Supporting Information

HBC-Porphyrin – Close contact chromophores

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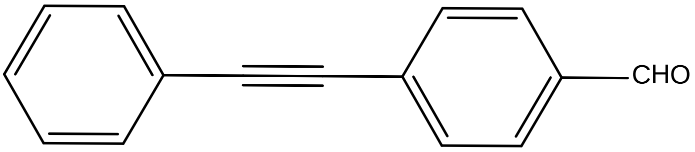
Experimental Section

All chemicals were purchased from chemical suppliers and used without further purification. All analytical reagent-grade solvents were purified by distillation. Hexakis-*tert.*butyl-hexaperibenzocoronene was synthesized following literature procedures.[1] Thin layer chromatography (TLC): Merck silica gel 60 F254. Detection: UV lamp (λ = 254 & 366 nm). Flash- chromatography (FC): Macherey–Nagel silica gel 60 M (230–400 mesh, 0.04–0.063 mm). Solvents were purified by distillation prior to use. Mass spectrometry: AXIMA Confidence MALDI TOF mass spectrometer, nitrogen UV laser, 50 Hz, λ=337 nm wavelength, Shimadzu. 3,5-dimethoxy-4-hydroxycinnamic acid (SIN), 2,5-dihydroxybenzoicacid (DHB) and 2-[(2*E*)-3-(4-*tert*-Butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) were used as matrix or without matrix (OM). High-resolution electrospray ionization (ESI) mass spectrometry: Bruker maXis 4G and Bruker microTOF II. NMR spectroscopy: JEOL JNM EX 400 and JEOL JNM GX 400 and Bruker Avance 300. Chemical shifts are referenced to residual protic impurities in the solvents (^{1}H) or the deuterated solvent itself (^{13}C) and reported relative to external $SiMe_4$. The resonance multiplicities are indicated as br (broad), s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet).

1. L. Zhai, R. Shukla, S. H. Wadumethrige and R. Rathore, *J. Org. Chem.*, 2010, **75**, 4748-4760.

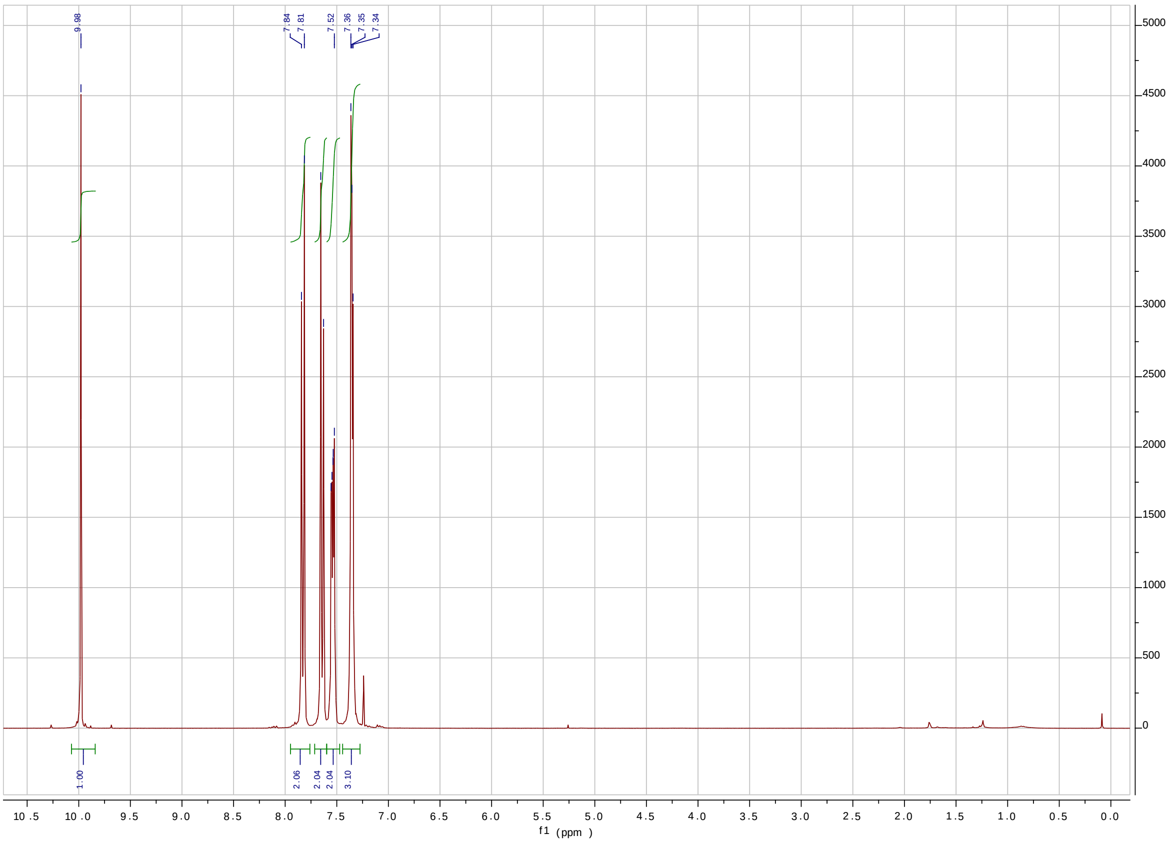
4-(phenylethynyl)benzaldehyde (**1**)

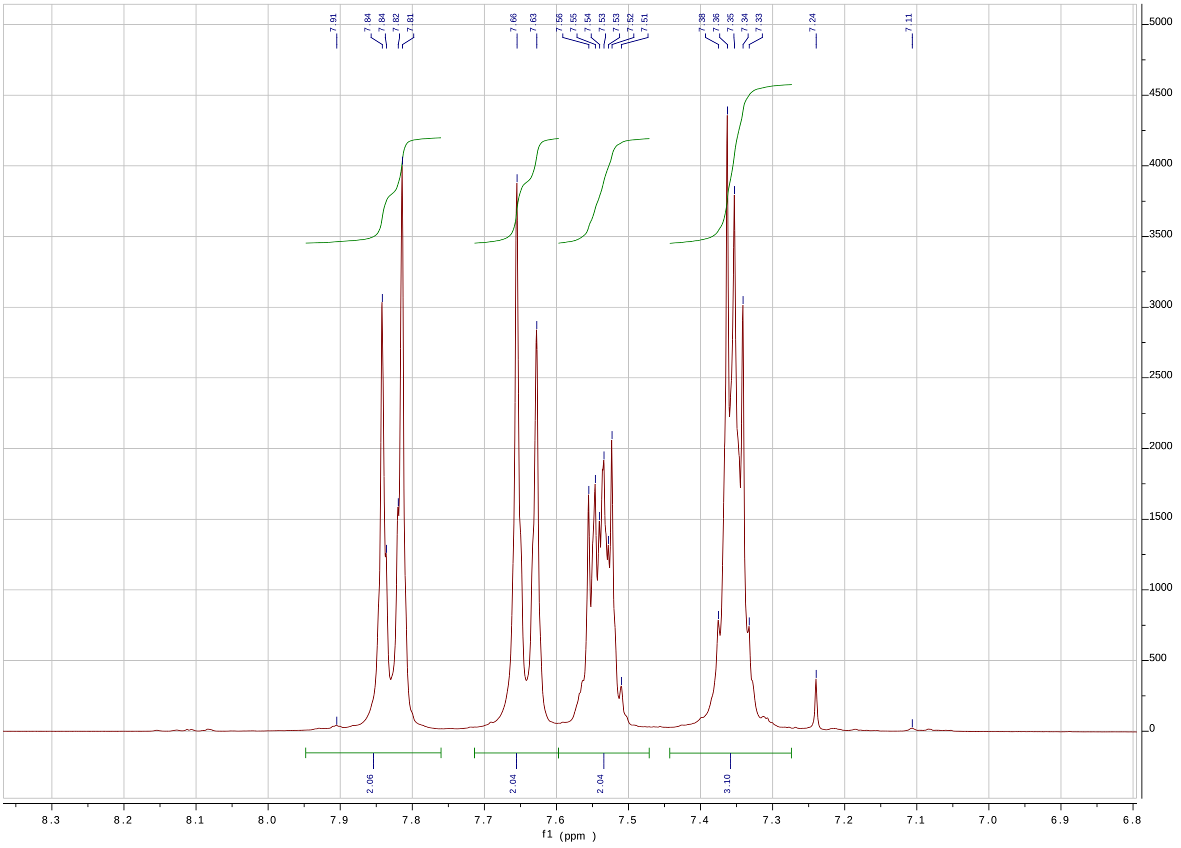


Chemical Formula: $C_{15}H_{10}O$
Exact Mass: 206,07
Molecular Weight: 206,24
m/z: 206.07 (100.0%), 207.08 (16.4%), 208.08 (1.5%)

To a solution of phenylacetylene (4.85 g, 47.6 mmol) and 4-bromobenzaldehyde (8.00 g, 43.2 mmol) in 150 ml dry MeCN with 15 ml NEt_3, copper(I)iodide (0.16 g, 0.9 mmol) and $Pd(Cl_2(PPh_3)_2$ (0.30 g, 0.04 mmol) were added under argon atmosphere. The reaction mixture was stirred under reflux overnight. After cooling to room temperature dichloromethane was added and the crude mixture was washed with water and diluted hydrochloric acid. The organic layer was dried over magnesium sulfate and after evaporation of the solvent the product was obtained as beige shining pellets in 60% yield after recrystallization from small amounts of *n*-hexane.

