Supporting Information

Zipping up Tetraazaperylenes: Synthesis of Tetraazacoronenes vis Doulbe Coupling in the Bay Positions

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Content

General Information

All chemicals and solvents were purchased from commercial suppliers and used without further purification. Solvents were dried according to standard procedures and water was degassed with argon. Deuterated solvents were bought from Sigma-Aldrich and used as received. The ^{1}H- and ^{13}C-spectra were recorded with a Bruker and 600II spectrometer and are referenced to the residual signal of $CDCl_3$ (^{1}H: 7.26 ppm and ^{13}C: 77.16 ppm).[1] Chemical shifts are given in ppm and coupling constants in Hz. The following abbreviations were used to describe the multiplicities: s = singlet, bs = broad singlet, d = doublet, q = quintet, m = multiplet. The mass spectra were recorded by the department of the organic Chemistry of the University of Heidelberg under the direction of Dr. J. Gross. MALDI spectra were measured on a Bruker ApexQe hybrid 9.4 T FT-ICR. The absorption spectra were recorded on a Cary 5000 UV/Vis spectrometer and were baseline and solvent corrected. The fluorescence spectra were recorded on a Varian Cary Eclipse Fluorescence spectrophotometer and emission quantum yields (Φ) were measured on a JASCO spectrofluorometer FP-8500 equipped with an ILF-835j100 mm integrating sphere. Cyclic voltammograms were recorded with a PalmSense EmStat3+ Blue instrument under inert atmosphere. Graphite was used as a working electrode, platinum wire as a counter electrode, silver wire as a reference electrode and ferrocene as internal standard. Measurements were carried out in a 0.1 M tetrabutylammonium hexafluorophosphate solution in anhydrous dichloromethane. IR-spectra were measured with a Varian 3100 FT-IR-Spectrometer (Excalibur Series) as KBr pellet. X-ray analyses were performed by Priv. Doz. Dr. Joachim Ballmann in the X-ray laboratory of the Department of Inorganic Chemistry at the University of Heidelberg with an Agilent Supernova E diffractometer. The obtained structures were solved and refined by Priv. Doz. Dr. Joachim Ballmann Unless otherwise stated, all preparative work was performed under an inert gas atmosphere using standard Schlenk glassware, which was flame dried.

Synthesis of Compounds

The literature known compounds (*Z*)-1,2-diphenyl-1,2-bis(pinacolboryl)ethene,[2] (*Z*)-2,2'-(oct-4-ene-4,5-diyl)bis(pinacolboran),[2] (*Z*)-1,2-bis(pinacolboryl)-1,2-di-*p*-tolylethene,[2,3] (*Z*)-1,2-bis(4-chlorophenyl)-1,2-bis(pinacolboryl)ethene,[4,5] and (*Z*)-1,2-bis(4-methoxyphenyl)-1,2-bis(pinacolboryl)ethene,[4] were synthesized according to literature procedures. If not commercially available, the corresponding alkynes were synthesized through double Stille cross coupling.[6] OAPPDO **1** was synthesized according to our reported procedure.[7]

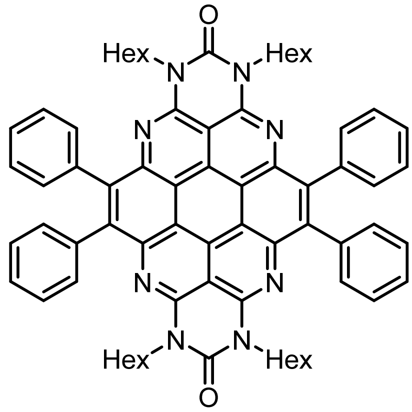
Synthesis of (*Z*)-1,2-bis(3,4-dimethoxyphenyl)-1,2-bis(pinacolboryl)ethene

According to a modified literature procedure,[4] [$Cu(OAc)_2$] (36 mg, 198 µmol, 0.10 equiv.) and tricyclohexylphosphine (194 mg, 692 µmol, 0.35 equiv.) were dissolved in methanol (3 ml) and stirred at 80°C for 30 min. The solvent was removed under reduced pressure and 1,2-bis(3,4-dimethoxyphenyl)ethyne (590 mg, 1.98 mmol, 1.00 equiv.) and bis(pinacolato)diboron (653 mg, 2.57 mmol, 1.30 equiv.) were added. Toluene (5 ml) was added, and the reaction mixture was stirred at 80°C for 18 h. After dilution with EtOAc, the mixture was filtered through a pad of Celite® and eluted with EtOAc. The solvent was removed under reduced pressure and the residue was recrystallized from boiling hexanes to give the title compound (*Z*)-1,2-bis(3,4-dimethoxyphenyl)-1,2-bis(pinacolboryl)ethene (380 mg, 688 µmol, 35%) as a colorless solid. **^{1}H-NMR ($CDCl_3$, 600.18 MHz, 295 K)** [ppm] = 6.65-6.64 (m, CH, 2H), 6.61-6.59 (m, CH, 2H), 6.47-6.46 (m, CH, 2H), 3.79 (s, CH_3, 6H), 3.53 (s, CH_3, 6H), 1.33 (bs, CH_3, 24H). **^{13}C-NMR ($CDCl_3$, 150.92 MHz, 295 K)** [ppm] = 148.1 (Cq), 147.2 (Cq), 134.2 (Cq), 121.7 (Cq), 113.1 (Cq), 110.5 (Cq), 84.2 (Cq), 55.8 (OCH_3), 55.5 (OCH_3), 25.1 (CH3). **MS(HR-MALDI$^+$)** m/z calcd. for $[C_{30}H_{42}O_8{}^{11}B_2]^+$: 552.3060, found 552.3068.

General Procedure for Double Suzuki-Miyaura Coupling

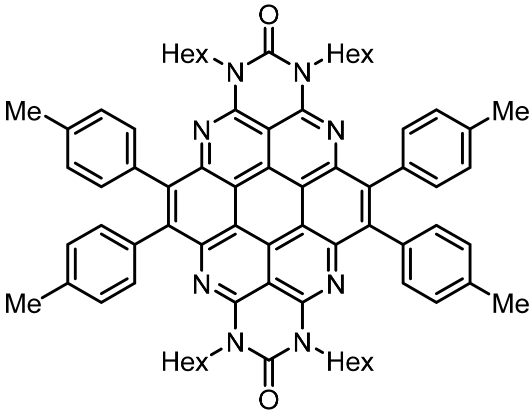
According to a modified literature procedure,[8] OAPPDO **1**, the corresponding bis(pinacolatoboryl)alkene, palladium catalyst and base were dissolved in tetrahydrofuran (20 ml). Water was added and the mixture was stirred at 80°C for 36 hours. The reaction mixture was extracted with CH_2Cl_2 (3x50 ml) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified accordingly.

Synthesis of Compound 2a



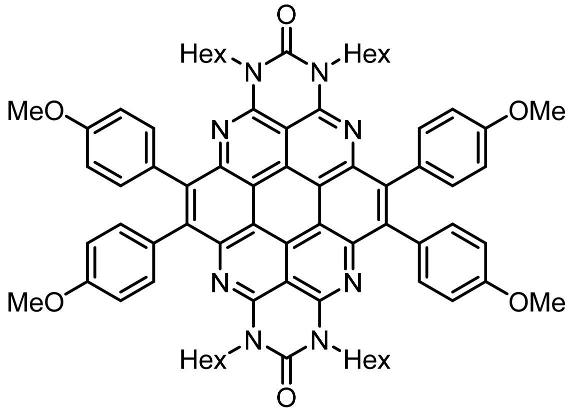
Compound **2a** was synthesized according to the general procedure for double Suzuki-Miyaura coupling using the following substances and quantities: OAPPDO **1** (100 mg, 119 µmol, 1.0 equiv.), (*Z*)-1,2-diphenyl-1,2-bis(pinacolboryl)ethene (108 mg, 249 µmol, 2.1 equiv.), $[Pd(PPh_3)_4]$ (41 mg, 36 µmol, 0.3 equiv.), K_2CO_3 (197 mg, 1.42 mmol, 12 equiv.) and water (214 µl, 12 mmol, 100 equiv.). The crude product was purified by washing with MeOH and hexanes and recrystallization from dichloromethane/MeOH. **2a** was obtained as an orange solid (62 mg, 59 µmol, 49%). **^{1}H-NMR ($CDCl_3$, 600.18 MHz, 295 K):** [ppm] = 7.46-7.45 (m, CH, 8H), 7.35-7.29 (m, CH, 12H), 4.28-4.25 (m, CH_2, 8H), 1.76-1.71 (m, CH_2, 8H), 1.33-1.26 (m, CH_2, 24H), 0.89 (t, $^3J_{H-H}$ = 6.87 Hz, CH_3, 12H), CH_3, 12H). **^{13}C-NMR ($CDCl_3$, 150.92 MHz, 295 K):** δ [ppm] = 152.2 (Cq), 148.6 (Cq), 142.9 (Cq), 142.3 (Cq), 137.8 (Cq), 132.3 (Cq), 131.8 (Cq), 127.3 (Cq), 126.9 (Cq), 112.9 (Cq), 100.3 (Cq), 43.0 (CH_2), 31.8 (CH_2), 27.4 (CH_2), 26.8 (CH_2), 22.8 (CH_2), 14.2 (CH_3). **MS(HR-MALDI$^+$):** m/z calcd. for $[C_{70}H_{72}N_8O_2]^+$: 1056.5773, found 1056.5759. **IR (KBr):** ṽ [cm^{-1}] = 2957 (m), 2928 (m), 2870 (m), 2857 (m), 1690 (s), 1641 (s), 1601 (m), 1560 (s), 1530 (m), 1477 (s), 1445 (m), 1366 (m), 1342 (m), 1258 (m), 1221 (w), 1204 (w), 1184 (w), 1152 (w), 1119 (w), 1099 (w), 1076 (w), 1057 (w), 1032 (w), 1001 (w), 883 (w), 814 (w), 787 (w), 760 (w), 750 (w), 725 (w), 698 (m), 658 (w), 644 (w).

Synthesis of Compound 2b



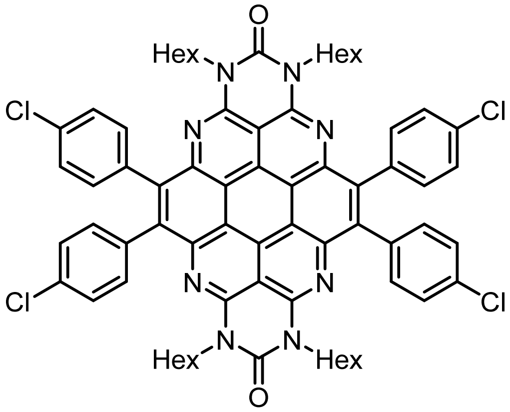
Compound **2b** was synthesized according to the general procedure for double Suzuki-Miyaura coupling using the following quantities: OAPPDO **1** (100 mg, 119 µmol, 1.0 equiv.), (*Z*)-1,2-bis(pinacolboryl)-1,2-di-p-tolylethene (115 mg, 249 µmol, 2.1 equiv.), $[Pd(PPh_3)_4]$ (41 mg, 36 µmol, 0.3 equiv.), K_2CO_3 (197 mg, 1.42 mmol, 12 equiv.) and water (214 µl, 12 mmol, 100 equiv.). The crude product was purified by washing with MeOH and hexanes and recrystallization from dichloromethane/MeOH. **2b** was obtained as an orange solid (12 mg, 11 µmol, 9%). **^{1}H-NMR ($CDCl_3$, 600.18 MHz, 295 K):** δ [ppm] = 7.31 (d, $^{3}J_{H\text{-}H}$ = 7.92, CH, 8H), 7.14 (d, $^{3}J_{H\text{-}H}$ = 7.89, CH, 8H), 4.26-4.23 (m, CH_2, 8H), 2.41 (s, CH_3, 12H), 1.75-1.70 (m, CH_2, 8H), 1.35-1.25 (m, CH_2, 12H), 0.91 (t, $^{3}J_{H\text{-}H}$ = 7.03 Hz, CH_3, 12H). **^{13}C-NMR ($CDCl_3$, 150.92 MHz, 295 K):** δ [ppm] = 152.2 (Cq), 148.3 (Cq), 143.0 (Cq), 142.1 (Cq), 136.2 (Cq), 134.9 (Cq), 132.2 (Cq), 131.7 (Cq), 128.0 (Cq), 112.8 (Cq), 100.1 (Cq), 43.0 (CH_2), 31.8 (CH_2), 27.4 (CH_2), 26.9 (CH_2), 22.9 (CH_2), 21.5 (CH_3), 14.2 (CH_3). **MS(HR-MALDI$^+$)** m/z calcd. for $[C_{74}H_{80}N_8O_2]^+$: 1112.6399, found 1112.6412. **IR (KBr):** ṽ [cm^{-1}] = 2957 (m), 2924 (m), 855 (m), 1734 (w), 1719 (m), 1695 (s), 1686 (s), 1641 (s), 1616 (m), 1603 (m), 1560 (s), 1541 (m), 1530 (m), 1514 (m), 1506 (m), 1477 (s), 1447 (m), 1420 (m), 1406 (m), 1395 (m), 1364 (s), 1342 (s), 1258 (s), 1202 (m), 1186 (m), 1169 (m), 1161 (m), 1144 (m), 1123 (m), 1113 (m), 1099 (m), 1074 (m),1040 (m), 1022 (m), 1003 (m), 995 (m), 984 (m), 972 (m), 959 (m), 941 (m), 918 (m), 885 (m), 874 (m), 862 (m), 851 (m), 839 (m), 818 (s), 800 (s), 777 (m), 748 (s), 737 (m), 727 (m), 696 (m), 660 (s), 646 (m), 625 (m).

Synthesis of Compound 2c



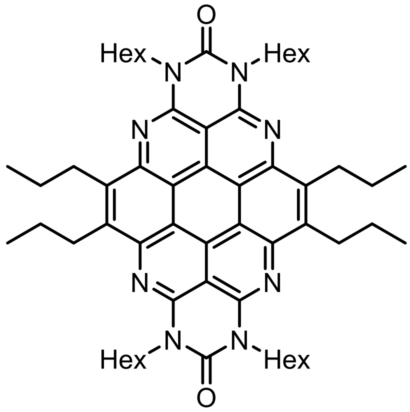
Compound **2c** was synthesized according to the general procedure for double Suzuki-Miyaura coupling using the following quantities: OAPPDO **1** (245 mg, 290 µmol, 1.0 equiv.), (*Z*)-1,2-bis(4-methoxyphenyl)-1,2-bis(pinacolboryl)ethene (300 mg, 610 µmol, 2.1 equiv.), [Pd(PPh_3)$_4$] (101 mg, 87 µmol, 0.3 equiv.), K_2CO_3 (481 mg, 3.48 mmol, 12 equiv.) and water (523 µl, 29 mmol, 100 equiv.). The crude product was purified by washing with MeOH and hexanes and recrystallization from dichloromethane/MeOH. **2c** was obtained as an orange solid (30 mg, 26 µmol, 9%). **^{1}H-NMR ($CDCl_3$, 600.18 MHz, 295 K):** [ppm] = 7.40 (d, $^3J_{H\text{-}H}$ = 8.68 Hz, CH, 8H), 6.90 (d, $^3J_{H\text{-}H}$ = 6.90 Hz, CH, 8H), 4.32-4.29 (m, CH_2, 8H), 3.87 (s, CH_3, 12H), 1.80-1.75 (m, CH_2, 8H), 1.39–1.26 (m, 24H), 0.89 (t, $^3J_{H\text{-}H}$ = 7.01 Hz, CH_3, 12H). **^{13}C-NMR ($CDCl_3$, 150.92 MHz, 295 K):** δ [ppm] = 158.5 (Cq), 152.2 (Cq), 148.4 (Cq), 143.0 (Cq), 141.8 (Cq), 133.6 (Cq), 131.8 (Cq), 130.3 (Cq), 128.2 (Cq), 112.8 (Cq), 100.2 (Cq), 55.3 (CH_3), 43.0 (CH_2), 31.8 (CH_2), 27.5 (CH_2), 27.0 (CH_2), 22.8 (CH_2), 14.2 (CH_3). **MS(HR-MALDI$^+$)** m/z calcd. for $[C_{74}H_{80}N_8O_6]^+$: 1176.6195, found 1176.6191. **IR (KBr):** ṽ [cm^{-1}] = 2955 (m), 2928 (m), 2857 (w), 1690 (s), 1639 (s), 1602 (s), 1560 (s), 1514 (s), 1477 (s), 1422 (m), 1414 (m), 1402 (m), 1364 (s), 1342 (s), 1290 (s), 1248 (s), 1204 (m), 1177 (s), 1109 (m), 1097 (m), 1067 (m), 1036 (s), 831 (w), 814 (w), 793 (w), 750 (w), 725 (w), 660 (w).

