Electronic Supporting Information (ESI)

Embedding a boroxazine ring into a nanographene scaffold by a concise bottom-up synthetic strategy

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Contents

1. Experimental and Computational Details

Experimental Details

Unless otherwise indicated, all reactions were done under inert conditions by flaming all glassware with a heat gun (at 630 °C) under vacuum and purging with argon. All chemicals and solvents were dried by known methods or were purchased from commercial suppliers in anhydrous form. Column chromatography were done with a medium pressure liquid chromatography (MPLC) system (PuriFlash 430 evo, Interchim), with Si-IR 20 μm columns in size of 12 g up to 120 g. Thin layer chromatography (TLC) was done using pre-coated polyester sheets (40 x 80 mm) from Machery-Nagel (POLYGAM®SIL G/UV254) with 0.2 mm silica gel 60 with fluorescence indicator. For visualization, UV light source (254 nm and 366 nm) was used. Melting points were measured with a Büchi B-540 apparatus. Nuclear magnetic resonance spectroscopy (NMR) was done on a Bruker Avance III HDX 600 (equipped with a dual (^{1}H/^{13}C) probe head. Chemical shifts (δ) are given in ppm, coupling constants in Hertz (Hz) and the multiplicities of the signals are designated as follows: s = singlet, br s = broad singlet, d = doublet, dd = doublet of doublet, t = triplet and m = multiplet. The signals of NMR solvents were calibrated (^{1}H/^{13}C): CD_2Cl_2 5.32/53.84 ppm and thf-d_8 3.58/67.21 ppm. Reference for ^{1}H and ^{13}C were tetramethyl silane (TMS) and for ^{11}B $BF_3{\cdot}OEt_3$ in $CDCl_3$. High resolution mass spectrometry was done with electron spray ionization time of flight mass spectrometry (ESI-TOF-MS) on a maXis 4G Bruker system or with an APCI source combined with a direct inlet probe (DIP) system. EI high resolution mass spectrometry was done on a Finnigan/MasCom MAT95. Optical spectra were recorded on a PerkinElmer Lambda 1050 spectrometer with a PerkinElmer 3D WB Det Module. Excitation and emission spectra were recorded on a Cary Variant SPVF spectrometer using Hellma Analytics quartz cuvettes. All measurements were done in spectroscopy grade solvents. The fluorescence quantum yield of **A** in 1,4-dioxane was measured with an excitation wavelength λ_{ex} = 362 nm (anthracene in ethanol as reference). Infrared spectroscopy was measured on a Bruker Tensor 27 with KBr pellets. The single crystal of **A** was measured on a Bruker Apex II with Cu K_α radiation.

Computational Details

Geometry optimizations of **A** on the S_0 potential energy surface (PES) were performed using the B3LYP[1, 2] functional as implemented in Gaussian 09[3] in conjunction with the 6-311+G** basis set.[4] Computation of the harmonic vibrational frequencies confirms that the resulting geometry corresponds to a minimum on the PES. Excited state energies and natural transition orbitals (NTO) were computed using the time-dependent (TD)[5] method in conjunction with the B3LYP functional and the 6-311+G** basis set. Nuclear-independent chemical shifts[6-8] were computed at the B3LYP/6-311+G** level using the GIAO method.[9] The anisotropy of current-induced density (ACID)[10, 11] was computed at the B3LYP/6-311+G** level using the AICD-2.0.0 program kindly provided by Professor Herges.

2. Synthesis

Synthesis of 2

To an ice-cold solution of **1** (1.9 g, 5.0 mmol, 1 equiv.) in a mixture of chloroform/DCM (1:1) (500 mL in total) was added over 2 h a solution of NBS (1.8 g, 10 mmol, 2 equiv.) in acetonitrile (120 mL). After complete addition the mixture was stirred at room temperature. After 12 h, all volatiles were removed under reduced pressure. Flash-chromatography (*n*-hexane/DCM 9:1, R_f = 0.21) yielded the desired product **2** as a colourless solid (2.1 g, 4.0 mmol, 80 %).

^{1}H-NMR (600 MHz, CD_2Cl_2): 8.14 (d, *J* = 8.0 Hz, 2H, H-3), 7.99 (d, *J* = 1.5 Hz, 2H, H-2), 7.79 (t, *J* = 8.0 Hz, 1H, H-4), 7.45 (d, *J* = 1.5 Hz, 2H, H-1), 7.05 (br s, H-5, 2H), 2.67 (t, *J* = 7.8 Hz, 4H, H-6), 1.70-1.63 (m, 4H, H-7), 1.45-1.37 (m, 4H, H-8), 0.97 (t, *J* = 7.4 Hz, 6H, H-9).

^{11}B-NMR (128 MHz, CD_2Cl_2): 27.0

^{13}C-NMR (151 MHz, CD_2Cl_2): 138.9 (C-7), 136.2 (C-5), 135.5 (C-2), 132.1 (C-1), 131.5 (C-10), 127.2 (br s, C-8), 124.0 (C-3), 123.8 (C-4), 120.0 (C-9), 113.4 (C-6), 35.4 (C-11), 34.3 (C-12), 22.7 (C-13), 14.2 (C-14).

HRMS (ESI): m/z $[M+H]^+$ calcd. for $C_{26}H_{27}BBr_2N_2$: 537.07144; found 537.07219 (Δ = 1.95 ppm)

Mp: 215 °C

Synthesis of 3

Under an inert atmosphere **2** (2.1 g, 4.0 mmol, 1 equiv.), bis(pinacolato) diboron (5.1 g, 20 mmol, 5 equiv.), potassium acetate (4.7 g, 48 mmol, 12 equiv.) and $Pd(dppf)Cl_2$ (0.3 g, 0.4 mmol, 0.1 equiv.) were dissolved in dry dioxane (250 mL) and stirred under reflux (90 °C oil bath temp.) for 18 h. After cooling down, 100 mL ethyl acetate were added and the mixture was washed with water (3 x 50 mL). The aqueous layer was extracted with dichloromethane (3 x 50 mL). All combined organic layers were dried over anhydrous sodium sulphate. All volatiles were removed under reduced pressure. Column chromatography (*n*-hexane/DCM 2:1, R_f = 0.2) yielded the desired compound **3** (1.7 g, 2.7 mmol, 68 %).

^{1}H-NMR (600 MHz, CD_2Cl_2): 8.58 (br s, 2H, H-5), 8.19 (d, *J* = 1.9 Hz, 2H, H-2), 8.17 (d, *J* = 8.0 Hz, 2H, H-3), 7.78 (t, *J* = 8.0 Hz, 1H, H-4), 7.64 (d, *J* = 1.9 Hz, 2H, H-1), 2.70 (t, *J* = 7.9 Hz, 4H, H-7), 1.71-1.65 (m, 4H, H-8), 1.48-1.39 (m, 4H, H-9), 1.46 (s, 24H, H-6), 0.98 (t, *J* = 7.4 Hz, 6H, H-10).

^{11}B-NMR (128 MHz, CD_2Cl_2): 31.4, 26.6.

^{13}C-NMR (151 MHz, CD_2Cl_2): 145.9 (C-5), 139.6 (C-9), 137.1 (C-1), 133.2 (C-2), 131.0 (C-12), 128.3 (C-3), 127.4 (C-10), 122.0 (C-4), 118.9 (C-11), 115.5 (C-6), 84.4 (C-7), 35.6 (C-13), 34.8 (C-14), 25.3 (C-8), 22.9 (C-15), 14.2 (C-16).

HRMS (EI): m/z $[M]^+$ calcd. for $C_{38}H_{51}B_3N_2O_4$: 632.412252; found: 632.40571 (Δ = 6.54 mmu)

Mp: decomposition

Synthesis of 4

3 (1.7 g, 2.7 mmol, 1 equiv.), Br-Bdan-benzene (2.2 g, 6.8 mmol, 2.5 equiv.), potassium carbonate (4.5 g, 32 mmol, 12 equiv.) and $Pd(PPh_3)_4$ (0.3 g, 0.3 mmol, 0.1 equiv.) were dissolved in a mixture of toluene (150 mL), ethanol (40 mL) and water (75 mL) and stirred under reflux (100 °C oil bath temp.) for 12 h. After cooling to rt, the reaction mixture was washed with water (3 x 30 mL) and the aqueous layer was extracted with DCM (4 x 50 mL). All combined organic layers were dried over anhydrous sodium sulphate and all volatiles were removed under reduced pressure. Flash chromatography (n-hexane/DCM 3:1 gradient to 3:2; R_f (3:2) = 0.1) yielded the desired compound **4** as a colourless solid (1.6 g, 1.9 mmol, 70 %).

