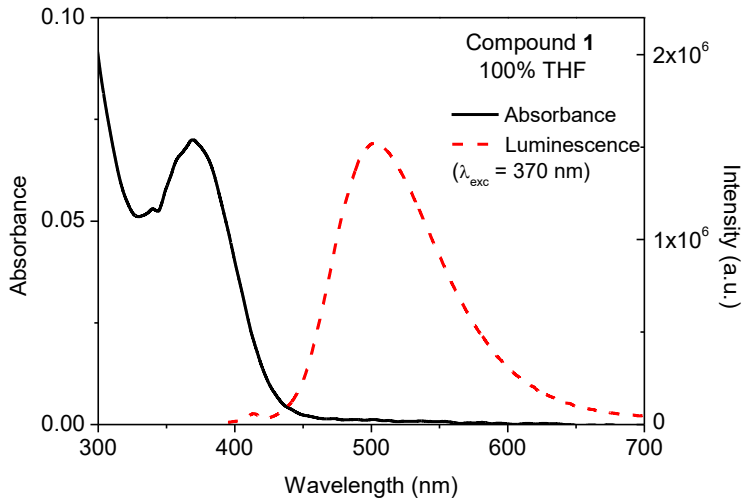


Figure S16. Absorption and fluorescence emission spectra of **1** in THF recorded in the 300-700 nm region. Emission was collected upon excitation at the absorption band maximum (λ_{exc} = 370 nm).

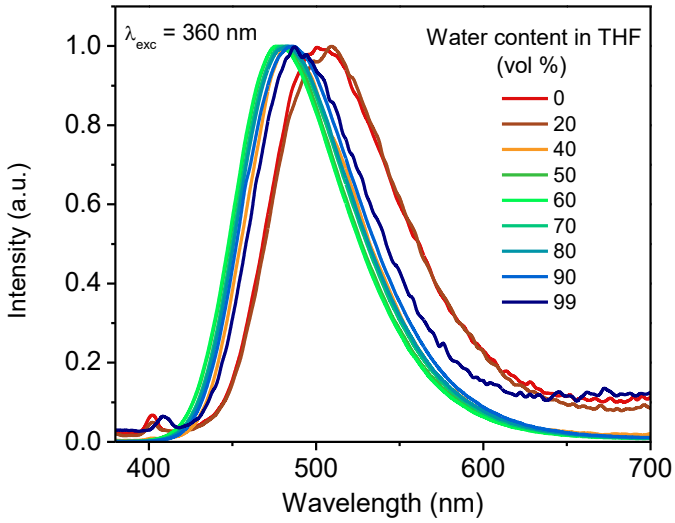


Figure S17. Normalized fluorescence spectra of **1** (λ_{exc} = 360 nm) showing the slight hypsochromic shift of the emission maxima due to the influence of the solvent composition (THF/Water).

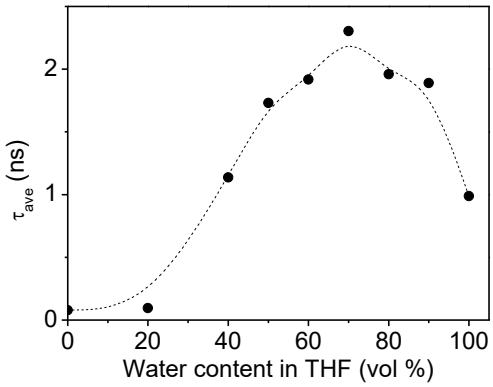


Figure S18. Excited state lifetime of **1** in THF/Water mixtures with increasing vol % of water.

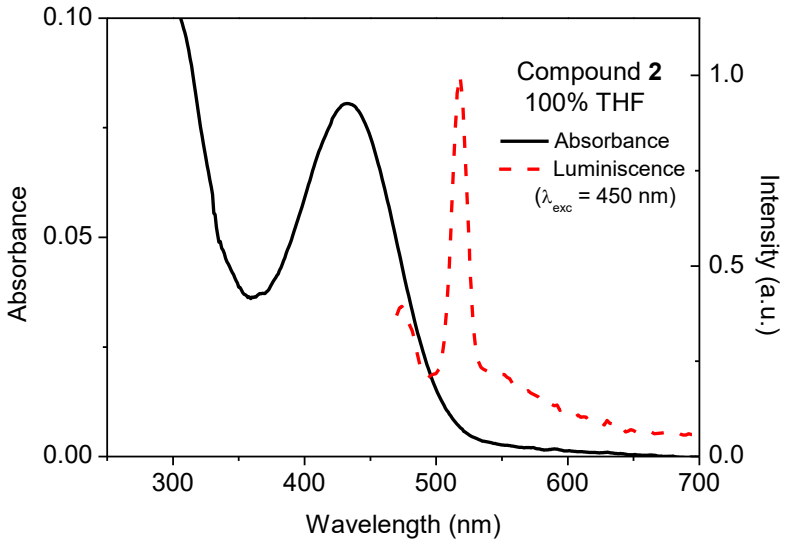


Figure S19. Absorption and emission spectra of **2** in THF. No emission of **2** was observed upon excitation at λ_{exc} = 450 nm. The sharp band in the emission spectra is due to the Raman signal from the residual water in THF. Based on the absence of emission an upper limit for emission quantum yield of 0.0001 can be estimated.

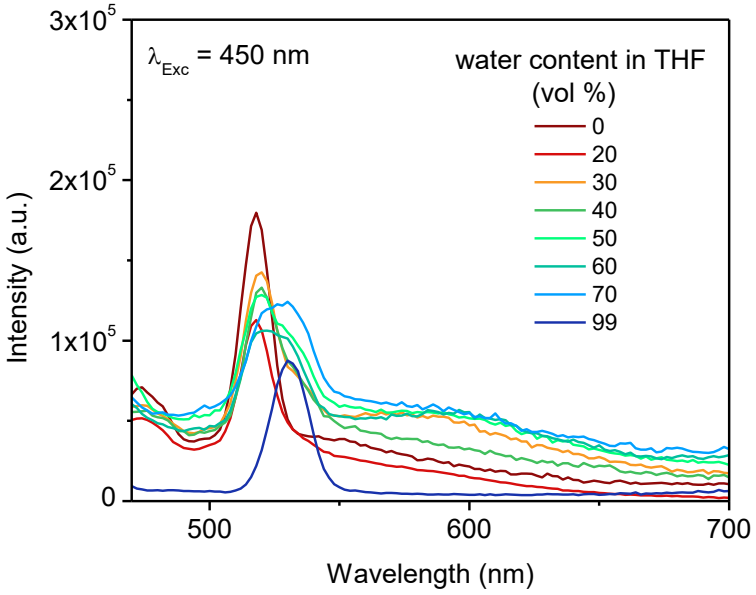


Figure S20. Influence of solvent composition (THF/Water) in fluorescence emission of **2** upon excitation at λ_{exc} = 450 nm. The sharp feature in the 520-550 nm region is the Raman signal from the residual water in THF.

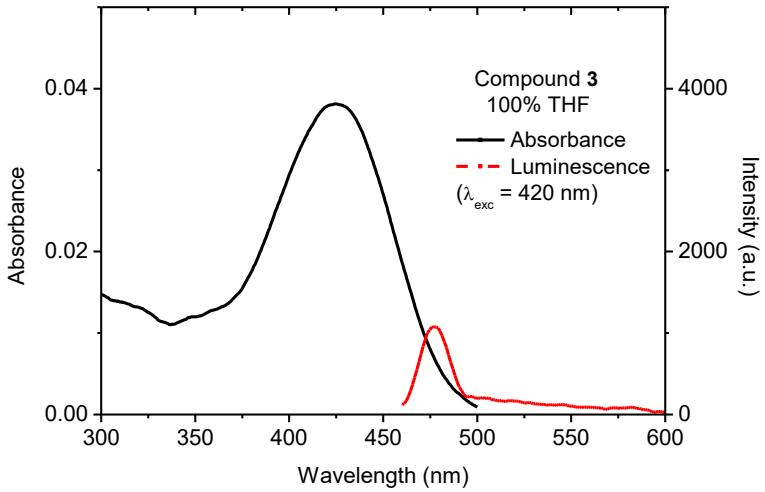


Figure S21. Absorption and emission spectra of **3** in THF. Emission was collected upon excitation at the absorption band maximum (λ_{exc} = 420 nm). The sharp band in the emission spectra is due to the Raman signal from the residual water in THF. Based on the absence of emission an upper limit for emission quantum yield of 0.0002 can be estimated.

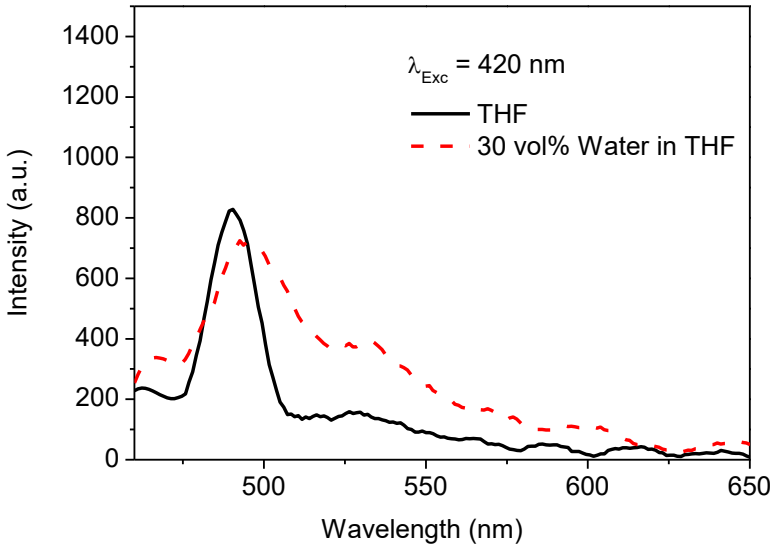


Figure S22. Fluorescence emission (λ_{exc} = 420 nm) of compound **3** in THF and 70 vol % water in THF. The sharp band at 490 nm corresponds to the Raman band of the water.

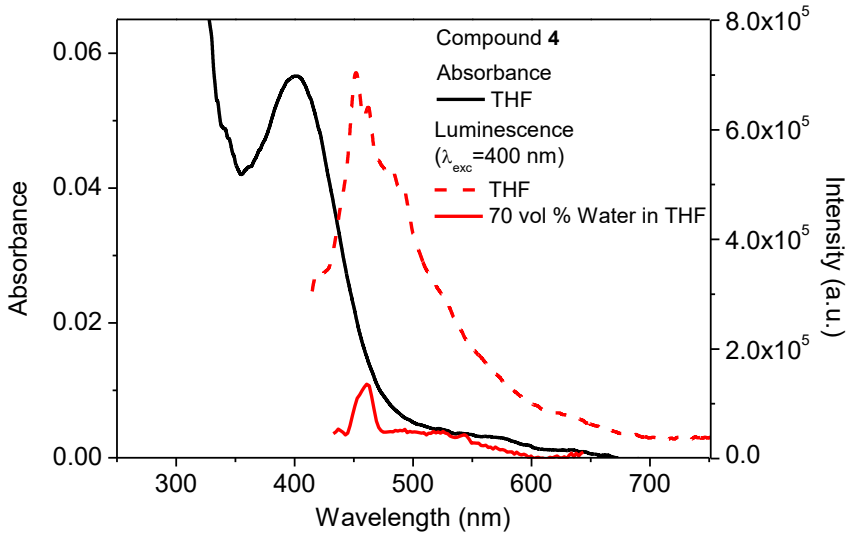


Figure S23. Absorption of **4** in THF and influence of solvent composition (THF/Water) in its fluorescence emission (λ_{exc} = 400 nm). The emission quantum yield measured in THF is 0.001.

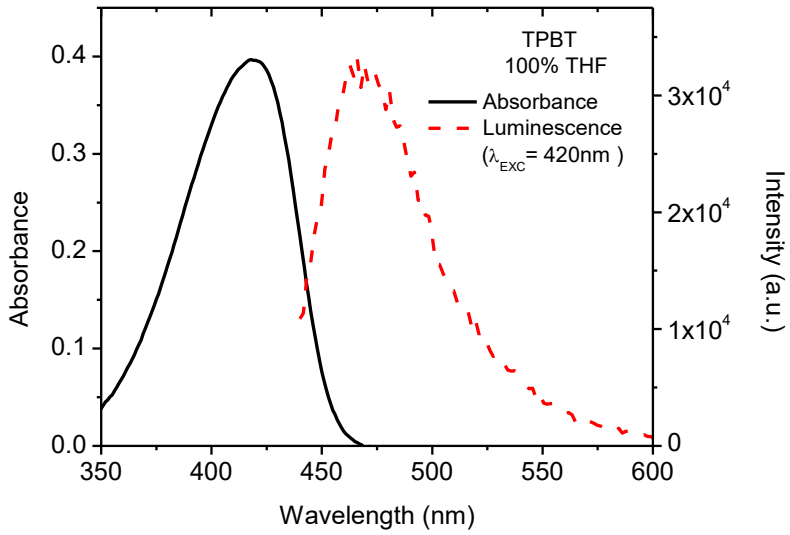


Figure S24. Absorption and emission spectra of TPBT in THF. Emission was collected upon excitation at the absorption maximum (λ_{exc} = 440 nm.). The quantum yield was estimated to be 0.002.