Synthesis of Compound 2d



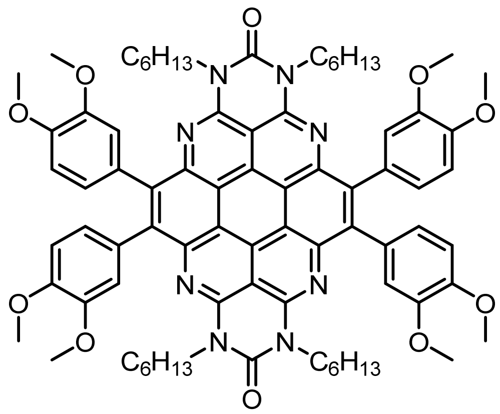
Compound **2d** was synthesized according to the general procedure for double Suzuki-Miyaura coupling using the following quantities: OAPPDO **1** (50 mg, 59 µmol, 1.0 equiv.), (*Z*)-1,2-bis(4-chlorophenyl)-1,2-bis(pinacolboryl)ethene (62 mg, 125 µmol, 2.1 equiv.), [(dppf)Pd(Cl)$_2$] (13 mg, 18 µmol, 0.3 equiv.), Cs_2CO_3 (232 mg, 712 µmol, 12 equiv.) and water (107 µl, 6 mmol, 100 equiv.). The crude product was purified by washing with MeOH and hexanes and recrystallization from dichloromethane/MeOH. **2d** was obtained as an orange solid (7.4 mg, 6 µmol, 10%). **^{1}H-NMR (CDCl$_3$, 600.18 MHz, 295 K):** δ [ppm] = 7.37 (dd, $^{3}J_{H\text{-}H}$ = 9.08 Hz, CH, 16H), 4.29-4.27 (m, CH_2, 8H), 1.76-1.71 (m, CH_2, 8H), 1.36-1.23 (m, CH_2, 24H), 0.91 (t, $^{3}J_{H\text{-}H}$ = 7.05 Hz, CH_3, 12H). **^{13}C-NMR (CDCl$_3$, 150.92 MHz, 295 K):** δ [ppm] = 152.0 (Cq), 148.8 (Cq), 142.7 (Cq), 141.0 (Cq), 135.9 (Cq), 133.5 (Cq), 133.3 (Cq), 131.7 (Cq), 127.8 (Cq), 113.1 (Cq), 100.5 (Cq), 43.2 (Cq), 31.8 (CH_2), 27.4 (CH_2), 26.9 (CH_2), 22.8 (CH_2), 14.2 (CH_3). **MS(HR-MALDI$^+$)** m/z calcd. for $[C_{70}H_{68}Cl_4N_8O_2]^+$: 1192.4214, found 1192.4219. **IR (KBr):** ṽ [cm^{-1}] = 2953 (m), 2926 (m), 2855 (m), 1690 (s), 1641 (s), 1605 (s), 1597 (m), 1564 (m), 1535 (m), 1495 (m), 1477 (s), 1445 (m), 1422 (m), 1400 (m), 1368 (s), 1342 (s), 1258 (m), 1236 (m), 1204 (m), 1188 (m), 1177 (m), 1152 (m), 1090 (s), 1042 (m), 1016 (s), 974 (m), 953 (m), 945 (m), 897 (m), 883 (m), 862 (m), 835 (m), 814 (s), 806 (m), 748 (m), 727 (m), 714 (m), 698 (m), 660 (m), 637 (m), 613 (m).

Synthesis of Compound 2e



Compound **2e** was synthesized according to the general procedure for double Suzuki-Miyaura coupling using the following quantities: OAPPDO 1 (100 mg, 119 µmol, 1.0 equiv.), (*Z*)-2,2'-(oct-4-ene-4,5-diyl)bis(pinacolboran) (91 mg, 250 µmol, 2.1 equiv.), [Pd(PPh_3)$_4$] (41 mg, 18 µmol, 0.3 equiv.), NaOH (3 M, 475 µl, 1.42 mmol, 12 equiv.). The crude product was purified by washing with MeOH, hexanes, diethyl ether and dichloromethane to furnish **2e** as an orange solid (11 mg, 12 µmol, 10%). **^{1}H-NMR (D_2SO_4, 600.18 MHz, 295 K):** δ [ppm] = 4.86 (s, CH_2, 8H), 1.68 (bs, CH_2, 8H), 1.57 (bs, CH_2, 8H), 1.27 (bs, CH_2, 8H), 1.06 (bs, CH_2, 8H), 1.00-0.95 (m, CH_2/CH_3, 28H), 0.52-0.50 (m, CH_3, 12H). **^{13}C-NMR (D_2SO_4, 150.92 MHz, 295 K):** δ [ppm] = 144.7 (Cq), 141.7 (Cq), 141.0 (Cq), 133.9 (Cq), 131.9 (Cq), 107.4 (Cq), 97.74 (Cq), 49.9 (CH_2), 27.2 (CH_2), 26.7 (CH_2), 22.5 (CH_2), 22.0 (CH_2), 20.2 (CH_2), 18.2 (CH_2), 10.3 (CH_3), 9.5 (CH_3). **MS(HR-MALDI$^+$)** m/z calcd. for $[C_{58}H_{80}N_8O_2]^+$: 920.6399, found 920.6400. **IR (KBr):** ṽ [cm^{-1}] = 3362 (w), 2957 (m), 2930 (m), 2870 (m), 2858 (m), 1693 (s), 1647 (s), 1609 (s), 1572 (s), 1539 (s), 1481 (s), 1425 (m), 1381 (s), 1344 (s), 1331 (s), 1302 (m), 1279 (m), 1256 (s), 1194 (m), 1155 (m), 1128 (m), 1090 (m), 1026 (m), 1001 (m), 945 (m), 885 (w), 826 (m), 810 (m), 797 (m), 775 (w), 750 (m), 725 (m), 708 (w), 694 (w), 637 (m), 627 (m).

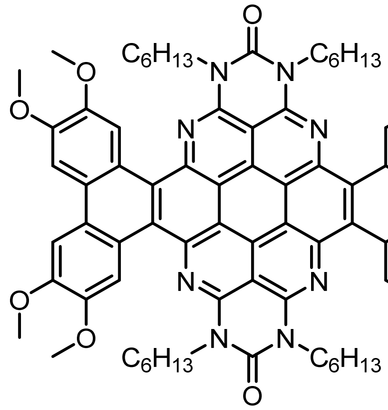
Synthesis of Compound 2f



Compound **2f** was synthesized according to the general procedure for double Suzuki-Miyaura coupling using the following quantities: OAPPDO **1** (100 mg, 119 µmol, 1.0 equiv.), (*Z*)-1,2-bis(3,4-dimethoxyphenyl)-1,2-bis(pinacolboryl)ethene (138 mg, 249 µmol, 2.1 equiv.), [Pd(PPh$_3$)$_4$] (41 mg, 36 µmol, 0.3 equiv.), K_2CO_3 (197 mg, 1.42 mmol, 12 equiv.) and water (214 µl, 12 mmol, 100 equiv.). The crude product was purified by washing with MeOH and hexanes and recrystallization from dichloromethane/MeOH. **2f** was obtained as an orange solid (78 mg, 60 µmol, 51%).

^{1}H-NMR ($CDCl_3$, 600.18 MHz, 295 K): δ [ppm] = 7.20 (bs, CH, 4H), 6.93 (d, $^3J_{H\text{-}H}$ = 8.58 Hz, CH_3, 8H), 4.35 (t, $^3J_{H\text{-}H}$ = 7.85 Hz, CH_2, 8H), 3.95 (s, OCH_3, 12H), 3.68 (bs, OCH_3, 12H), 1.82-1.768 (m, CH_2, 8H), 1.38-1.32 (m, CH_2, 8H)), 1.31-1.25 (m, CH_2, 16H), 0.88-0.86 (m, CH_3, 12H). **^{13}C-NMR ($CDCl_3$, 150.92 MHz, 295 K):** δ [ppm] = 152.1 (Cq), 148.5 (Cq), 148.1 (Cq), 147.9 (Cq), 142.8 (Cq), 141.8 (Cq), 130.4 (Cq), 125.0 (Cq), 115.6 (Cq), 112.8 (Cq), 109.9 (Cq), 101.1 (Cq), 100.1 (Cq), 55.8 (OCH_3), 55.8 (OCH_3), 42.8 (CH_2), 31.6 (CH_2), 27.3 (CH_2), 26.7 (CH_2), 22.6 (CH_2), 14.0 (CH_3). **MS(HR-MALDI$^+$)** m/z calcd. for $[C_{78}H_{88}N_8O_{10}]^+$: 1296.6618, found 1296.6619. **IR (KBr):** ṽ [cm^{-1}] = 2995 (w), 2955 (m), 2930 (m), 2870 (m), 2857 (m), 2835 (m), 1686 (s), 1639 (s), 1603 (s), 1582 (s), 1558 (s), 1541 (s), 1516 (s), 1476 (s), 1414 (s), 1358 (s), 1317 (s), 1294 (s), 1261 (s), 1236 (s), 1188 (s), 1175 (s), 1140 (s), 1097 (m), 1030 (s), 970 (m), 935 (m), 916 (m), 893 (m), 870 (m), 841 (m), 827 (m), 814 (m), 800 (m), 764 (m), 750 (m), 737 (m), 727 (m), 700 (m), 679 (m), 656 (m), 623 (m).

Synthesis of Compound 3



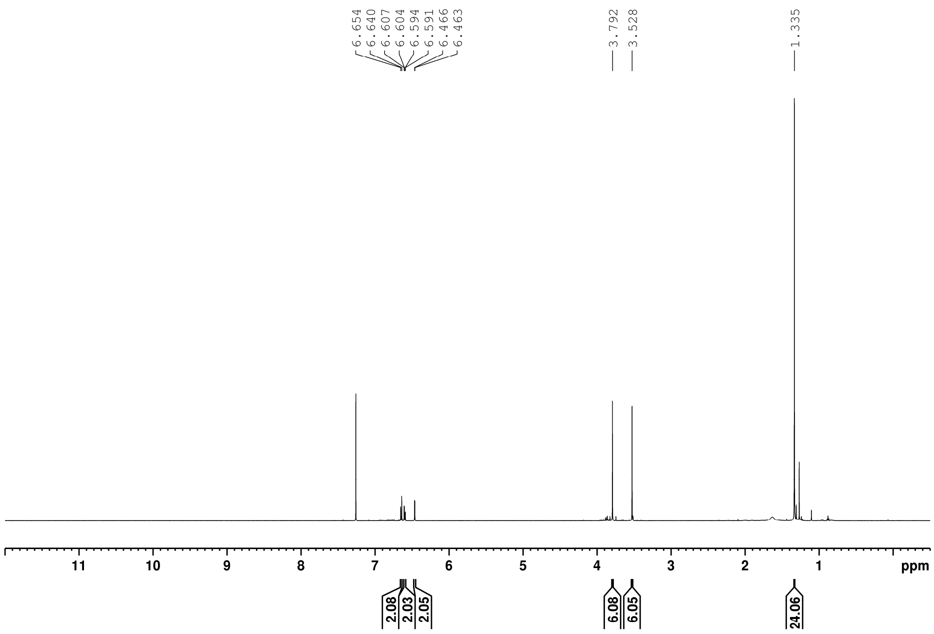
Compound **2f** (10 mg, 7.7 µmol, 1.0 equiv.) was dissolved in dry dichloromethane (1 ml) and cooled to 0 °C. Me_3SO_3H (0.1 ml) was added, and the mixture was stirred for 10 minutes. After addition of DDQ (3.7 mg, 16 µmol, 2.1 equiv.), the mixture was stirred for another 20 minutes at 0 °C, during which the mixture turned deep green. The mixture was neutralized with $NaHCO_3$ (aq.), diluted with dichloromethane and the organic phase was separated. Washing with water and drying over Na_2SO_4 furnished compound **3** as a red-purple solid (9.8 mg, 7.6 µmol, 98%). **^{1}H-NMR ($CDCl_3$, 600.18 MHz, 295 K):** δ [ppm] = 9.98 (s, CH, 4H), 8.02 (s, CH, 4H), 4.87 (t, $^3J_{H\text{-}H}$ = 7.65 Hz, CH_2, 8H), 4.26 (s, OCH_3, 12H), 4.18 (s, OCH_3, 12H), 1.91 (q, $^3J_{H\text{-}H}$ = 7.65 Hz, CH_2, 8H), 1.46 (q, $^3J_{H\text{-}H}$ = 7.57 Hz, CH_2, 8H), 1.31-1.18 (m, CH_2, 24H), (q, $^3J_{H\text{-}H}$ = 7.65 Hz, CH_2, 8H), 0.76 (t, $^3J_{H\text{-}H}$ = 7.31 Hz, CH_3, 12H). **^{13}C-NMR ($CDCl_3$, 150.92 MHz, 295 K):** δ [ppm] = 152.1 (Cq), 150.4 (Cq), 148.3 (Cq), 147.9 (Cq), 142.2 (Cq), 132.6 (Cq), 128.3 (Cq), 126.6 (Cq), 124.4 (Cq), 113.1 (Cq), 111.7 (Cq), 103.8 (Cq), 99.8 (Cq), 56.8 (OCH_3), 56.0 (OCH_3), 42.8 (CH_2), 31.4 (CH_2), 27.3 (CH_2), 26.7 (CH_2), 22.5 (CH_2), 13.9 (CH_3). **MS(HR-MALDI$^+$)** m/z calcd. For $[C_{78}H_{84}N_8O_{10}]^+$: 1292.6305, found 1292.6304. **IR (KBr):** ṽ [cm^{-1}] = 3123 (w), 2997 (w), 2955 (m), 2926 (m), 2872 (m), 2853 (m), 1693 (s), 1639 (s), 1601 (s), 1553 (s), 1522 (s), 1506 (s), 1466 (s), 1422 (s), 1375 (s), 1356 (s), 1335 (s), 1273 (s), 1261 (s), 1207 (s), 1173 (s), 1153 (s), 1125 (s), 1090 (s), 1030 (s), 995 (s), 912 (s), 883 (s), 862 (s), 822 (s), 810 (s), 773 (s), 752 (s), 725 (s), 685 (s), 670 (s), 615 (s).

Characterization of Compounds

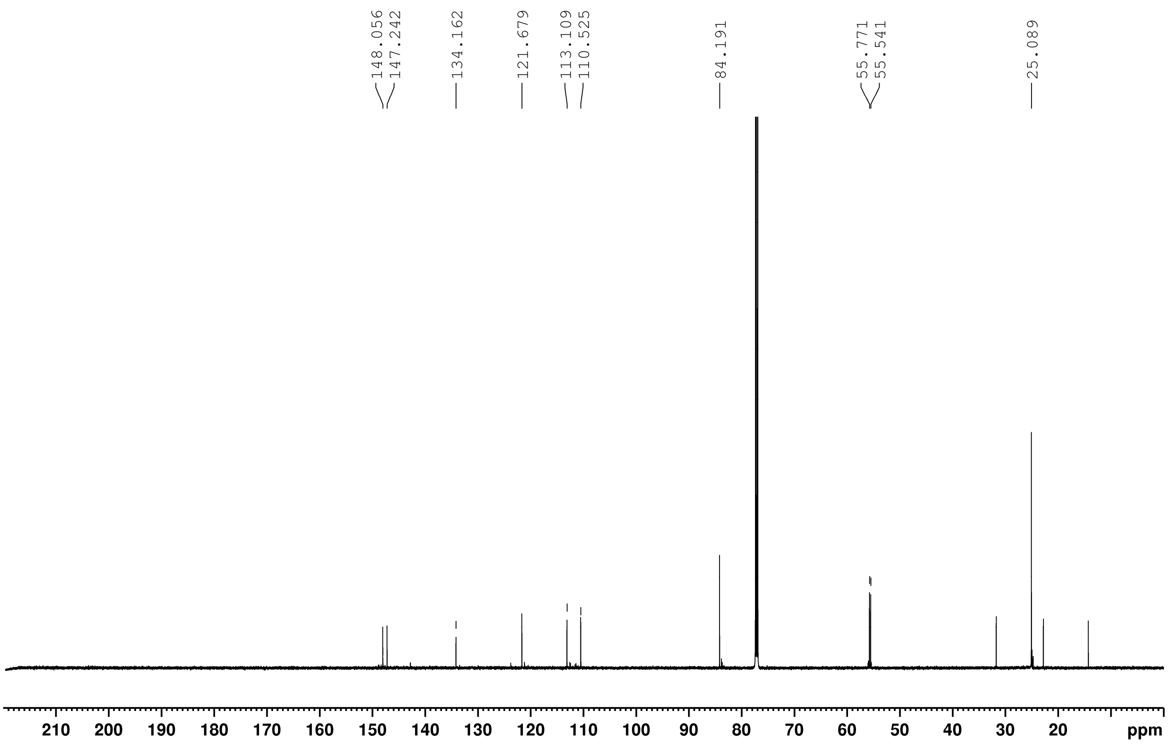
^{1}H- and ^{13}C-spectra

(*Z*)-1,2-bis(3,4-dimethoxyphenyl)-1,2-bis(pinacolboryl)ethene

^{1}H NMR (600.13 MHz, $CDCl_3$, 295 K):