^{1}H-NMR (600 MHz, CD_2Cl_2): 8.31-8.28 (m, 2H, H-3), 8.18-8.16 (m, 2H, H-2), 7.89-7.85 (m, 1H, H-4), 7.81-7.77 (m, 2H, H-8), 7.58-7.48 (m, 4H, H-6, H-7), 7.42 (dd, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H, H-12), 7.37 (dd, *J* = 7.3 Hz, *J* = 1.1 Hz, 1H, H-5), 7.08-7.06 (m, 2H, H-1), 6.95-6.92 (m, 2H, H-10), 6.87-6.79 (m, 6H, H-11, H-18, H-19), 6.18 (s, 1H, NH1), 6.16 (s, 1H, NH2), 5.97 (dd, *J* = 7.3 Hz, *J* = 0.7 Hz, 2H, H-9), 5.89 (dd, *J* = 7.3 Hz, *J* = 0.8 Hz, 2H, H-13), 5.65 (s, 2H, NH3), 5.58 (s, 2H, NH4), 2.73-2.67 (m, 4H, H-14), 1.64-1.55 (m, 4H, H-15), 1.35-1.26 (m, 4H, H-16), 0.81-0.74 (m, 6H, H-17).

^{11}B-NMR (128 MHz, CD_2Cl_2): 29.1, 26.6.

^{13}C-NMR (151 MHz, CD_2Cl_2): 143.6 (C-11), 143.5 (C-10), 141.4 (C-19), 141.3 (C-18), 139.5 (C-5), 139.4 (C-6), 136.5 (C-), 136.4 (C-), 135.2 (C-13), 134.9 (C-12), 134.2 (C-3), 133.7 (C-17), 133.6 (C-16), 131.5 (C-), 131.4 (C-8), 131.3 (C-14), 131.1 (C-15), 130.7 (C-), 130.6 (C-), 130.5 (C-1), 130.3 (C-2), 128.0 (C-), 127.8 (C-22), 127.8 (C-), 127.3 (C-9), 124.2 (C-4), 122.6 (C-), 122.6 (C-), 119.8 (C-), 119.8 (C-7), 119.7 (C-), 117.6 (C-), 117.5 (C-), 106.0 (C-20), 106.0 (C-21), 35.6 (C-23), 34.6 (C-24), 22.6 (C-25), 14.0 (C-26). All other signals could not be assigned due to the two multiplet signals in the ^{1}H NMR with 4H and 6H.

HRMS (EI): m/z $[M]^+$ calcd. for $C_{58}H_{51}B_3N_6Na$: 887.43717; found: 887.43794 (Δ = 0.8 mmu)

Mp: decomposition

Synthesis of A

Under an inert atmosphere **4** (112 mg, 0.13 mmol, 1 equiv.) was dissolved in degassed THF (50 mL). A degassed H_2SO_4 solution (3.1 mL, 2 M in water, 6.28 mmol, 48 equiv.) was added dropwise. The mixture was stirred for 3 days at 50 °C. After cooling to rt, the obtained solid was filtered and washed with concentrated $NaHCO_3$ solution, water, acetone and thf until a white solid was obtained. Sublimation in a quartz ampule (10^{-3} mbar, 300 °C) yielded the desired compound **A** as colourless needles (66.2 mg, 0.12 mmol, 90 %).

^{1}H-NMR (600 MHz, 80 °C, dioxane-d_8): 8.74-8.72 (m, 2H, H-1), 8.55 (d, *J* = 8.0 Hz, 2H, H-4), 8.48-8.42 (m expected as d + s; d, 2H, H-7; s, 4H, H-5, H-6), 7.98-7.94 (m, 1H, H-8), 7.84-7.79 (m, 2H, H-3), 7.66-7.61 (m, 2H, H-2), 2.98 (t, *J* = 7.7 Hz, 4H, H-9), 1.95-1.86 (m, 4H, H-10), 1.63-1.53 (m, 4H, H-11), 1.07 (t, *J* = 7.4 Hz, 6H, H-12).

^{11}B-NMR (128 MHz, 80 °C, dioxane-d_8): 30.5 (br s).

^{13}C-NMR (151 MHz, 80 °C, dioxane-d_8): 142.4 (C-5), 140.4 (C-12), 138.1 (C-6), 136.6 (C-8), 134.5 (C-11), 133.4 (C-1), 132.9 (C-14), 132.3 (C-3), 126.9 (C-2), 126.0 (C-10), 125.0 (C*-7), 124.9 (C*-9), 123.1 (C-4), 120.8 (C-13), 36.0 (C-15), 34.3 (C-16), 22.7 (C-17), 13.8 (C-18). C* could be interchanged due to overlap in ^{1}H-NMR. C-B are not found due to quadrupole moment.

IR (KBr) ν (cm^{-1}): 3069, 3037, 2951, 2926, 2869, 2853, 1602, 1585, 1573, 1556, 1547, 1483, 1460, 1430, 1395, 1380, 1328, 1294, 1251, 813, 780, 459, 738, 675, 621.

UV/vis (1,4-dioxane) λ_{max} (log ε): 204 (5.16), 207 (5.17), 210 (5.17), 224 (5.07), 240 (4.99), 248 (5.00), 264 (4.90), 291 (4.48), 334 (4.16), 348 (4.42), 350 (4.42), 363 (4.39), 367 (4.48).

HRMS (DIP-APCI): m/z $[M+H]^+$ calcd. for $C_{38}H_{33}B_3N_2O$: 567.29627; found 567.29583 (Δ = 0.81 ppm)

EA: calcd. for $C_{38}H_{33}B_3N_2O$: N 4.95 %, C 80.62 %, H 5.88 %; found: N 4.96, C 80.97, H 5.89 %.

