Electronic Supplementary Material (ESI) for Chemical Science.

UNRAVELLING THE CONDUCTANCE PATH THROUGH SINGLE PORPHYRIN JUNCTIONS

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SUPPORTING INFORMATION

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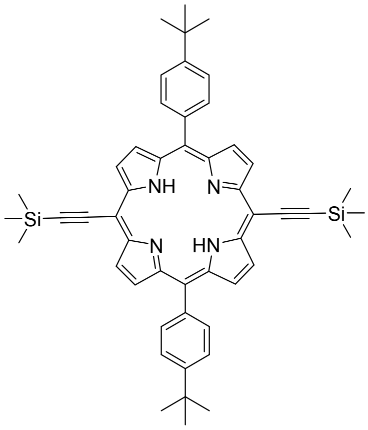
EXPERIMENTAL PROCEDURES

GENERAL REMARKS

Reagents and solvents: All commercially available compounds were purchased from Sigma-Aldrich, Acros, Apollo Scientific, Alfa Aesar and Fluorochem and used without further purification, but 1*H*-pyrrole which was filtered Al_2O_3 prior to use. Anhydrous solvents were purchased from Sigma-Aldrich and stored over molecular sieves (4 Å). THF was dried by distilation over sodium and benzophenone. Net3 was dried by filtering over Al_2O_3. Column chromatography was performed on silica gel P60 (40-63 µm) from SilicycleTM, the solvents were technical grade. TLC was performed with silica gel 60 F254 glass plates purchased from Merck.

Analytics and instruments: NMR experiments were performed on Bruker Avance III NMR spectrometers operating at 250, 400, 500 or 600 MHz proton frequencies. The instruments were equipped with a direct-observe 5 mm BBFO smart probe (250, 400 and 600 MHz), or an indirect-detection 5 mm BBI probe (500 MHz). All probes were equipped with actively shielded z-gradients (10 A). The chemical shifts are reported in ppm relative to tetramethylsilane or referenced to residual solvent peak and the J values are given in Hz (±0.1 Hz). Standard Bruker pulse sequences were used, and the data was processed on Topspin 3.2 (Bruker) using twofold zero-filling in the indirect dimensio. MALDI-TOF mass spectra were recorded on a Bruker MicroFlex LRF spectrometer using tetracyanoquinodimethane (TCNQ) as a matrix. High resolution mass spectra (HRMS) were measured on a Bruker solariX spectrometer with a MALDI source for HR-MALDI-ToF MS or on a maX-isTM4G instrument from Bruker for HR-ESI-ToF MS. Melting points were measured on a Büchi M-565 melting point apparatus and are uncorrected.

SYNTHESIS AND CHARACTERIZATION



1

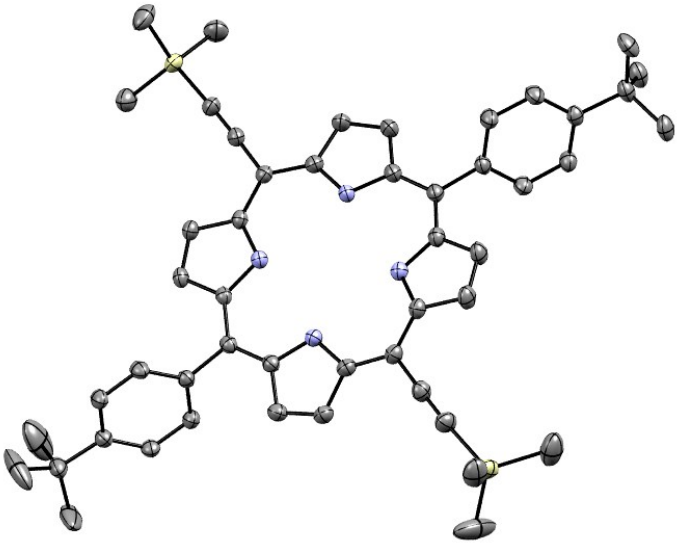
5,15-bis(4-(*tert*-butyl)phenyl)-10,20-bis((trimethylsilyl)ethynyl)-porphyrin (1): A solution of 3-(trimethylsilyl)propiolaldehyde (1.5 mL, 10.0 mmol, 1.0 eq) and 2,2'-((4-(*tert*-butyl)phenyl)-methylene)bis(1*H*-pyrrole)[1] (2.78 g, 10.0 mmol, 1.0 eq.) in CH_2Cl_2 (1000 mL)was purged with argon for 20 min at 0 °C. Trifluoroborate diethyl etherate (0.13 mL, 1.00 mmol, 0.1 eq.) was added and the reaction mixture was stirred for 5 min at 0 °C. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (2.50 g, 11.0 mmol, 1.1 eq.) was added and the mixture was stirred for 1 h at rt. The reaction mixture was filtered over a plug of silica eluted with CH_2Cl_2 and was concentrated under reduced pressure. Crystallisation from CH_2Cl_2/CH_3OH gave the title compound **1** (1.16 g, 1.52 mmol, 30%) as a microcrystalline purple solid.