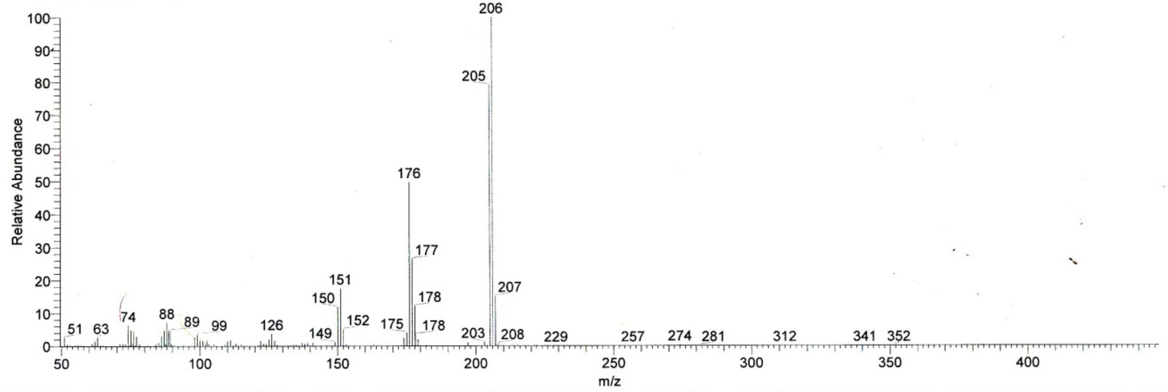
^{1}H NMR (400 MHz, CDCl$_3$, rt): $\delta = 9.98$ (s, 1H, CHO), 7.83 (d, 2H, ^3J = 8 Hz, H-C$_{\text{arom}}$), 7.65 (d, 2H, ^3J = 8 Hz, H-C$_{\text{arom}}$), 7.54 (m, aromatic), 7.35 (m, aromatic) ppm.

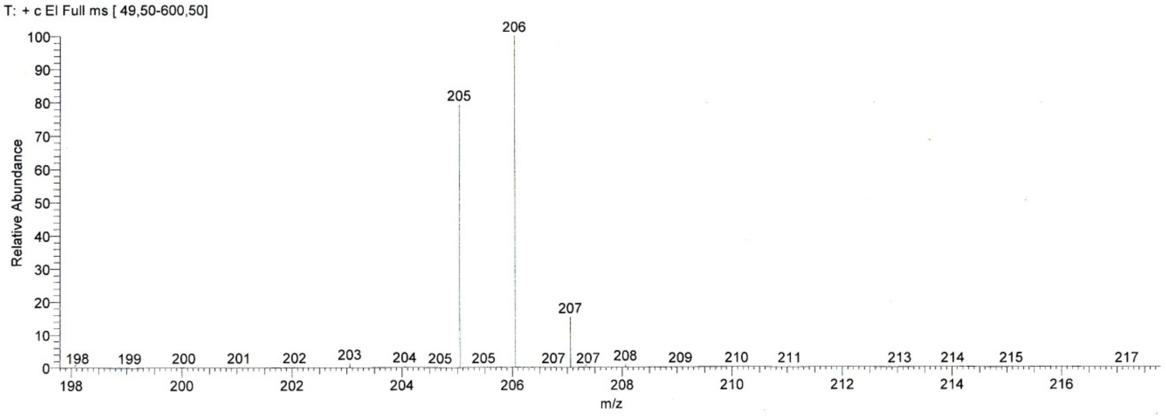




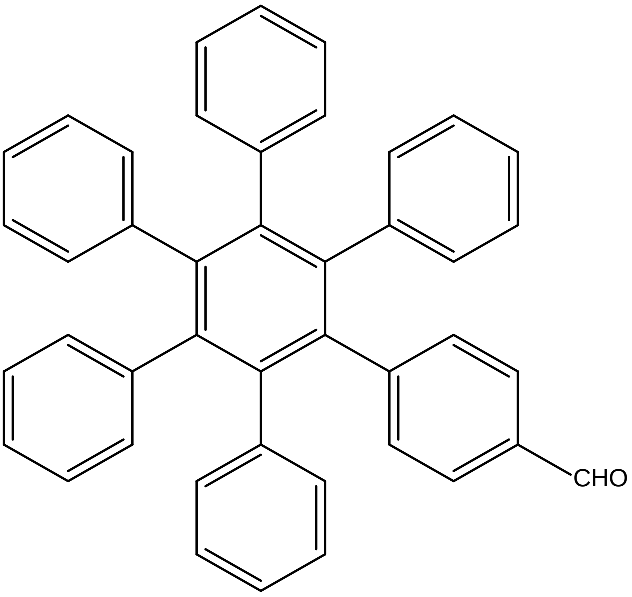
^{13}C NMR (100 MHz, $CDCl_3$, rt): δ = 191.5, 135.4, 132.2, 131.9, 129.6, 129.6, 129.1, 128.6, 122.5 ppm.

MS-EI(+): $^{m}/_{z}$ [M^+] $C_{15}H_{10}O$: calc.: 206.07, found: 206.





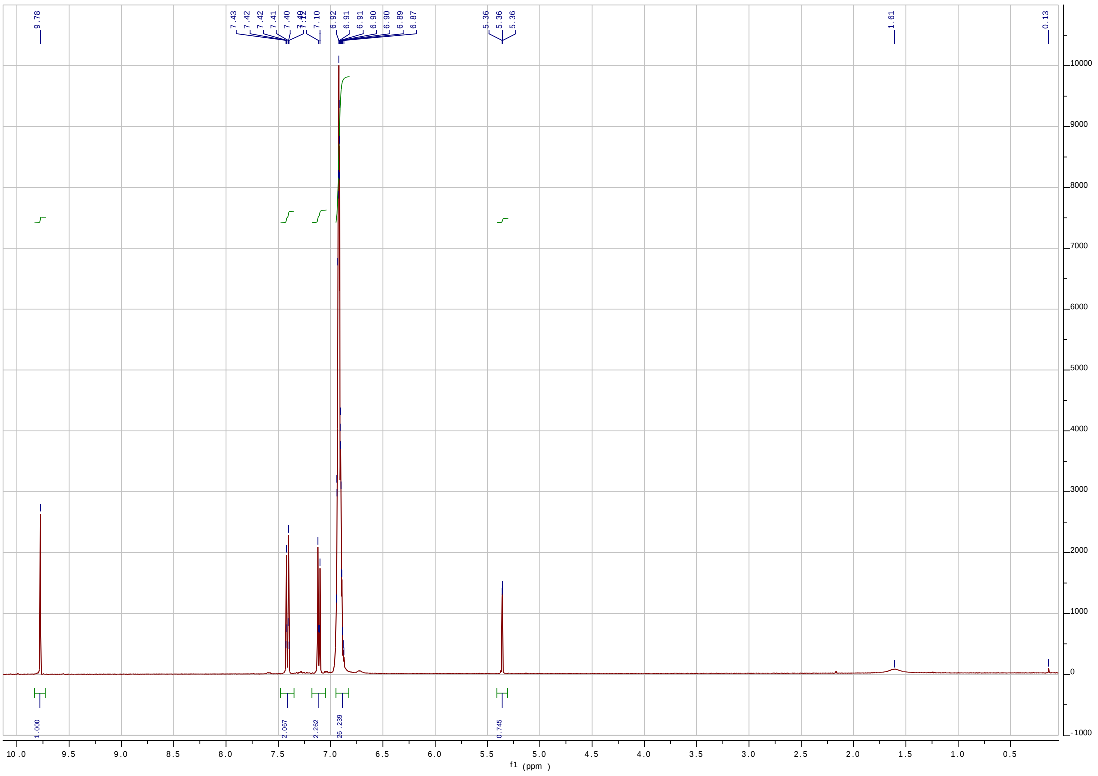
3',4',5',6'-tetraphenyl-[1,1':2',1''-terphenyl]-4-carbaldehyde – HPB-CHO (**2**)

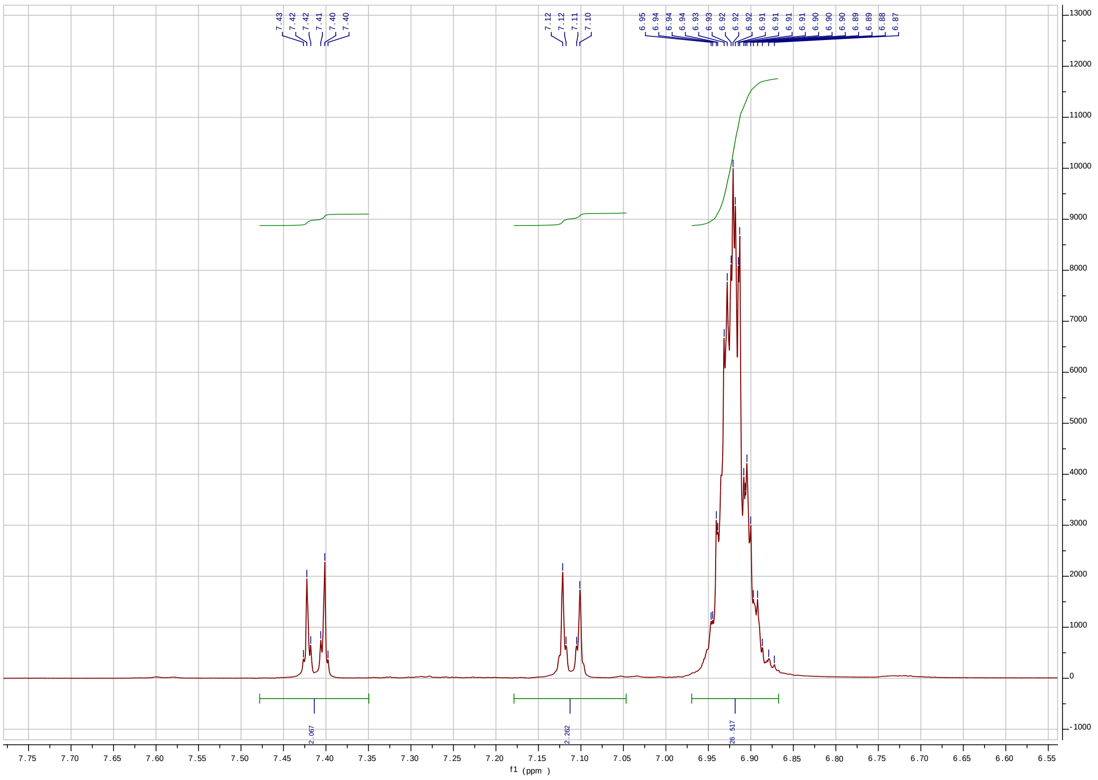


Chemical Formula: $C_{43}H_{30}O$
Exact Mass: 562,23
Molecular Weight: 562,70
m/z: 562.23 (100.0%), 563.23 (46.5%), 564.24 (10.7%), 565.24 (1.7%)