Mp: 320 °C

3. Cartesian Coordinates of Stationary Points

Given in Å and computed at B3LYP/6-311+G**

Compound $\mathbf{A_H}$ (C_{2V})

```
53
scf done: -1413.43740047

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6        0.000000000      2.551803000      3.596188000
6        0.000000000      0.000000000     -2.268365000
6        0.000000000      1.236596000     -2.950048000
6        0.000000000      2.490197000     -2.165773000
6        0.000000000      2.482153000     -0.739258000
6        0.000000000      3.711852000     -0.014551000
6        0.000000000      3.743902000      1.464606000
6        0.000000000     -2.551803000      3.596188000
6        0.000000000     -2.532604000      2.190431000
6        0.000000000     -3.743902000      1.464606000
6        0.000000000     -3.711852000     -0.014551000
6        0.000000000     -2.482153000     -0.739258000
6        0.000000000     -1.236596000     -2.950048000
6        0.000000000     -2.490197000     -2.165773000
6        0.000000000      3.726754000     -2.824494000
1        0.000000000      3.758515000     -3.905093000
6        0.000000000      4.909189000     -0.743251000
1        0.000000000      5.855227000     -0.220441000
6        0.000000000      1.214504000     -4.352375000
1        0.000000000      2.126224000     -4.934050000
6        0.000000000     -1.214504000     -4.352375000
1        0.000000000     -2.126224000     -4.934050000
6        0.000000000     -3.726754000     -2.824494000
1        0.000000000     -3.758515000     -3.905093000