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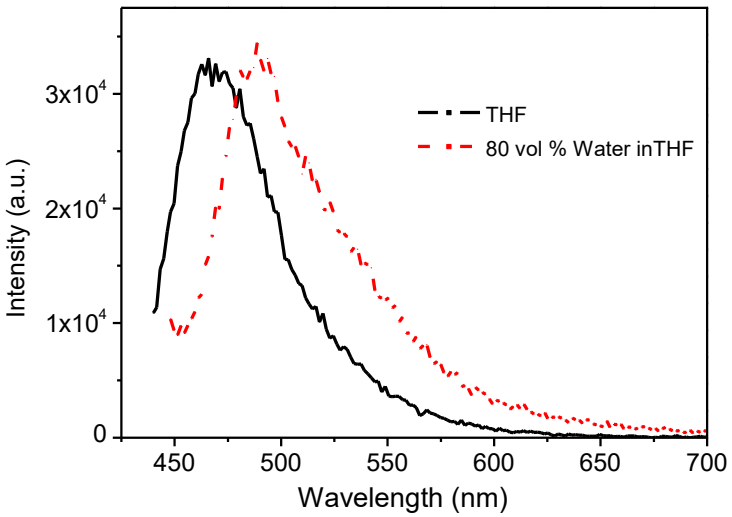

Figure S25. Fluorescence emission (λ_{exc} = 440 nm) of TPBT in THF and 80 vol % water in THF.

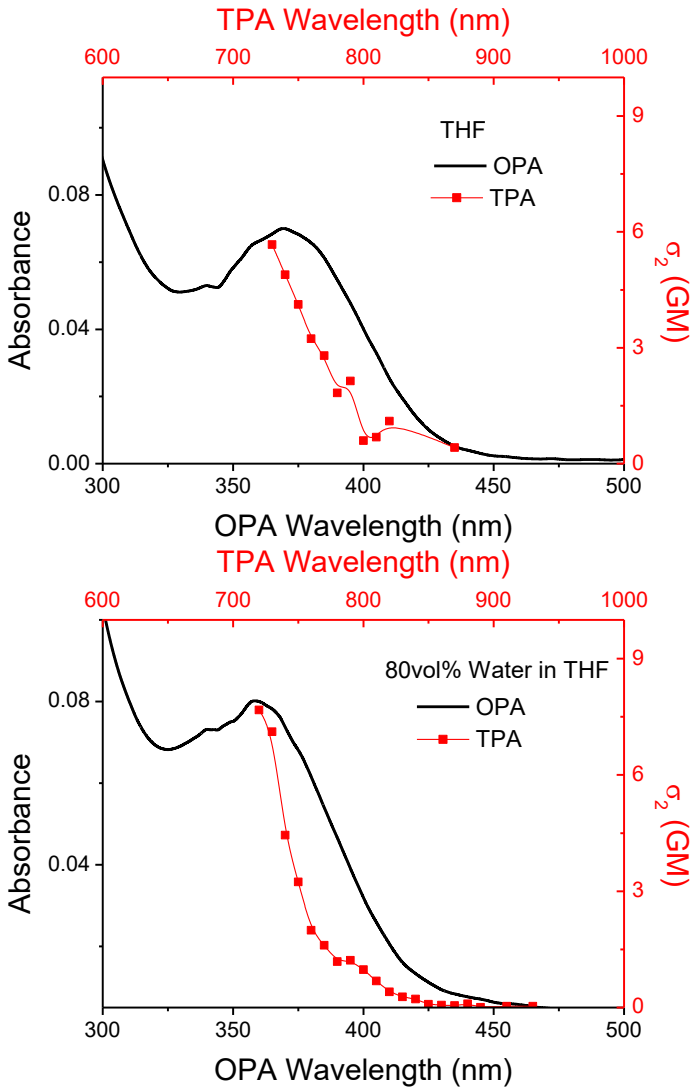

Figure S26. Two-photon absosorption (TPA) and one-photon absorption (OPA) of **1** in THF (top) and 80 vol % water content in THF (down).

Single crystal X-Ray Analysis

X-ray diffraction quality single crystals of **1** were grown by slow evaporation of a solution of **1** in a $CHCl_3$/hexane solvent mixture. Single crystals of **3**, **8** and TPBT were obtained by slow evaporation of a solution of the compound in a CH_2Cl_2/hexane mixture. The X-ray diffraction data were collected on a Bruker D8 Venture diffractometer equipped with a Photon 100 detector using Mo or Cu radiation sources. The structures were solved with the SHELXT[S6] or SIR2014 software (direct methods) and refined using the full-matrix least-squares against F^2 procedure with SHELX 2016[S7] using the WinGX32[S8] software. Hydrogen atoms were placed in idealized positions (U_{eg}(H) = 1.2U_{eg}(C) or U_{eg}(H) = 1.5U_{eg}(C)) and were allowed to ride on their parent atoms. A summary of the X-ray diffraction measurement and refinement data is given in Table S1. CCDC-1817321 (**1**), CCDC-1817322 (**3**), CCDC-1817323 (**8**), CCDC-1817320 (TPBT) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/?

Compound **1** crystallized exclusively as its *syn* conformer, in agreement with the results reported for **2**, for which the *syn* conformer was obtained when the compound was crystallised from chloroform or hexane. Due to the limited quality of the crystals obtained for *syn*-**1**, the thermal ellipsoids of some atoms had to be modelled by using ISOR restraints. Moreover, there was some disorder in a chloroform solvent molecule which was modelled by using SIMU and DELU restraints. In the crystal structure of **8,** the OMe and OH groups are disordered as they partially occupy the same positions in the unit cell, attached to each of the 7-membered rings. These disorder was modelled using EADP, EXYZ, FREE, BIND and PART instructions, with an occupancy factor of 0.5 for the atomsin volved. One of the *t*butyl groups showed thermal disorder which was modelled with SIMU, DELU and ISOR restraints.

The unit cell data measured for TPBT match those previously reported in the literature.[S9] The crystal structures of TPE[S10] and **2**[S11] were previously reported and the data were obtained from the Cambridge Crystallographic Data Centre (CCDC-1275289 and CCDC-823689-823690, respectively)

Table S1. Summary of X-ray diffraction crystallography measurement and refinement data for compounds **1**, **3**, **8** and TPBT[S9]

	1·5CHCl$_3$	**3**	**8**	**TPBT**
Chemical formula	$C_{109}H_{93}Cl_{15}$	$C_{30}H_{20}$	$C_{105}H_{92}O_2$	$C_{28}H_{20}$
M_r	1934.58	380.46	1385.78	356.44
Crystal size [mm^3]	0.210 x 0.160 x 0.110	0.400 x 0.200 x 0.150	0.194 x 0.130 x 0.111	0.379 x 0.150 x 0.145
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Wavelength [Å]	1.54178 (Cu Kα)	0.71073 (Mo Kα)	1.54178 (Cu Kα)	0.71073 (Mo Kα)
Space group	*P*212121	*P*21/*n*	*P*21/*n*	*P*-1
a [Å]	11.3561(10)	14.7030(17)	11.1208(5)	9.9154(12)
b [Å]	27.561(3)	8.1421(10)	22.2219(11)	10.0178(12)
c [Å]	31.571(3)	17.264(2)	16.4054(9)	10.4437(12)
α [°]	90	90	90	92.162(5)
β [°]	90	101.638(2)	108.564(2)	104.822(5)
γ [°]	90	90	90	105.321(4)
V [Å^3]	9881.1(15)	2024.3(4)	3843.2(3)	961.0(2)
Z	4	4	2	2
ρ_{calcd} [Mg m^{-3}]	1.300	1.248	1.198	1.232
μ [mm^{-1}]	4.188	0.071	0.526	0.070
F(000)	4008	800	1476	376
θ range [°]	2.128 to 59.072	1.662 to 28.343	3.469 to 44.573	2.121 to 24.801
hkl ranges	-12/9,-30/29,-33/35	-19/19,-10/9,-15/22	-9/10,-20/20,-14/14	-11/11,-11/11,-12/12
Reflections collected	73156	12686	20635	24447
Independent reflections	14174	4543	3017	3304
R_{int}	0.0578	0.0364	0.0327	0.0411
Completeness [%]	99.6	99.4	99.3	99.8
Absorption correction	Numerical	Multi-scan	Numerical	Numerical
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.1095, wR_2 = 0.3178	R_1 = 0.0457, wR_2 = 0.1126	R_1 = 0.0806, wR_2 = 0.1836	R_1 = 0.0351, wR_2 = 0.0914
R indices (all data)	R_1 = 0.1130, wR_2 = 0.3233	R_1 = 0.0615, wR_2 = 0.1270	R_1 = 0.0911, wR_2 = 0.1914	R_1 = 0.0383, wR_2 = 0.0958
Goodness-of-fit on F^2	1.588	0.961	1.094	1.098

[a]In common: Temperature, 100 K. Refinement method, full-matrix least-squares on F^2.

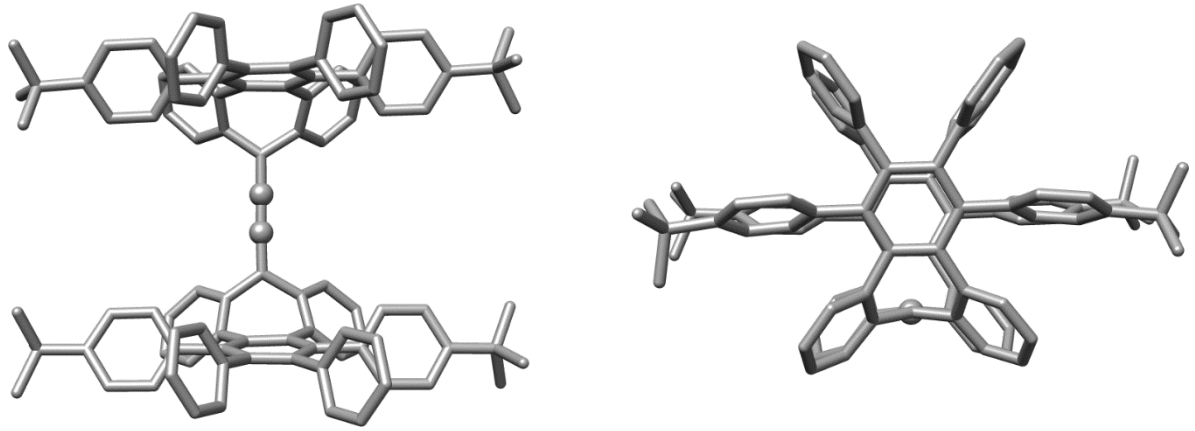

Figure S27. Top (left) and front (right) views of the stick representation of the crystal structure of **1**. Hydrogen atoms and solvent molecules have been omitted and the [3]cumulene central C atoms have been represented in the ball-and-stick model for clarity.

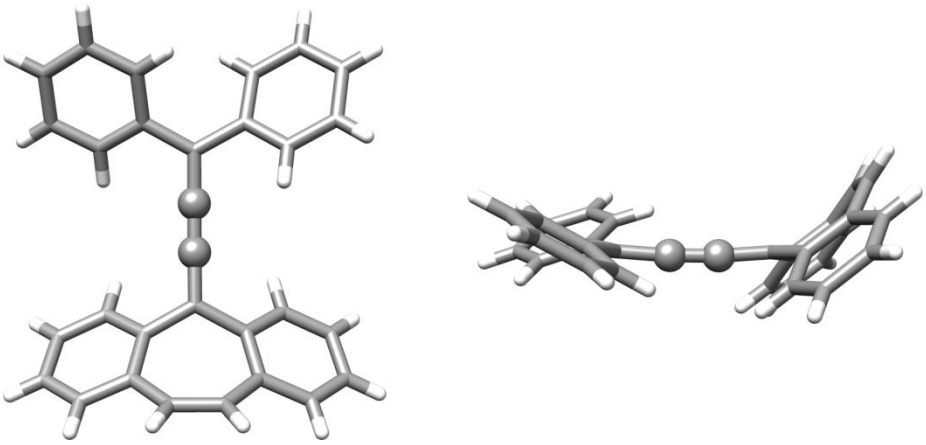

Figure S28. Top (left) and side (right) views of the crystal structure of **3**.