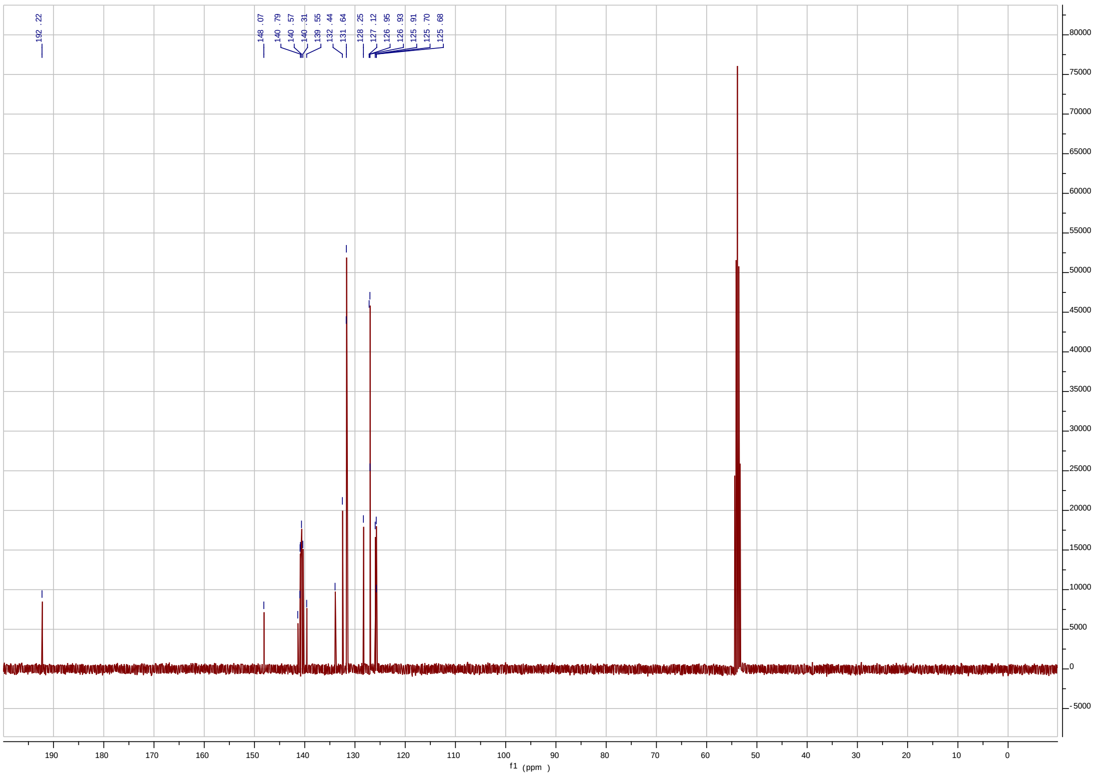
4.85 g (12.6 mmol) neat tetraphenylcyclopentadienone were mixed with 5.2 g (25.3 mmol) **1** in a 30 cm long Schlenck tube equipped with a bubble counter under low, but, constant argon stream. The tube was heated to 240°C in a mono mode laboratory microwave oven (CEM discover – open vessel dynamic) under dynamic irradiation with peakpower of 300W. After 30 minutes the tube was removed from the oven and cooled down to room temperature. The crude product was dissolved in as little dichloromethane as possible and transferred to a 300 mL Erlenmeyer flask. After evaporation to dryness the raw product was repeatedly washed and filtered from boiling ethanol to yield HPB-CHO (**2**) as white powder in typically >60 % yield.

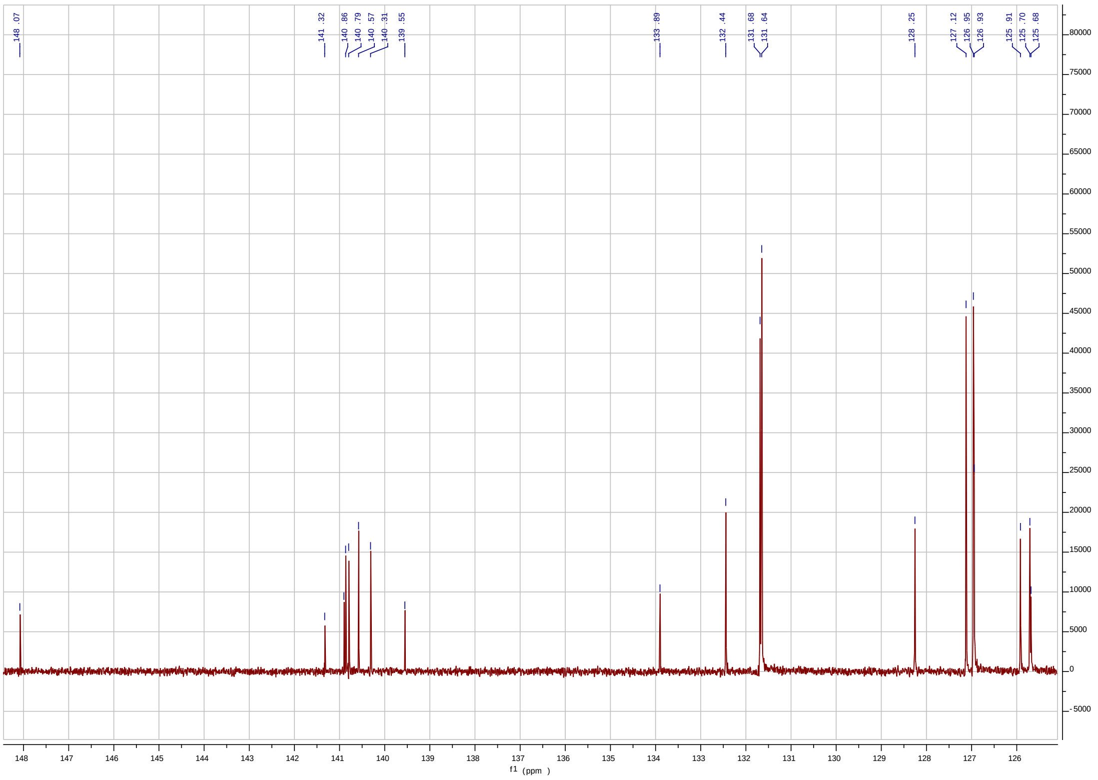
^{1}H NMR (400 MHz, CD_2Cl_2, rt): $\delta = 9.78$ (s, 1H, CHO), 7.42 (d, 2H, $^3J = 8$ Hz, H-$C_{arom,CHO}$), 7.11 (d, 2H, $^3J = 8$ Hz, H-$C_{arom,CHO}$), 6.91 (m, 25H, H-$C_{arom.}$) ppm.



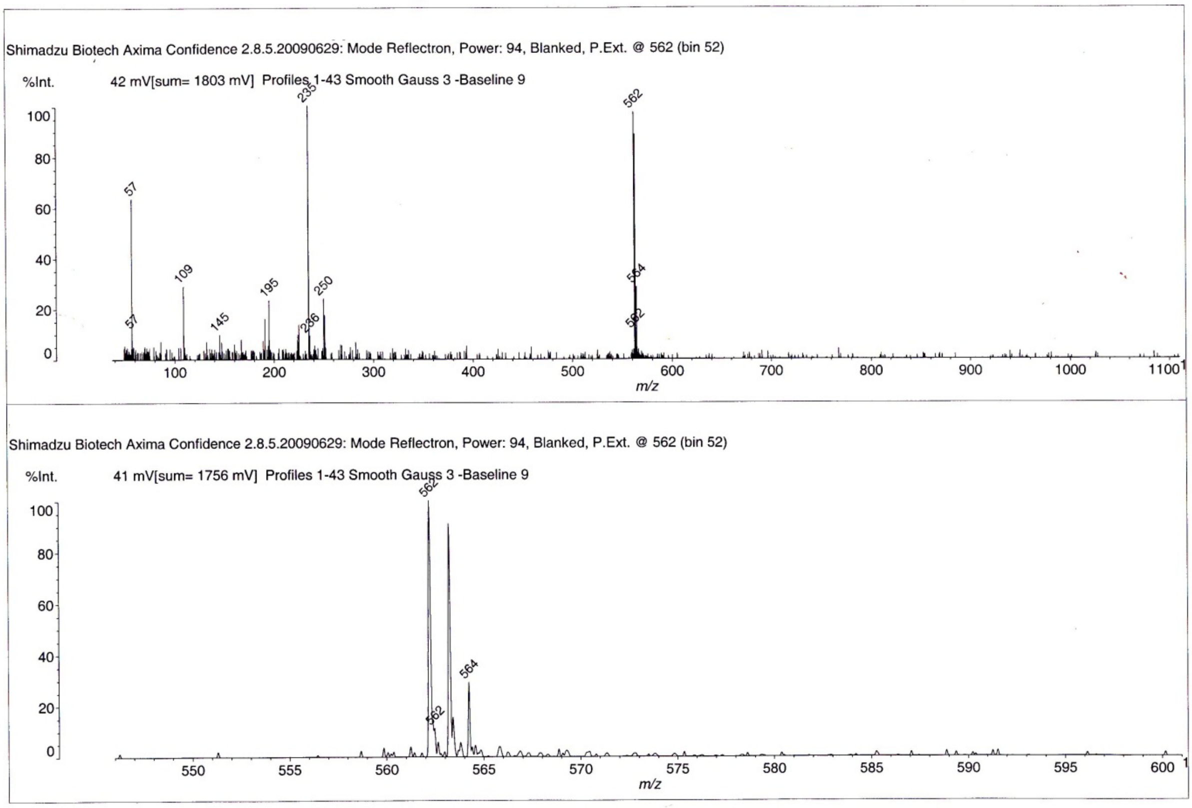


^{13}C NMR (100.5 MHz, CD_2Cl_2, rt): δ = 192.22, 148.07, 140.79, 140.57, 140.31, 139.55, 132.44, 131.64, 128.25, 127.12, 126.95, 126.93, 125.91, 125.70, 125.68