6        0.000000000     -4.909189000     -0.743251000
1        0.000000000     -5.855227000     -0.220441000
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1        0.000000000     -5.907766000      1.688366000
6        0.000000000     -3.747272000      4.295260000
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1        0.000000000      3.755672000      5.379624000
6        0.000000000      4.951431000      2.193546000
1        0.000000000      5.907766000      1.688366000
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1        0.000000000      5.866344000     -2.663380000
6        0.000000000      0.000000000     -5.029783000
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6        0.000000000      4.950151000      3.579888000
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5        0.000000000      1.222483000      1.401360000
7        0.000000000      1.256642000     -0.040863000
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8        0.000000000      0.000000000      2.034216000
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4. Spectra

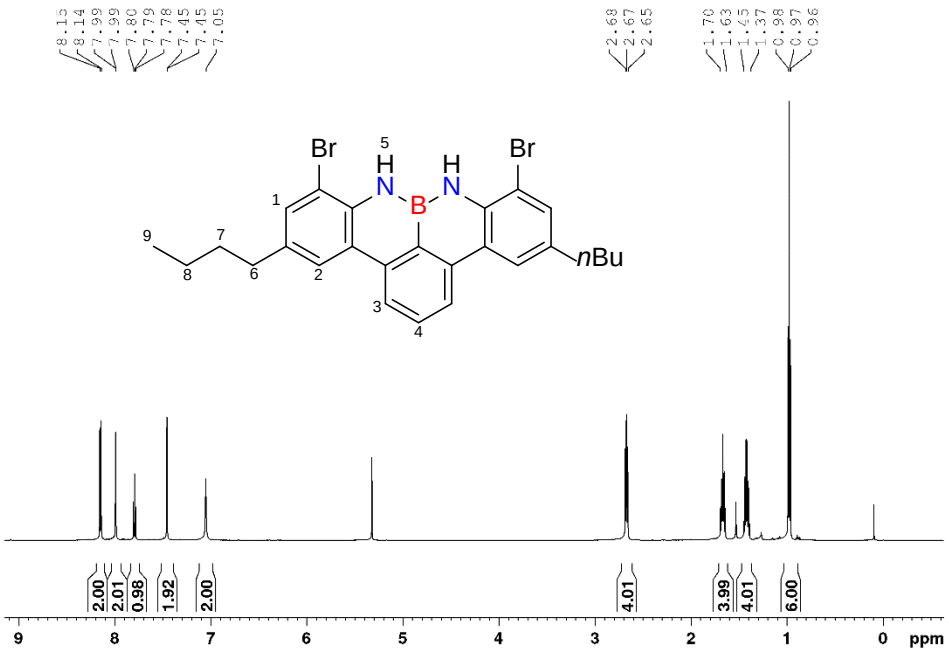


Figure S1: ^{1}H-NMR of **2** in CD_2Cl_2.

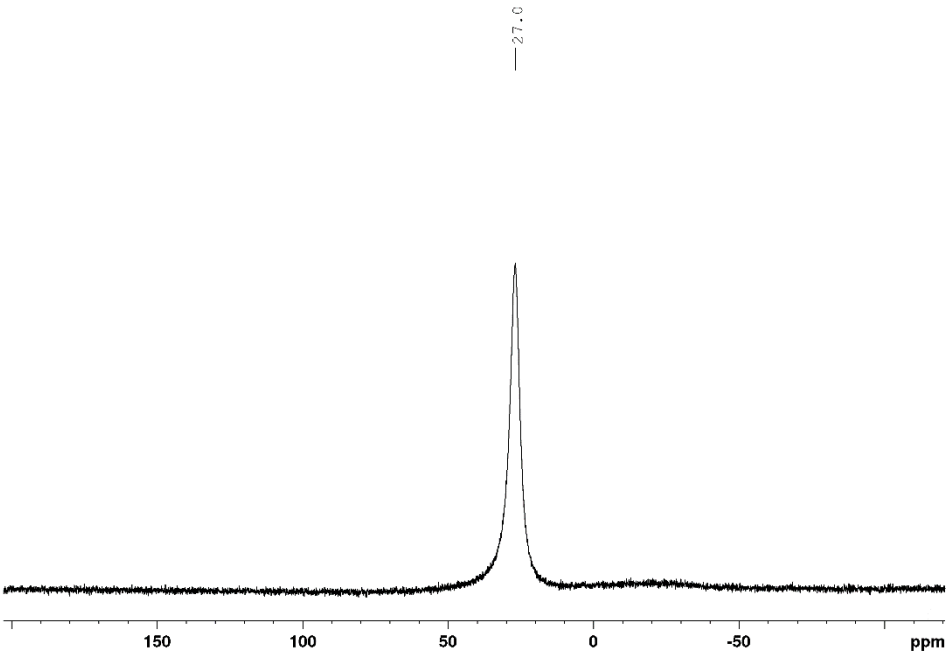


Figure S2: ^{11}B-NMR of **2** in CD_2Cl_2.

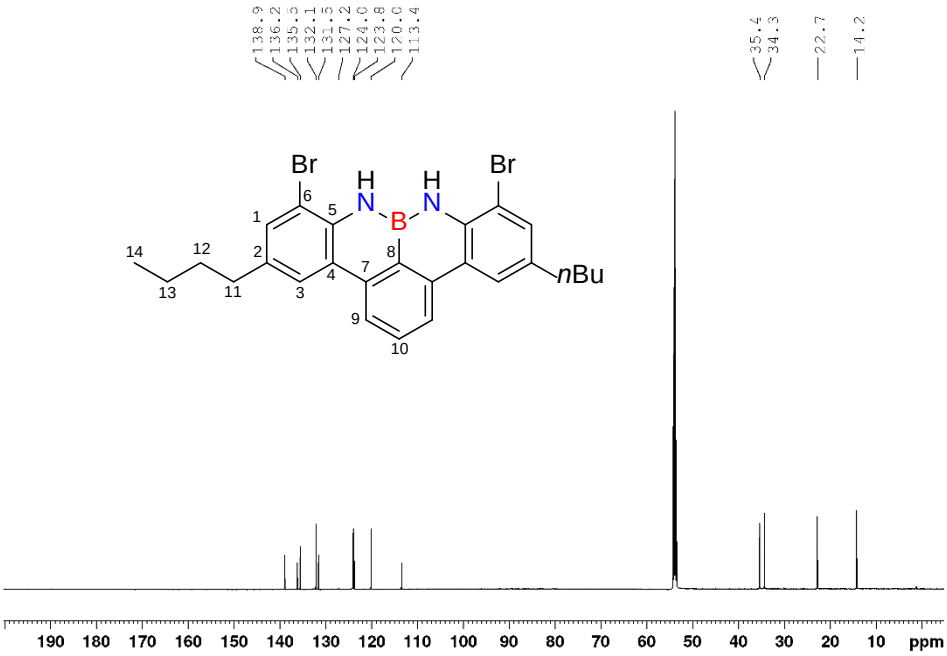


Figure S3: ^{13}C-NMR of **2** in CD_2Cl_2.

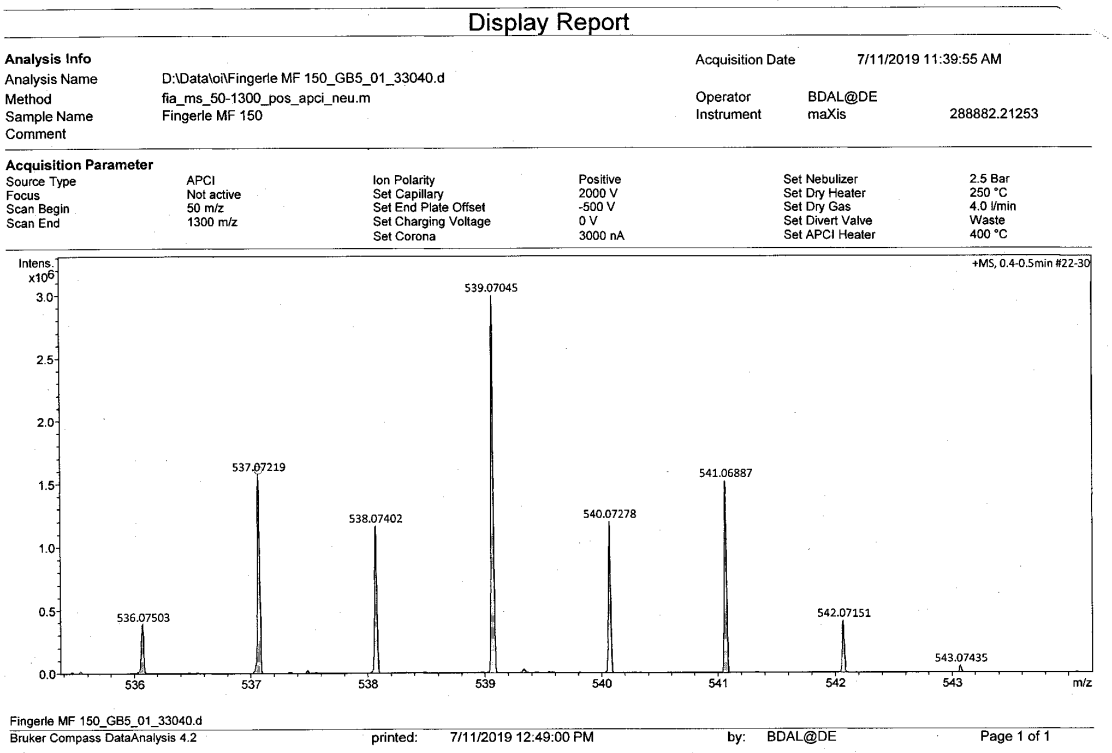


Figure S4: HR-APCI of **2**.

High Resolution MS

☐ **FT-ICR-MS**

☒ **ESI- oder APCI-TOF-MS** (MS/MS möglich)

☐ **egal (je nach freien Kapazitäten)**