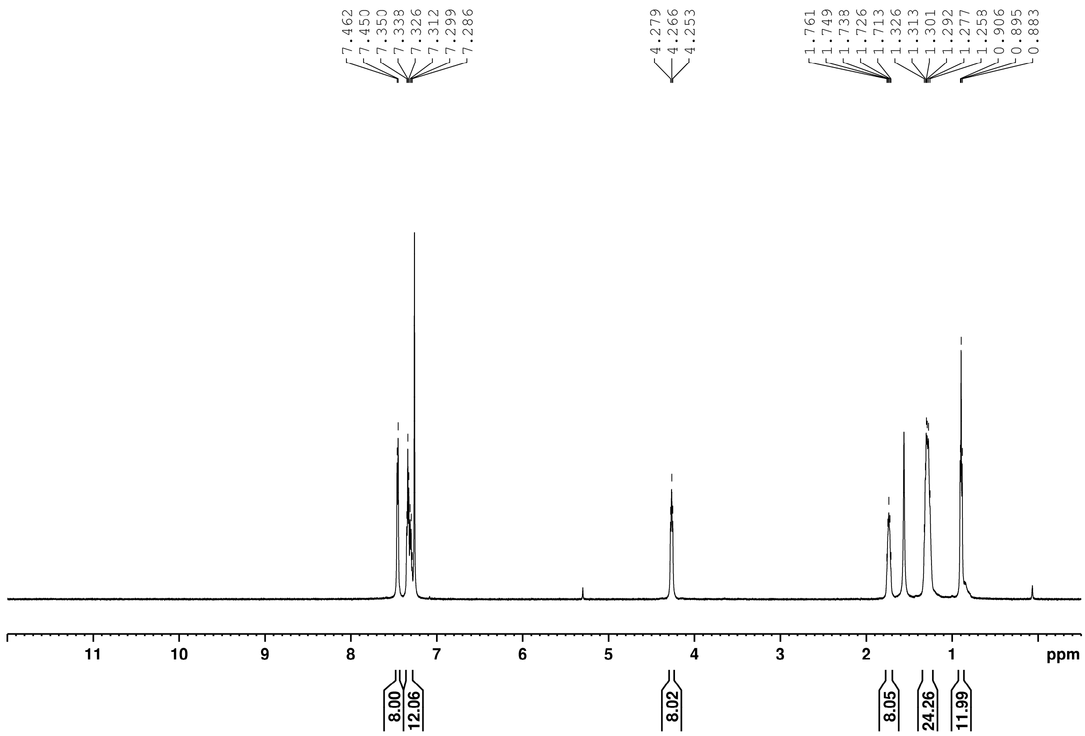


^{13}C NMR (150.90 MHz, $CDCl_3$, 295 K):

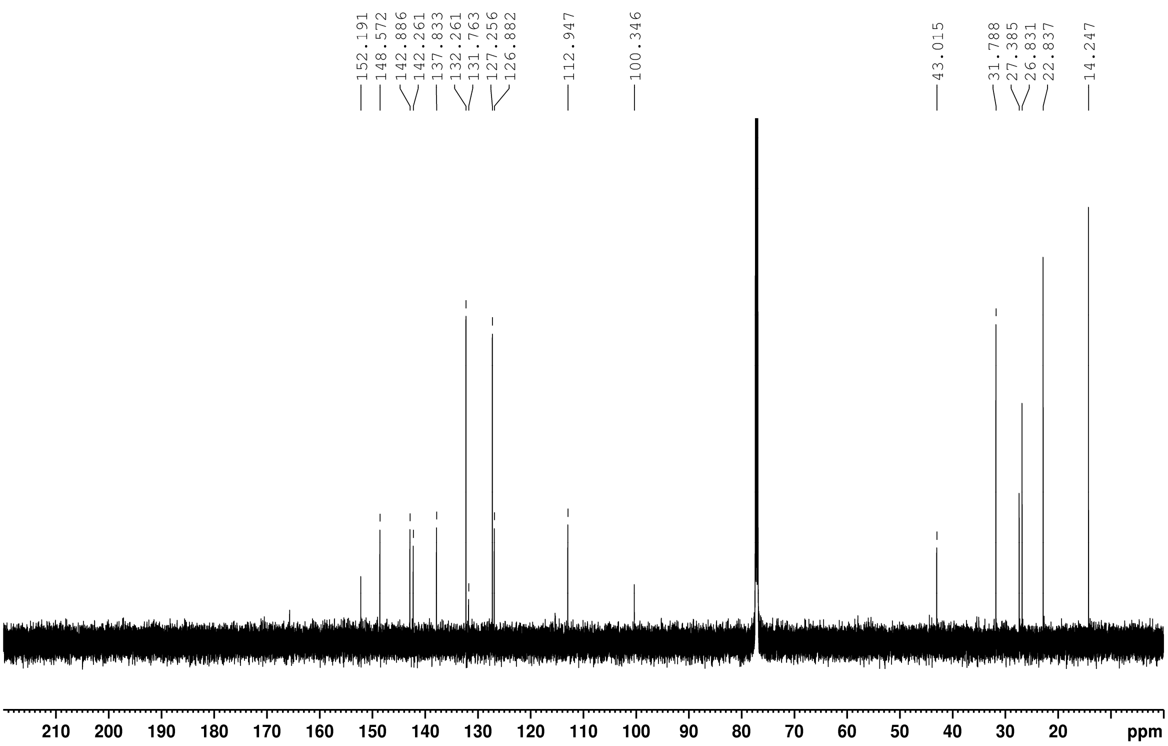


Compound **2a**

^{1}H NMR (600.13 MHz, $CDCl_3$, 295 K):

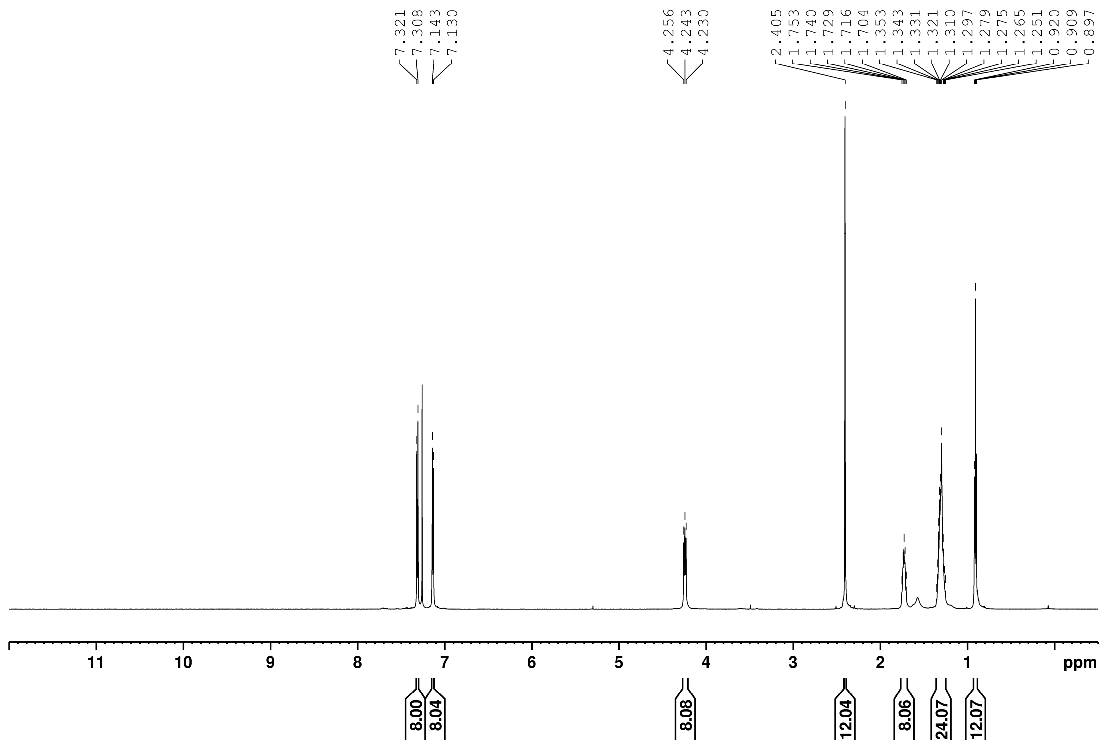


^{13}C NMR (150.90 MHz, $CDCl_3$, 295 K):

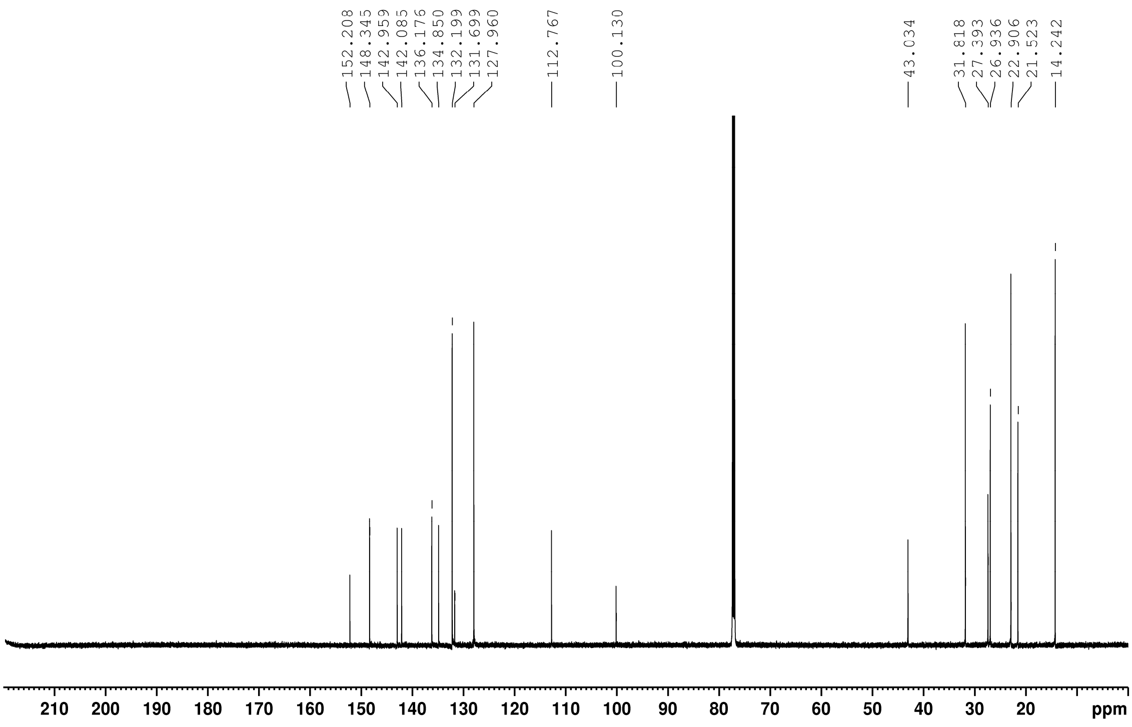


Compound **2b**

^{1}H NMR (600.13 MHz, $CDCl_3$, 295 K):

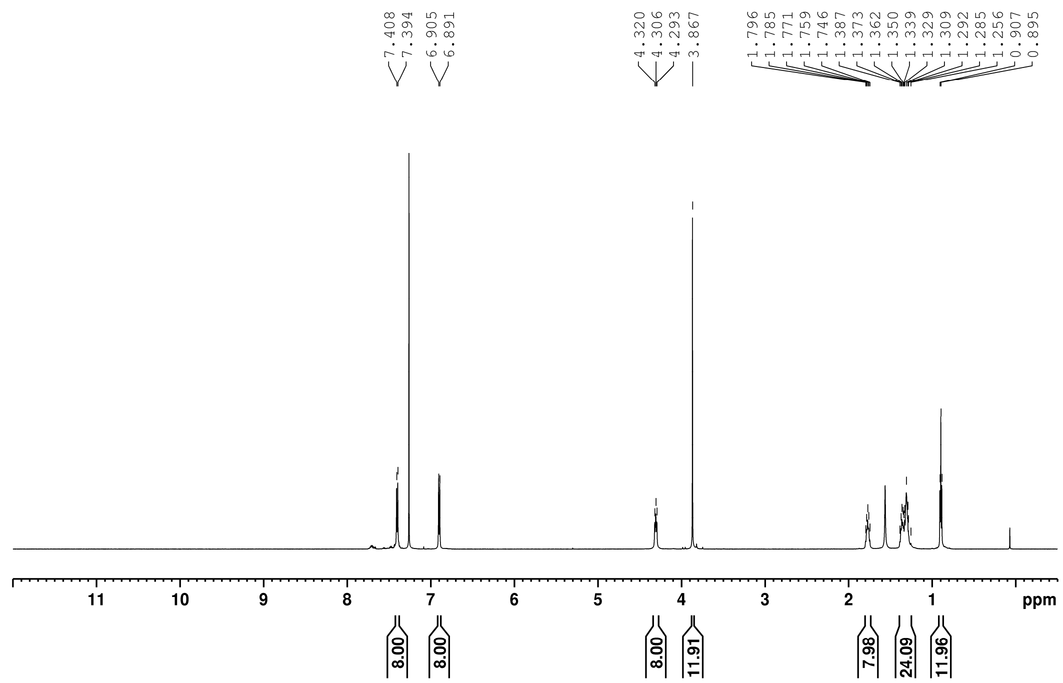


^{13}C NMR (150.90 MHz, $CDCl_3$, 295 K):

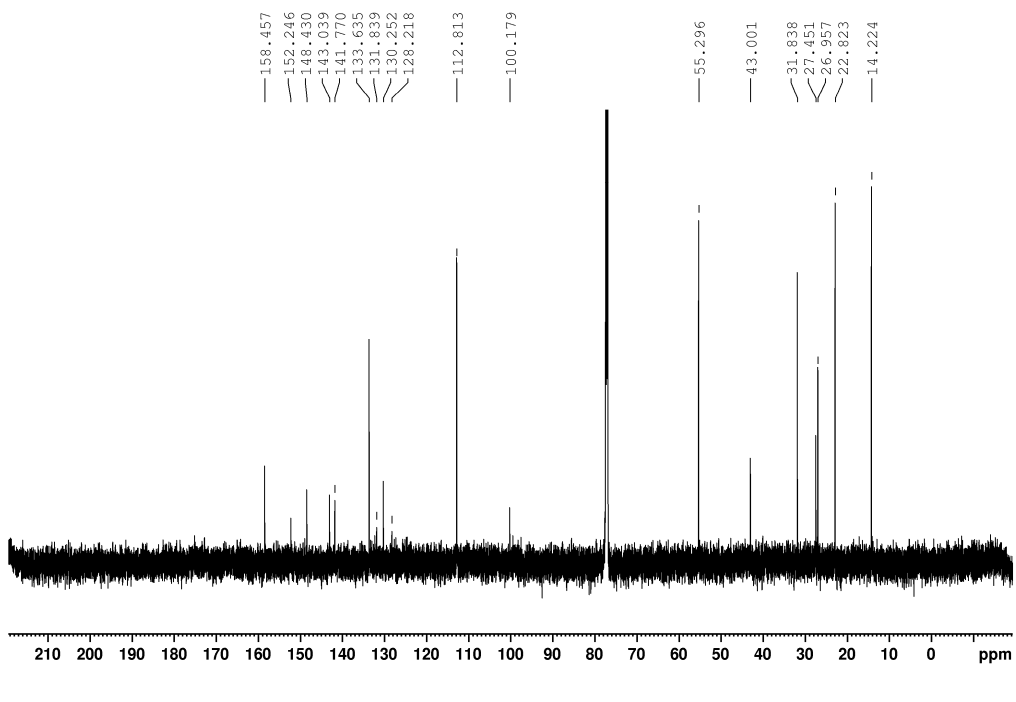


Compound **2c**

^{1}H NMR (600.13 MHz, $CDCl_3$, 295 K):