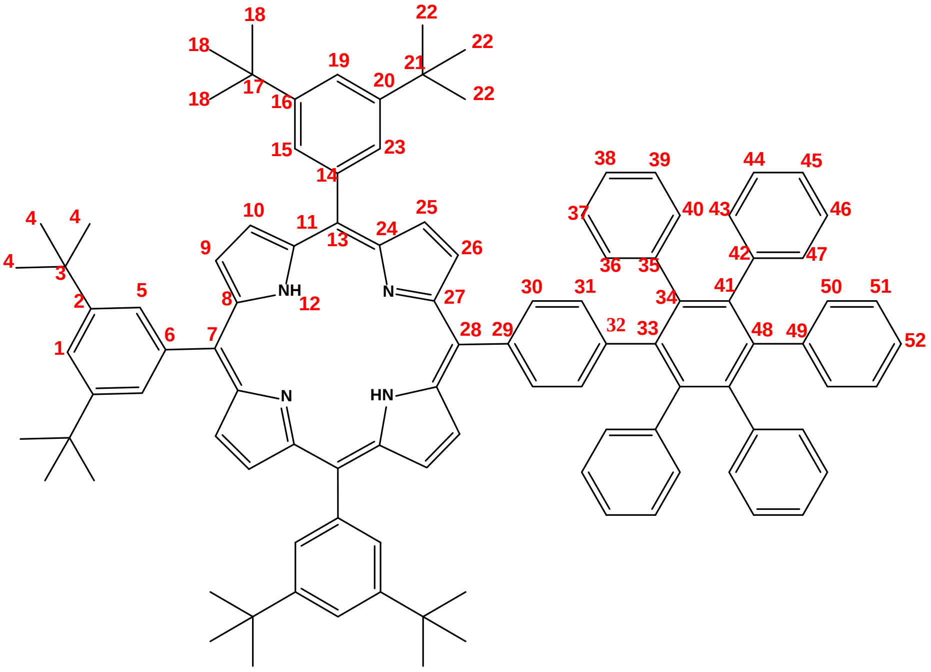




MALDI-TOF-MS (DCTB): $^{m}/_{z}$ [M^{+}] $C_{43}H_{30}O$: calc.: 562.23, found: 562.



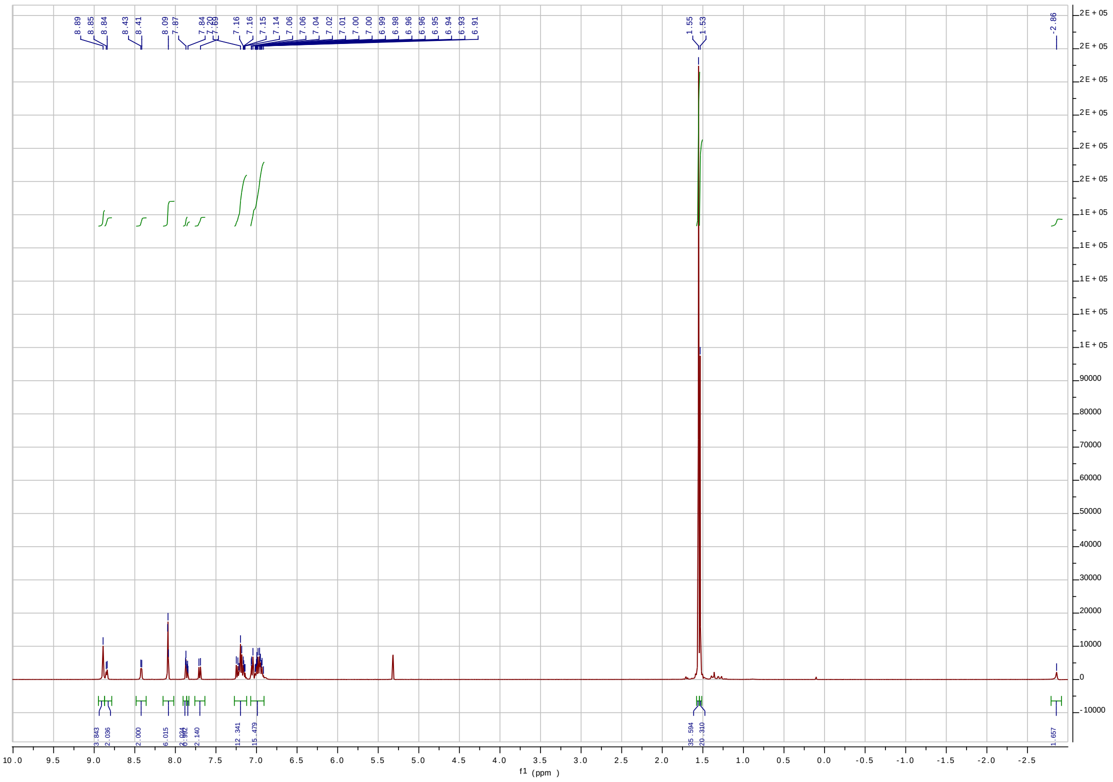
5-(*4’*-2’’,3’’,4’’,5’’,6’’-pentaphenyl-phenyl)-10,15,20-tris(3’,5’-*tert*-butyl-phenyl)-porphyrin – mono-HPB-porphyrin (**3**)

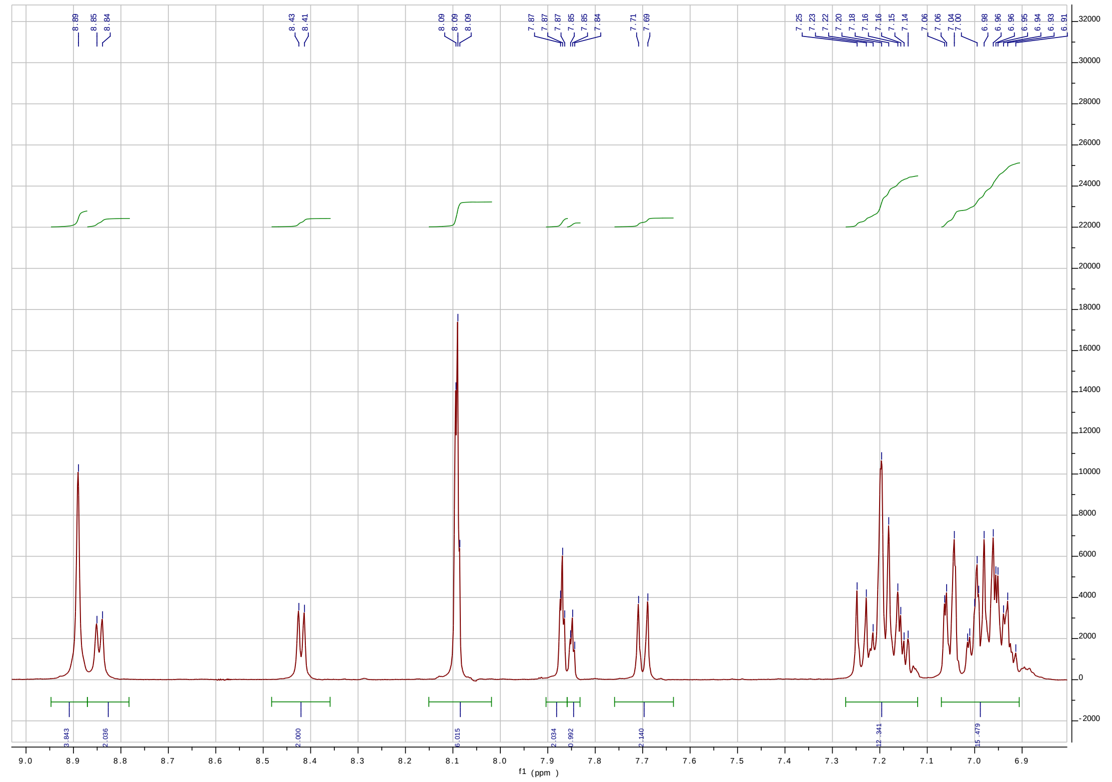


Chemical Formula: $C_{104}H_{102}N_4$
Exact Mass: 1406,81
Molecular Weight: 1407,95
m/z: 1407.81 (100.0%), 1406.81 (87.7%), 1408.82 (56.1%), 1409.82 (20.9%), 1410.82 (5.8%), 1408.81 (1.5%), 1411.83 (1.2%), 1407.82 (1.0%)

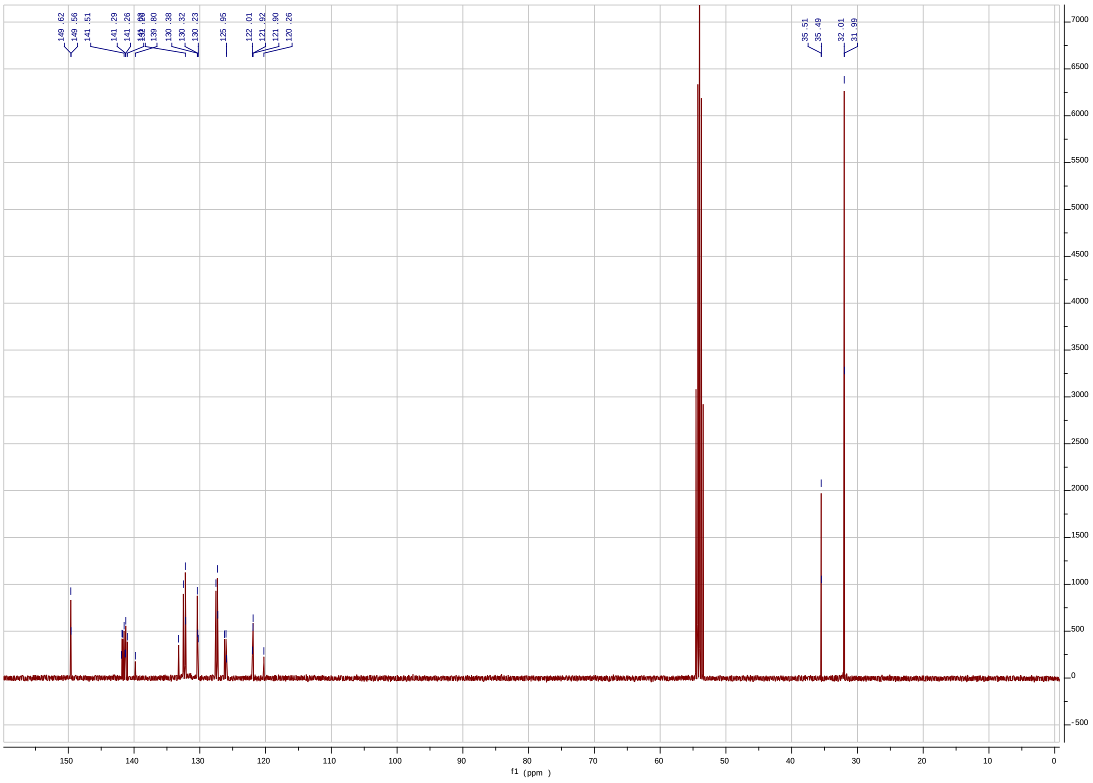
In 1.4 L dichloromethane and 10 mL EtOH compound **2** (2.00 g, 3.55 mmol) together with 3,5-*tert*-butylbenzaldehyde (2.33 g, 10.66 mmol) and pyrrole (2.15 g, 31.98 mmol) was dissolved and purged with nitrogen. After addition of $BF_3{\cdot}OEt_2$ (0.05 g, 0.36 mmol) the reaction mixture was stirred for one hour at room temperature. DDQ (1.21 g, 5.33 mmol) was added and the reaction mixture stirred for two hours at room temperature. The solvent was evaporated and the crude reaction mixture first purified by a plug followed by column chromatography with hexane:dichloromethane (5:1) as eluent. The purple crystals of porphyrin **3** were obtained as second fraction and recrystallized from MeOH/hexane in up to 19 % yield.