TLC (SiO_2, CH_2Cl_2/cyclohexane (1:2)): $R_f = 0.39$.

MP: > 300 °C

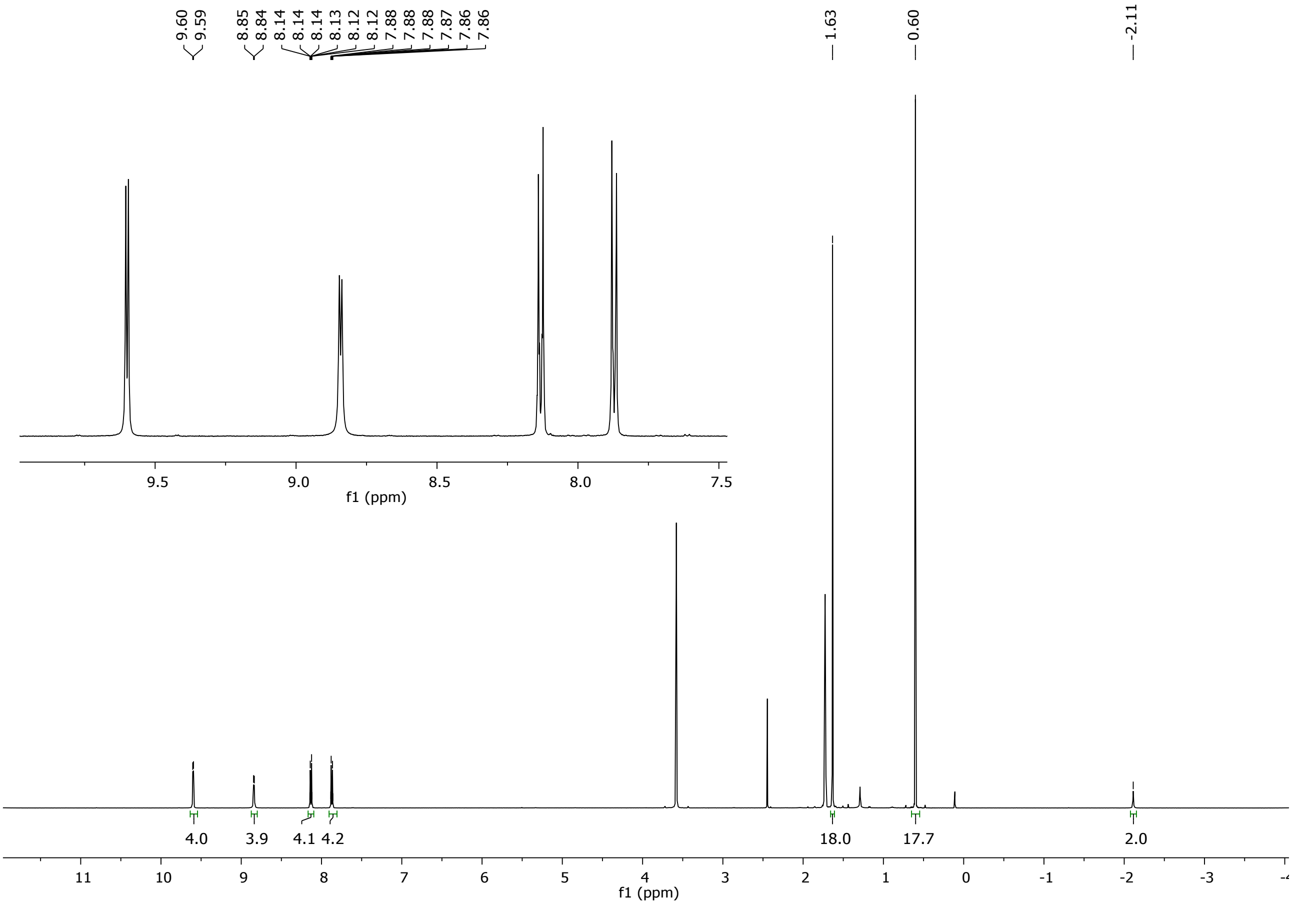
^{1}H-NMR (500 MHz, THF-d_8, 298 K, δ/ppm): 9.60 (d, $^3J_{HH} = 4.8$ Hz, 4H, H_β), 8.84 (d, $^3J_{HH} = 4.7$ Hz, 4H, H_β), 8.16 – 8.09 (m, 4H, H_{Ph}), 7.90 – 7.83 (m, 4H, H_{Ph}), 1.63 (s, 18H, H_{tBu}), 0.60 (s, 18H, H_{TMS}), -2.11 (s, 2H, H_{NH}).