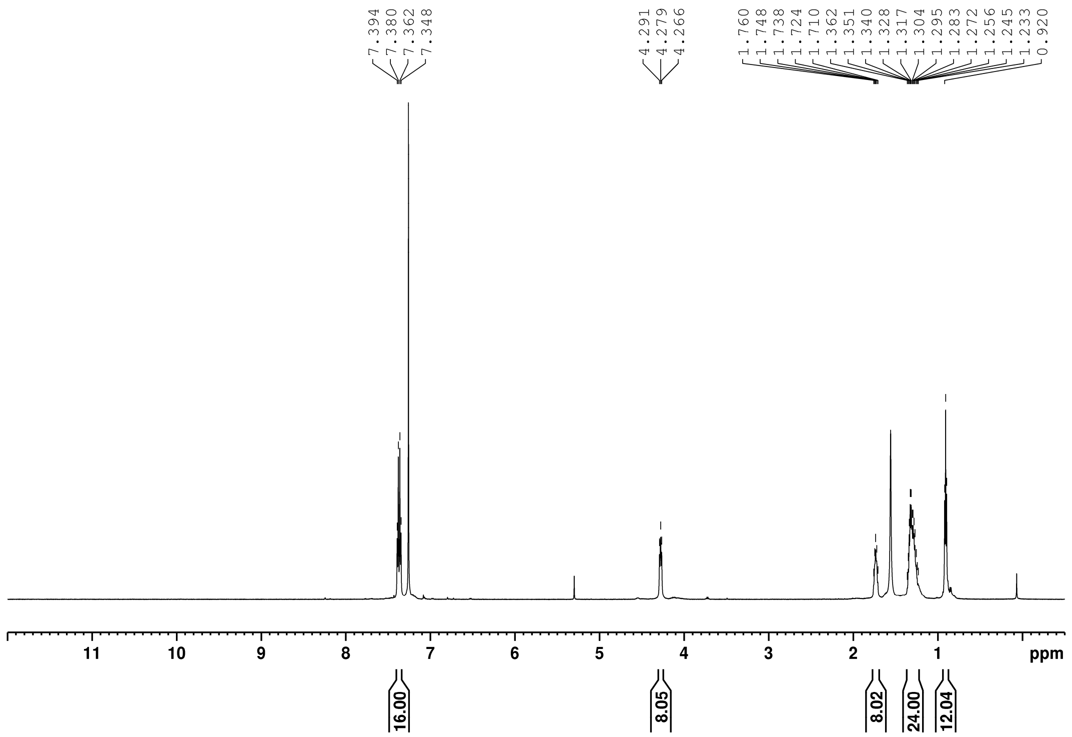


^{13}C NMR (150.90 MHz, $CDCl_3$, 295 K):

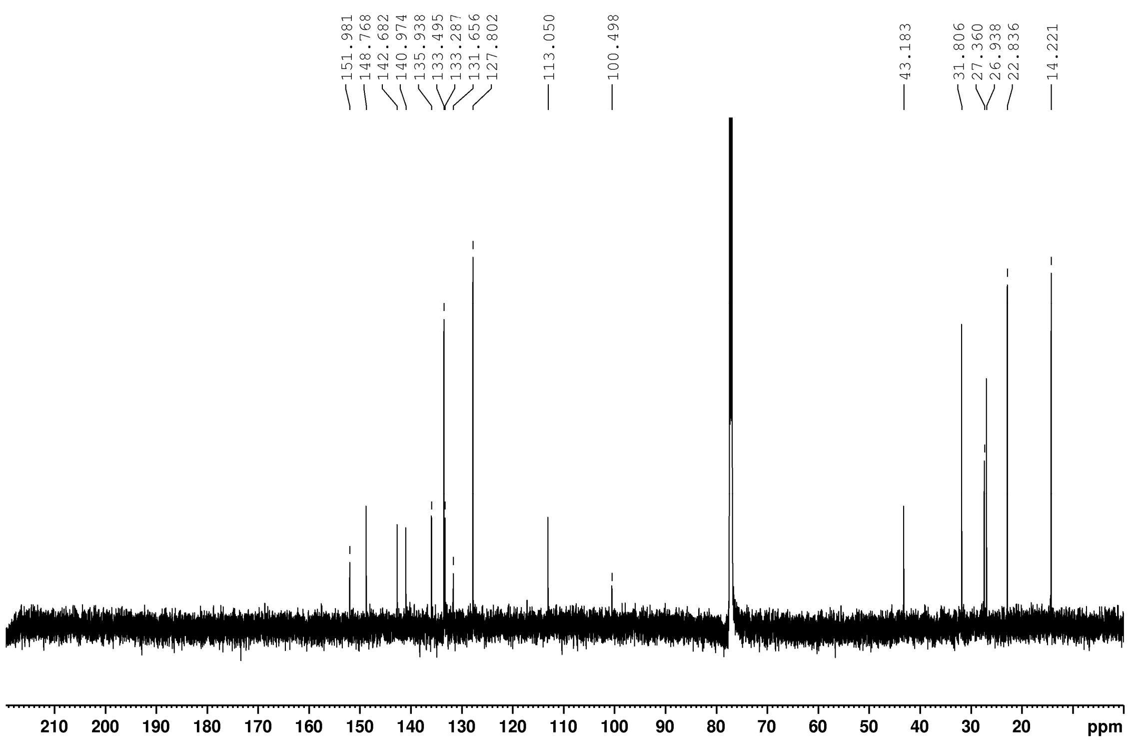


Compound **2d**

^{1}H NMR (600.13 MHz, $CDCl_3$, 295 K):

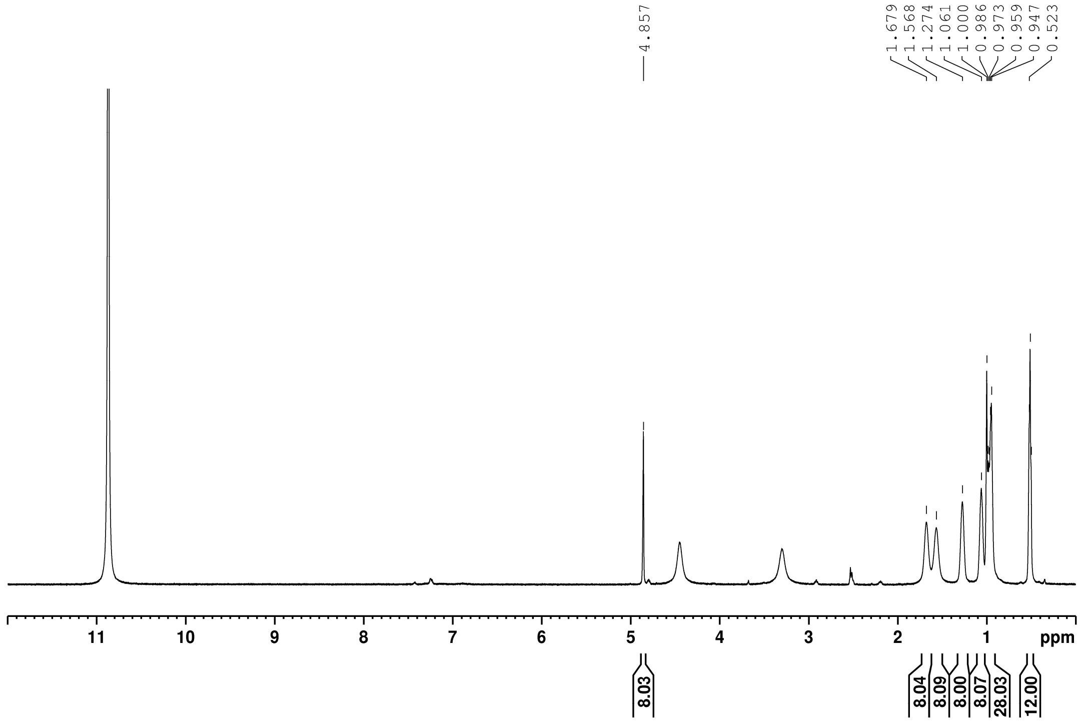


^{13}C NMR (150.90 MHz, $CDCl_3$, 295 K):

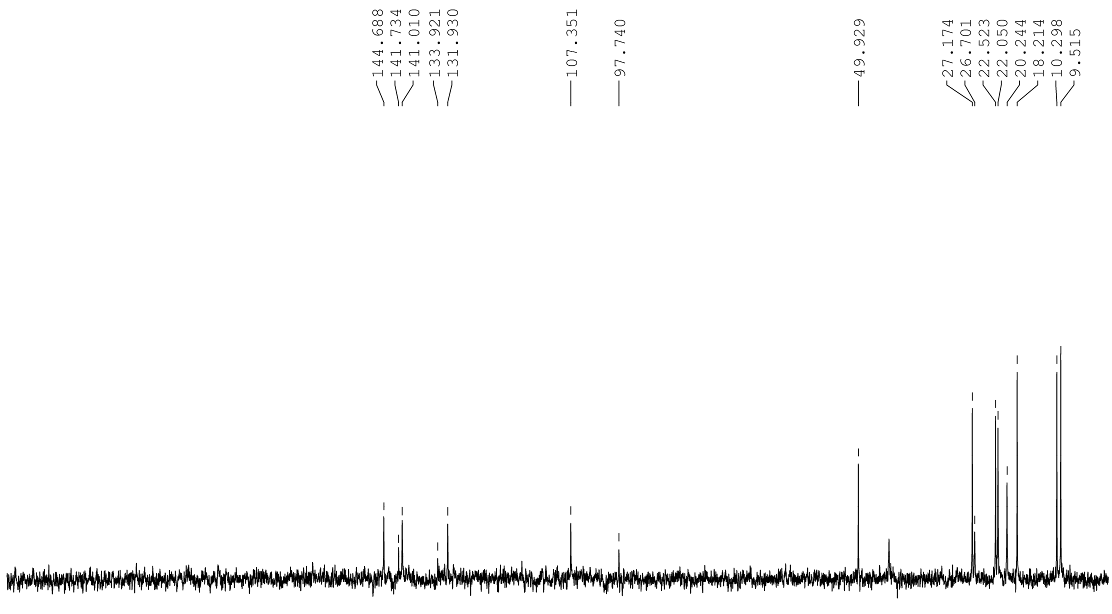


Compound **2e**

^{1}H NMR (600.13 MHz, D_2SO_4, 295 K):

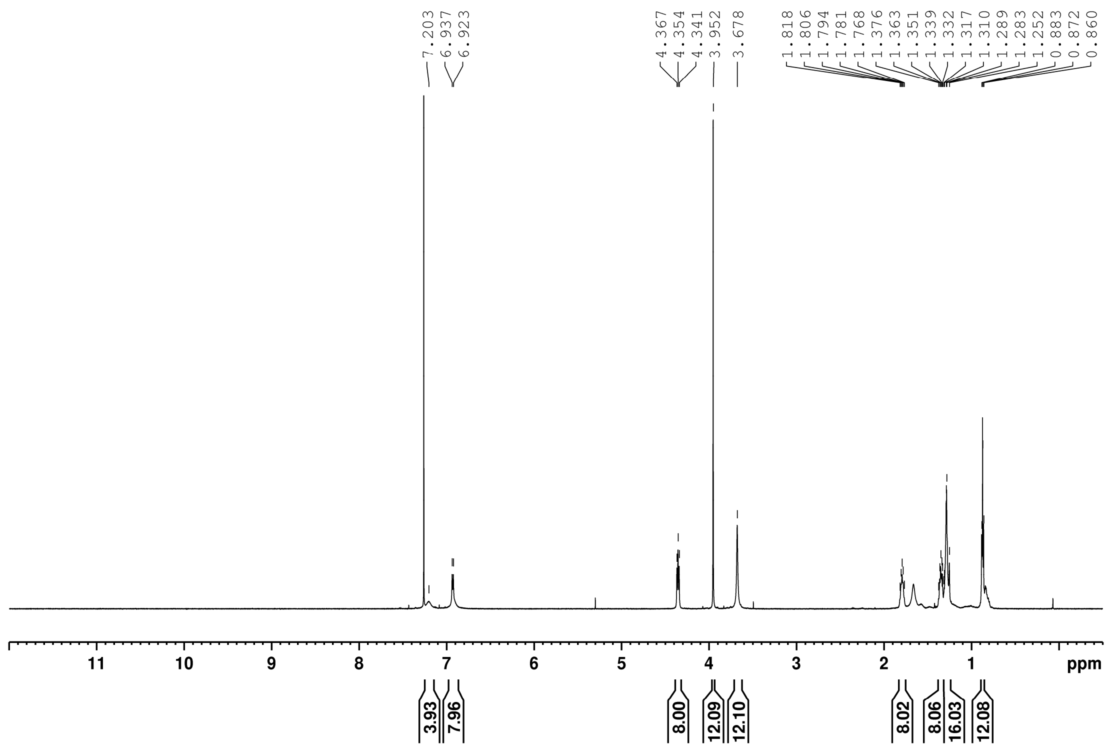


^{13}C NMR (150.90 MHz, D_2SO_4, 295 K):

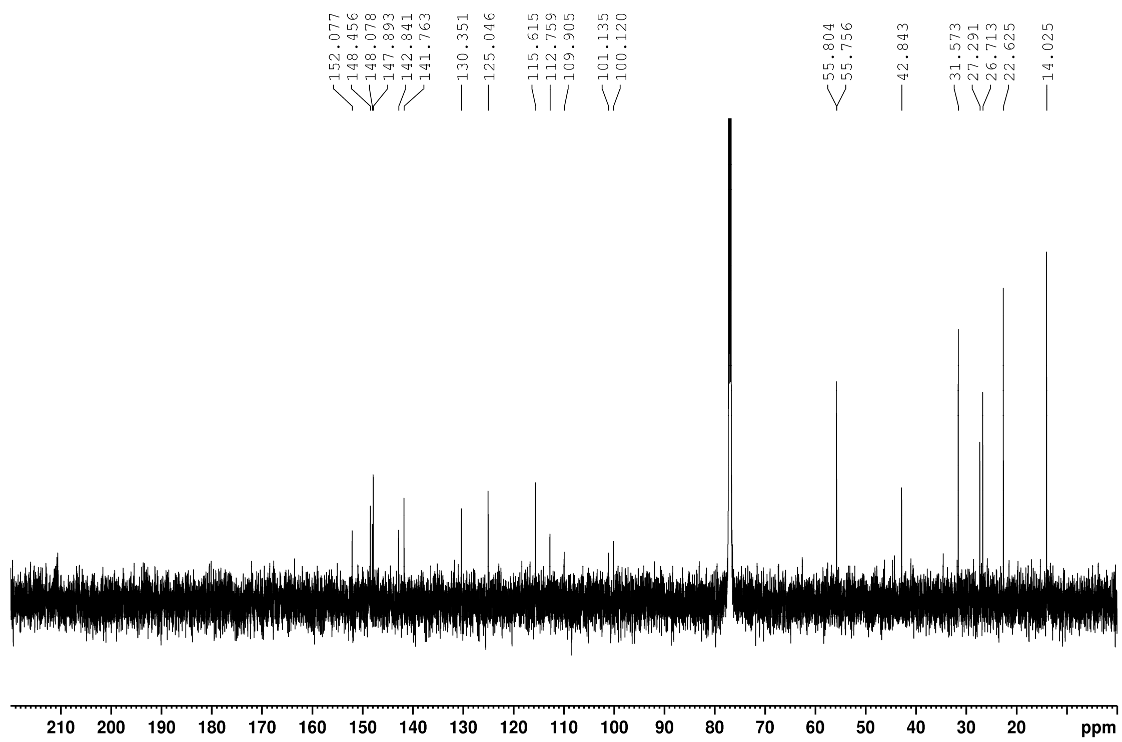


Compound **2f**

^{1}H NMR (600.13 MHz, $CDCl_3$, 295 K):

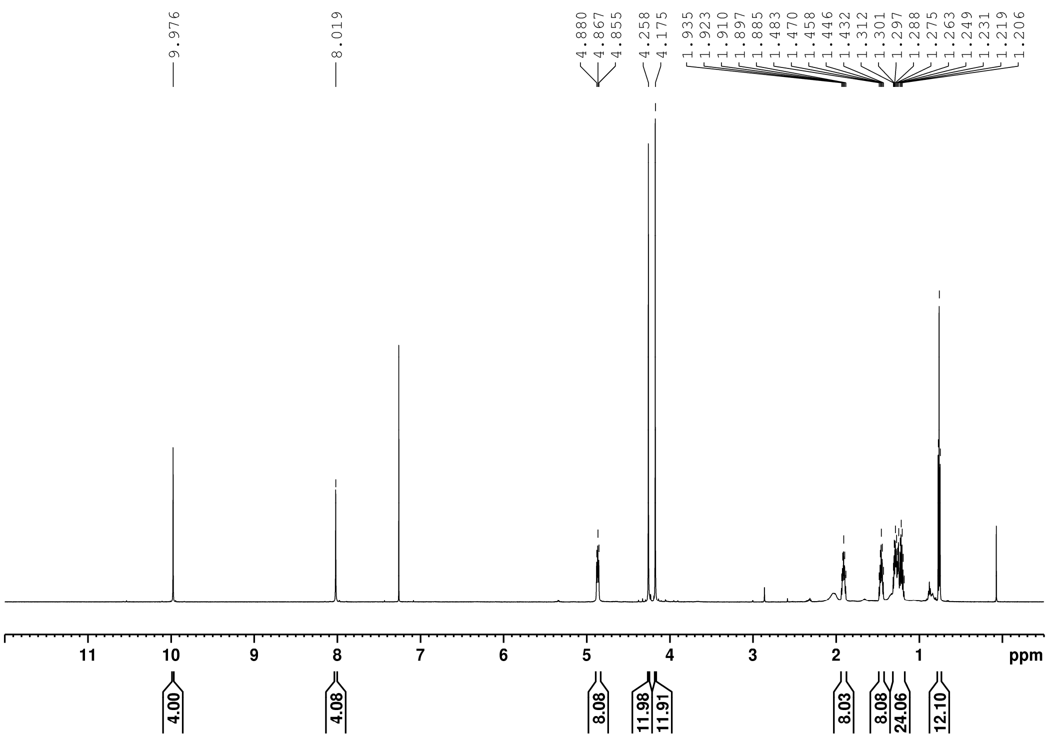


^{13}C NMR (150.90 MHz, $CDCl_3$, 295 K):