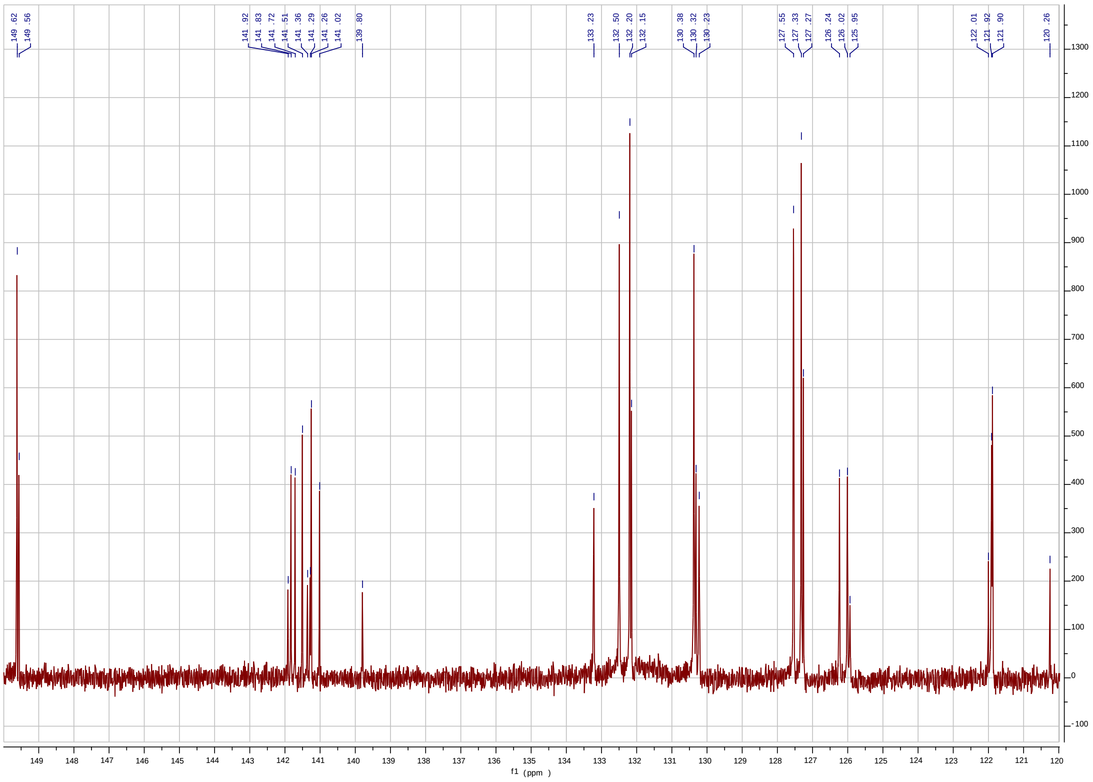
^{1}H NMR (400 MHz, CD$_2$Cl$_2$, rt): δ [ppm] = 8.89 (s, 4H, *9/10*), 8.85 (d, 2H, 3J = 4.7 Hz, *25*), 8.42 (d, 2H, 3J = 4.7 Hz, *26*), 8.09 (m, 6H, *15/19/23*), 7.87 (t, 2H, 4J = 1.7 Hz, *5*), 7.85 (t, 1H, 4J = 1.7 Hz, *1*), 7.70 (d, 2H, 3J = 7.8 Hz, *30*), 7.25-7.14 (m, 12H, *31/36/40/43/47/50*), 7.06-6.91 (m, 15H, *37-39/44-46/51/52*), 1.55 (s, 36H, *18/22*), 1.53 (s, 18H, *4*), -2.86 (s, 2H, *12*)



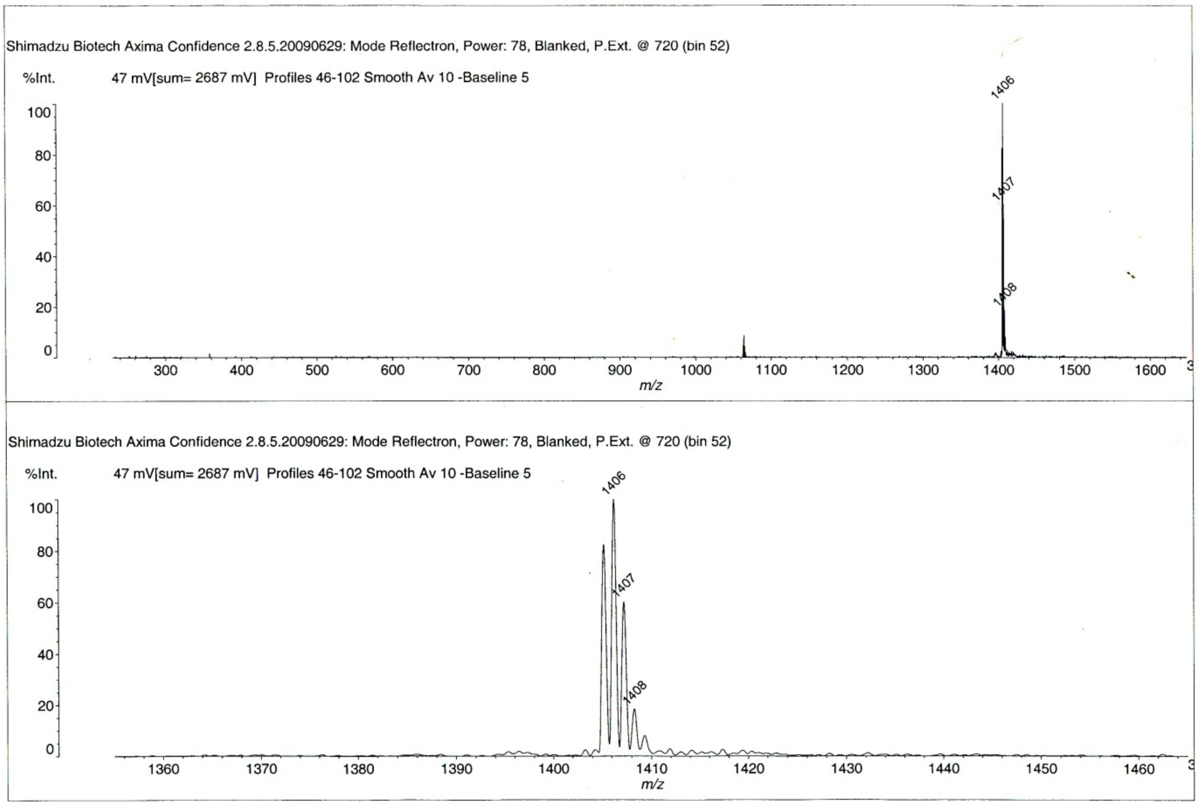


^{13}C NMR (100 MHz, CD_2Cl_2, rt): δ [ppm] = 149.62, 149.56, 141.92, 141.83, 141.72, 141.51,141.36, 141.29, 141.26, 141.02, 139.80, 131.23, 132.50, 132.20, 132.15, 130.38, 130.32, 130.23, 127.55, 127.33, 127.27, 126.24, 126.02, 125.95, 122.01, 121.92, 121.90, 120.26, 35.51, 35.49, 32.01, 31.99

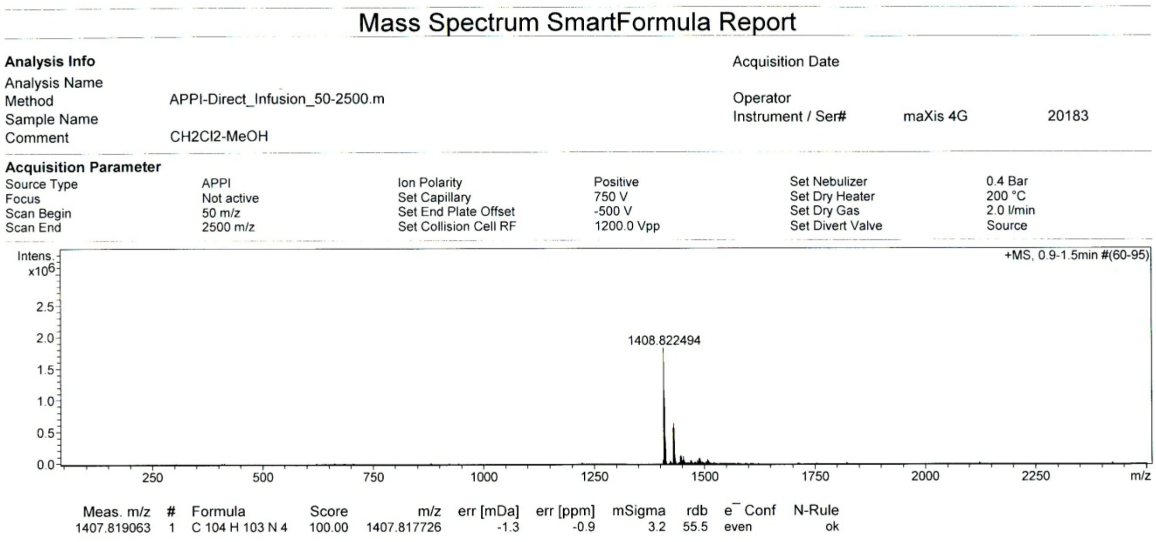




MALDI-TOF-MS (OM): $^{m}/_{z}$ $[M^+]$ $C_{104}H_{102}N_4$: calc.: 1407.95, found: 1405.