Name: Fingerle AK: Bettinger

Tel. email:

Datum:

Probenbezeichnung: MF150 nominelle Masse:

Falls Masse nicht bekannt, welcher Massenbereich soll gemessen werden:

Summenformel (falls bekannt): $C_{26}H_{27}BBr_2N_2$

Strukturformel (falls bekannt):

Einwaage (zwischen 0,1mg und 2 mg):

Löslich in:

Falls schon gelöst, in welchem Lösemittel und in welcher Konzentration:

Hinweise bezüglich Zersetzlichkeit:

Hinweise bezüglich Toxizität (wenn bekannt):

Hohe Massengenauigkeit erwünscht? ja/nein

Massenanalyse erwünscht?

Wenn ja, welche Elemente sollen berücksichtigt werden?

MS/MS erwünscht?:

Ergebnis:

$[M+H]^+_{(theor.)}$ = 537,07114 ~~68~~

Gemessen = 537,07219

Relative Massenabweichung = 1,95 ppm

Figure S5: Data sheet of HR-APCI of **2**.

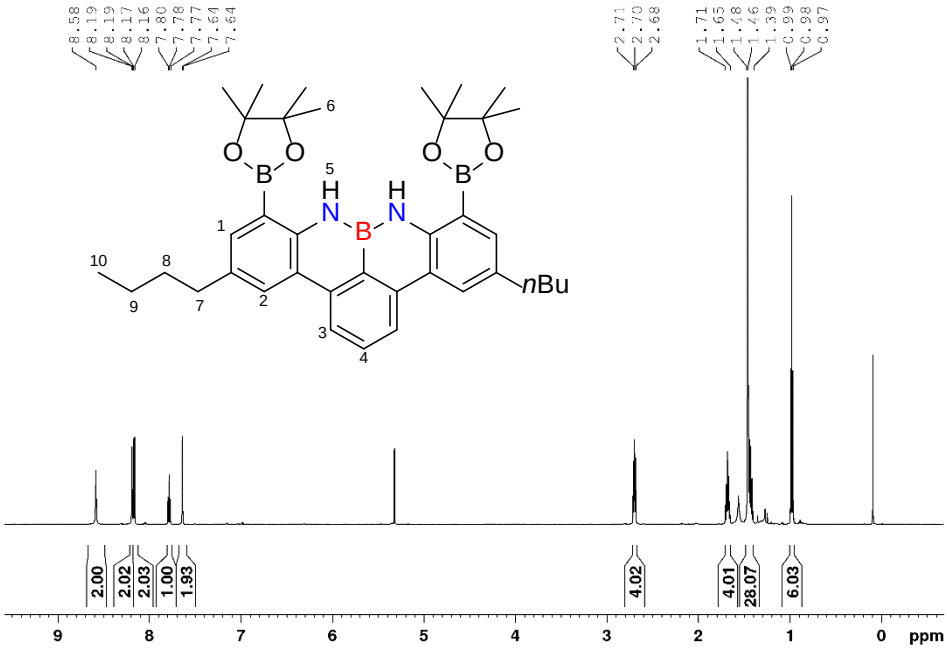


Figure S6: ^{1}H-NMR of **3** in CD_2Cl_2.

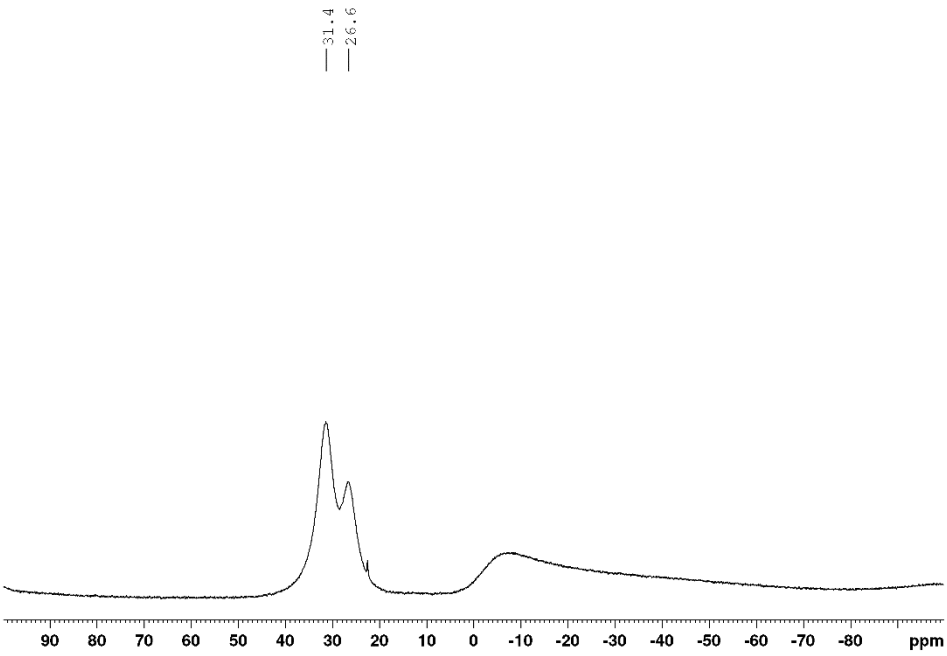


Figure S7: ^{11}B-NMR of **3** in CD_2Cl_2.

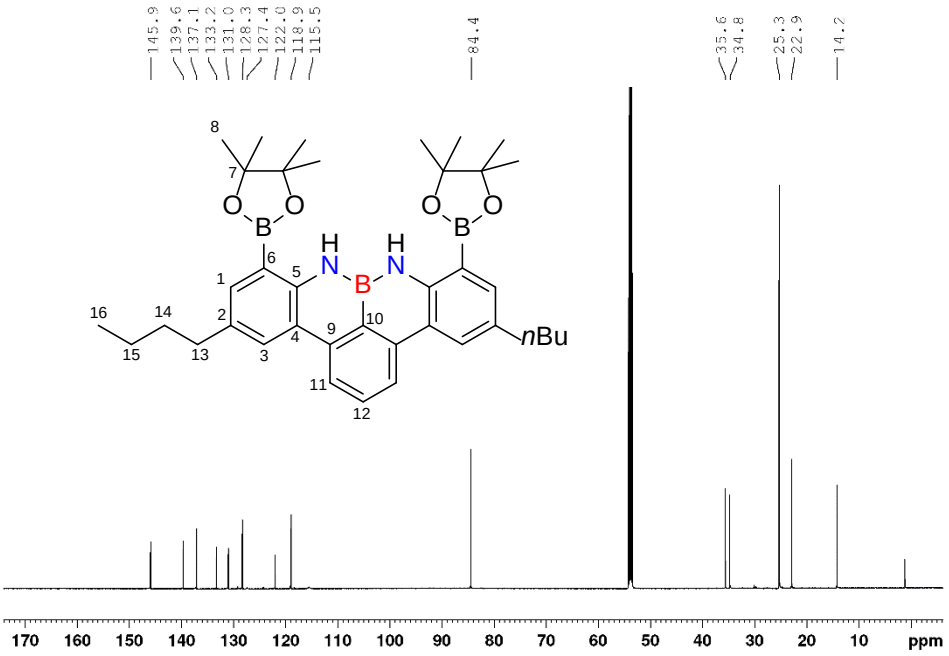


Figure S8: ^{13}C-NMR of **3** in CD_2Cl_2.

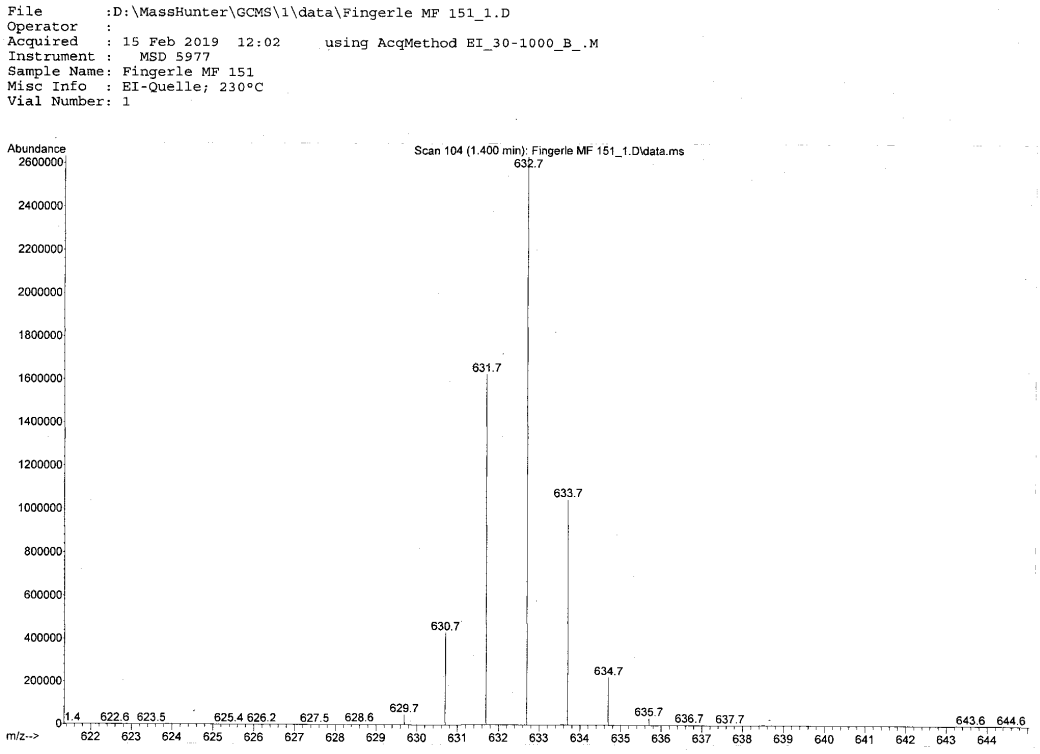


Figure S9: EI-MS spectra of **3**.

M a s s e n f e i n b e s t i m m u n g

Name: Fingerle Probenbezeichnung: MF 151

Ionisierungsmethode: **EI** ..X... **FAB** .....

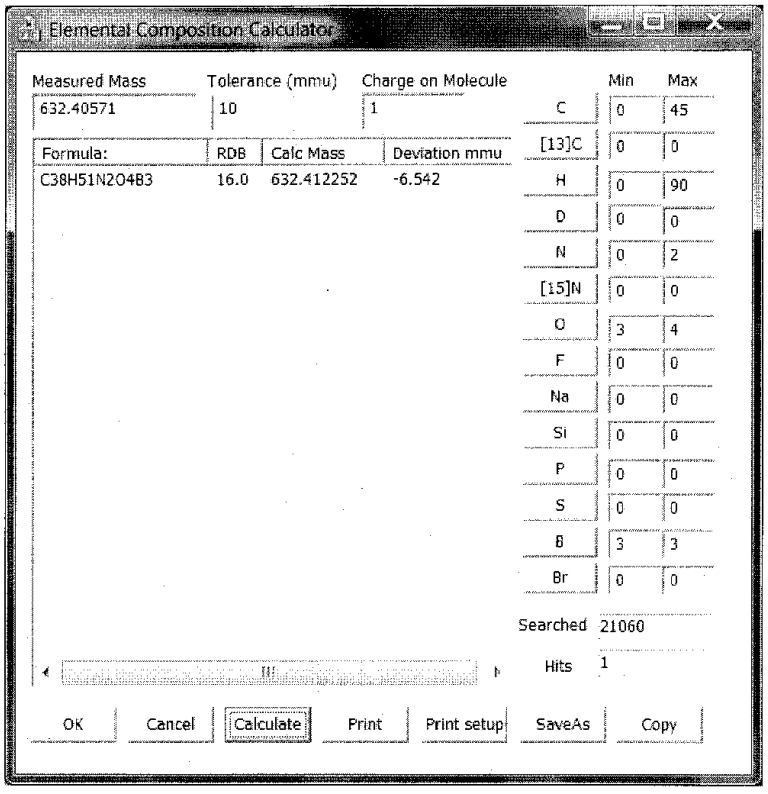
Massenspektrometer: **MAT 95**

Referenz - Ion und seine **exakte Masse:**

$C_{12}F_{24}N^+$ 614 613,96418

die **gefundene exakte Masse** erhält man zu: 632,40571

damit ergibt/ergeben sich folgende **Elementkombination(en)** :