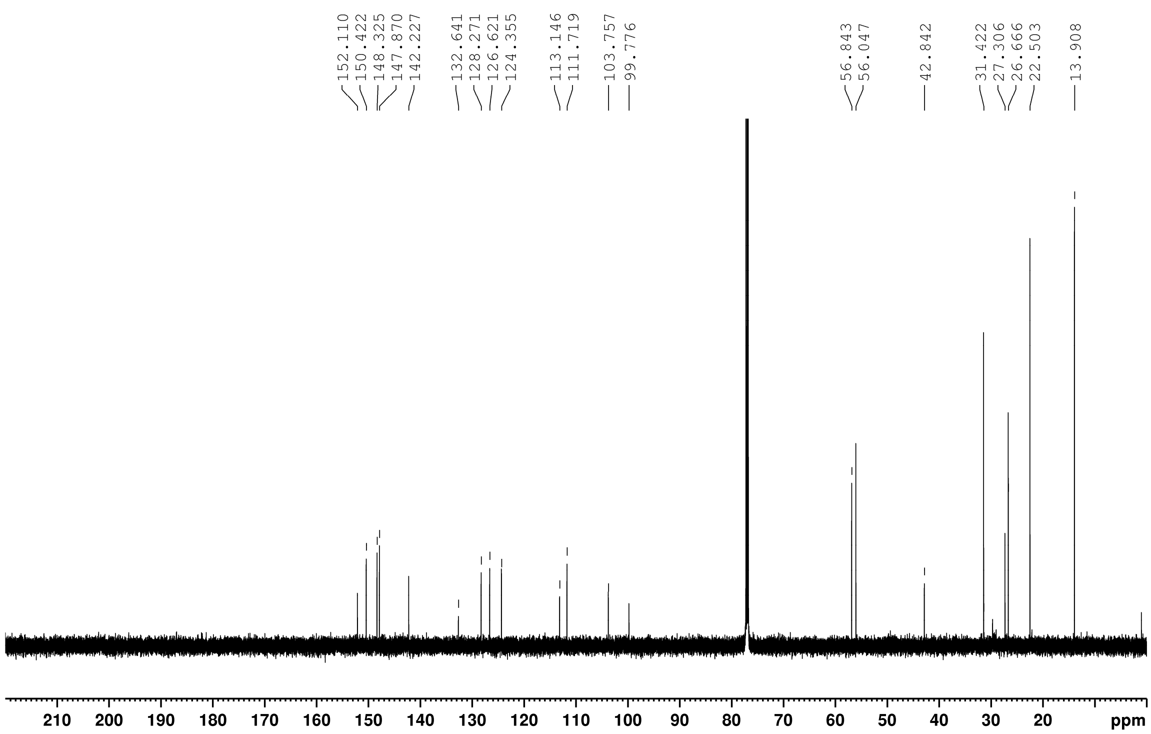


Compound **3**

^{1}H NMR (600.13 MHz, $CDCl_3$, 295 K):

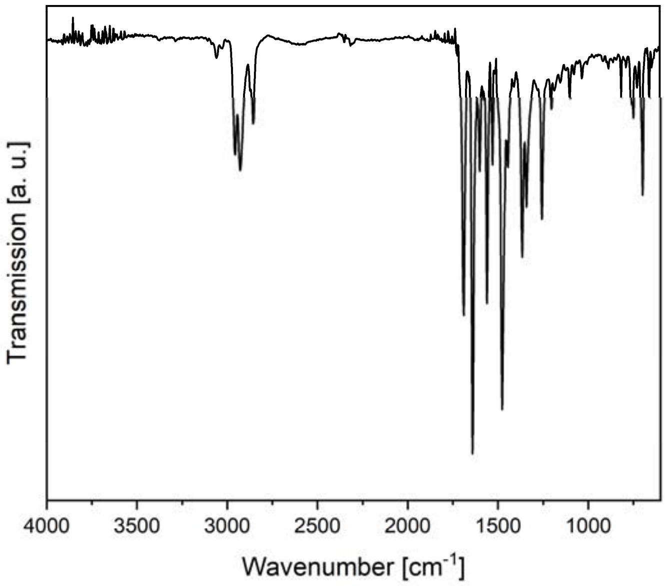


^{13}C NMR (150.90 MHz, $CDCl_3$, 295 K):

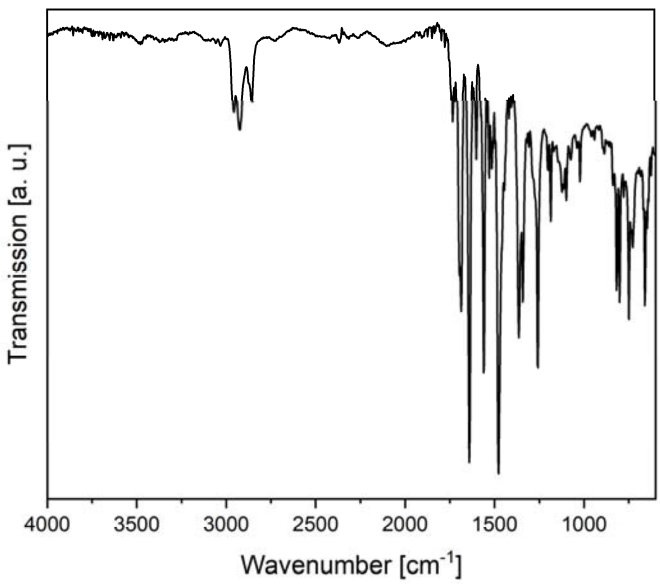


IR Spectra

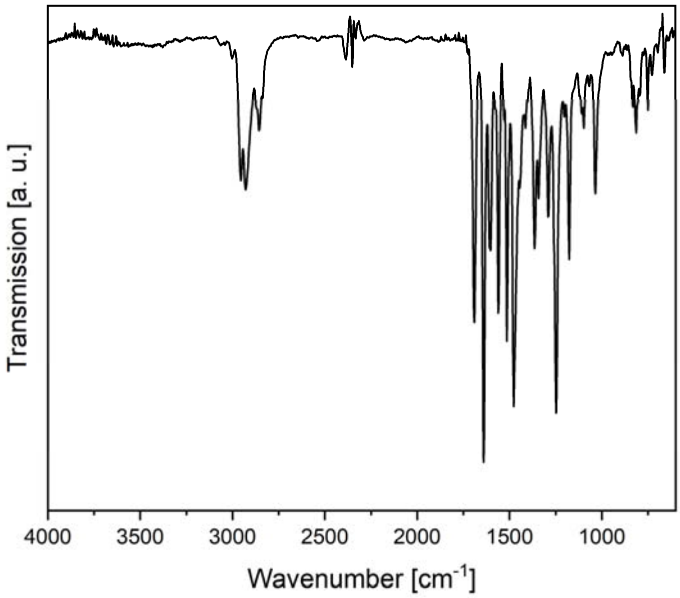
Compound **2a**:



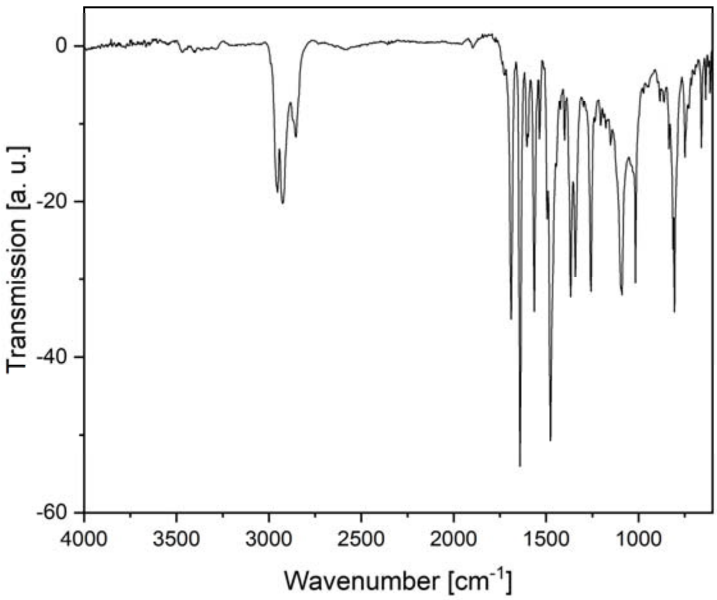
Compound **2b**:



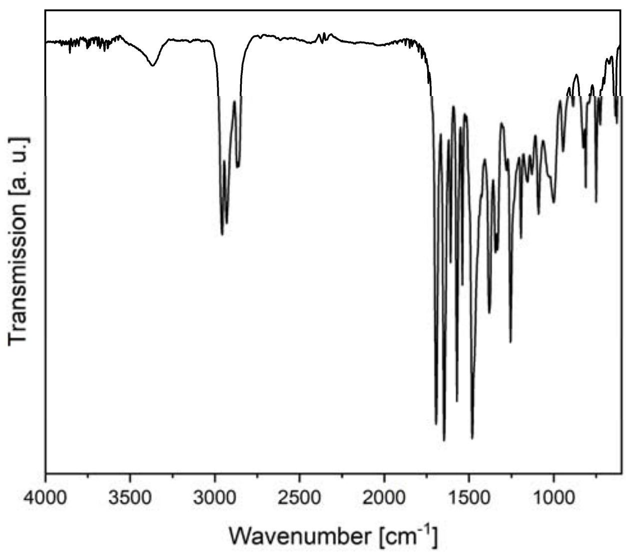
Compound **2c**:



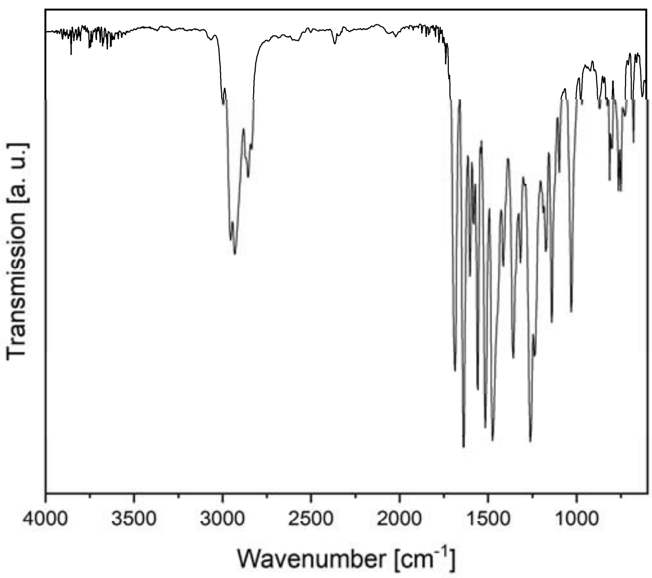
Compound **2d**:



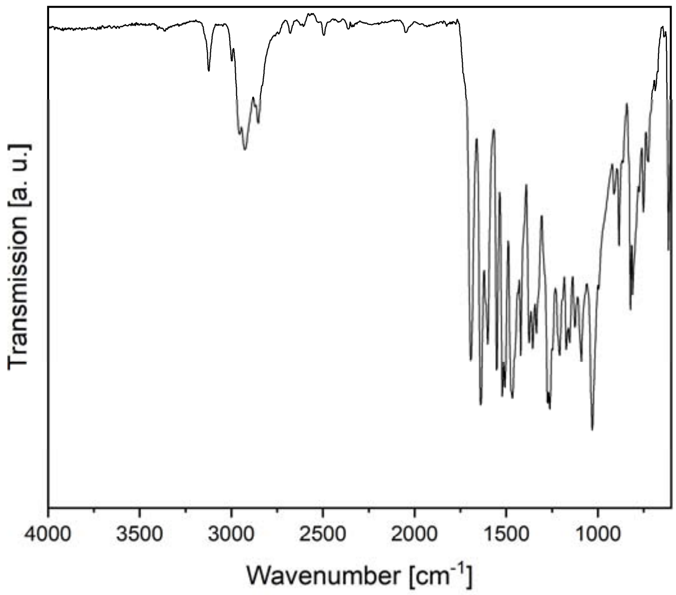
Compound **2e**:



Compound **2f**:



Compound **3**:



Transmission [a. u.]
4000
3500
3000
2500
2000
1500
1000
Wavenumber [cm-1]

Photophysical Properties

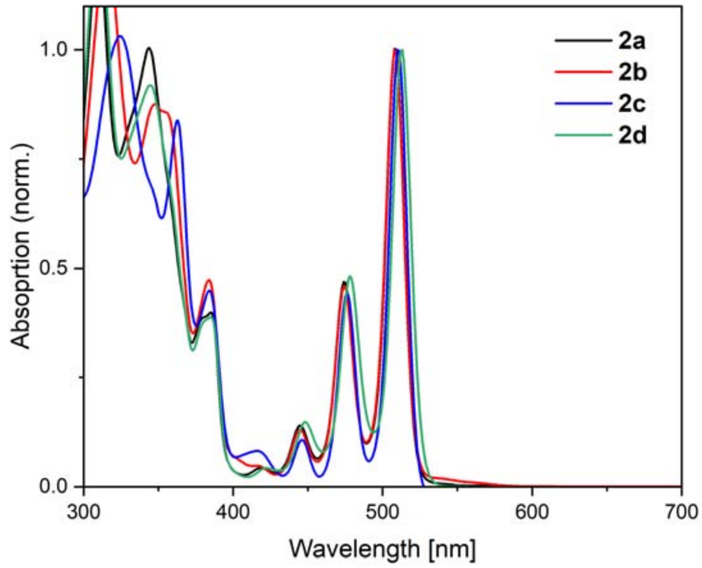


Figure S1: UV/Vis spectra of tetraazacoronenes **2a-2d** (DCM, c ≈ 10^{-5}).

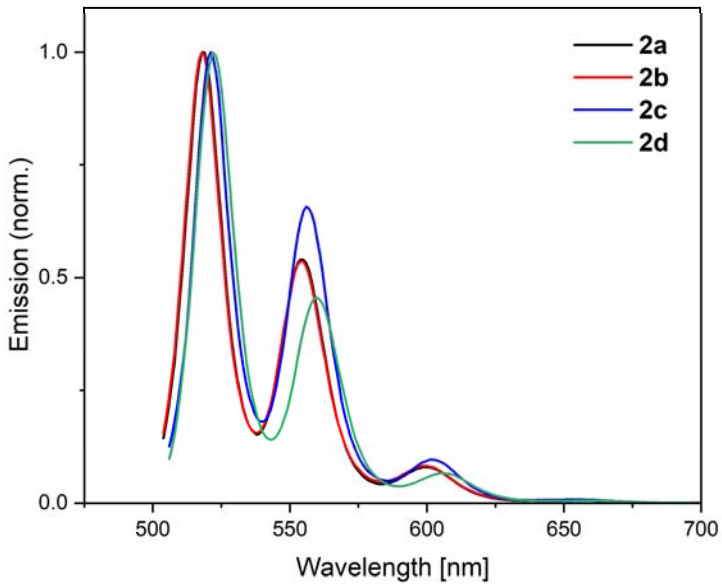


Figure S2: Fluorescence spectra of tetraazacoronenes **2a-2d** (DCM, c ≈ 10^{-5}, excitation wavelength: $\lambda_{abs,max}$ − 5 nm).