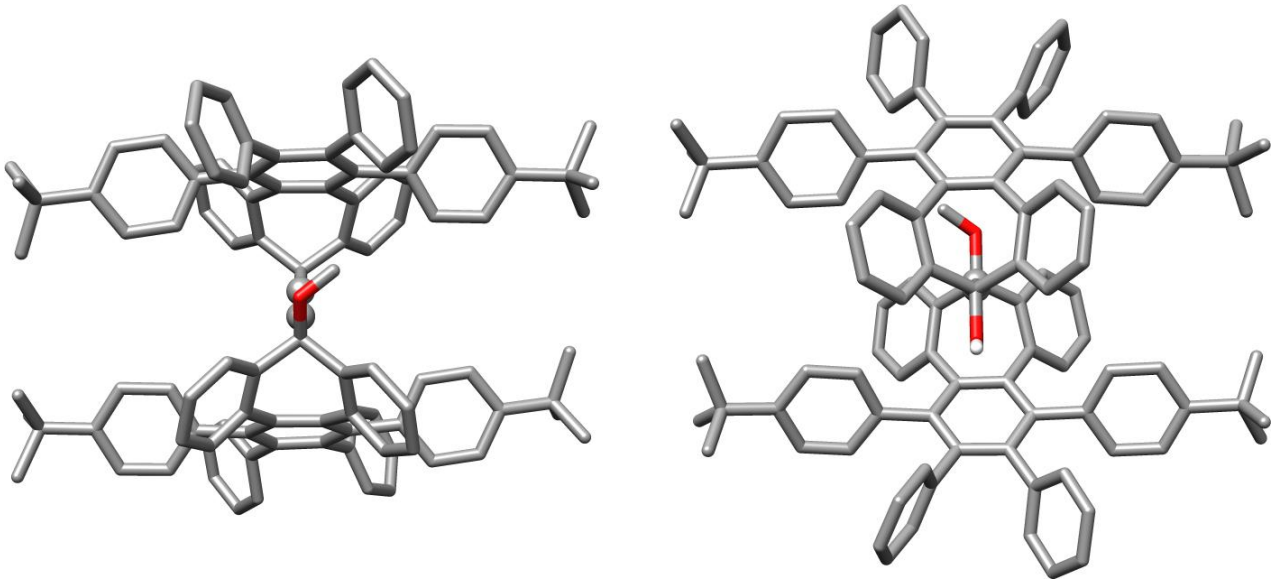

Figure S29. Top (left) and front (right) views of the crystal structure of **8**. Hydrogen atoms apart from that of the OH group have been omitted and the [3]cumulene central C atoms have been represented as balls for clarity.

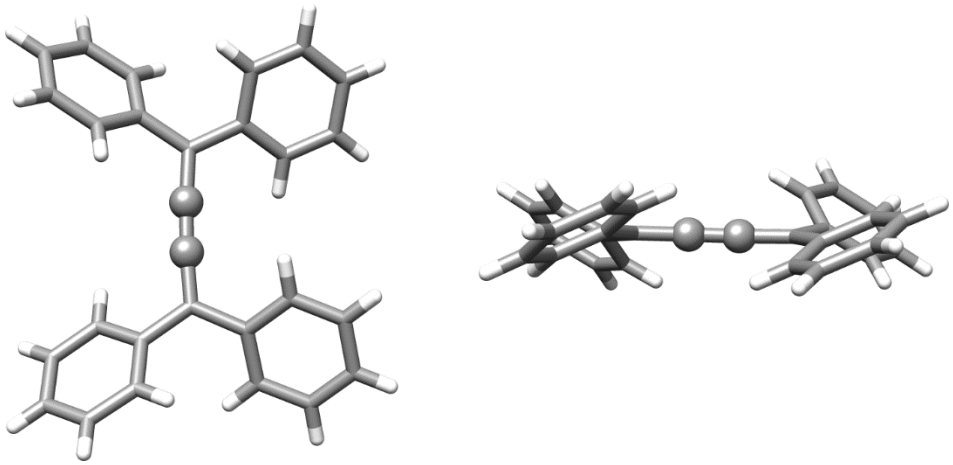

Figure S30. Top (left) and side (right) views of the X-ray crystal structure of TPBT.

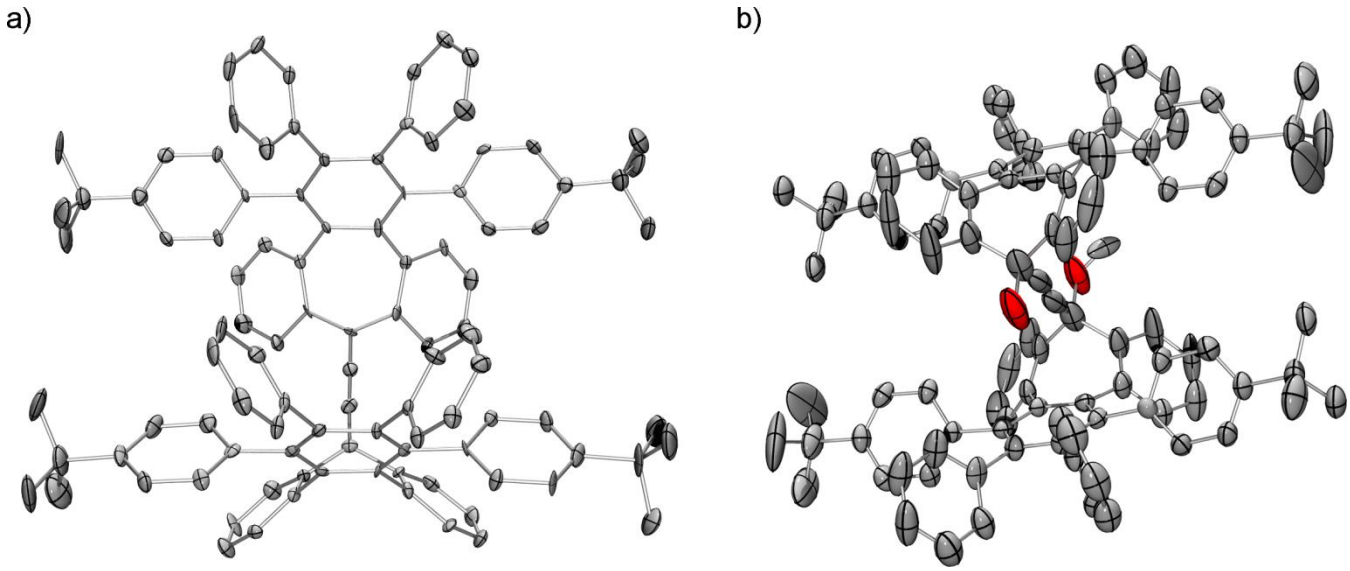

Figure S31. ORTEP representation of the crystal structure of: a) **1**; b) **8**. Thermal displacement ellipsoids are shown at 50% probability. Hydrogen atoms and solvent molecules have been omitted for clarity**.**

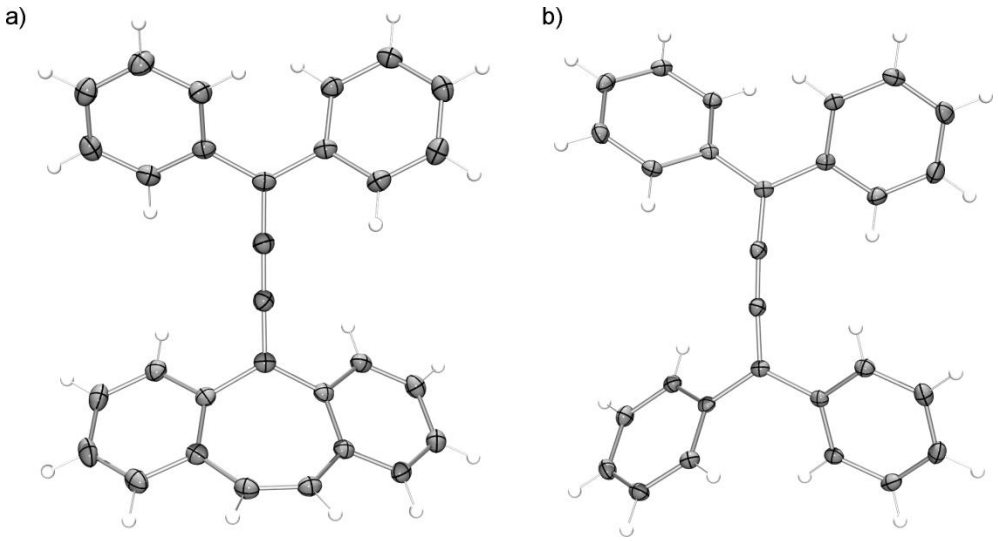

Figure S32. ORTEP drawing with the thermal displacement ellipsoids shown at 50% probability of the X-ray crystal structure of: a) **3**; b) TPBT.

Theoretical calculations

Calculations were done using Gaussian 09.[S12] Ground state geometry optimizations were performed in vacuum for the different molecules at the B3LYP/6-31G(d,p) level, and frequency calculations were used to ensure that a minimum was reached. TDDFT calculations were done at the same level of approximation to estimate the Franck − Condon transition energies and the corresponding configuration interaction coefficients, transition dipole moments, and oscillator strengths for one-photon absorption.

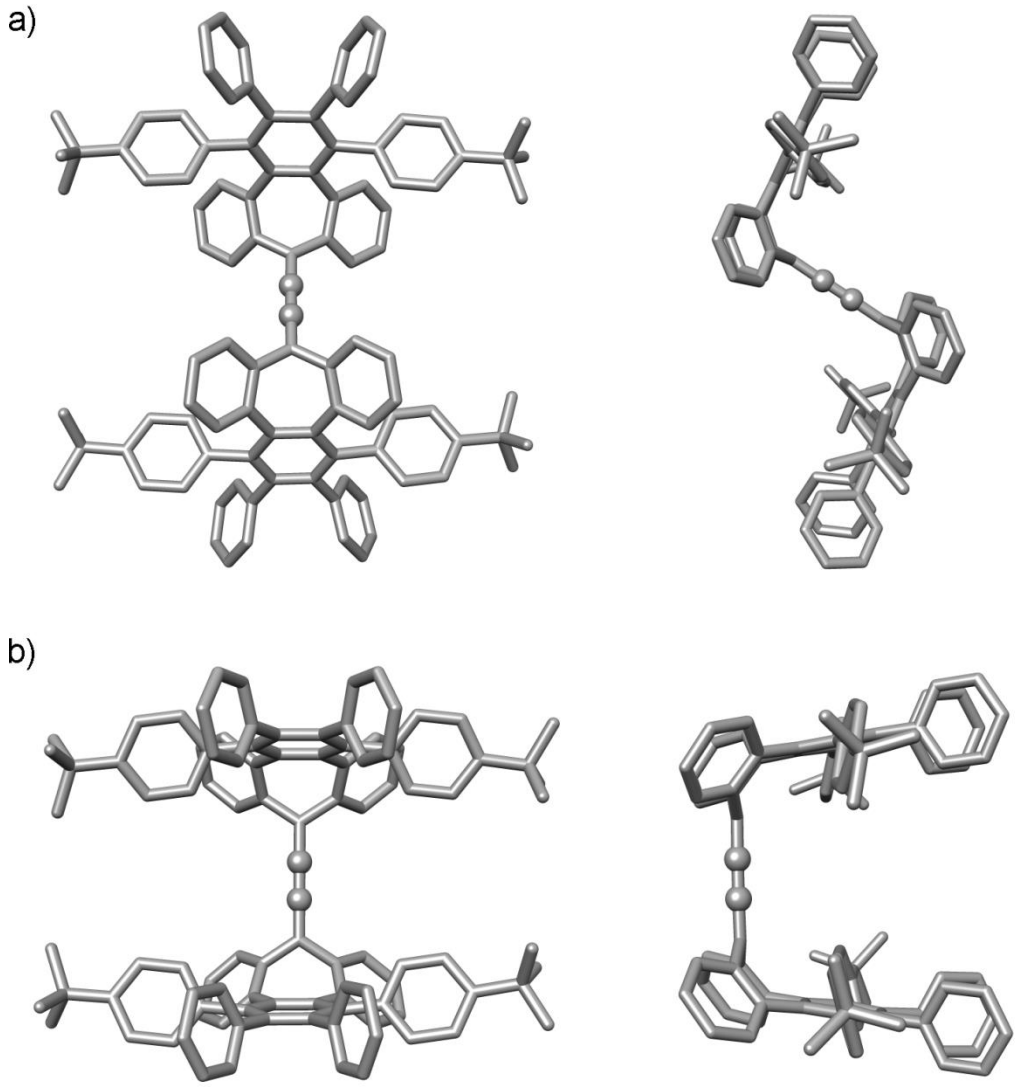

Figure S33. Top (left) and lateral (right) views of DFT (B3LYP/6-31G(d,p)) calculated structure of: a) *anti*-**1**; b) *syn*-**1** Hydrogen atoms have been omitted and the [3]cumulene central C atoms have been represented as balls for clarity.