HRMS (ESI$^-$) for [M-H$^+$] $C_{104}H_{103}N_4$: calc.: 1407.817726, found: 1407.819063.



Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name
Method APPI-Direct_Infusion_50-2500.m
Sample Name
Comment CH2Cl2-MeOH

Acquisition Date
Operator
Instrument / Ser# maXis 4G 20183

Acquisition Parameter

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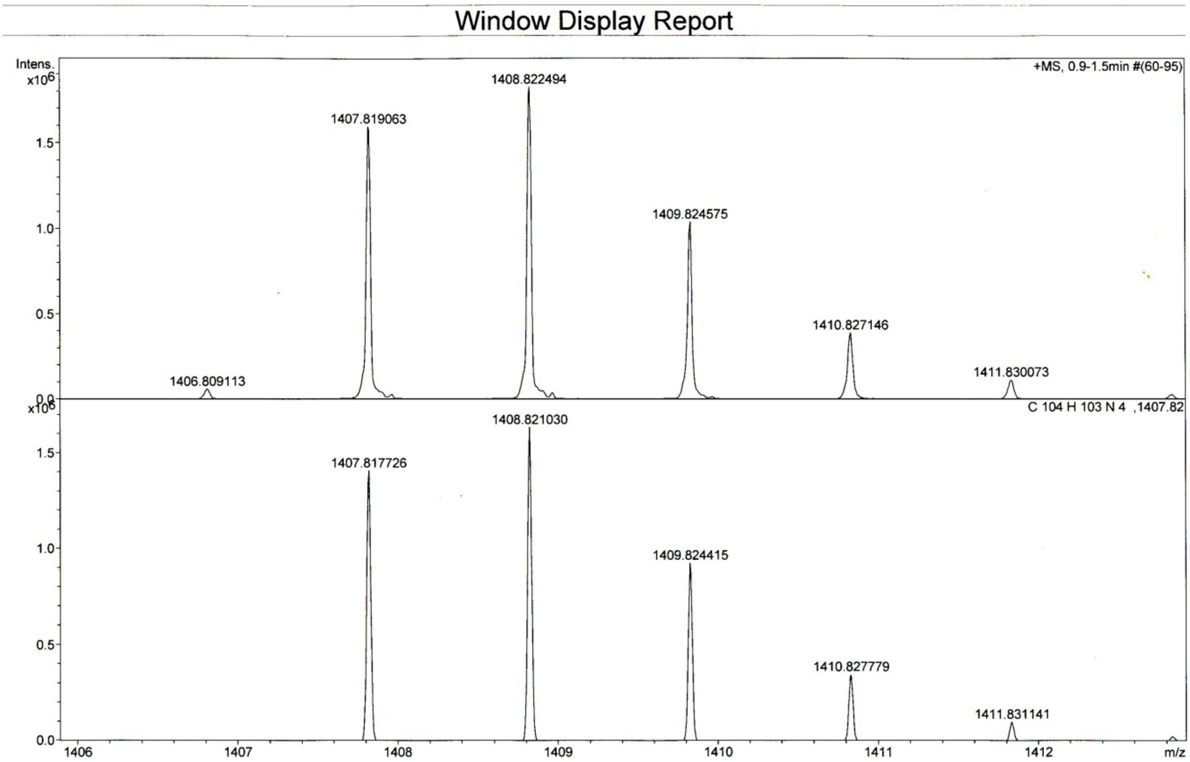
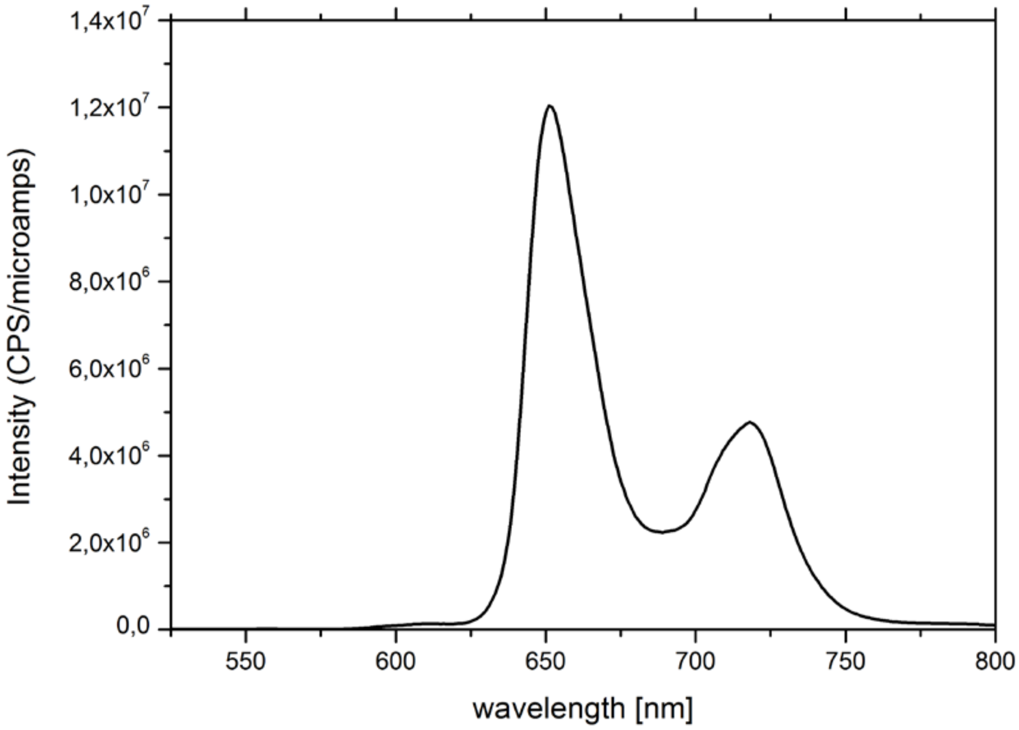
Focus	Not active	Set Capillary	750 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	2.0 l/min
Scan End	2500 m/z	Set Collision Cell RF	1200.0 Vpp	Set Divert Valve	Source

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1407.819063	1	C 104 H 103 N 4	100.00	1407.817726	-1.3	-0.9	3.2	55.5	even	ok



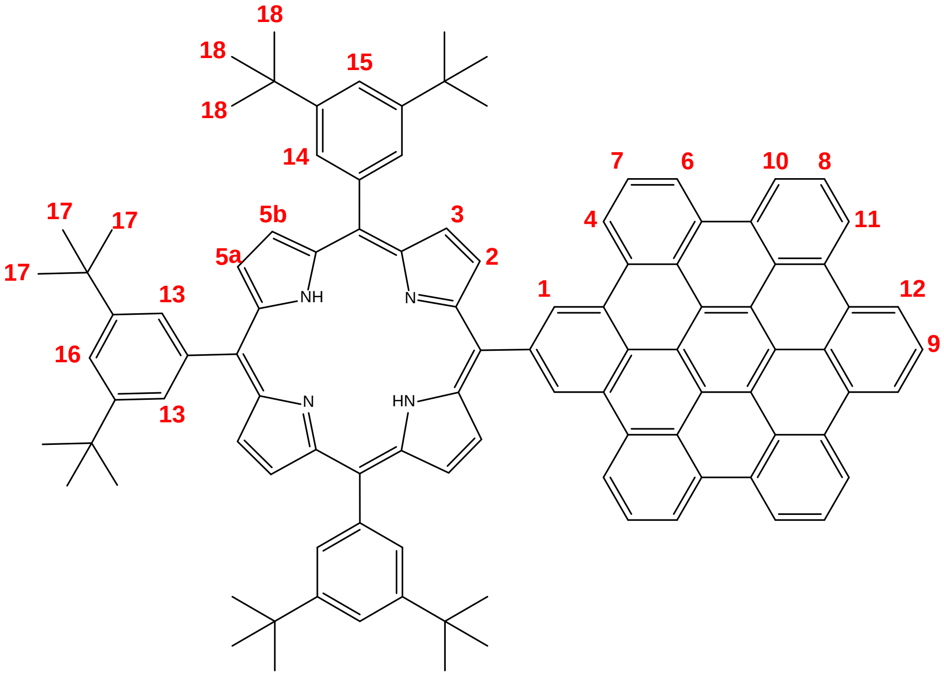
Window Display Report

UV/Vis (THF): $\lambda_{max}(\varepsilon[M^{-1}cm^{-1}])$ = 419 (472200), 515 (14500), 549 (6000), 592 (1700), 647 (1300) nm.



Emission spectra of the HPB-Porphyrin **3** after excitation at 515 nm.

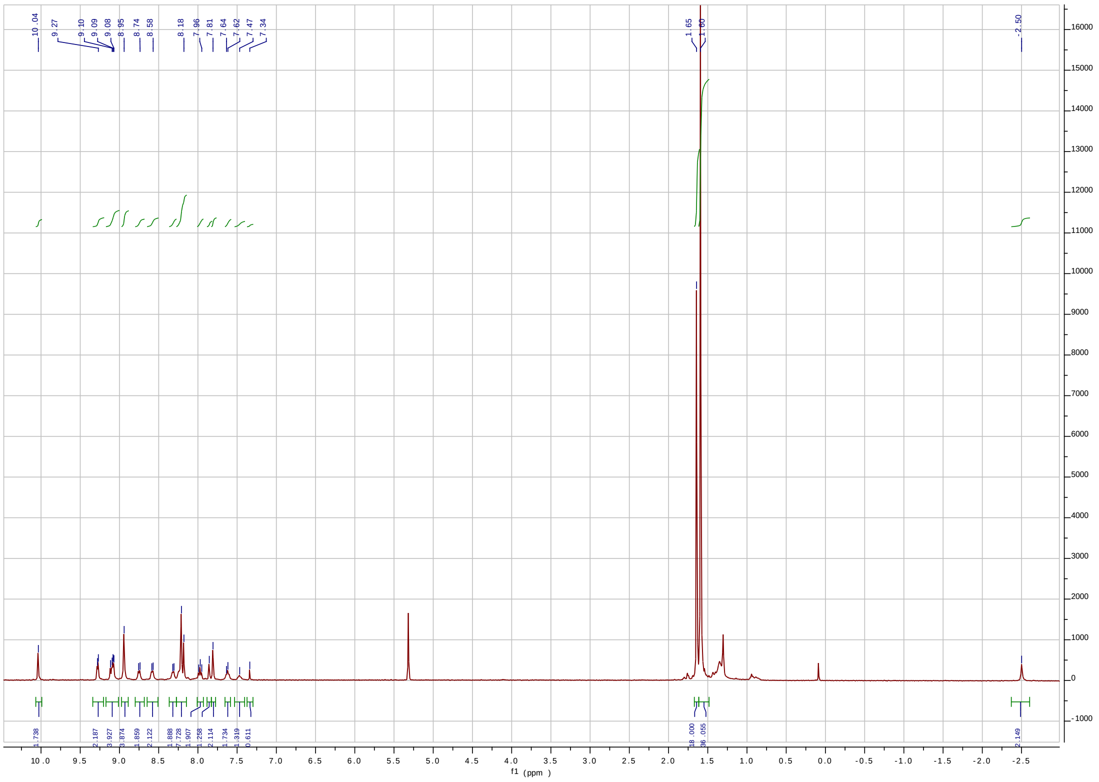
5-(HBC)-10,15,20-tris(3',5'-*tert*-butyl-phenyl)-porphyrin – mono-HBC-porphyrin (**4**)