Datum: 25. Feb. 2019 MS – Nummer: 190054

Figure S10: Data sheet of HR-EI of **3**.

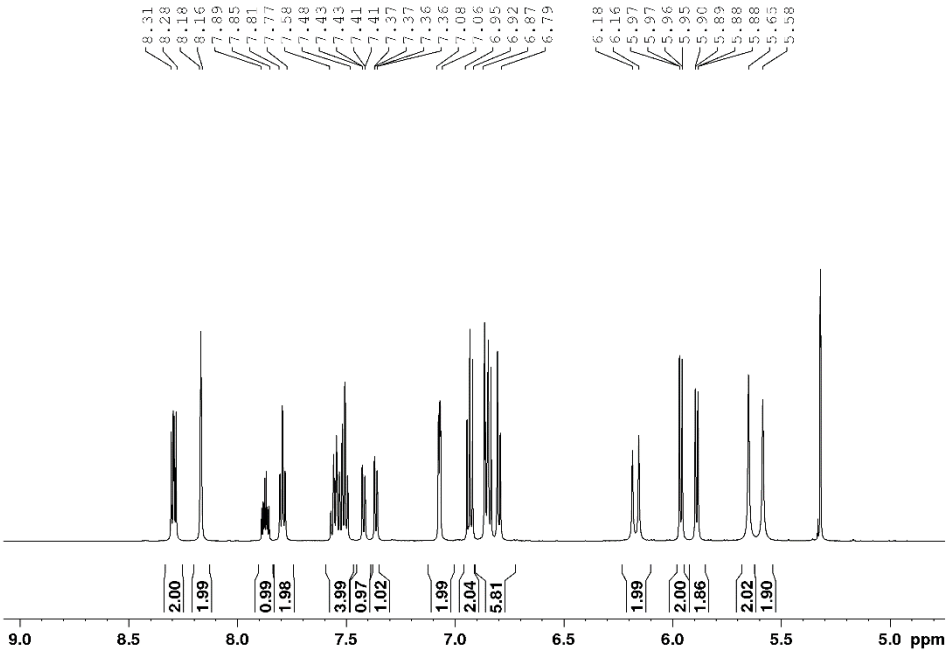


Figure S11: ^{1}H-NMR (aromatic signals) of **4** in CD_2Cl_2.

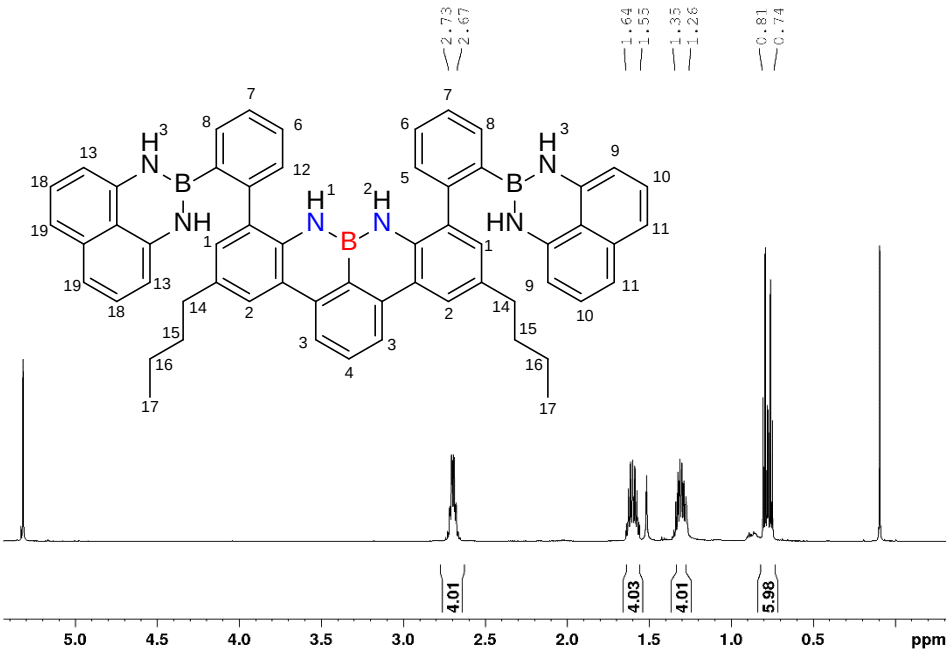


Figure S12: ^{1}H-NMR (non-aromatic signals) of **4** in CD_2Cl_2.

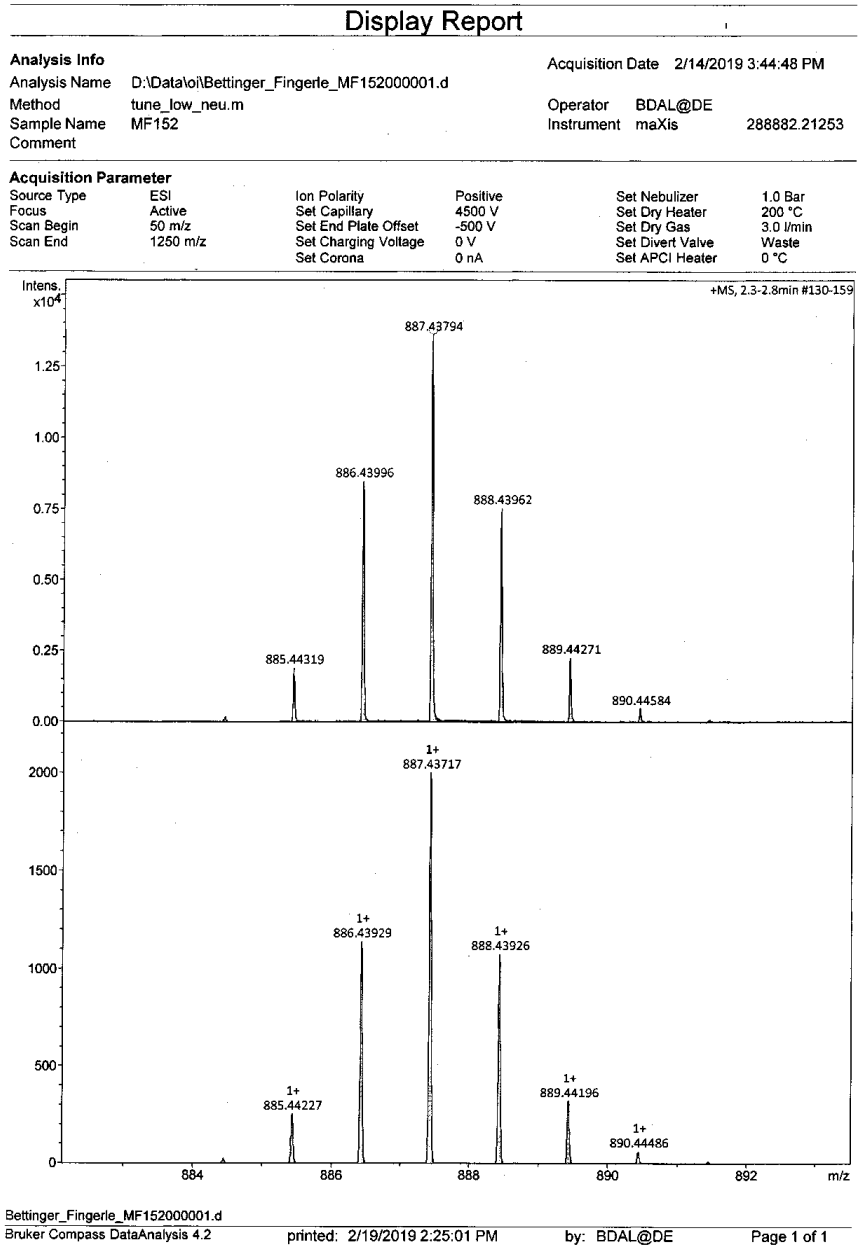


Figure S13: HR-APCI of **4**.

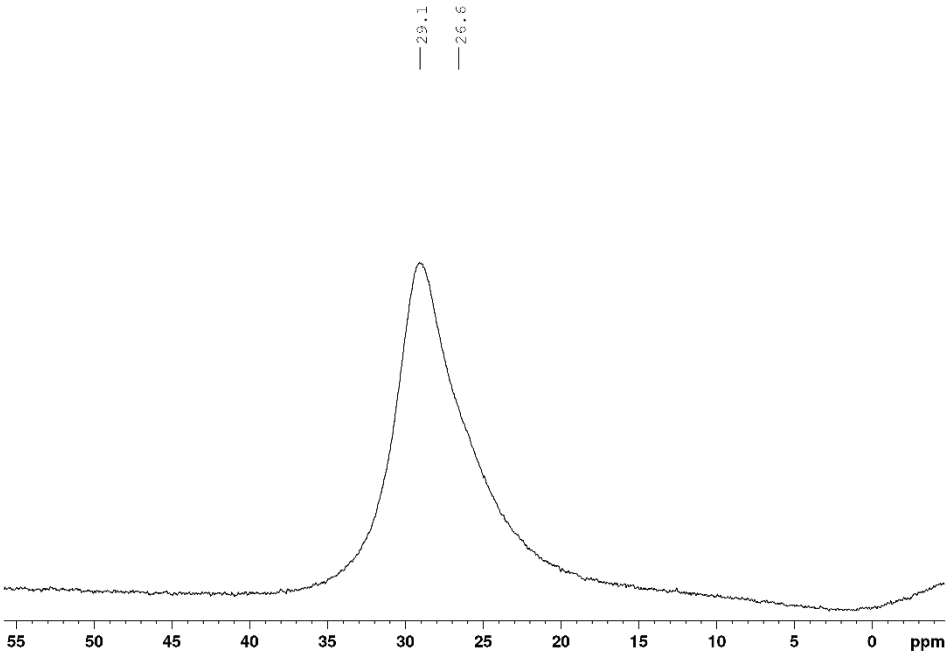


Figure S14: ^{11}B-NMR of **4** in CD_2Cl_2.

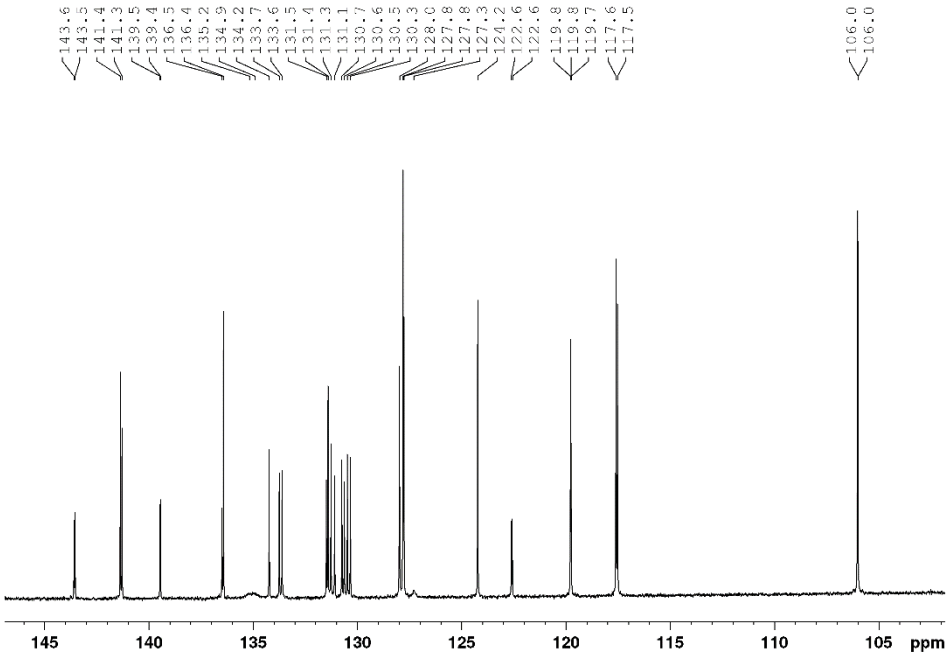


Figure S15: ^{13}C-NMR (aromatic signals) of **4** in CD_2Cl_2.

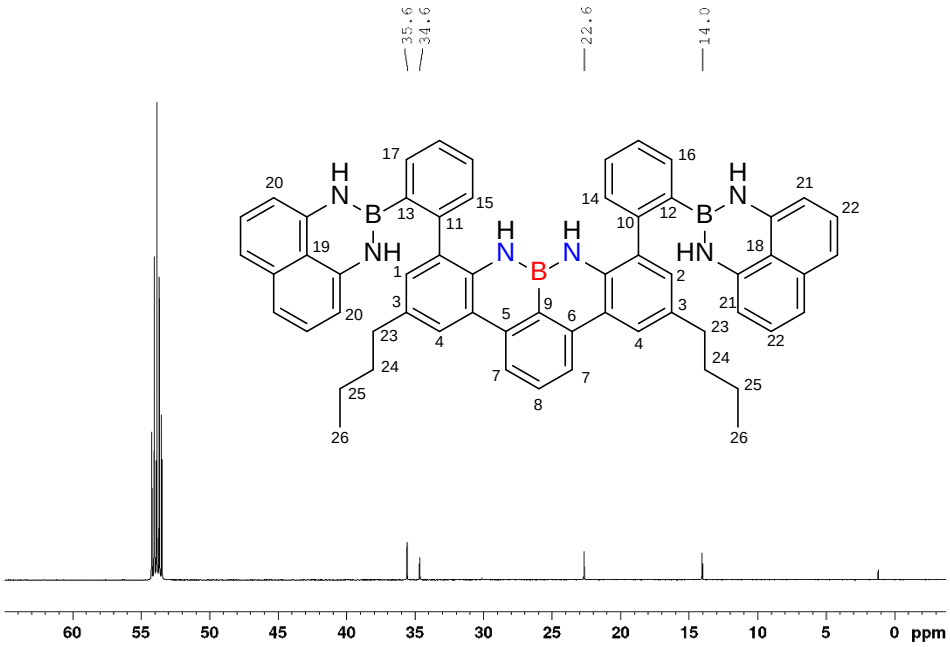


Figure S16: ^{13}C-NMR (non-aromatic signals) of **4** in CD_2Cl_2.

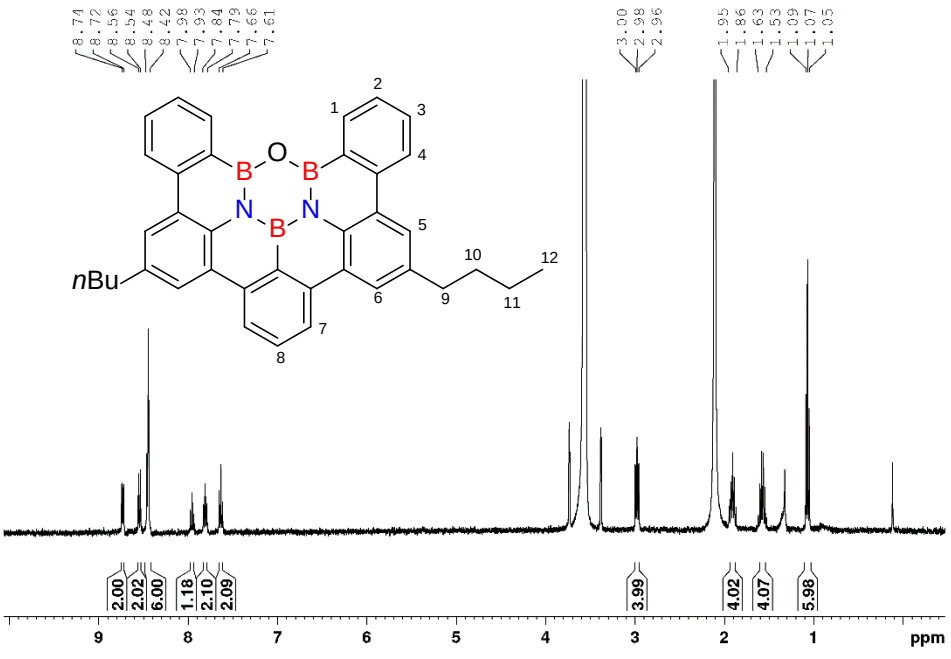


Figure S17: ^{1}H-NMR (aromatic signals) of **A** in dioxane-d_8 at 80 °C.

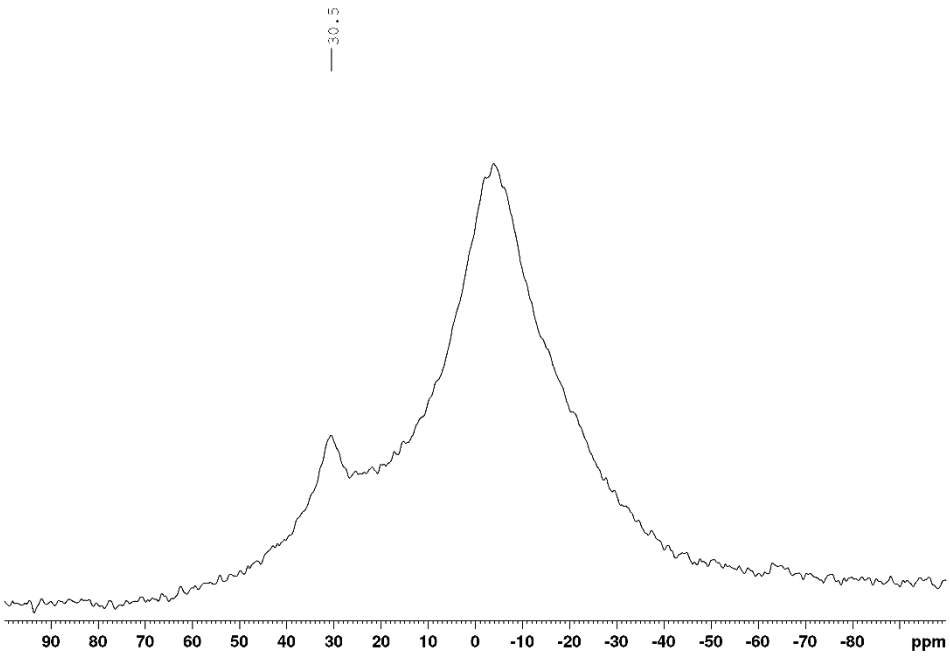


Figure S18: ^{11}B-NMR of **A** in dioxane-d_8 at 80 °C.

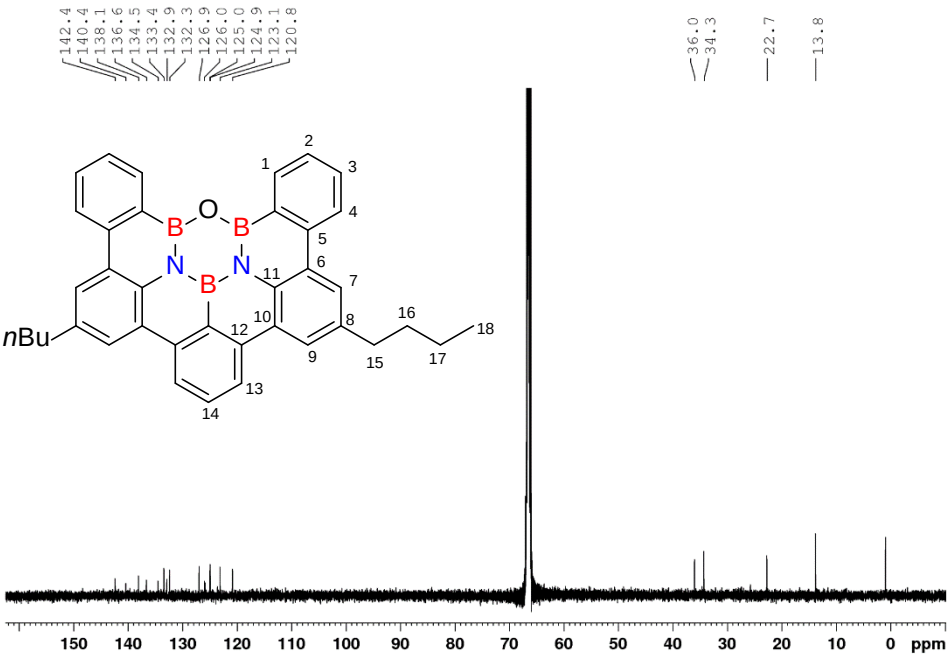


Figure S19: ^{13}C-NMR of **A** in dioxane-d_8 at 80 °C.

EuroEA Elemental Analyser

AutoRun name : AG Bettinger-052219 (125)
Date of Analysis : 22 May 2019
Time of Analysis : 13:16:11
Analysed by : ea

Signed By : ea
Operator Group : GRP1
Configuration : CHNS

Calibration Type : K-Factor

Results Summary for Element %

#	Type	Name	N %	C %	H %	S %	O %	Weight (mg)
1	Blk	Blank	-	-	-	-	-	-
2	Blk	Blank	-	-	-	-	-	-
3	Std	Sulphanilamide	16.430	42.021	4.718	18.641	-	1.724
4	Std	Sulphanilamide	16.107	41.677	4.649	18.601	-	1.139
5	Smp	MF 153	5.118	80.879	5.900	-	-	1.078
6	Smp	MF 153	4.960	80.969	5.889	-	-	1.053