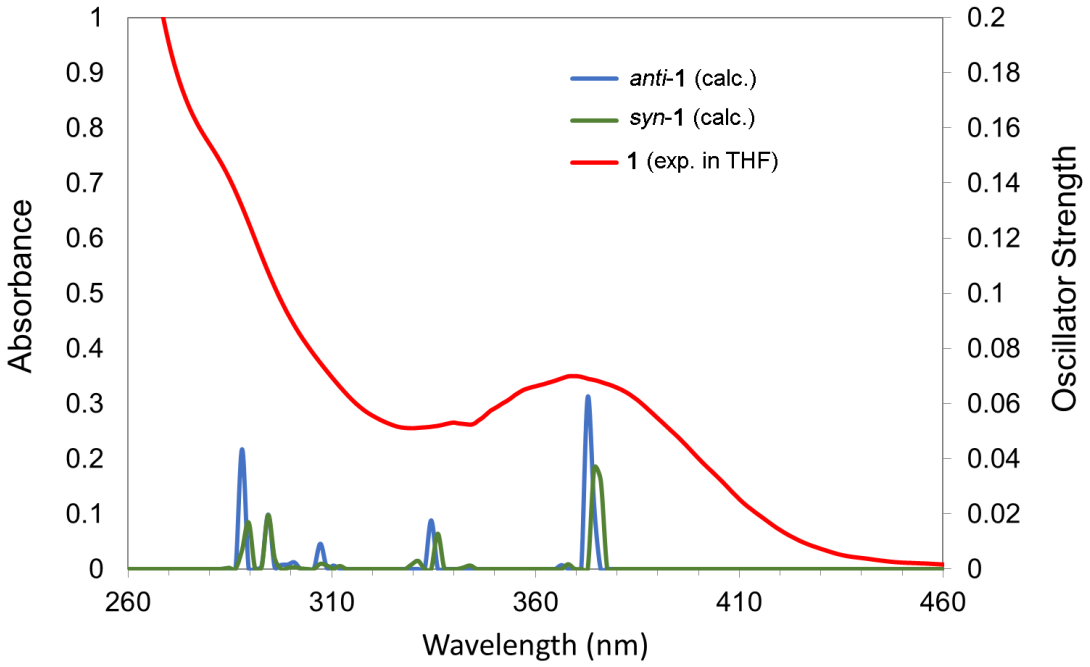

Figure S34. Conformationally resolved absorption spectra of **1**.

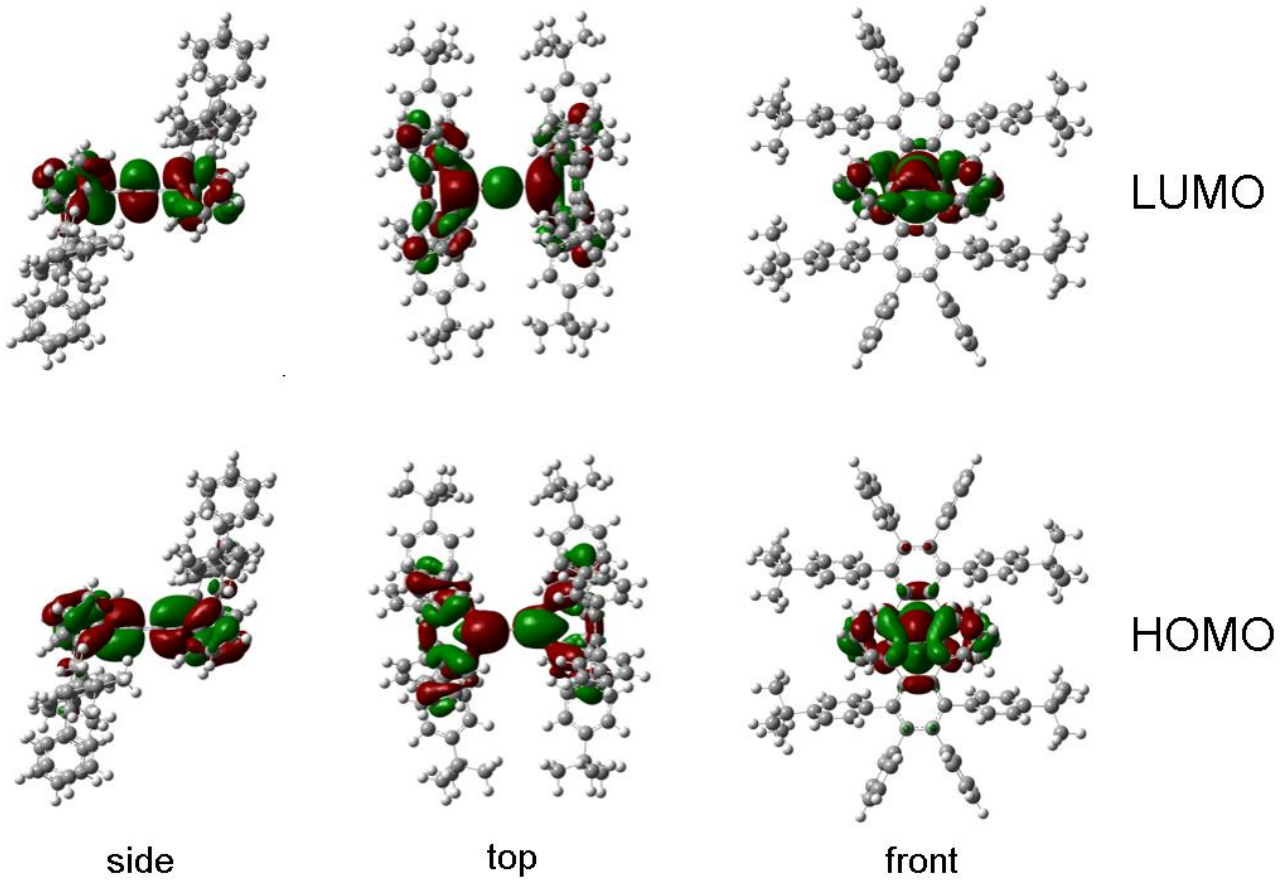

Figure S35. Different views of the frontier molecular orbitals of *anti*-**1** participating in the $S_1 \leftarrow S_0$ transition responsible for the absorption at 360 nm.

Table S2. Atomic coordinates for the DFT optimized structure of *anti*-**1**.

Atom	X	Y	Z
C	0	0	0
C	0	0	1.4123596
C	1.2787586	0	2.1874141
C	2.2744581	-0.9770180	1.9536789
C	2.0882702	-2.0354586	0.9130426
C	1.7588246	-1.7021453	-0.4204214
C	2.0634436	-4.0195031	-1.0930698
H	2.0664096	-4.7765222	-1.8718814
C	1.7804171	-2.6946265	-1.4117707
H	1.5365631	-2.4140854	-2.4317403
C	2.3057314	-4.3696345	0.2355758
H	2.4909721	-5.4048200	0.5061563
C	2.3264514	-3.3841536	1.2188134
H	2.5500269	-3.6590444	2.2429717
C	-1.2332922	0.0889110	2.0757554
H	-1.2502233	0.0608777	3.1591618
C	-2.4280653	0.2347322	1.3761435
H	-3.3665009	0.2969790	1.9189312
C	-2.4111283	0.3158922	-0.0167345
H	-3.3347241	0.4506746	-0.5721134
C	-1.2033762	0.1873965	-0.6962887
H	-1.1790474	0.1966661	-1.7815779
C	1.4949001	1.0105146	3.1587995
C	2.6693973	0.9986441	3.9388084
C	3.6590263	0.0194501	3.7123325
C	3.4801773	-0.9466712	2.7004168
C	4.6176314	-1.8695983	2.3746459
C	5.0653858	-2.8455752	3.2701416
H	4.5672265	-2.9625015	4.2276359
C	6.1419278	-3.6766467	2.9563380
H	6.4439210	-4.4196697	3.6854957
C	6.8255656	-3.5629747	1.7392037
C	6.3736949	-2.5756687	0.8472451
H	6.8698226	-2.4438139	-0.1100954
C	5.2963141	-1.7504454	1.1529220
H	4.9706939	-1.0049414	0.4333280
C	4.9419782	0.0719781	4.4922034
C	5.0185758	-0.4489176	5.7909871
H	4.1378354	-0.9039020	6.2346965
C	6.2099419	-0.3947285	6.5144005
H	6.2493862	-0.8061136	7.5191281
C	7.3461622	0.1862449	5.9503990
H	8.2742548	0.2305163	6.5129371
C	7.2818415	0.7100250	4.6585941
H	8.1607859	1.1648854	4.2106264
C	6.0899795	0.6526695	3.9365118
H	6.0471865	1.0568257	2.9296501
C	2.9234321	2.0901921	4.9397266
C	2.6527819	1.9065420	6.3022663
H	2.2455913	0.9583562	6.6414170
C	2.8960654	2.9255994	7.2232475
H	2.6780723	2.7644226	8.2752732
C	3.4183869	4.1467021	6.7955473
H	3.6093707	4.9405359	7.5118553
C	3.6942735	4.3406569	5.4416666
H	4.1017632	5.2874679	5.0987163
C	3.4483696	3.3208085	4.5226287
H	3.6610747	3.4776352	3.4694849
C	-0.2075899	2.3647831	4.4740133
H	-0.1156298	1.6654003	5.2991190
C	0.5393517	2.1580522	3.3059108
C	0.3903263	3.0871669	2.2707293
H	0.9505304	2.9529909	1.3499095
C	-0.4706247	4.1783016	2.3953738
H	-0.5467610	4.8676991	1.5624104
C	-1.2239385	4.3885880	3.5573537
C	-1.0696781	3.4505328	4.5919335
H	-1.6311937	3.5655939	5.5146983
C	8.0222883	-4.4546212	1.3621517
C	9.2721291	-3.5697607	1.1415016
H	10.1332481	-4.1874375	0.8619261
H	9.5284110	-3.0211754	2.0536761
H	9.1149668	-2.8369058	0.3446885
C	8.3517921	-5.4857513	2.4577285
H	7.5133047	-6.1651225	2.6431543
H	8.6173256	-5.0037442	3.4041427
H	9.2068322	-6.0945618	2.1465646
C	7.7036027	-5.2229833	0.0576768
H	7.5019212	-4.5441685	-0.7760184
H	6.8248378	-5.8632782	0.1860229
H	8.5498475	-5.8584424	-0.2274218
C	-2.1858047	5.5778391	3.7306499
C	-3.6192192	5.0487394	3.9733044
H	-3.9635196	4.4500837	3.1236731
H	-4.3174116	5.8828272	4.1076994
H	-3.6745711	4.4213667	4.8676374
C	-1.7413060	6.4269166	4.9450922
H	-1.7385419	5.8431815	5.8701535
H	-2.4203990	7.2752784	5.0878546
H	-0.7306424	6.8210022	4.7973569
C	-2.2159342	6.4917608	2.4911702
H	-1.2330636	6.9261932	2.2812417
H	-2.9128526	7.3190959	2.6597934