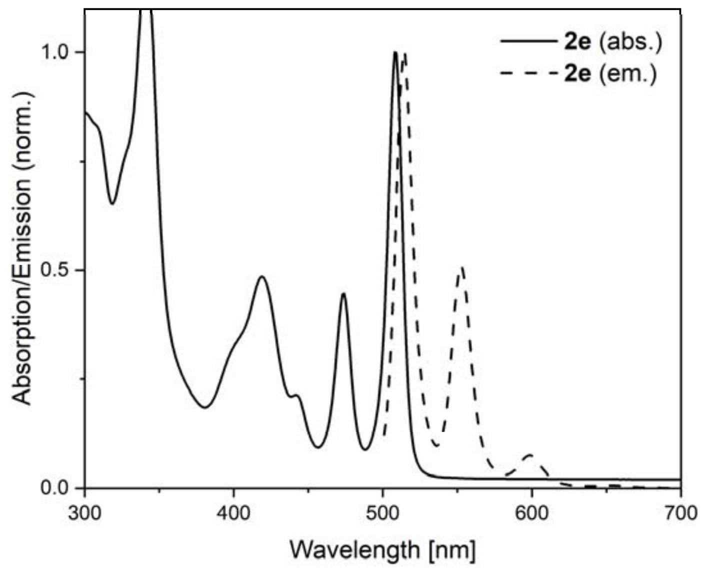


Figure S3: Absorption and emission spectra of tetraazacoronene **2e** (H_2SO_4, c ≈ 10^{-5}, excitation wavelength: $\lambda_{abs,max}$ − 5 nm).

Table S1: Photophysical properties of **2e** (H_2SO_4, c ≈ 10^{-5}, excitation wavelength: $\lambda_{abs,max}$ − 5 nm). Fluorescence quantum yields measured with an Ulbricht sphere (E < 0.1).

	$\lambda_{abs,max}$ [nm]	log ε	Φ [%]	$\lambda_{em,\ max}$ [nm]	Δ_{Stokes} cm^{-1}
2e	508	4.48	19	514	230

Redox Properties

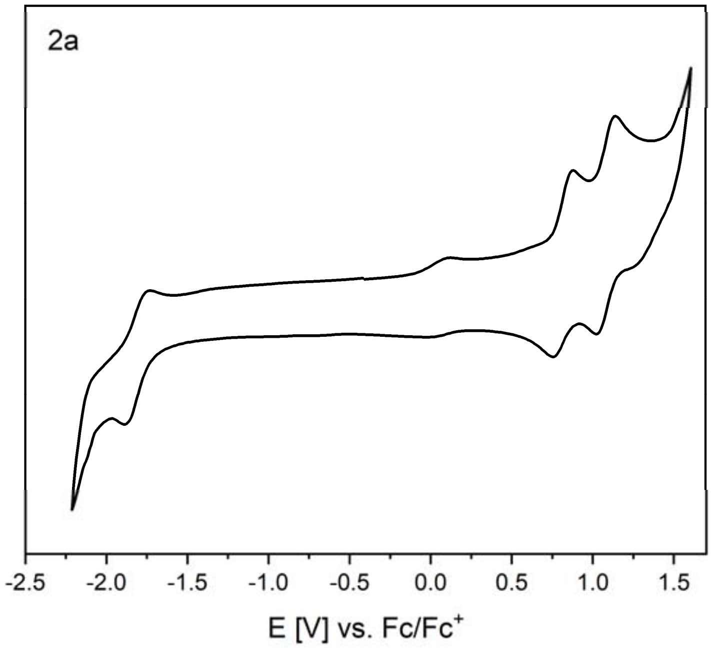


Figure S4: Cyclic voltammogram of tetraazacoronene **2a** (DCM, *n*-Bu_4NPF_6).

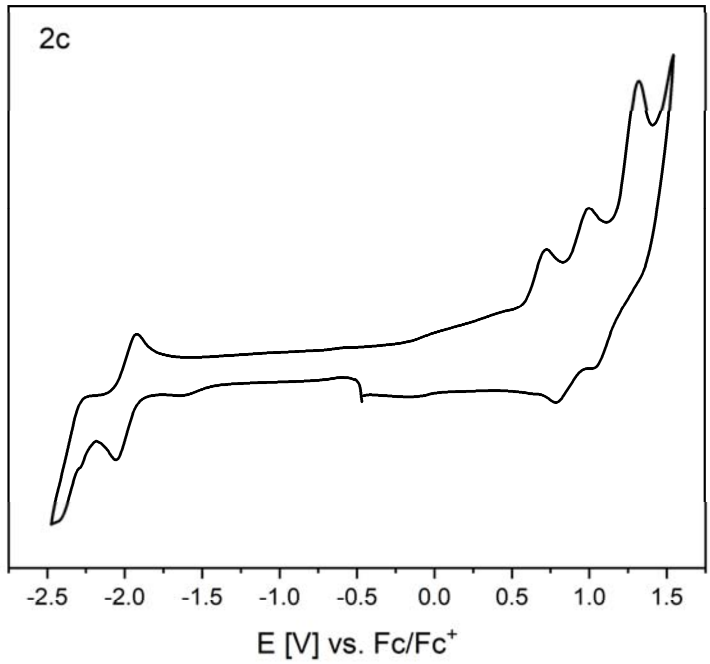


Figure S5: Cyclic voltammogram of tetraazacoronene **2c** (DCM, *n*-Bu_4NPF_6).

Table S2: Redox properties of tetraazacoronenes **2a** and **2c** (DCM, *n*-Bu_4NPF_6). E_{HOMO} and E_{LUMO} were calculated according to: $E_{HOMO} = -(E_{Ox1} + 5.15\ eV)$ or $E_{LUMO} = -(E_{Red1} + 5.15\ eV)$.[9]

	E_{ox1} [V] vs. Fc/Fc$^+$	E_{ox2} [V] vs. Fc/Fc$^+$	E_{Red} [V] vs. Fc/Fc$^+$	E_{HOMO} [eV] vs. Fc/Fc$^+$	E_{LUMO}[eV] vs. Fc/Fc$^+$
2a	0.80	1.06	−1.83	−5.95	−3.32
2c	0.89	1.17	−1.99	−6.04	−3.16

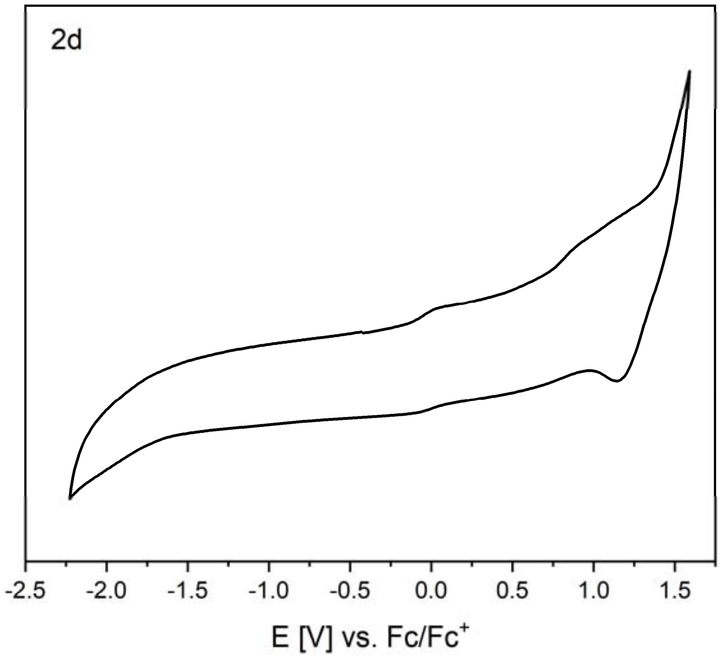


Figure S6: Cyclic voltammogram of tetraazacoronene **2d** (DCM, *n*-Bu_4NPF_6).

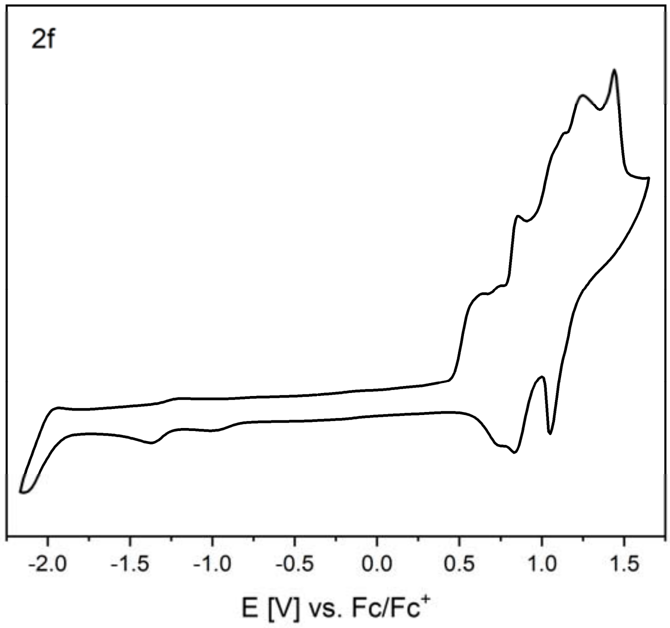


Figure S7: Cyclic voltammogram of tetraazacoronene **2f** (DCM, *n*-Bu_4NPF_6).

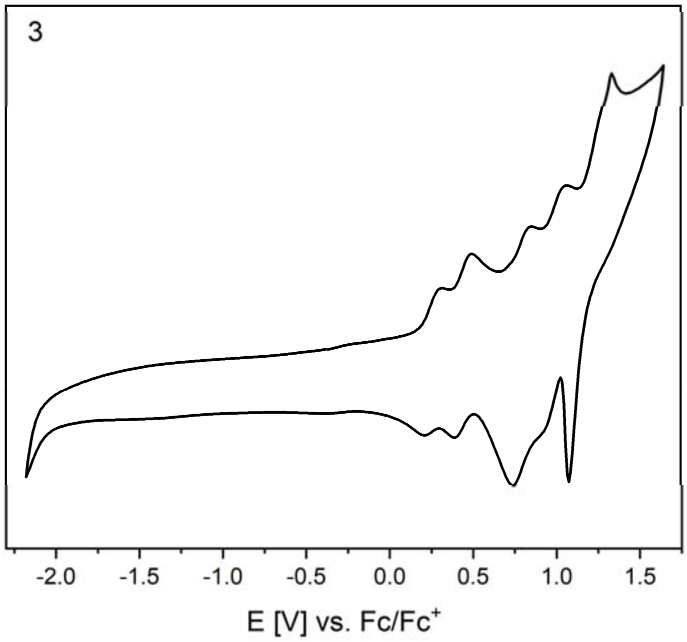


Figure S8: Cyclic voltammogram of **3** (DCM, *n*-Bu_4NPF_6).

Computational Details

All DFT calculations were performed in the gas phase using the Gaussian 16 program suit (G16RevC.01).[10] The B3LYP[11] functional was used to optimize the geometries on the valence triple-ζ basis set Def2-TZVPP.[12] The resulting ground state structures were confirmed as energy minima through frequency calculations showing no negative eigenvalue in the Hessian matrix. Grimme's dispersion correction D3[13] with Becke-Johnson damping[14] were considered in all calculations. TD-DFT calculations for molecular properties on the excited state (singlet excitations) were performed at the triple-ζ level of theory (Def2-TZVPP) with B3LYP using 10 roots, or at the 6-31G*[15] level of theory using 30 roots. For the calculations of **3**, the *meso* conformer was considered. The simulated UV/Vis spectra and the molecular structures were depicted using ChemCraft (v1.8).[16] Anisotropy of the induced current density (ACID) plots were calculated according to R. Herges (B3LYP/6-311G** level of theory).[17,18] Only occupied π-orbitals, analyzed and determined using the Multiwfn 3.6 software,[19,20] were considered.

Optimized Coordinates

xyz-coordinates for **2a**:

atom	x	y	z
N	2.409229	2.810486	-0.027121
C	1.247516	3.426934	-0.03674
C	2.428391	1.440531	-0.002603
C	1.236403	0.701104	-0.00056
C	-0.000001	1.379104	-0.0065
C	-0.000001	2.759826	-0.022581
C	-1.247518	3.426935	-0.036771
C	-1.236405	0.701103	-0.000561
C	-2.428393	1.440531	-0.002606
N	-2.40923	2.810485	-0.02713
N	1.198029	4.810006	-0.064413
N	-1.198027	4.810006	-0.064533
C	0.000001	5.534682	-0.074016
O	-0.000001	6.748785	-0.091295
C	-1.236405	-0.701104	0.000477
C	-0.000001	-1.379104	0.006411
C	1.236402	-0.701104	0.000473
C	2.428391	-1.440531	0.002548
C	-0.000001	-2.759825	0.022509
N	2.409229	-2.810485	0.027092
C	-1.247518	-3.426934	0.036726
C	-2.428394	-1.440531	0.00256
N	-2.40923	-2.810485	0.02711
C	1.247515	-3.426934	0.036702

N	1.198028	-4.810005	0.064416
N	-1.198028	-4.810005	0.064492
C	0	-5.534681	0.074048
O	-0.000001	-6.748781	0.091492
C	-2.459721	5.548874	-0.080869
C	2.459732	5.548862	-0.080666
C	-2.459726	-5.548865	0.08089
C	2.459731	-5.548858	0.080759
H	3.02654	-5.329611	-0.822131
H	2.228388	-6.604457	0.138275
H	3.054848	-5.234603	0.93528
H	-3.055083	-5.23408	0.935043
H	-2.228389	-6.604428	0.139089
H	-3.026285	-5.330194	-0.822304
H	3.026467	5.329647	0.822279
H	2.228391	6.604459	-0.138231
H	3.054919	5.23458	-0.935127
H	-3.055336	5.233665	-0.934679
H	-2.228392	6.604408	-0.139631
H	-3.02601	5.330667	0.822612
C	-3.660739	0.699495	-0.004125
C	-3.660738	-0.699495	0.0041
C	3.660735	-0.699495	0.004087
C	3.660735	0.699494	-0.004124
C	5.253102	2.375229	0.956066
C	6.450688	3.075391	0.921864
C	4.934671	1.462124	-0.049379
H	6.688425	3.771129	1.715502
C	7.341228	2.886032	-0.128974
C	5.832265	1.282483	-1.101542
H	8.273678	3.433441	-0.15716
H	5.595698	0.578415	-1.886533
C	7.02514	1.990715	-1.14362
H	7.709563	1.839172	-1.96733
H	4.559387	2.530464	1.769819
C	-6.450686	3.075445	0.921753
C	-5.253102	2.375281	0.955992
C	-7.341225	2.886039	-0.129076
H	-4.559386	2.530558	1.769735
H	-8.273674	3.433449	-0.15729
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C	-7.025139	1.990672	-1.143679
H	-7.70956	1.839092	-1.967384
C	-5.832267	1.282439	-1.101566
H	-5.5957	0.578333	-1.886522
H	-6.68842	3.771223	1.715358
C	-5.832246	-1.282445	1.10158
C	-4.934671	-1.462126	0.049406
C	-7.025116	-1.99068	1.143713

H	-7.709522	-1.839105	1.967431
C	-5.253118	-2.375276	-0.955993
C	-7.34122	-2.886042	0.129112
H	-4.559418	-2.530545	-1.769752
H	-8.273667	-3.433454	0.15734
C	-6.450701	-3.075442	-0.921736
H	-6.68845	-3.771216	-1.715339
H	-5.595666	-0.578342	1.886536
C	5.832244	-1.282485	1.101546
C	7.025117	-1.990719	1.143647
C	4.934669	-1.462125	0.049366
H	7.709525	-1.839177	1.96737
C	7.341222	-2.886038	0.129007
C	5.253118	-2.375231	-0.956073
H	8.273671	-3.433448	0.157211
H	4.559417	-2.530465	-1.769838
C	6.450702	-3.075396	-0.921847
H	6.688452	-3.771134	-1.715481
H	5.595663	-0.578416	1.886531

xyz-coordinates for **2f**:

atom	x	y	z
N	-2.401952	2.806169	-0.107329
C	-1.241169	3.424528	-0.117038
C	-2.416384	1.435548	-0.106382
C	-1.222506	0.698069	-0.104707
C	0.012175	1.378775	-0.117932
C	0.007783	2.759962	-0.126469
C	1.253511	3.429843	-0.128836
C	1.250371	0.704008	-0.116342
C	2.441059	1.446321	-0.132683
N	2.416707	2.816834	-0.131328
N	-1.194313	4.808328	-0.114521
N	1.201063	4.813682	-0.125097
C	0.001983	5.535652	-0.121478
O	-0.000909	6.750161	-0.123335
C	1.253649	-0.698068	-0.088937
C	0.018693	-1.378868	-0.076383
C	-1.219576	-0.704142	-0.078776
C	-2.409964	-1.447277	-0.062565
C	0.021254	-2.75996	-0.064639
N	-2.388159	-2.817695	-0.058467
C	1.270211	-3.423923	-0.069339
C	2.447856	-1.434532	-0.07855
N	2.430378	-2.805251	-0.074059
C	-1.224576	-3.430398	-0.060408
N	-1.171161	-4.814223	-0.060006
N	1.224091	-4.808094	-0.069959