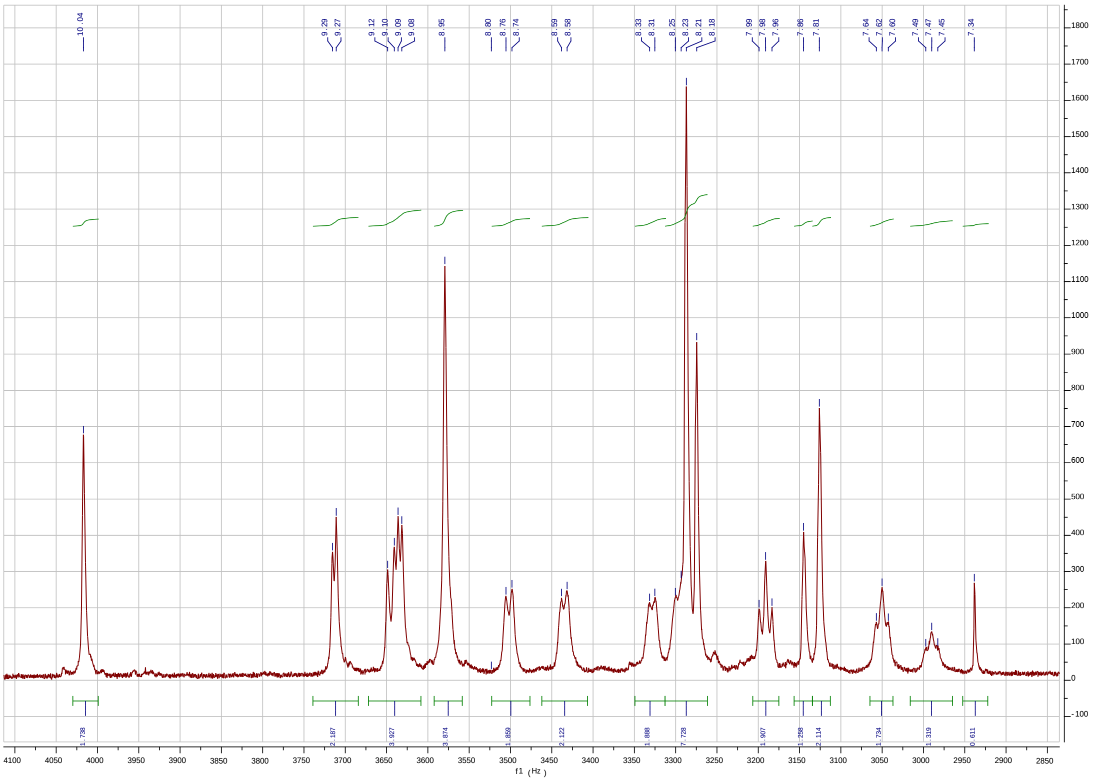


Chemical Formula: $C_{104}H_{90}N_4$
Exact Mass: 1394,72
Molecular Weight: 1395,85
m/z: 1395.72 (100.0%), 1394.72 (88.1%), 1396.72 (56.7%), 1397.73 (20.9%), 1398.73 (5.7%), 1395.71 (1.3%), 1399.73 (1.3%), 1396.73 (1.0%)

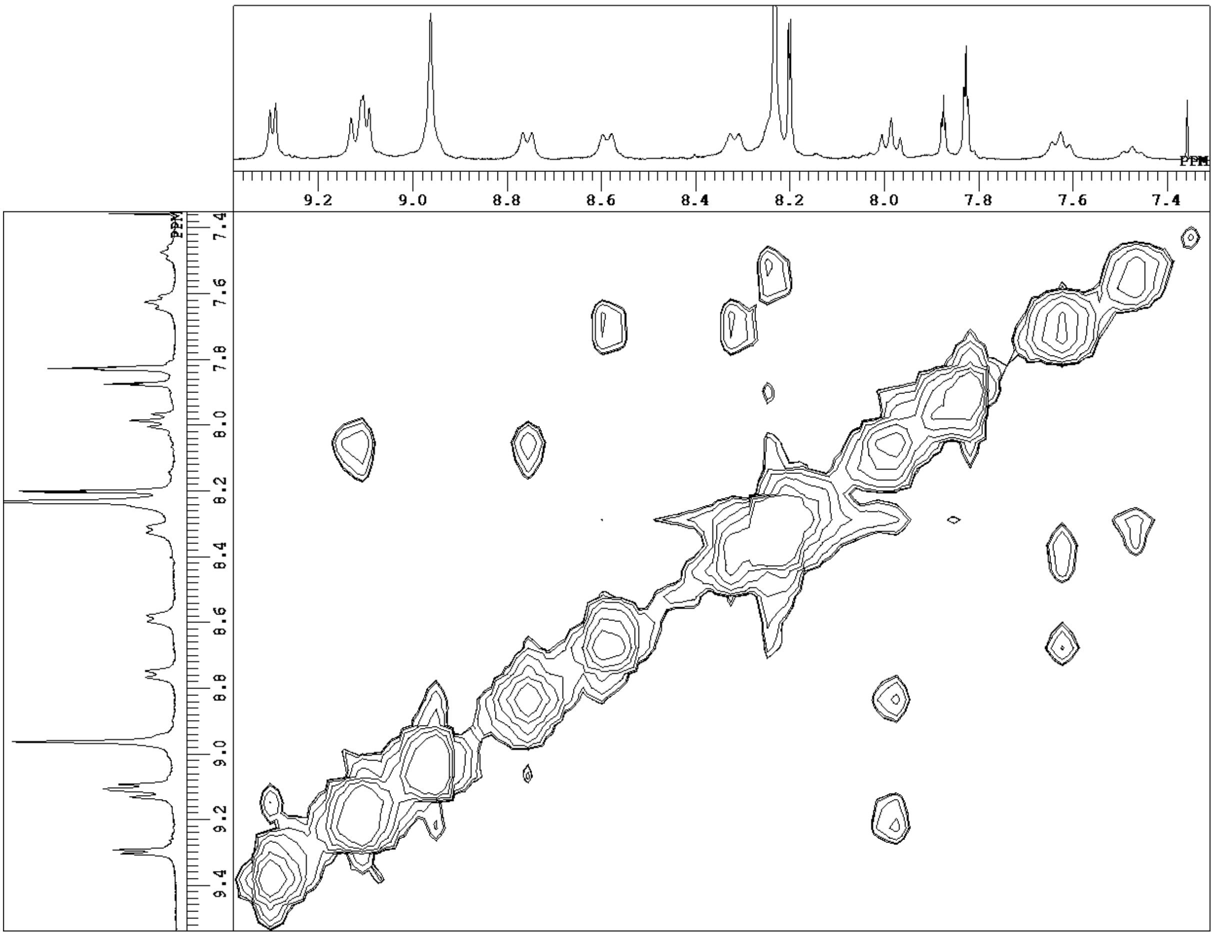
To an ice cooled, argon saturated solution of 15 mg (0.011 mmol) of **4** in 50 mL dry dichloromethane 0.57 ml of a freshly prepared solution of 300 mg/mL water free iron(III)chloride in dry nitromethane are added dropwise by syringe through a pressure equilibrated septum while maintaining a low but constant stream of argon bubbling through the solution. Cooling is maintained for typically one hour and evaporated solvent is replaced if necessary. Subsequently, the flask is sealed, stirred for 8 hours then quenched by addition of 50 mL cold methanol and neutralized with sat. $NaHCO_3$. The mixture is poured into 200 mL water/cyclohexane (1:1 v/v), the organic layer is washed two times with distilled water and the solvent is removed under reduced pressure. Further purification can be performed by column chromatography (silica gel, DCM/Hexane 1:2), if necessary. The final product is obtained as bronze solid in good to quantitative yields.