H	-2.5505287	5.9554111	1.5972568	C	4.7988208	-1.7850536	-9.3796590
C	1.2305486	-0.3518019	-0.7638785	C	4.2852921	-2.6155136	-7.1977399
C	1.6606818	0.3583741	-1.8053131	H	2.8557307	-1.4877555	-6.0613187
C	2.0722274	1.0513312	-2.7802810	H	-0.6890547	2.5085351	-10.6729948
C	2.4826457	1.7797553	-3.8170439	C	-2.7308511	1.8659835	-10.8961921
C	1.9278241	3.1281141	-4.1263127	C	-3.6237731	0.5472724	-9.0858908
C	3.7052169	1.4617825	-4.6074144	H	-2.2788182	0.1661883	-7.4484554
C	1.5616950	3.4748585	-5.4455788	C	-3.2491265	4.8341096	-6.0503375
C	1.9105947	4.1047603	-3.1193955	H	-2.9678487	5.7721743	-7.9778503
C	3.6861709	1.4976327	-6.0202578	H	-3.1848879	3.6533399	-4.2421410
C	4.9208891	1.2769047	-3.9319940	H	1.2440629	0.7323763	-11.2396773
C	1.3786931	2.4296507	-6.4991416	C	0.7083840	-1.2414351	-11.9092049
C	1.2865605	4.8220832	-5.7253544	C	0.1359266	-2.8202135	-10.1791062
C	1.5934758	5.4281446	-3.4110756	H	0.2310386	-2.0791005	-8.1602815
H	2.1833245	3.8140644	-2.1096210	H	5.3317514	-1.8380502	-10.3220661
C	2.3968814	1.4885657	-6.7789119	C	5.0140848	-2.7537042	-8.3911879
C	4.9127665	1.4505422	-6.7002888	H	4.4130177	-3.3406338	-6.3990472
C	6.1217685	1.1877570	-4.6297944	H	-2.8513459	2.3463690	-11.8631282
H	4.9108491	1.2395675	-2.8470920	C	-3.7918005	1.1599088	-10.3281342
C	0.1539167	2.3782690	-7.2123729	H	-4.4434125	-0.0053858	-8.6354742
H	1.0324229	5.1066459	-6.7398916	C	-4.4556560	5.7114898	-5.6708263
C	1.3104591	5.7929419	-4.7278165	H	0.8464609	-1.0003293	-12.9594787
H	1.5944109	6.1733214	-2.6209172	C	0.3086809	-2.5237589	-11.5316985
C	2.1909462	0.5046148	-7.7797715	H	-0.1755051	-3.8154772	-9.8748425
C	6.1189934	1.3079733	-6.0198050	C	5.9898484	-3.9309813	-8.5679548
H	4.9159897	1.5080569	-7.7824772	H	-4.7417254	1.0873162	-10.8497820
H	7.0547252	1.0542202	-4.0899849	C	-4.0271641	7.1980259	-5.6596638
C	-0.0204861	1.4357631	-8.2464387	C	-5.5845186	5.5120978	-6.7097138
C	-1.0056517	3.2461313	-6.8202715	C	-5.0171838	5.3643248	-4.2792002
H	1.0964841	6.8278444	-4.9775089	H	0.1332036	-3.2859299	-12.2854023
C	0.9979320	0.5026676	-8.5321400	C	5.2100917	-5.2634551	-8.4666730
C	3.1827970	-0.6002974	-7.9968845	C	6.7069116	-3.8970704	-9.9305876
H	7.0512018	1.2782940	-6.5759037	C	7.0650116	-3.8825275	-7.4565263
C	-1.3308552	1.3481440	-8.9765633	H	-3.2333655	7.3700971	-4.9254418
C	-1.5186485	4.2373587	-7.6684598	H	-4.8769887	7.8393414	-5.3993699
C	-1.6363492	3.0628199	-5.5850871	H	-3.6540460	7.5204748	-6.6360385
C	0.7631008	-0.5496718	-9.5782658	H	-5.2607427	5.7824598	-7.7189536
C	3.8996489	-0.7345589	-9.1897842	H	-6.4500429	6.1358598	-6.4586133
C	3.3938752	-1.5657311	-7.0014996	H	-5.9129930	4.4680323	-6.7342040
C	-1.5110025	1.9569932	-10.2256967	H	-5.3687941	4.3286432	-4.2284567
C	-2.4037132	0.6413727	-8.4167278	H	-5.8694159	6.0132629	-4.0529481
H	-1.0560879	4.4060646	-8.6359148	H	-4.2719978	5.5112915	-3.4906571
C	-2.6095964	5.0128805	-7.2885365	H	5.8912603	-6.1145327	-8.5802017
H	-1.2601455	2.3067775	-4.9019993	H	4.4478657	-5.3305682	-9.2497400
C	-2.7342200	3.8384750	-5.2103981	H	4.7062068	-5.3663956	-7.5011724
C	0.9314305	-0.2635923	-10.9398321	H	7.3031561	-2.9870674	-10.0545938
C	0.3616686	-1.8413030	-9.2116282	H	6.0002341	-3.9593419	-10.7644136
H	3.7574279	-0.0086264	-9.9844076	H	7.3876042	-4.7507511	-10.0109105

H	6.6222873	-3.9473168	-6.4583730	H	7.7646012	-4.7191333	-7.5655457
H	7.6376774	-2.9507710	-7.5071361				

Zero-point correction = 1.598861
Thermal correction to Energy = 1.689511
Thermal correction to Enthalpy = 1.690455
Thermal correction to Gibbs Free Energy = 1.457606
Sum of electronic and zero-point Energies = –4014.600216
Sum of electronic and thermal Energies = –4014.509566
Sum of electronic and thermal Enthalpies = –4014.508622
Sum of electronic and thermal Free Energies = –4014.741472
(0 imaginary frequencies)

Table S3. Atomic coordinates for the DFT optimized structure of *syn*-**1**.

Atom	X	Y	Z	H	-7.553981	-3.481575	0.488279
C	-0.705280	-1.847591	-3.222138	C	-5.433756	-3.503615	0.252723
C	-2.150416	-2.175472	-3.383379	H	-5.365552	-4.561936	0.484933
C	-2.781547	-3.121556	-2.545038	C	-3.144344	-3.718562	2.442134
C	-2.160496	-3.543828	-1.251991	C	-3.236816	-2.475892	3.083600
C	-0.833263	-4.029458	-1.205262	H	-2.741659	-1.614132	2.646439
C	-0.011016	-4.148405	-2.449155	C	-3.959025	-2.335887	4.268441
C	0.173554	-3.048047	-3.316268	H	-4.018252	-1.364266	4.750671
C	-2.842464	-1.654083	-4.487033	C	-4.603594	-3.437601	4.832186
H	-2.343891	-0.920078	-5.112433	H	-5.167025	-3.328977	5.754399
C	-4.122324	-2.097988	-4.806036	C	-4.519516	-4.679891	4.202687
H	-4.639298	-1.689474	-5.669445	H	-5.017979	-5.544026	4.632901
C	-4.716217	-3.094949	-4.031394	C	-3.794252	-4.817990	3.019222
H	-5.698261	-3.479869	-4.289404	H	-3.734061	-5.787486	2.533269
C	-4.052772	-3.588804	-2.911630	C	-0.424713	-4.693041	2.542768
H	-4.534513	-4.338384	-2.294738	C	-0.611438	-5.957595	3.116995
C	1.096664	-3.138297	-4.368409	H	-1.204165	-6.699684	2.589872
H	1.232874	-2.276648	-5.014507	C	-0.041822	-6.274226	4.350264
C	1.794862	-4.317693	-4.610142	H	-0.196617	-7.260952	4.777723
H	2.499117	-4.372516	-5.435133	C	0.722021	-5.327197	5.033194
C	1.555568	-5.434067	-3.808118	H	1.164786	-5.571974	5.994331
H	2.064590	-6.372523	-4.006525	C	0.912237	-4.063423	4.473146
C	0.670451	-5.340779	-2.737682	H	1.504696	-3.318698	4.997030
H	0.514973	-6.202004	-2.098240	C	0.343842	-3.750261	3.238509
C	-2.914194	-3.432471	-0.055600	H	0.499257	-2.766977	2.804862
C	-2.361061	-3.861118	1.168440	C	1.193669	-4.750695	0.146382
C	-1.036040	-4.341853	1.215950	C	1.630446	-6.022596	0.528943
C	-0.260887	-4.398262	0.039003	H	0.901239	-6.799731	0.735454
C	-4.268321	-2.786356	-0.052032	C	2.989889	-6.315621	0.649526
C	-4.403718	-1.423908	-0.338545	H	3.272517	-7.319042	0.946561
H	-3.520816	-0.840323	-0.582485	C	3.972810	-5.349429	0.401091
C	-5.653615	-0.803188	-0.328434	C	3.525766	-4.073105	0.019809
H	-5.701687	0.254843	-0.559459	H	4.246514	-3.286552	-0.184211
C	-6.823619	-1.515376	-0.035938	C	2.172450	-3.778362	-0.107123
C	-6.678591	-2.882439	0.254594	H	1.866700	-2.781561	-0.411271

C	-0.234638	-0.601505	-3.242132	C	0.638441	5.988597	3.074571
C	0.216157	0.580541	-3.244739	H	1.234796	6.720607	2.537498
C	0.690563	1.825314	-3.230692	C	3.148706	3.708654	2.418786
C	-0.183461	3.028878	-3.328173	C	3.234373	2.465375	3.060075
C	0.010150	4.135024	-2.470194	H	2.735540	1.606117	2.622143
C	0.835572	4.021282	-1.227853	C	3.954708	2.321371	4.245576
C	2.159108	3.525262	-1.273871	H	4.008787	1.349241	4.727379
C	2.775207	3.092085	-2.565553	C	4.604070	3.419751	4.810326
C	2.136800	2.145643	-3.397811	H	5.166027	3.308126	5.733089
C	2.823281	1.615263	-4.500663	C	4.526519	4.662664	4.181179
H	2.319159	0.881182	-5.121495	H	5.028715	5.524247	4.612174
C	4.104951	2.050275	-4.824566	C	3.803135	4.804733	2.997047
H	4.617595	1.634818	-5.687231	H	3.748364	5.774626	2.511355
C	4.706575	3.047005	-4.055631	C	4.263973	2.759455	-0.073285
H	5.690330	3.424803	-4.317617	C	4.388928	1.391929	-0.358639
C	4.048587	3.549911	-2.936669	H	3.502309	0.816214	-0.607496
H	4.536075	4.299108	-2.323844	C	5.630805	0.765692	-0.335910
C	-1.110890	3.115691	-4.376884	H	5.678264	-0.295438	-0.563474
H	-1.254055	2.249767	-5.015722	C	6.809048	1.468420	-0.032322
C	-1.804239	4.296602	-4.624920	C	6.676047	2.833533	0.251174
H	-2.511765	4.348456	-5.447311	H	7.548714	3.429514	0.492484
C	-1.555300	5.418175	-3.833187	C	5.431208	3.464553	0.235958
H	-2.059868	6.357871	-4.036990	H	5.371459	4.523932	0.465689
C	-0.666018	5.328650	-2.765914	C	5.480408	-5.631956	0.529980
H	-0.502865	6.194553	-2.134819	C	6.171276	-5.380324	-0.831166
C	0.270172	4.404942	0.015030	H	5.765583	-6.041088	-1.604130
C	1.047286	4.349422	1.190647	H	7.248153	-5.568303	-0.752998
C	2.367043	3.854472	1.144438	H	6.036755	-4.349410	-1.171396
C	-1.179753	4.775555	0.125412	C	5.768899	-7.084601	0.953420
C	2.914509	3.415066	-0.078529	H	5.331860	-7.318727	1.929565
C	-2.171092	3.814578	-0.099947	H	6.850060	-7.239394	1.030304
H	-1.881626	2.807626	-0.386267	H	5.383773	-7.805075	0.224428
C	-3.524958	4.126699	0.031375	C	6.091015	-4.690082	1.594821
H	-4.250655	3.342355	-0.151130	H	5.959761	-3.636668	1.329724
C	-3.949441	5.412911	0.388534	H	7.166131	-4.876010	1.698542
C	-2.947830	6.372938	0.609423	H	5.622029	-4.848039	2.571355
H	-3.222726	7.386373	0.887052	C	-8.221240	-0.870347	-0.029298
C	-1.596861	6.064208	0.486674	C	-9.113109	-1.569834	-1.082462
H	-0.855209	6.835000	0.671636	H	-8.689920	-1.460509	-2.086341
C	0.442005	4.718781	2.515324	H	-10.117188	-1.130489	-1.086381
C	-0.330910	3.789138	3.223804	H	-9.218334	-2.639641	-0.879666
H	-0.493755	2.801913	2.802021	C	-8.174357	0.632266	-0.364299
C	-0.893943	4.120270	4.456203	H	-7.577894	1.193863	0.362189
H	-1.489854	3.385521	4.990175	H	-9.188002	1.045763	-0.348585
C	-0.693955	5.389062	5.001299	H	-7.759683	0.814641	-1.361050
H	-1.132623	5.647697	5.960671	C	-8.859172	-1.032676	1.370725
C	0.074302	6.323132	4.305619	H	-8.961409	-2.084796	1.652059
H	0.236850	7.313601	4.721381	H	-9.858813	-0.583812	1.388948

H	-8.250965	-0.540944	2.136803	C	8.162588	0.735632	-0.019432
C	-5.431940	5.797297	0.542200	C	8.430039	0.120370	-1.413462
C	-6.375141	4.611500	0.265486	H	9.389155	-0.409941	-1.419830
H	-6.203126	3.784356	0.962122	H	8.465730	0.897645	-2.183678
H	-6.261490	4.229848	-0.754324	H	7.652723	-0.594382	-1.698779
H	-7.415471	4.931301	0.384000	C	8.126473	-0.391727	1.039299
C	-5.689758	6.290562	1.985857	H	9.082989	-0.926292	1.061927
H	-5.457238	5.506478	2.713635	H	7.341455	-1.123711	0.826839
H	-6.741784	6.571229	2.111310	H	7.940369	0.015987	2.038104
H	-5.080277	7.164627	2.233237	C	9.333605	1.676380	0.322097
C	-5.776437	6.929635	-0.454184	H	9.221279	2.122758	1.315460
H	-6.827179	7.223668	-0.350785	H	9.431565	2.486836	-0.407699
H	-5.614279	6.604537	-1.487046	H	10.272743	1.113619	0.317520
H	-5.163734	7.820104	-0.285010				