C	0.028359	-5.535648	-0.056182
O	0.031611	-6.750159	-0.042697
C	2.461107	5.555095	-0.129228
C	-2.457161	5.544748	-0.104967
C	2.487094	-5.544067	-0.078188
C	-2.430482	-5.556679	-0.058083
H	-2.988424	-5.33487	0.849969
H	-2.196677	-6.611964	-0.111894
H	-3.035271	-5.248205	-0.907755
H	3.086772	-5.226322	-0.927996
H	2.258493	-6.600162	-0.1383
H	3.04783	-5.326267	0.829202
H	-3.030008	5.304424	-0.998627
H	-2.227565	6.60181	-0.072381
H	-3.045317	5.248484	0.760862
H	3.05948	5.261833	0.73058
H	2.227775	6.611291	-0.095109
H	3.025795	5.316088	-1.028352
C	3.675789	0.710387	-0.121378
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C	-3.642221	-0.709701	-0.074095
C	-3.643677	0.691925	-0.080007
C	-5.304613	2.304239	-1.05152
C	-6.552493	2.910763	-1.037032
C	-4.929373	1.434004	-0.030167
H	-6.8591	3.574311	-1.833878
C	-7.447509	2.668137	-0.001719
C	-5.820068	1.213748	1.018746
H	-5.56767	0.537635	1.822363
C	-7.070616	1.808189	1.037228
H	-4.624377	2.493901	-1.868764
C	6.484464	3.00247	-1.17253
C	5.245084	2.376253	-1.134798
C	7.450552	2.737439	-0.214992
H	4.513893	2.58131	-1.901738
C	4.9527	1.469738	-0.121969
C	7.162413	1.824769	0.815536
C	5.912832	1.223678	0.862114
H	5.690985	0.506545	1.634663
H	6.734292	3.69528	-1.964183
C	5.923857	-1.20681	-1.085665
C	4.959193	-1.444688	-0.103647
C	7.166092	-1.807719	-1.041553
C	5.264715	-2.34604	0.909325
C	7.475244	-2.699539	0.001685
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C	6.508938	-2.965845	0.968222
H	6.716311	-3.654482	1.772877
H	5.731026	-0.513628	-1.8911

C	-5.845703	-1.226189	-1.129556
C	-7.091467	-1.82105	-1.130414
C	-4.926136	-1.453253	-0.103153
C	-7.454627	-2.683076	-0.0804
C	-5.279441	-2.333905	0.911254
H	-4.581599	-2.538253	1.709901
C	-6.532223	-2.938438	0.930888
H	-6.781851	-3.605303	1.741701
H	-5.609106	-0.555064	-1.942015
O	8.689001	3.305656	-0.348637
O	-8.69848	3.228308	-0.05455
O	-8.706255	-3.210125	-0.13833
O	8.720783	-3.241517	-0.017537
C	-8.978243	4.198033	0.959075
H	-9.996149	4.53722	0.78349
H	-8.292562	5.044515	0.871681
H	-8.897467	3.762584	1.954628
C	-9.101477	-4.106414	0.884796
H	-10.115889	-4.410018	0.641995
H	-9.09177	-3.62272	1.86521
H	-8.455917	-4.987673	0.912247
C	9.074323	4.217802	0.6804
H	10.052081	4.599575	0.396919
H	9.139483	3.721037	1.647633
H	8.363868	5.046752	0.739006
C	9.062363	-4.168531	0.996896
H	10.081266	-4.481155	0.78664
H	8.403895	-5.040477	0.976922
H	9.021133	-3.709538	1.98845
O	8.077554	-1.544741	-2.028782
O	-7.947942	-1.587093	-2.174436
O	-7.924051	1.541965	2.082827
O	8.167995	1.555732	1.694001
C	7.97986	0.488572	2.61013
H	8.921457	0.38334	3.142118
H	7.744314	-0.441528	2.0881
H	7.184563	0.711432	3.325925
C	9.10762	-0.626794	-1.649587
H	9.744009	-0.502631	-2.522045
H	9.697313	-1.022176	-0.821126
H	8.679236	0.337555	-1.368531
C	-8.997131	-0.661565	-1.887338
H	-9.6417	-1.035053	-1.089993
H	-9.575023	-0.558299	-2.802393
H	-8.585197	0.309734	-1.602895
C	-8.952391	0.600894	1.765162
H	-9.544612	0.474733	2.668422
H	-8.515175	-0.357093	1.474086
H	-9.586045	0.972089	0.957971

xyz-coordinates for **3**^{meso}:

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C	1.149297	3.400928	0.615605
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C	1.196715	0.732325	0.070149
C	-0.056212	1.373759	0.196296
C	-0.079752	2.730362	0.463903
C	-1.330975	3.366915	0.578111
C	-1.286067	0.696573	0.041973
C	-2.489631	1.413155	0.112555
N	-2.476146	2.750644	0.405818
N	1.081814	4.749706	0.926339
N	-1.309911	4.71772	0.886966
C	-0.126212	5.443353	1.056833
O	-0.145984	6.631701	1.307514
C	-1.263907	-0.683421	-0.223192
C	-0.012402	-1.322667	-0.361523
C	1.218598	-0.646019	-0.201768
C	2.424085	-1.357707	-0.290682
C	0.008174	-2.673422	-0.662961
N	2.407135	-2.687634	-0.617463
C	-1.223766	-3.336969	-0.840611
C	-2.445903	-1.433367	-0.320218
N	-2.389298	-2.761896	-0.655389
C	1.262734	-3.300494	-0.802822
N	1.249687	-4.641573	-1.151323
N	-1.140577	-4.664607	-1.242933
C	0.068574	-5.349239	-1.380814
O	0.075675	-6.523813	-1.692643
C	-2.58185	5.429254	0.999682
C	2.329294	5.495782	1.08074
C	-2.347521	-5.429617	-1.544423
C	2.521901	-5.348735	-1.278542
H	3.178202	-4.793586	-1.944516
H	2.316703	-6.336324	-1.671719
H	3.007473	-5.426852	-0.306443
H	-2.526387	-6.179319	-0.77482
H	-2.22223	-5.942227	-2.493697
H	-3.176577	-4.733455	-1.588497
H	2.987223	4.955757	1.75687
H	2.087605	6.475487	1.472417
H	2.832316	5.594137	0.119134
H	-3.058684	5.506149	0.022957
H	-2.379212	6.417984	1.390791
H	-3.24418	4.87544	1.660175
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C	-3.704025	-0.742635	-0.107151
C	3.661894	-0.631441	-0.071434
C	3.641846	0.790951	-0.011254
C	4.940231	2.902215	-0.451135
C	6.11039	3.577666	-0.675575
C	4.895968	1.519291	-0.163777
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C	6.128615	0.830743	-0.130603
C	7.32598	1.531643	-0.369101
H	4.031325	3.466657	-0.513759
C	-6.262688	3.359874	-0.902965
C	-5.076533	2.734415	-0.62463
C	-7.46947	2.625973	-0.863265
H	-4.184374	3.325544	-0.6905
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C	-7.42018	1.287158	-0.53947
C	-6.20641	0.637938	-0.244674
C	-6.179833	-0.764631	0.104992
C	-4.950989	-1.461423	0.128225
C	-7.356368	-1.449915	0.455675
C	-4.96839	-2.821928	0.512653
C	-7.358089	-2.769476	0.82811
H	-4.039421	-3.355859	0.536159
C	-6.132546	-3.471763	0.86006
C	6.145602	-0.591219	0.13847
C	7.345513	-1.26017	0.434623
C	4.933342	-1.323054	0.119413
C	7.39132	-2.610109	0.691546
C	5.007905	-2.706182	0.387642
H	4.116328	-3.301273	0.384948
C	6.193365	-3.346799	0.652757
O	-8.599349	3.304658	-1.181992
O	8.454062	3.610927	-0.896225
O	8.600881	-3.201006	0.948401
O	-8.547617	-3.378127	1.117139
C	9.703706	2.941291	-0.912946
H	10.446266	3.699457	-1.144414
H	9.725761	2.16432	-1.680653
H	9.928535	2.49545	0.059234
C	8.757922	-3.72197	2.272295
H	9.751694	-4.160887	2.310163
H	8.006867	-4.48038	2.49118
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H	-9.733416	-4.200623	2.53344
H	-8.675481	-2.902415	3.136561
H	-7.99923	-4.515565	2.780923
H	-8.308404	-0.94339	0.475026
H	-8.330252	0.713342	-0.547601

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H	-10.58613	3.316617	-1.483484
H	-10.062017	2.182049	-0.216767
H	-9.802888	1.784889	-1.935067
H	8.27846	-0.723322	0.501685
H	8.254766	0.989237	-0.381532
O	-6.200753	-4.773208	1.24968
O	6.174911	-4.695473	0.924236
O	-6.248066	4.673486	-1.296697
O	6.058501	4.904399	-1.017184
C	-6.776889	5.59697	-0.346583
H	-6.685221	6.583849	-0.793759
H	-6.199202	5.562315	0.581583
H	-7.825627	5.389314	-0.132381
C	6.536585	5.807269	-0.021099
H	6.419737	6.807123	-0.431964
H	7.587327	5.62665	0.206943
H	5.94201	5.716824	0.89245
C	6.73711	-5.512007	-0.105205
H	6.668829	-6.539291	0.244475
H	7.780533	-5.252898	-0.289777
H	6.16585	-5.40247	-1.030652
C	-4.997364	-5.51884	1.30481
H	-5.275304	-6.512035	1.646321
H	-4.285336	-5.076849	2.006331
H	-4.533022	-5.588318	0.320547

xyz-coordinates for **3**$^{\textbf{\textit{helical}}}$:

atom	x	y	z
N	2.334019	2.880543	0.041919
C	1.167007	3.476474	-0.032017
C	2.398733	1.513013	0.052099
C	1.22398	0.752369	-0.036466
C	-0.029551	1.400702	-0.076649
C	-0.058221	2.783308	-0.085551
C	-1.311175	3.423807	-0.148452
C	-1.255186	0.700217	-0.10904
C	-2.460164	1.41029	-0.205235
N	-2.452785	2.7797	-0.211648
N	1.095286	4.85951	-0.058168
N	-1.295747	4.80886	-0.143358
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O	-0.141285	6.773715	-0.113885
C	-1.227423	-0.704406	-0.058405
C	0.026977	-1.354121	-0.064264
C	1.253189	-0.652474	-0.074345
C	2.462913	-1.358471	-0.144752
C	0.055979	-2.738881	-0.061546

N	2.456809	-2.7292	-0.125171
C	-1.176567	-3.427626	-0.051919
C	-2.406996	-1.459963	0.018508
N	-2.343448	-2.829784	0.005765
C	1.31639	-3.375331	-0.069819
N	1.293895	-4.763353	-0.00362
N	-1.094574	-4.813365	-0.120359
C	0.114836	-5.503108	-0.061798
O	0.140625	-6.718705	-0.062115
C	-2.569238	5.522581	-0.216106
C	2.340073	5.626027	-0.00737
C	-2.298744	-5.631087	-0.230844
C	2.532699	-5.52946	0.096618
H	2.737134	-6.049143	-0.838727
H	2.433985	-6.273372	0.881933
H	3.333805	-4.834736	0.319626
H	-2.497807	-6.147917	0.707144
H	-2.155726	-6.378708	-1.005507
H	-3.12404	-4.972887	-0.47538
H	2.814267	5.513469	0.96669
H	2.100187	6.666464	-0.184117
H	3.024837	5.249427	-0.76271
H	-3.028391	5.374594	-1.19307
H	-2.373067	6.574803	-0.055049
H	-3.243924	5.130309	0.540721
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C	-3.668423	-0.743774	0.05978
C	3.693886	-0.591749	-0.185684
C	3.663647	0.802162	0.103007
C	4.927694	2.739087	1.086476
C	6.085837	3.339516	1.503324
C	4.90522	1.472223	0.460479
C	7.322973	2.684892	1.309997
C	6.142343	0.809258	0.297992
C	7.32748	1.43537	0.728585
H	4.012257	3.27353	1.249631
C	-6.222154	3.0614	-1.675088
C	-5.038384	2.51921	-1.250558
C	-7.429091	2.353197	-1.478611
H	-4.145553	3.081528	-1.441884
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C	-7.382611	1.123922	-0.856931
C	-6.171243	0.562263	-0.411059
C	-6.146312	-0.722988	0.250517
C	-4.917278	-1.39306	0.443108
C	-7.325752	-1.312309	0.738756
C	-4.937826	-2.629366	1.129053
C	-7.3304	-2.510922	1.404267
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C	4.969144	-1.200805	-0.542275
C	7.438176	-2.28748	-1.387344
C	5.038078	-2.435751	-1.226862
H	4.123911	-2.955652	-1.432474
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O	-8.55622	2.938777	-1.953419
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O	8.645982	-2.74535	-1.833049
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C	9.694537	2.74095	1.517661
H	10.430644	3.445659	1.893676
H	9.874601	2.557657	0.45578
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C	9.097549	-3.979016	-1.27165
H	10.076543	-4.167442	-1.705003
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H	9.191595	-3.889829	-0.186013
C	-8.722827	-3.108471	3.228593
H	-9.720262	-3.515886	3.373278
H	-8.670907	-2.108625	3.667895
H	-7.98797	-3.757396	3.702886
H	-8.27802	-0.816997	0.633096
H	-8.292559	0.561537	-0.741617
C	-9.782663	2.240076	-1.819479
H	-10.540407	2.877616	-2.265792
H	-10.026869	2.063981	-0.768863
H	-9.753372	1.284712	-2.348547
H	8.323762	-0.566759	-0.608258
H	8.264028	0.919619	0.611176
O	-6.177027	-4.360582	2.286229
O	6.341014	-4.112179	-2.391462
O	-6.2051	4.249906	-2.359058
O	6.023899	4.593388	2.054547
C	-6.739348	5.365549	-1.648281
H	-6.646816	6.223799	-2.309433
H	-6.16591	5.545914	-0.734487
H	-7.788833	5.210137	-1.396614
C	6.32183	4.667858	3.448407
H	6.210142	5.71219	3.729675
H	7.34107	4.341061	3.65447
H	5.617209	4.059098	4.021712
C	5.149655	-4.758827	-2.805084
H	5.46283	-5.605364	-3.40971
H	4.525946	-4.091586	-3.404592
H	4.573144	-5.115148	-1.950081
C	-4.974695	-5.071315	2.522281

H	-5.255522	-5.958005	3.083776
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TD-DFT Spectra

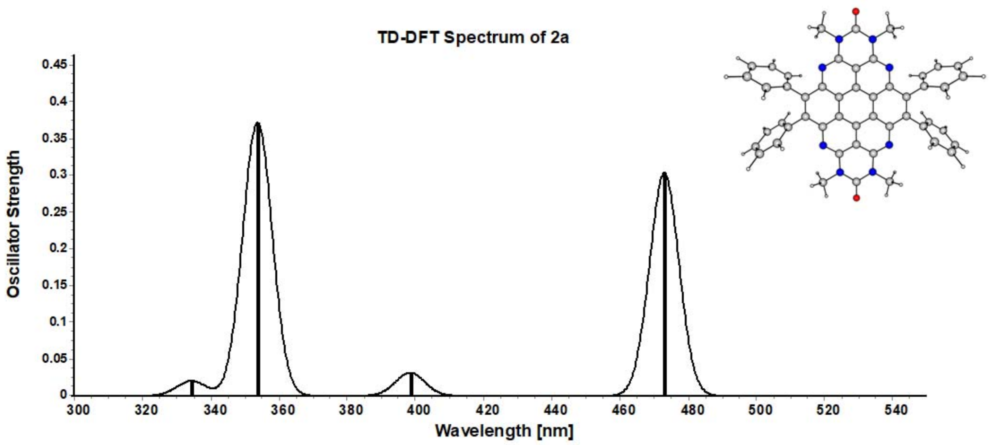

Figure S9: Plot of the TD-DFT UV/Vis spectrum of **2a** (B3LYP-GD3(BJ)/Def2-TZVPP).

Table S3: Excited states (singlets) of **2a** in the gas phase (B3LYP-GD3(BJ)/Def2-TZVPP).