^{1}H NMR (400 MHz, CS_2, CD_2Cl_2, rt): δ [ppm] = 10.04 (s, 2H, *1*), 9.28 (d, 2H, 3J = 4.7 Hz, *2*), 9.11 (d, 2H, ^3J = 7.9 Hz, *4*), 9.09 (d, 2H, ^3J = 4.7 Hz, *3*), 8.95 (s, 4H, *5a/5b*), 8.75 (d, 2H, ^3J = 7.2 Hz, *6*), 8.59 (d, 2H, ^3J = 6.7 Hz, *10*), 8.32 (d, 2H, ^3J = 6.4 Hz, *11*), 8.24 (d, 2H, *12*), 8.21 (s, 4H, *14*), 8.18 (s, 2H, *13*), 7.98 (t, 2H, ^3J = 7.6 Hz, *7*), 7.86 (s, 1H, *16*), 7.81 (s, 2H, *15*), 7.62 (t, 2H, ^3J = 7.3, *8*), 7.47 (t, 1H, ^3J = 7.7 Hz, *9*), 1.65 (s, 18H, *17*), 1.60 (s, 36H, *18*)

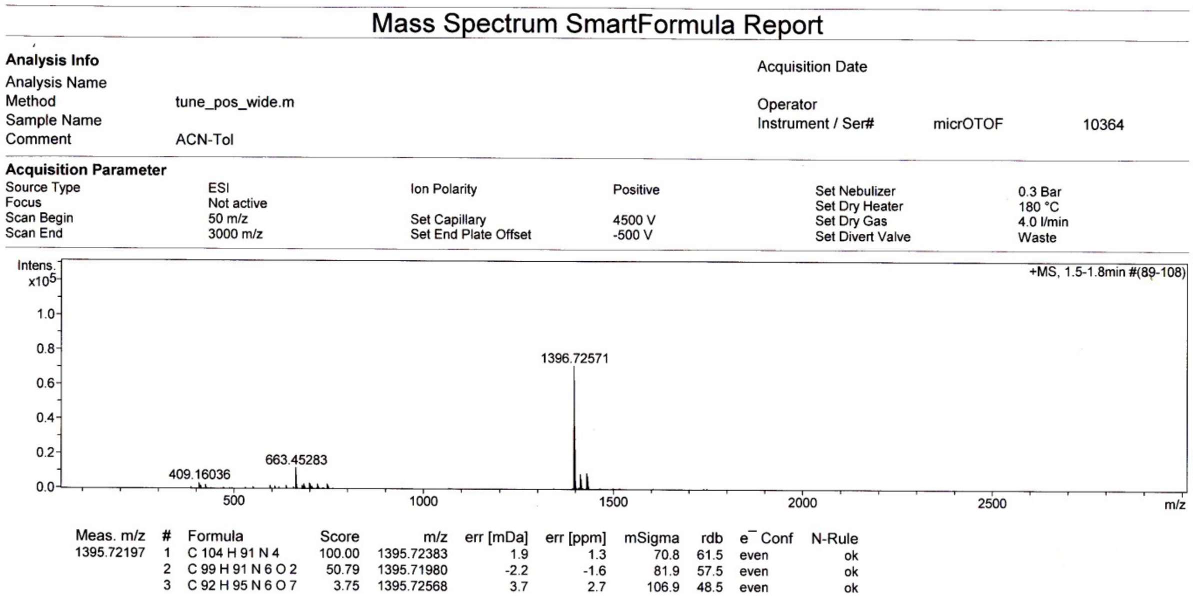




COSY-2D NMR (400 MHz, CS_2/CD_2Cl_2) – aromatic region



HRMS (ESI$^-$) for $C_{104}H_{90}N_4$: calc.: 1395.72383, found: 1395.72197



Mass Spectrum SmartFormula Report

Analysis Info
Analysis Name
Method tune_pos_wide.m
Sample Name
Comment ACN-Tol

Acquisition Date

Operator
Instrument / Ser# micrOTOF 10364

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
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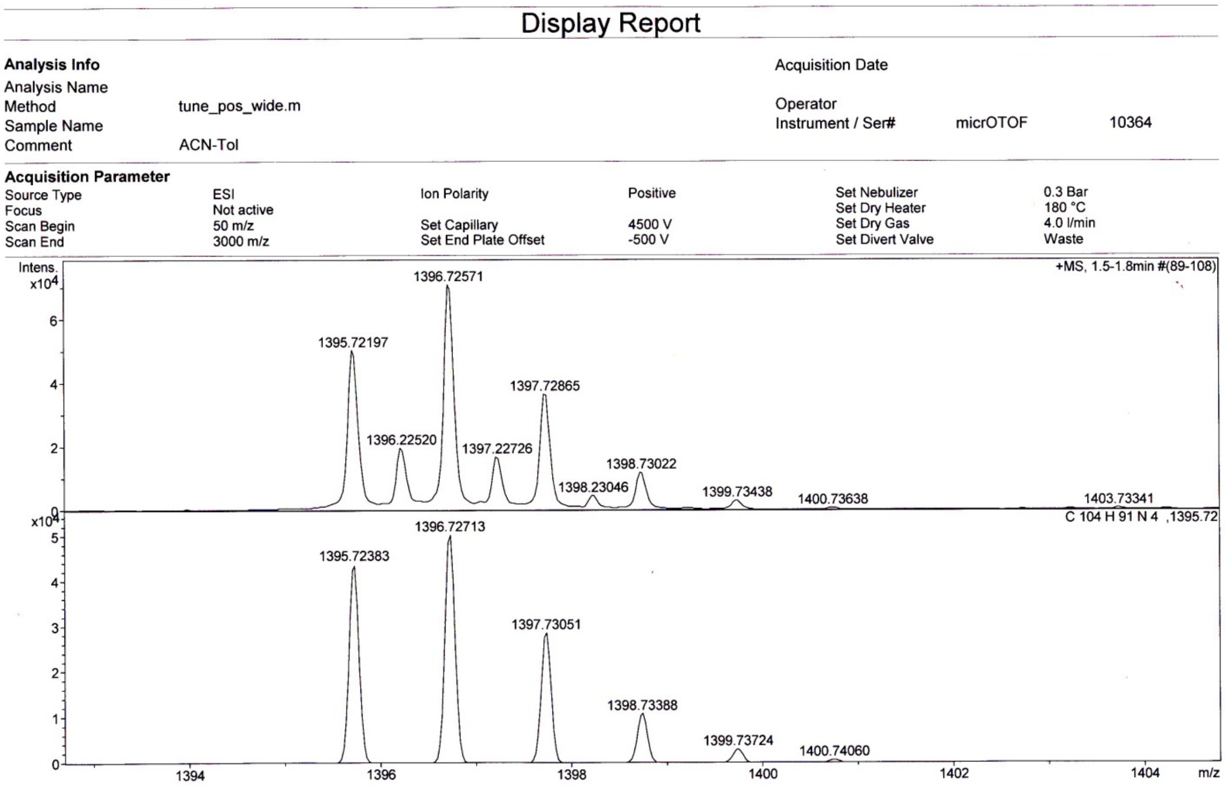
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1395.72197	1	C 104 H 91 N 4	100.00	1395.72383	1.9	1.3	70.8	61.5	even	ok
	2	C 99 H 91 N 6 O 2	50.79	1395.71980	-2.2	-1.6	81.9	57.5	even	ok
	3	C 92 H 95 N 6 O 7	3.75	1395.72568	3.7	2.7	106.9	48.5	even	ok



Display Report

Analysis Info
Analysis Name
Method tune_pos_wide.m
Sample Name
Comment ACN-Tol

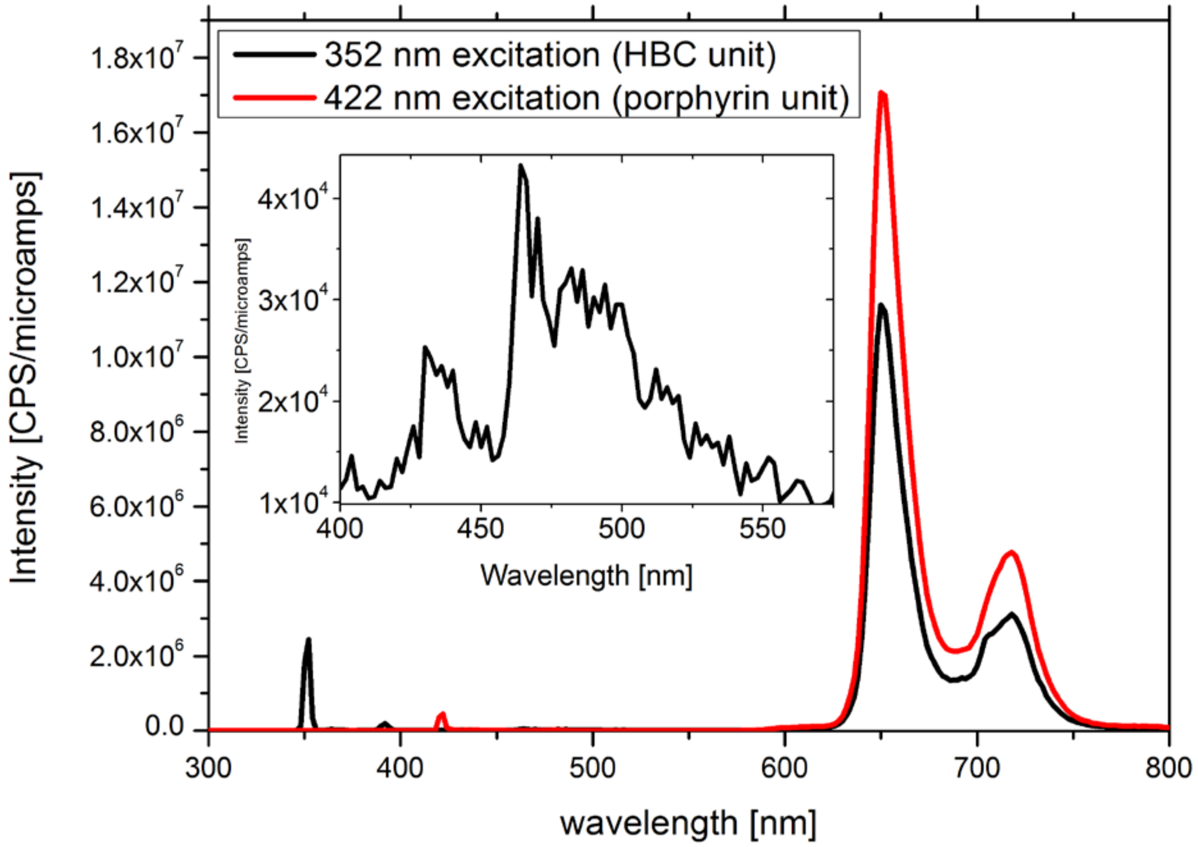
Acquisition Date

Operator
Instrument / Ser# micrOTOF 10364

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

UV/Vis (THF): $\lambda_{max}(\varepsilon[M^{-1}cm^{-1}])$ = 353 (64400), 426 (208400), 516 (11000), 552 (6000), 591 (2900), 648 (2600) nm.



Emission spectra of HBC-porphyrin **4** for different excitation wavelengths are shown, which excite either the HBC (352 nm) or the porphyrin (422 nm) unit of the conjugate. In both cases strong emission of the porphyrin is observed. When the HBC unit is excited emission from the HBC is completely suppressed as deduced from the zoomed region of the expected emission in the inset.