Zero-point correction= 1.598821 (Hartree/Particle)
Thermal correction to Energy= 1.689447
Thermal correction to Enthalpy= 1.690392
Thermal correction to Gibbs Free Energy= 1.459264
Sum of electronic and zero-point Energies= –4014.599990
Sum of electronic and thermal Energies= –4014.509363
Sum of electronic and thermal Enthalpies= –4014.508419
Sum of electronic and thermal Free Energies= –4014.739546
(0 imaginary frequencies)

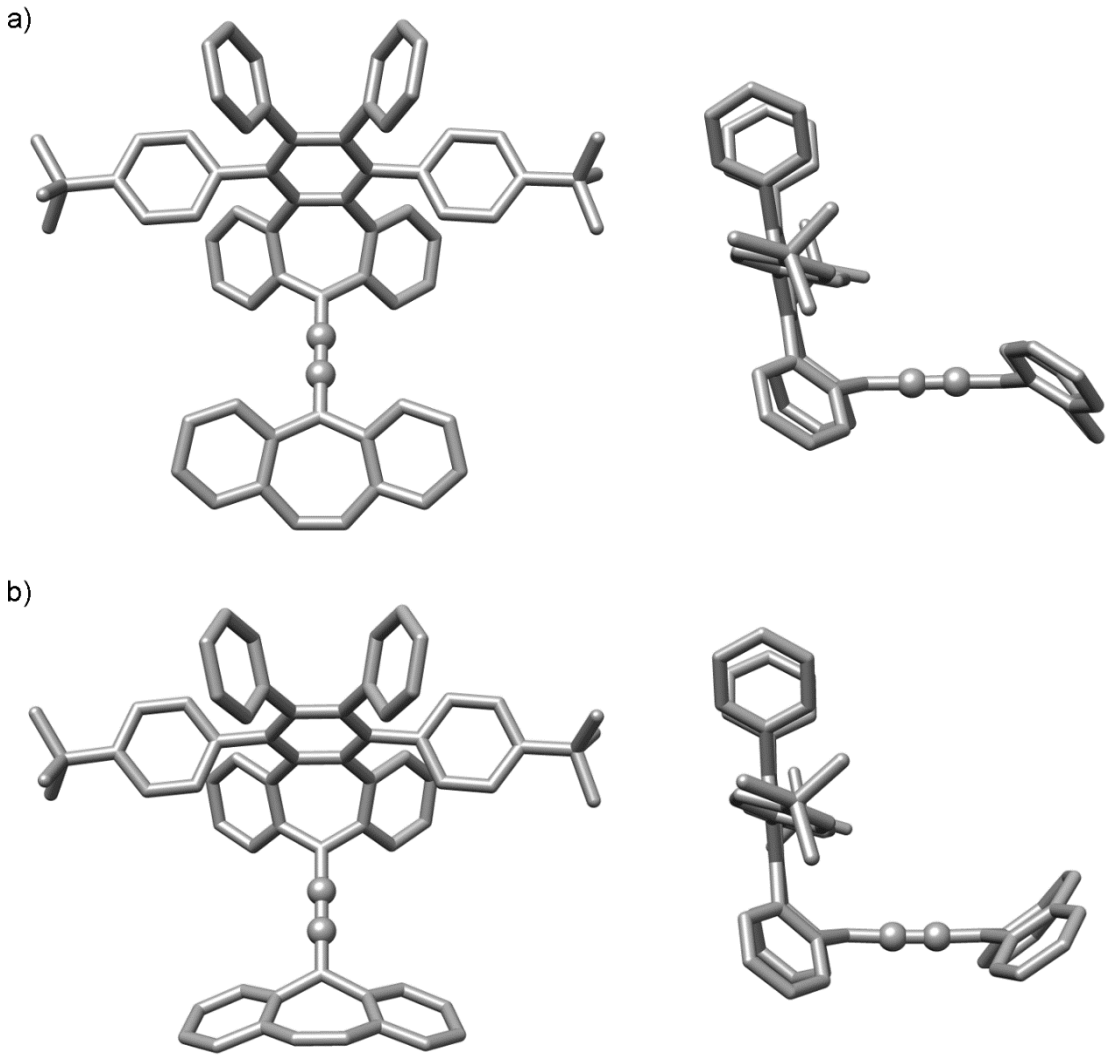

Figure S36. Top (left) and lateral (right) views of DFT (B3LYP/6-31G(d,p)) calculated structure of: a) *anti*-**4**; b) *syn*-**4**. Hydrogen atoms have been omitted and the [3]cumulene central C atoms have been represented as balls for clarity.

Table S4. Atomic coordinates for the DFT optimized structure of *anti*-**4**.

Atom	X	Y	Z
C	1.182007	1.286571	2.330660
C	1.496534	-0.090999	2.362149
C	0.774750	-1.069361	1.491140
C	-0.637284	-1.149591	1.499618
C	-1.455852	-0.256723	2.377127
C	-1.298921	1.147436	2.339414
C	-3.238322	1.418584	3.781905
H	-3.930575	2.068872	4.308686
C	-2.212863	1.968073	3.018066
H	-2.082842	3.044455	2.965037
C	-3.345022	0.031910	3.893656
H	-4.115917	-0.411520	4.516756
C	-2.468627	-0.789120	3.189152
H	-2.580208	-1.865383	3.251486
C	2.568845	-0.508182	3.164979
H	2.801587	-1.565171	3.222722
C	3.352291	0.404295	3.866424
H	4.173117	0.048703	4.482029
C	3.088805	1.770416	3.760987
H	3.707044	2.493078	4.285522
C	2.002447	2.203024	3.006268
H	1.751715	3.258085	2.957896
C	1.524023	-1.911645	0.630259
C	0.864432	-2.862892	-0.175247
C	-0.543529	-2.942331	-0.167238
C	-1.296762	-2.071384	0.647022
C	-2.791842	-2.077665	0.518684
C	-3.569595	-3.168335	0.919672
H	-3.088130	-4.035801	1.360449
C	-4.956963	-3.163788	0.766427
H	-5.511508	-4.034506	1.097247

C	-5.628100	-2.073574	0.198363
C	-4.839397	-0.982870	-0.204829
H	-5.309648	-0.111526	-0.651374
C	-3.457236	-0.981198	-0.048738
H	-2.882524	-0.115931	-0.365888
C	-1.236904	-3.885594	-1.108811
C	-1.414782	-5.237489	-0.785883
H	-1.050088	-5.610089	0.167020
C	-2.057284	-6.105020	-1.669382
H	-2.187036	-7.149474	-1.399988
C	-2.530318	-5.634046	-2.894606
H	-3.029579	-6.308935	-3.583822
C	-2.356917	-4.290358	-3.228457
H	-2.720793	-3.913798	-4.180246
C	-1.715753	-3.424790	-2.342559
H	-1.586310	-2.379225	-2.605301
C	1.649030	-3.727114	-1.120888
C	1.966028	-5.053660	-0.799101
H	1.644411	-5.461780	0.154771
C	2.692151	-5.850587	-1.684301
H	2.929610	-6.876027	-1.415318
C	3.110518	-5.333435	-2.910691
H	3.674565	-5.953187	-3.601699
C	2.798857	-4.014652	-3.243440
H	3.119344	-3.602808	-4.196225
C	2.075353	-3.219051	-2.355407
H	1.839837	-2.191928	-2.617245
C	3.906871	-2.751948	0.885672
H	3.526314	-3.667297	1.328126
C	3.009339	-1.751155	0.487994
C	3.545430	-0.592011	-0.082709
H	2.876975	0.203802	-0.398035
C	4.922503	-0.435621	-0.246943
H	5.284295	0.482527	-0.695528
C	5.825682	-1.428039	0.154947
C	5.279374	-2.589348	0.726524
H	5.935402	-3.390044	1.055306
C	-7.154612	-2.035716	0.004927
C	-7.478465	-1.876565	-1.499729
H	-8.562874	-1.846129	-1.655507
H	-7.074487	-2.714430	-2.077084
H	-7.057513	-0.954576	-1.911486
C	-7.839563	-3.319727	0.508980
H	-7.671813	-3.477441	1.579420
H	-7.486269	-4.206754	-0.026751
H	-8.920689	-3.247826	0.352032
C	-7.745056	-0.836677	0.784122
H	-7.326618	0.115220	0.444514
H	-7.539564	-0.926686	1.855757
H	-8.831704	-0.790970	0.648383
C	7.350690	-1.289492	-0.000825
C	8.016536	-1.347595	1.394572
H	7.659384	-0.532193	2.031962
H	9.104873	-1.256449	1.303003
H	7.803599	-2.289984	1.907930
C	7.889646	-2.447823	-0.873248
H	7.679277	-3.424973	-0.428955
H	8.975878	-2.362761	-0.991814
H	7.435983	-2.430940	-1.869467
C	7.751884	0.039539	-0.667965
H	7.330299	0.133560	-1.674132
H	8.841504	0.091936	-0.760814
H	7.429166	0.904599	-0.079545
C	-0.091519	1.767565	1.726510
C	-0.153512	2.819169	0.907202
C	-0.212343	3.801610	0.116678
C	-0.275440	4.861593	-0.703219
C	0.998250	5.457239	-1.188471
C	-1.610852	5.300109	-1.190023
C	1.216967	6.853473	-1.314829
C	2.060025	4.581436	-1.480357
C	-1.997162	6.659604	-1.315475
C	-2.557754	4.302462	-1.486430
C	0.217589	7.881577	-1.047610
C	2.499432	7.300821	-1.693900
C	3.309543	5.045920	-1.874246
H	1.885780	3.514790	-1.386982
C	-1.129174	7.800512	-1.047409
C	-3.323618	6.948733	-1.696648
C	-3.853462	4.612546	-1.882791
H	-2.255426	3.264640	-1.395233
H	2.669439	8.371617	-1.768490
C	3.534235	6.420470	-1.978575
H	4.104377	4.339313	-2.093504
C	-4.243368	5.949788	-1.984992
H	-3.621753	7.991165	-1.770667
H	-4.555932	3.815066	-2.105750
H	4.506484	6.800319	-2.277705
H	-5.253908	6.209296	-2.285825
H	0.635207	8.875033	-0.895217
H	-1.663159	8.736636	-0.895226

Zero-point correction = 1.005505 (Hartree/Particle)

Thermal correction to Energy = 1.062724

Thermal correction to Enthalpy = 1.063668
Thermal correction to Gibbs Free Energy = 0.907040
Sum of electronic and zero-point Energies = –2622.799294
Sum of electronic and thermal Energies = –2622.742075
Sum of electronic and thermal Enthalpies = –2622.741131
Sum of electronic and thermal Free Energies = –2622.897759
(0 imaginary frequencies)

Table S5. Atomic coordinates for the DFT optimized structure of *syn*-**4**.

Atom	X	Y	Z
C	-0.045102	1.740600	1.929157
C	1.213870	1.201922	2.516173
C	1.495407	-0.181925	2.469277
C	0.746984	-1.091163	1.547203
C	-0.666910	-1.134540	1.554118
C	-1.461173	-0.271807	2.482467
C	-1.264196	1.126666	2.526451
C	2.048607	2.057951	3.249576
H	1.818916	3.118969	3.266858
C	3.122703	1.557909	3.980138
H	3.753645	2.233791	4.550050
C	3.358130	0.182828	4.001722
H	4.169987	-0.226247	4.595600
C	2.556714	-0.669337	3.246757
H	2.765561	-1.732855	3.242481
C	-2.143214	1.930857	3.266652
H	-1.978136	3.003849	3.282143
C	-3.178681	1.367062	4.006534
H	-3.844633	2.003839	4.581610
C	-3.329851	-0.019734	4.030463
H	-4.110199	-0.476910	4.631449
C	-2.484522	-0.822184	3.268873
H	-2.628124	-1.896436	3.266820
C	1.473197	-1.903816	0.639847
C	0.788497	-2.795603	-0.211245
C	-0.621155	-2.838130	-0.204963
C	-1.350826	-1.989886	0.653393
C	2.960473	-1.765795	0.495987
C	3.513559	-0.588049	-0.018096
H	2.858682	0.235929	-0.285933
C	4.891865	-0.450048	-0.188767
H	5.266309	0.482995	-0.593915
C	5.778671	-1.479969	0.150067
C	5.215438	-2.658530	0.667413
H	5.859249	-3.487784	0.945983
C	3.841556	-2.802990	0.832604
H	3.447169	-3.733313	1.229564
C	1.549637	-3.629963	-1.201604
C	1.990576	-3.069534	-2.408109
H	1.784301	-2.023788	-2.615022
C	2.691571	-3.837347	-3.337627
H	3.024079	-3.384965	-4.267631
C	2.965194	-5.180248	-3.075394
H	3.511538	-5.778503	-3.798843
C	2.532086	-5.749367	-1.877458
H	2.740310	-6.793932	-1.663398
C	1.829003	-4.979969	-0.950263
H	1.496199	-5.428438	-0.018585
C	-1.339518	-3.712038	-1.193440
C	-1.563034	-5.071191	-0.936007
H	-1.216873	-5.500392	-0.000107
C	-2.227983	-5.874469	-1.862647
H	-2.393124	-6.925740	-1.643860
C	-2.678325	-5.330587	-3.065985
H	-3.195166	-5.955262	-3.788791
C	-2.459770	-3.978908	-3.334502
H	-2.805903	-3.545821	-4.268709
C	-1.796238	-3.177516	-2.405756
H	-1.631812	-2.125403	-2.617923
C	-2.844701	-1.940124	0.520142
C	-3.661370	-3.021928	0.863353
H	-3.212613	-3.926039	1.263198
C	-5.046688	-2.962867	0.702449
H	-5.632520	-3.829044	0.987902
C	-5.676208	-1.824688	0.183100
C	-4.848501	-0.742981	-0.162052
H	-5.285311	0.163807	-0.570158
C	-3.468280	-0.794992	0.002922
H	-2.863269	0.064545	-0.270218
C	-0.080895	2.803320	1.124508
C	-0.114915	3.784246	0.329652
C	-0.150736	4.799635	-0.545628
C	1.135235	5.420382	-0.963712
C	1.421494	5.816952	-2.295554
C	0.483968	5.734408	-3.409626
C	-0.864561	5.692890	-3.404233
C	-1.796731	5.716966	-2.282853