Excited State	Wavelength [nm]	Oscillator Strength
1	472.99	0.3023
2	398.46	0.0306
3	389.14	0.0000
4	353.70	0.3714
5	349.02	0.0000
6	343.42	0.0000
7	335.04	0.0000
8	334.30	0.0195
9	332.20	0.0000
10	325.58	0.0000

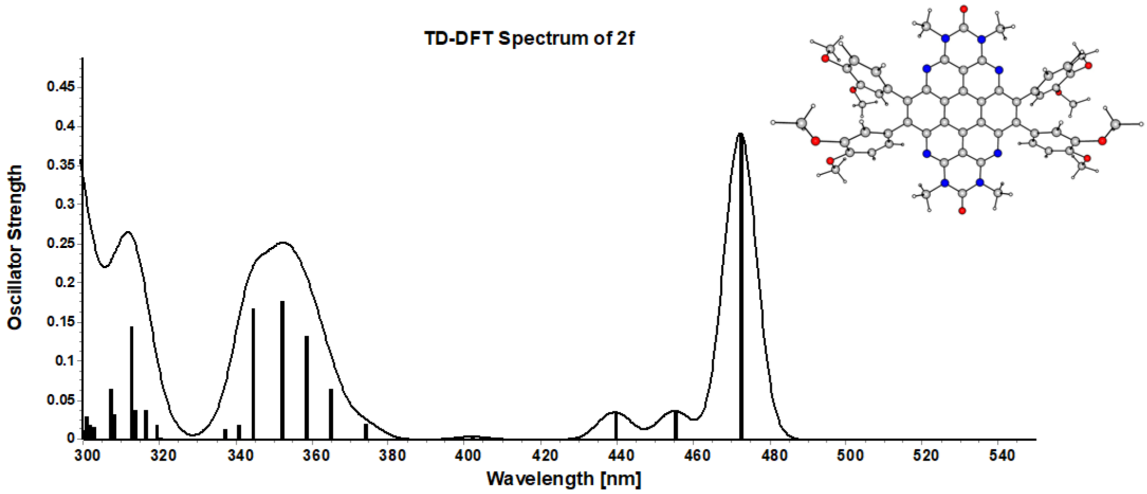

Figure S10: Plot of the TD-DFT UV/Vis spectrum of **2f** (B3LYP-GD3(BJ)/6-31G*).

Table S4: Excited states (singlets) of **2f** in the gas phase (B3LYP-GD3(BJ)/6-31G*).

Excited State	Wavelength [nm]	Oscillator Strength
1	472.34	0.3912
2	455.07	0.0365
3	439.41	0.0347
4	401.97	0.0036
5	373.94	0.0197
6	364.77	0.0634
7	358.50	0.1333
8	351.97	0.1767
9	344.28	0.1679
10	340.58	0.0185
11	337.54	0.0009
12	336.87	0.0132
13	323.55	0.0007
14	320.10	0.0021
15	319.13	0.0180
16	316.28	0.0377
17	313.47	0.0378
18	312.50	0.1442
19	307.86	0.0314
20	307.25	0.0655
21	302.57	0.0161
22	301.58	0.0176
23	300.85	0.0289
24	299.65	0.0122
25	298.53	0.1221
26	294.88	0.2531
27	290.75	0.0444
28	289.70	0.0079
29	283.41	0.0612

30	282.85	0.0003

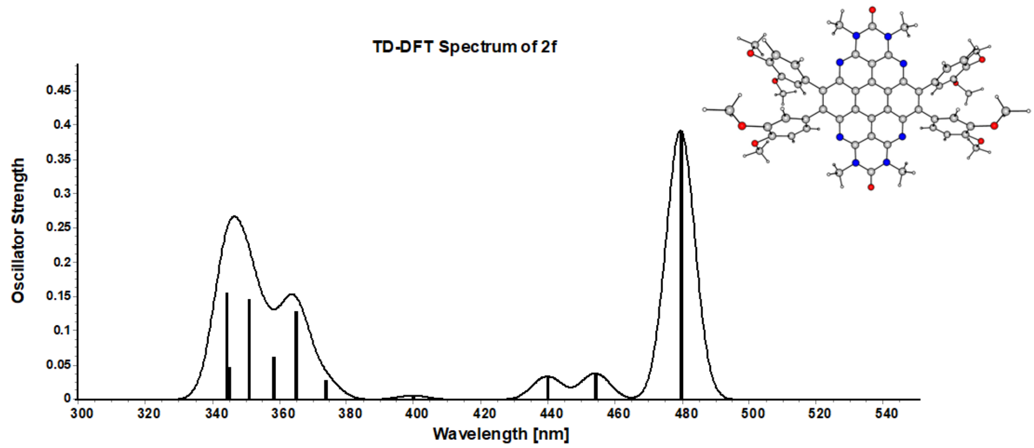

Figure S11: Plot of the TD-DFT UV/Vis spectrum of **2f** (B3LYP-GD3(BJ)/Def2-TZVPP).

Table S5: Excited states (singlets) of **2f** in the gas phase (B3LYP-GD3(BJ)/Def2-TZVPP).

Excited State	Wavelength [nm]	Oscillator Strength
1	479.57	0.3924
2	454.21	0.0381
3	439.86	0.0334
4	399.71	0.0056
5	373.56	0.0277
6	364.87	0.1290
7	358.11	0.0610
8	350.77	0.1462
9	344.79	0.0467
10	344.23	0.1549

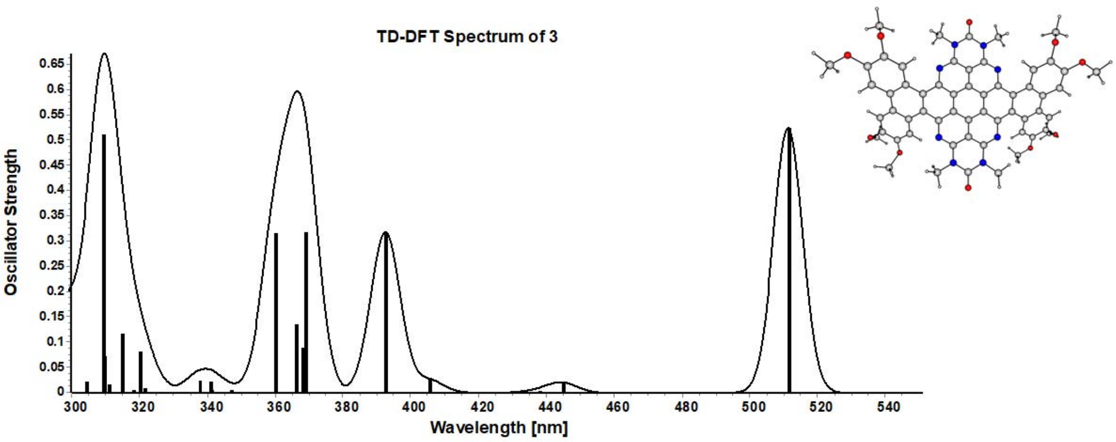

Figure S12: Plot of the TD-DFT UV/Vis spectrum of **3***meso* (B3LYP-GD3(BJ)/6-31G*).

Table S6: Excited states (singlets) of **3**^{meso} in the gas phase (B3LYP-GD3(BJ)/6-31G*).

Excited State	Wavelength [nm]	Oscillator Strength
1	511.35	0.5229
2	444.73	0.0191
3	437.84	0.0042
4	427.46	0.0003
5	405.56	0.0242
6	392.55	0.3171
7	368.78	0.3177
8	368.07	0.0880
9	366.04	0.1356
10	360.16	0.3155
11	347.04	0.0054
12	341.15	0.0047
13	340.98	0.0211
14	337.60	0.0239
15	331.74	0.0020
16	324.88	0.0001
17	321.57	0.0093
18	320.19	0.0802
19	318.00	0.0052
20	314.76	0.1161
21	312.86	0.0018
22	310.99	0.0154
23	309.63	0.0717
24	309.25	0.5108
25	306.32	0.0005
26	304.23	0.0210
27	299.37	0.0133
28	298.52	0.0792
29	297.35	0.0197
30	296.69	0.0575

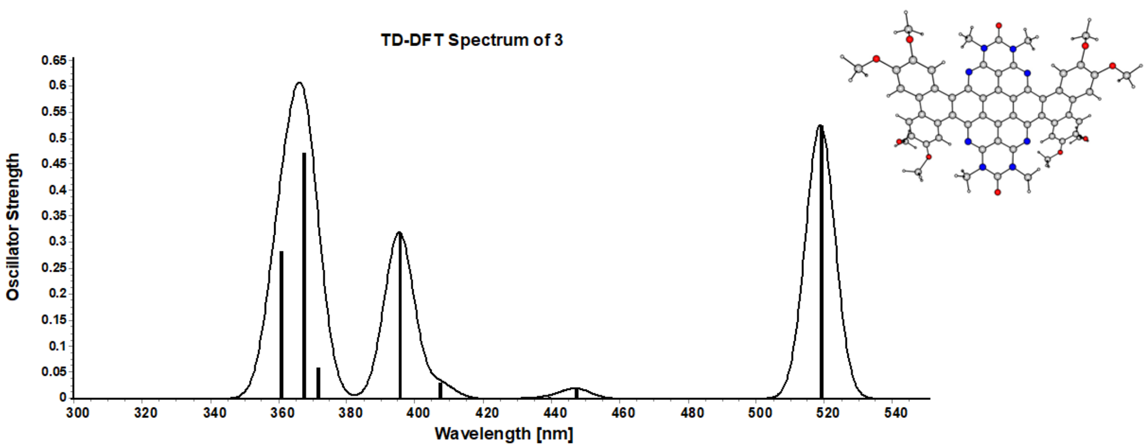

Figure S13: Plot of the TD-DFT UV/Vis spectrum of **3**^{meso} (B3LYP-GD3(BJ)/Def2-TZVPP).

Table S7: Excited states (singlets) of **3**^{meso} in the gas phase (B3LYP-GD3(BJ)/Def2-TZVPP).

Excited State	Wavelength [nm]	Oscillator Strength
1	518.81	0.5250
2	447.12	0.0188
3	439.25	0.0027
4	430.04	0.0004
5	407.19	0.0290
6	395.33	0.3186
7	378.83	0.0002
8	371.39	0.0600
9	367.28	0.4728
10	360.70	0.2823

Thermodynamic stability of 3^{meso} versus 3^{helical}

The DFT calculations of the helical chiral and *meso* conformer of **3** in the gas phase were performed to investigate the thermodynamic stability of the two diastereomers (Figure S14). On this basis, the free energy of the *meso* conformation is nearly the same as the helical isomer (ΔE = 0.7 kcal mol^{-1}), which is in stark contrast to the not core aza-substituted analogue, whose *meso* conformer is thermodynamically more stable (ΔE = 17.5 kcal mol^{-1} at the B3LYP/6-311G++(d,p) level of theory).[20] This illustrates the less Pauli repulsion of the H atoms of the phenanthro moiety and the lone pairs of the N atoms of the azacoronene core, compared to the H-H repulsion of the non-aza analogue, which is further manifesting in a smaller twist of the moieties of 15.8° compared to 44.2° and 41.2° (X-ray crystal structure).[21]

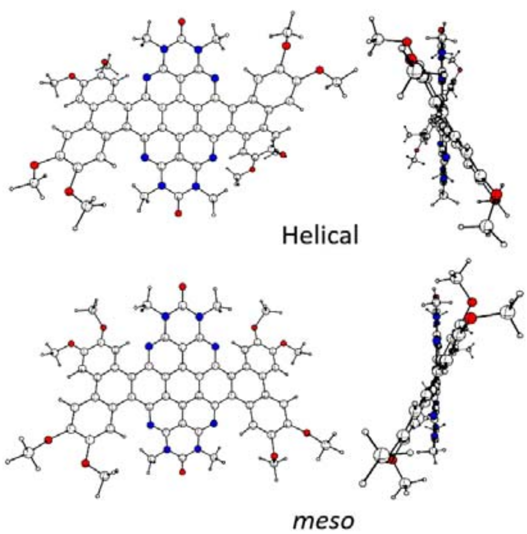

Figure S14: Optimized molecular structures of **3**^{helical} and **3**^{meso} (B3LYP-GD3(BJ)/Def2-TZVPP).

Calculation of Fluorescence Lifetimes

Fluorescence lifetimes were calculated according to the Strickler-Berg equation:[22]

$$\frac{1}{\tau_0} = 2.88 \times 10^{-9} \eta^2 \frac{\int I(\nu) d\nu}{\int \nu^{-3} I(\nu) d\nu} \int \frac{g(\nu)}{\nu} d\nu \qquad (1)$$

(A) (B)

Absorption and emission spectra were recorded in diluted (10^{-5} M) solutions. η is the refractive index of the solvent (dichloromethane, 1.4125[26]). To obtain A two curves were plotted, one of the corrected fluorescence intensity against the frequency in wavenumbers, and the other one additionally multiplied by ν^{-3}. The ratio of the areas under the curve gives A. B was obtained by plotting the absorption spectra in molar absorption coefficients divided by the wavenumber against the wave numbers and integrated over the lowest absorption band including the vibrational shoulders.

Crystallographic Details

Crystal data and details of the structure determinations are compiled in Table S8. Full shells of intensity data were collected at 120(1) K with an Agilent Technologies Supernova-E CCD diffractometer (Cu-K_α radiation, microfocus X-ray tube, multilayer mirror optics). Detector frames (typically ω-, occasionally φ-scans, scan width 1.0°) were integrated by profile fitting.[23,24] Data were corrected for air and detector absorption, Lorentz and polarization effects[24] and scaled essentially by application of appropriate spherical harmonic functions.[24,25,26] Absorption by the crystal was treated spherically (**2a**) or numerically (**2c**, Gaussian grid).[23-27] An illumination correction was performed as part of the numerical absorption correction.[25]

Using OLEX2,[28] the structures were solved with SHELXT[29] (intrinsic phasing) and refined with SHELXL[30] by full-matrix least squares methods based on F^2 against all unique reflections. All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were generally input at calculated positions and refined with a riding model.[31] Split atom models were used to refine disordered groups and/or solvent molecules. When found necessary, suitable geometry and adp restraints were applied.[31,32]

Single crystals of **2a** were found to degrade to powder over a period of 5 to 10 hours at 120 Kelvin. This phase transition was also observed at 200 Kelvin within a similar time frame. Hence, a fairly large (0.1×0.1×0.1) crystal was selected and the data collection strategy was optimized for minimal time. In several attempts using a new crystal each time, we were able to collect the data set reported here within only 6 hours. A certain degree of crystal degradation was still observed. Hence, the data were corrected for sample decay during absorption correction (B-factor refinement as implemented in CrysAlisPro).[24,25]

Due to severe disorder and fractional occupancy, electron density attributed to the solvents of crystallisation was removed from the structure of **2c** (presumably CH_2Cl_2, MeOH and water) using OLEX2 solvent masks (an OLEX2 implementation of the BYPASS procedure).[33] Contributions from the masked solvents to $F(000)$, ρ_{calc} and μ were taken into consideration during absorption correction.

CCDC 2290320 (**2a**) and 2290321 (**2c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre's and FIZ Karlsruhe's joint Access Service via https://www.ccdc.cam.ac.uk.

Table S8: Details of the crystal structure determinations of **2a** and **2c**.

Compound	**2a**	**2c**
Empirical formula	$C_{70}H_{72}N_8O_2$	$C_{74}H_{80}N_8O_6$, [+ solvents]
Formula weight	1057.35	1303.43
Temperature [K]	120(1)	120(1)
Crystal system	*triclinic*	*triclinic*
Space group (number)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
a [Å]	15.5792(4)	13.3834(2)
b [Å]	18.9640(5)	15.0836(2)
c [Å]	21.4149(5)	17.5480(2)
α [°]	72.501(2)	106.6270(10)
β [°]	78.358(2)	96.5330(10)
γ [°]	71.564(2)	91.8250(10)
Volume [Å^3]	5684.5(3)	3364.53(8)
Z	4	2
ρ_{calc} [g·cm^{-3}]	1.235	1.287
μ [mm^{-1}]	0.586	1.369
transmission factors (max, min)	0.80447, 0.79645	1.000,0.659
F(000)	2256	1386
Radiation	Cu-K_α (λ=1.54184 Å)	Cu-K_α (λ=1.54184 Å)
2θ range [°]	6.0 to 133.2	6.7 to 142.5
Index ranges	±18, ± 22, ±25	±16, ±18, ±21
Reflections collected	91456	97860
Independent reflections	19732 [R_{int} = 0.0993]	12847 [R_{int} = 0.0691]
observed [$I \geq 2\sigma(I)$]	9732	10532
Completeness to θ	98.2 % (θ = 66.6°)	99.8 % (θ = 67.7°)
Data / Restraints / Parameters	19732 / 315 / 1472	12847 / 375 / 926
Goodness-of-fit on F^2	0.951	1.027
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0905 wR_2 = 0.2339	R_1 = 0.0566 wR_2 = 0.1470
Final *R* indexes [all data]	R_1 = 0.1746 wR_2 = 0.2852	R_1 = 0.0667 wR_2 = 0.1546
Largest peak/hole [*e*·Å^{-3}]	0.67/−0.48	0.56/−0.34
CCDC number	2290320	2290321

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