berechnet 4,95 80,62 5,88 %

Figure S20: Elementary analysis of **A**.

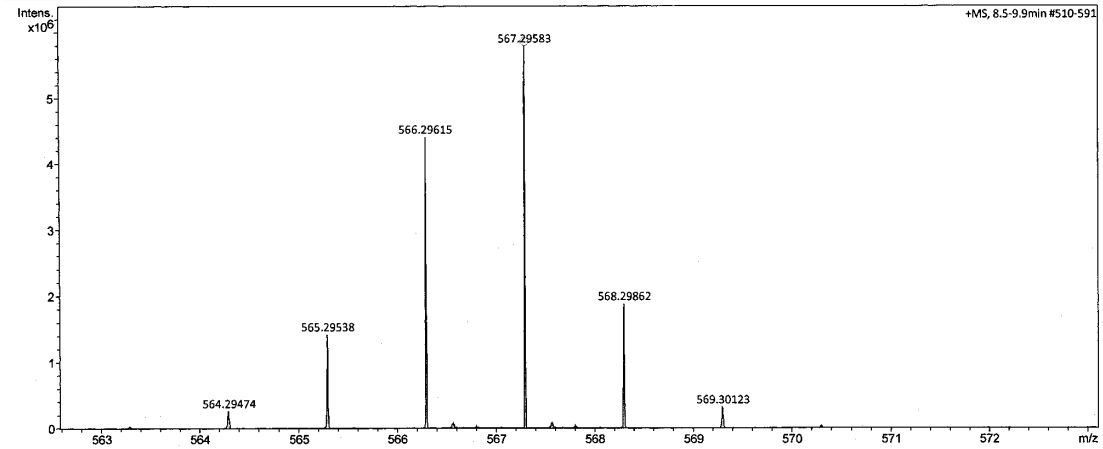
Display Report

Analysis Info
Analysis Name D:\Data\oi\Fingerle_MF 153000001.d
Method tune_low_apci_DIP_neu.m
Sample Name
Comment

Acquisition Date 1/13/2020 2:26:56 PM
Operator BDAL@DE
Instrument maXis 288882.21253

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	220 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	2200 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	4000 nA	Set APCI Heater	400 °C



Fingerle_MF 153000001.d
Bruker Compass DataAnalysis 4.2 printed: 1/13/2020 2:52:22 PM by: BDAL@DE Page 1 of 1

Figure S21: HR-APCI of **A**.

High Resolution MS

☐ **FT-ICR-MS**

☐ **ESI- oder APCI-TOF-MS** (MS/MS möglich)

☐ **egal (je nach freien Kapazitäten)**

Name: AK:

Tel. email:

Datum:

Probenbezeichnung: MF153 nominelle Masse:

Falls Masse nicht bekannt, welcher Massenbereich soll gemessen werden:

Summenformel (falls bekannt):

Strukturformel (falls bekannt):

Einwaage (zwischen 0,1mg und 2 mg):

Löslich in:

Falls schon gelöst, in welchem Lösemittel und in welcher Konzentration:

Hinweise bezüglich Zersetzlichkeit:

Hinweise bezüglich Toxizität (wenn bekannt):

Hohe Massengenauigkeit erwünscht? ja/nein

Massenanalyse erwünscht?

Wenn ja, welche Elemente sollen berücksichtigt werden?

MS/MS erwünscht?:

Ergebnis:

$[M+H]^+_{(theor.)}$ = 567,29448 (567,29627)

Gemessen = 567,29583

Relative Massenabweichung = 0,81 ppm

Figure S22: Data sheet of HR-APCI of **A**.