C	-1.476714	5.337226	-0.953801	H	-7.605232	-3.879257	-0.168089
C	-2.482066	5.413250	0.027177	H	-9.008660	-2.891407	0.250032
H	-2.231318	5.124981	1.042405	H	-7.779738	-3.229076	1.472941
C	-3.772346	5.834739	-0.272245	C	-7.502544	-1.475706	-1.515957
H	-4.521515	5.881672	0.512404	H	-7.046101	-0.548354	-1.874306
C	-4.096302	6.187938	-1.584098	H	-8.583725	-1.400235	-1.679078
H	-5.101338	6.511981	-1.836946	H	-7.120762	-2.295008	-2.133670
C	-3.118109	6.119515	-2.566594	C	7.304125	-1.366281	-0.020957
H	-3.364987	6.389017	-3.590054	C	7.990250	-1.528075	1.356213
C	2.140459	5.562392	0.010070	H	7.662257	-0.747508	2.050384
H	1.915529	5.262245	1.027895	H	9.078815	-1.455220	1.251869
C	3.399738	6.063039	-0.299385	H	7.763646	-2.496448	1.812125
H	4.149791	6.158940	0.479943	C	7.726815	-0.007695	-0.611234
C	3.692130	6.431842	-1.614326	H	7.294261	0.157184	-1.603448
H	4.673314	6.816991	-1.875019	H	8.816151	0.026142	-0.716534
C	2.713176	6.300336	-2.589621	H	7.431326	0.826843	0.032943
H	2.935433	6.582443	-3.615320	C	7.800981	-2.479906	-0.973161
C	-7.198899	-1.725255	-0.019412	H	7.571920	-3.477339	-0.587081
C	-7.754938	-0.549252	0.817998	H	8.887233	-2.414115	-1.103833
H	-7.562938	-0.703782	1.884795	H	7.332992	-2.389278	-1.958676
H	-8.837992	-0.457765	0.676778	H	0.955497	5.785672	-4.389229
H	-7.299832	0.403575	0.532733	H	-1.346189	5.714928	-4.380016
C	-7.932120	-3.009592	0.411107				

Zero-point correction = 1.005533 (Hartree/Particle)
Thermal correction to Energy = 1.062745
Thermal correction to Enthalpy = 1.063690
Thermal correction to Gibbs Free Energy = 0.907506
Sum of electronic and zero-point Energies = –2622.798957
Sum of electronic and thermal Energies = –2622.741744
Sum of electronic and thermal Enthalpies = –2622.740800
Sum of electronic and thermal Free Energies = –2622.896984
(0 imaginary frequencies)

Transmission Electron Microscopy

One drop of a suspension of **1**-aggregates in 70 vol % of water content in THF was placed on a copper grid coated with carbon. The deposit was dried under vacuum. The electron microscopy studies were performed using a LIBRA 120 PLUS Carl Zeiss SMT TEM instrument.

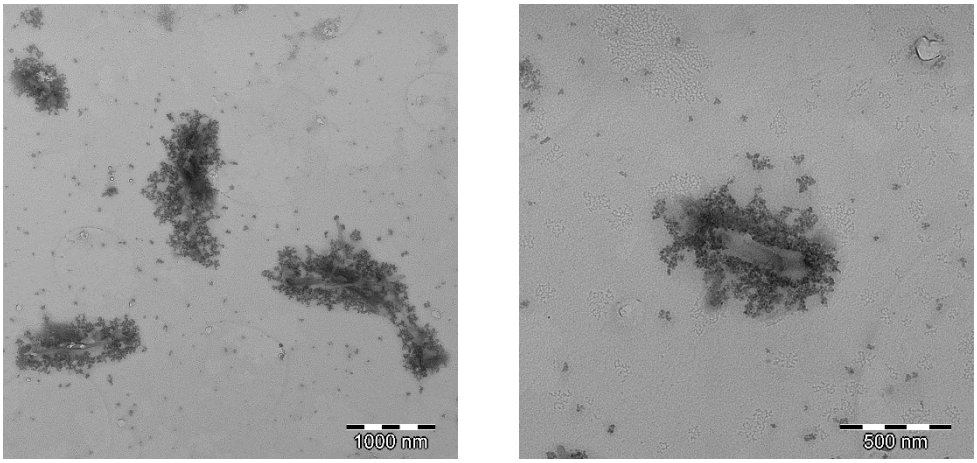

Figure S37. TEM images of **1**-aggregates formed in a THF/water mixture with 70 vol % water content deposited on a copper grid coated with carbon.

Dynamic-Light Scattering

Hydrodynamic diameters (D_H) of the aggregates were obtained using a Zetasizer Nano ZS (Malvern, model ZEN3600) equipped with a 4 mW He–Ne solid-state laser operating at 633 nm and backscattered light was detected at 173°. The auto-correlated functions were analyzed by the CONTIN method. The concentration of **1** was kept at 5.1×10^{-6} M in all samples. Mixtures of 10-90 vol % of milli-Q water in THF were prepared and analyzed.

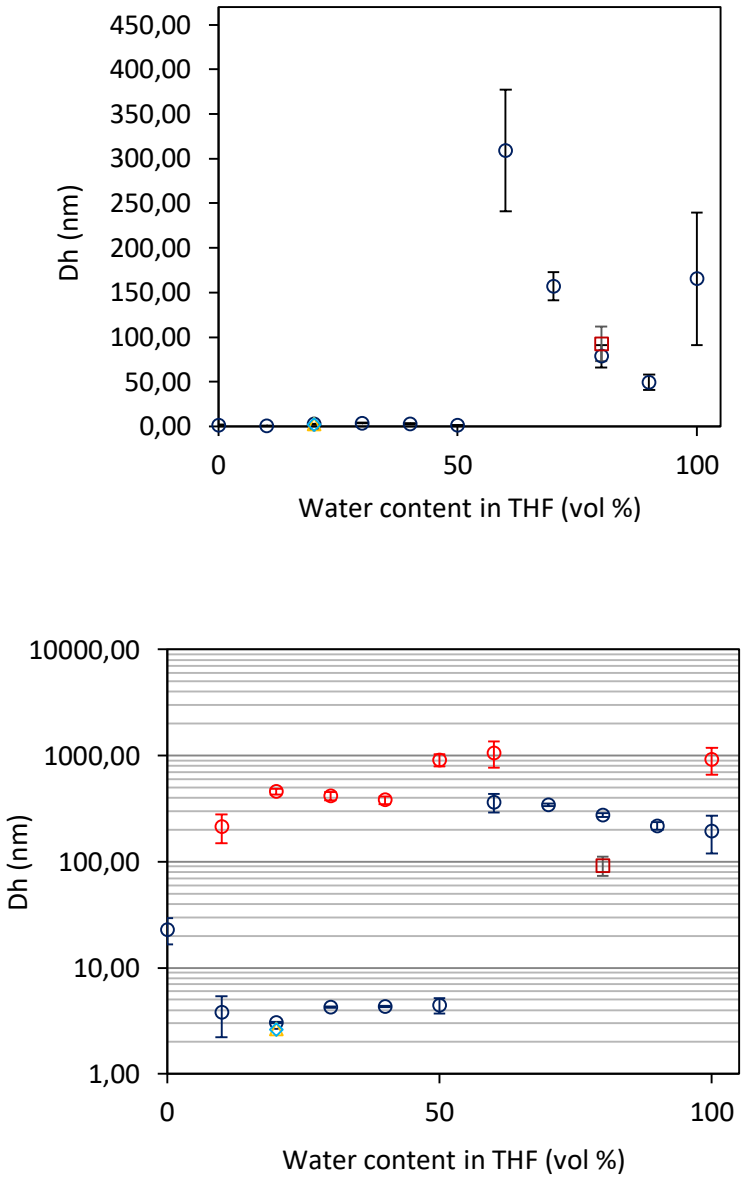

Figure S38. DLS measurements of **1** in THF/water mixtures: Peak by number (top) and peak by intensity (bottom) graphs.

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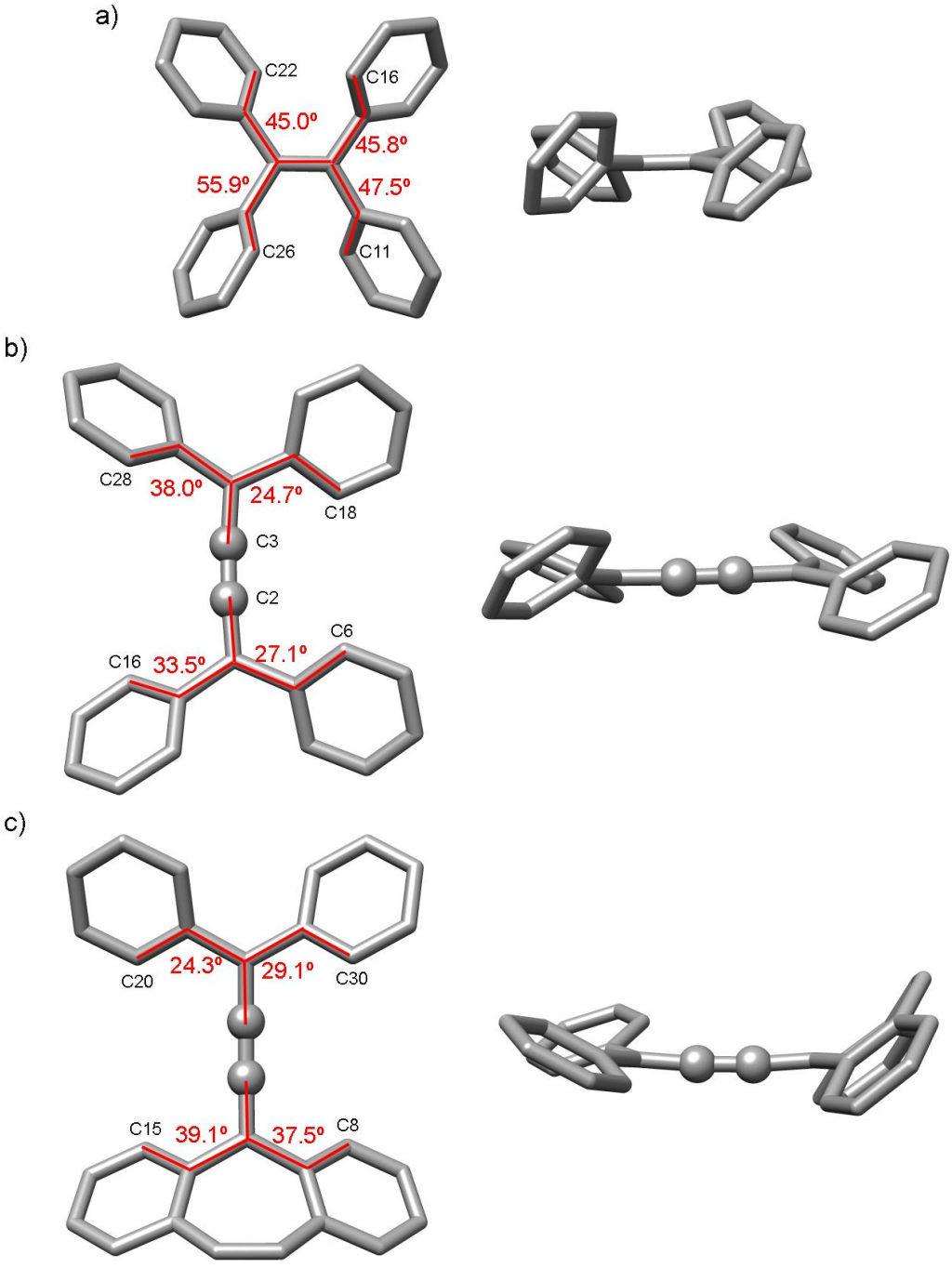
Study of the planarity



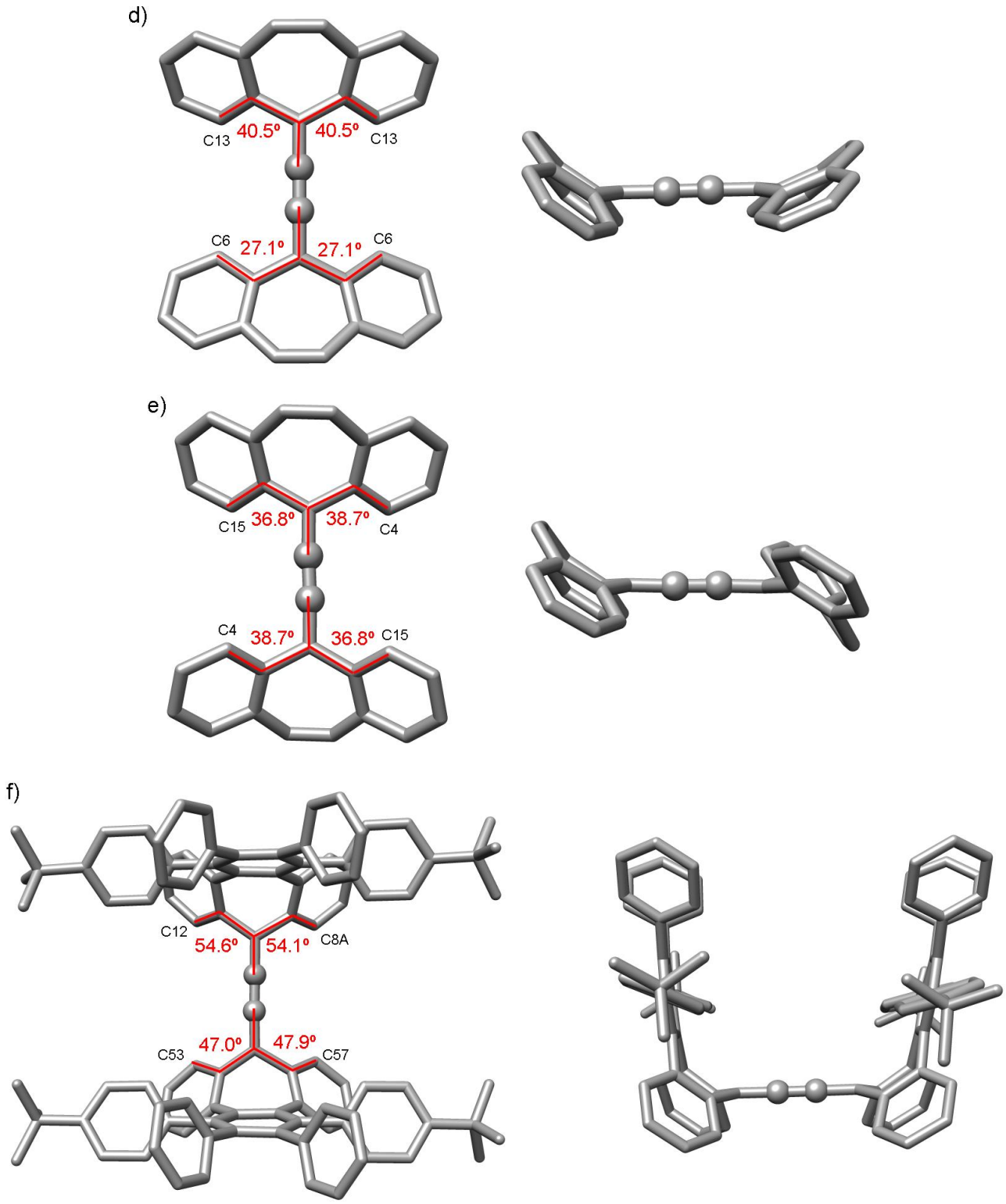


Figure S39. Top (left) and side (right) views of the crystal structure of: a) TPE;[S10] b) TPBT, c) **3**; d) *syn*-**2**;[S11] e) *anti*-**2**;[S11] f) *syn*-**1**; showing the absolute value of the dihedral angles between the double bonds and the corresponding aromatic rings attached to them. H atoms have been omitted and [3]cumulene central C atoms have been represented as balls for clarity.

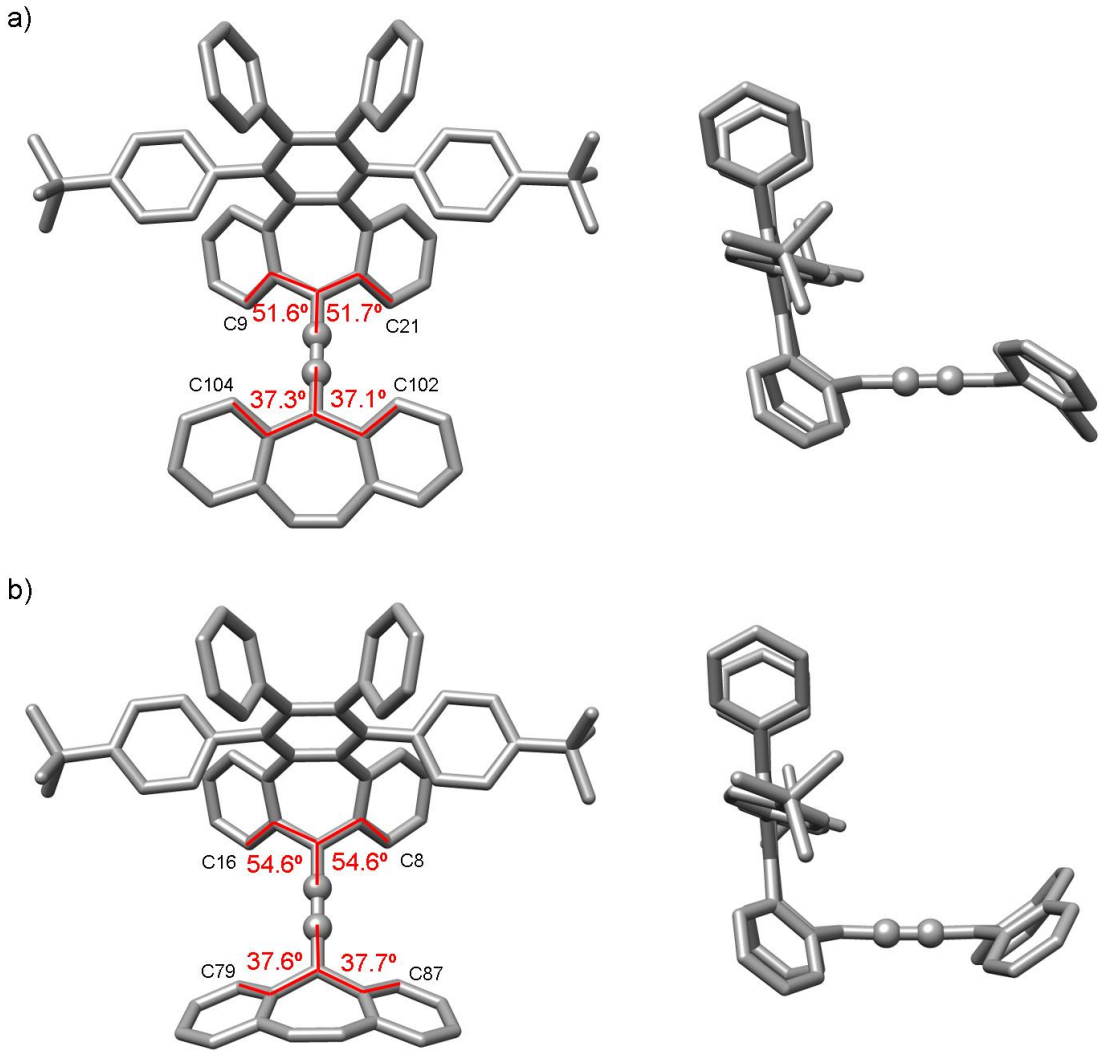


Figure S40. Top (left) and lateral (right) views of DFT (B3LYP/6-31G(d,p)) calculated structure of: a) *anti*-**4**; b) *syn*-**4**. The dihedral angles between the double bonds and the corresponding rings attached to them and their correspondent absolute values are represented in red. Hydrogen atoms have been omitted and the [3]cumulene central C atoms have been represented as balls for clarity.

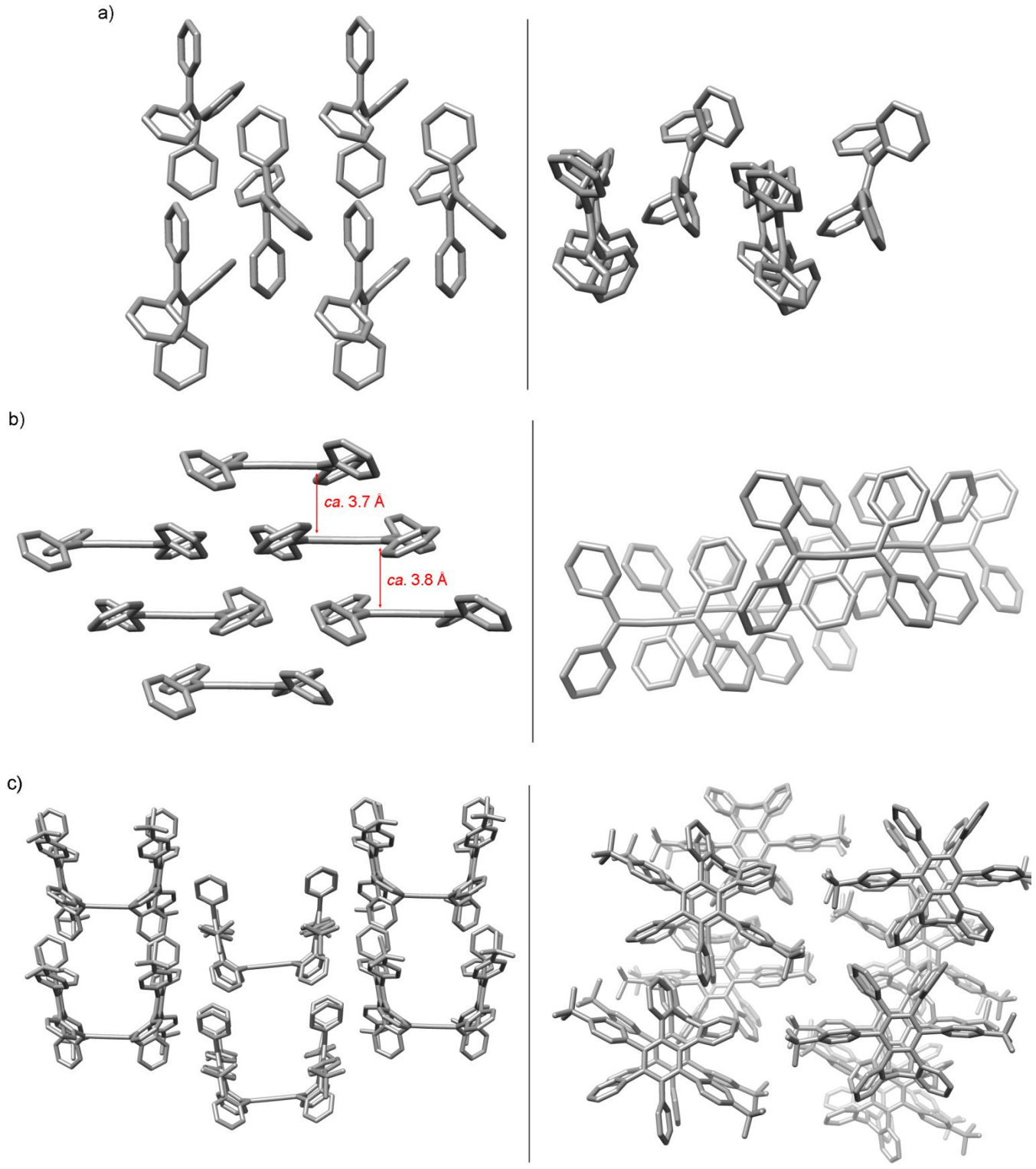


Figure S41. Different views of the crystal packing of: a) TPE;[S10] b) TPBT (distances shown: C4–centroid(C3–C4) and C1-centroid(C1–C2)); c) *syn*-**1**. Hydrogen atoms have been omitted for clarity.

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