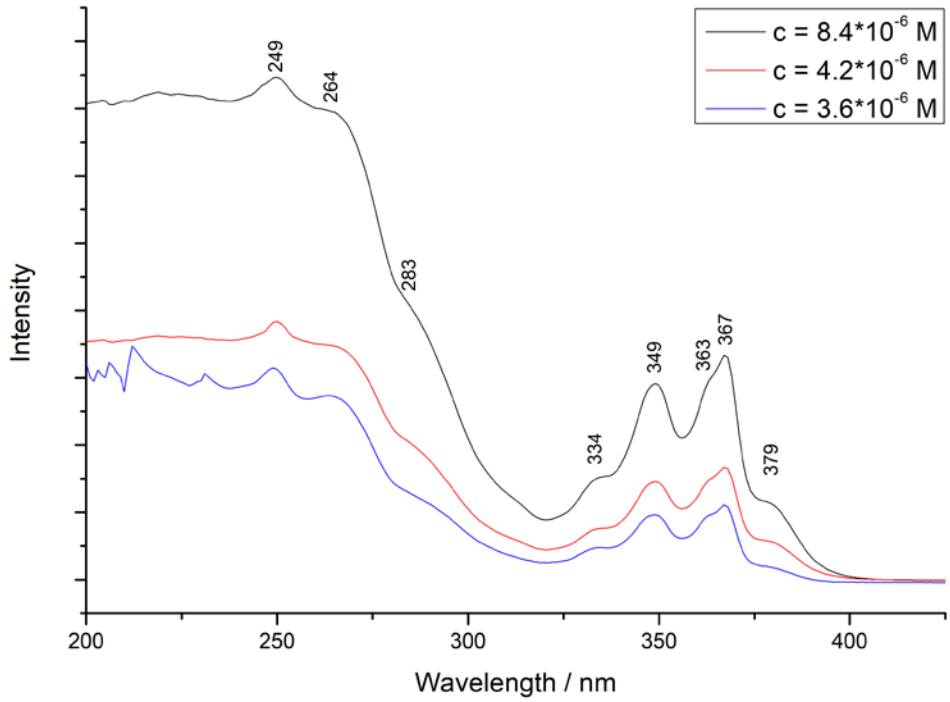


Figure S23: UV-Vis spectra of **A** in dioxane (various concentrations).

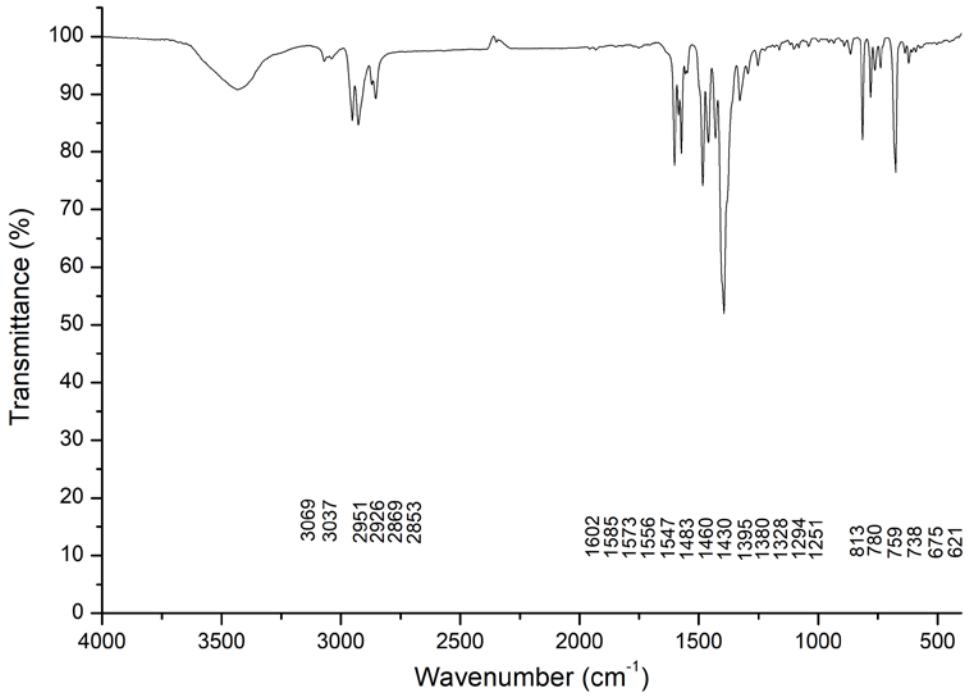


Figure S24: IR (KBr) spectra of **A**.

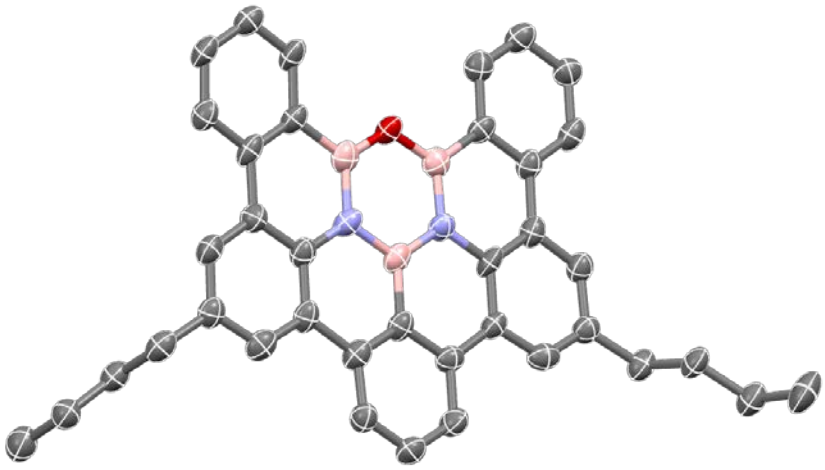


Figure S25: Molecular structure of **A** (hydrogens are omitted for clarity).

References

1. K. Kim and K. D. Jordan, *J. Phys. Chem.*, 1994, **98**, 10089-10094.
2. P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623-11627.
3. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, W. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B.

G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, J. E. P. Jr., F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 09*, Revision A.02; Gaussian, Inc.: Wallingford CT, 2009.

4. R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650-654.
5. R. E. Stratmann, G. E. Scuseria and M. J. Frisch, *J. Chem. Phys.*, 1998, **109**, 8218-8224.
6. Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta and P. v. R. Schleyer, *Chem. Rev.*, 2005, **105**, 3842-3888.
7. P. v. R. Schleyer, H. Jiao, N. J. R. v. E. Hommes, V. G. Malkin and O. L. Malkina, *J. Am. Chem. Soc.*, 1997, **119**, 12669-12670.
8. G. E. Herberich, H.-W. Marx, S. Moss, P. v. R. Schleyer and T. Wagner, *Chem. Eur. J.*, 1996, **2**, 458-461.
9. K. Wolinski, J. F. Hinton and P. Pulay, *J. Am. Chem. Soc.*, 1990, **112**, 8251-8260.
10. D. Geuenich, K. Hess, F. Köhler and R. Herges, *Chem. Rev.*, 2005, **105**, 3758-3772.
11. R. Herges and D. Geuenich, *J. Phys. Chem. A*, 2001, **105**, 3214-3220.