MALDI-TOF *m/z* (%) = 766 [M^+].

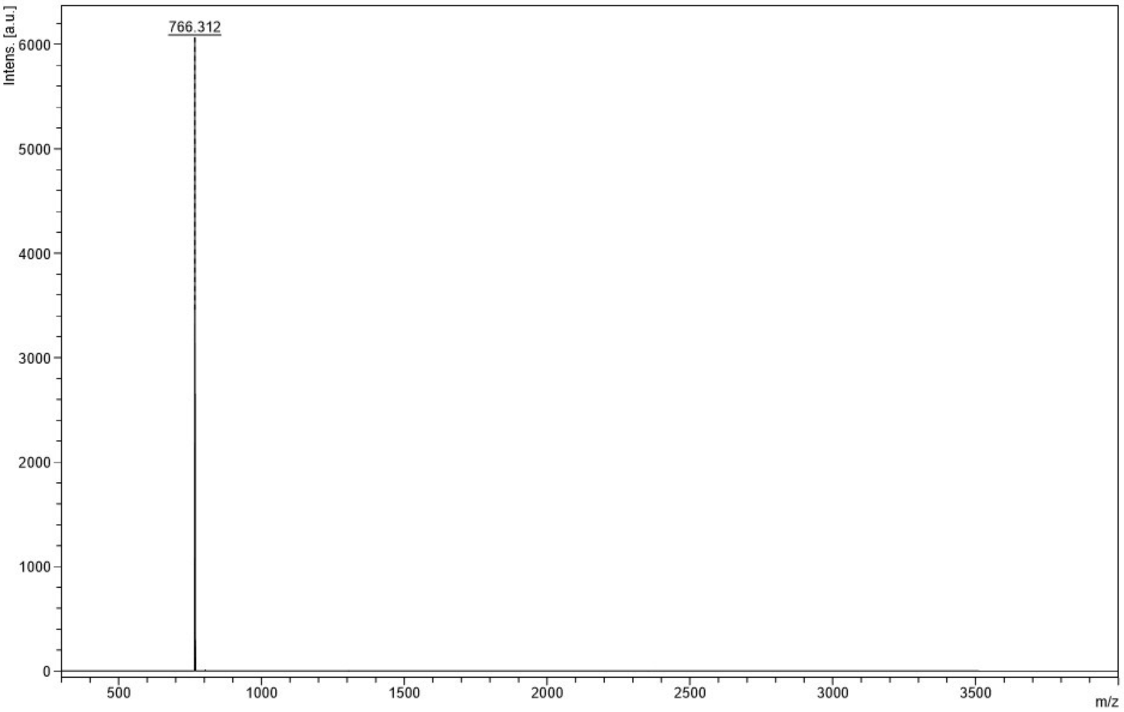


S 1: **ORTEP-representation of the solid state structure of 1.** Thermal ellipsoids are plotted on a 50% probability level. Protons and solvent molecules are omitted for clarity.

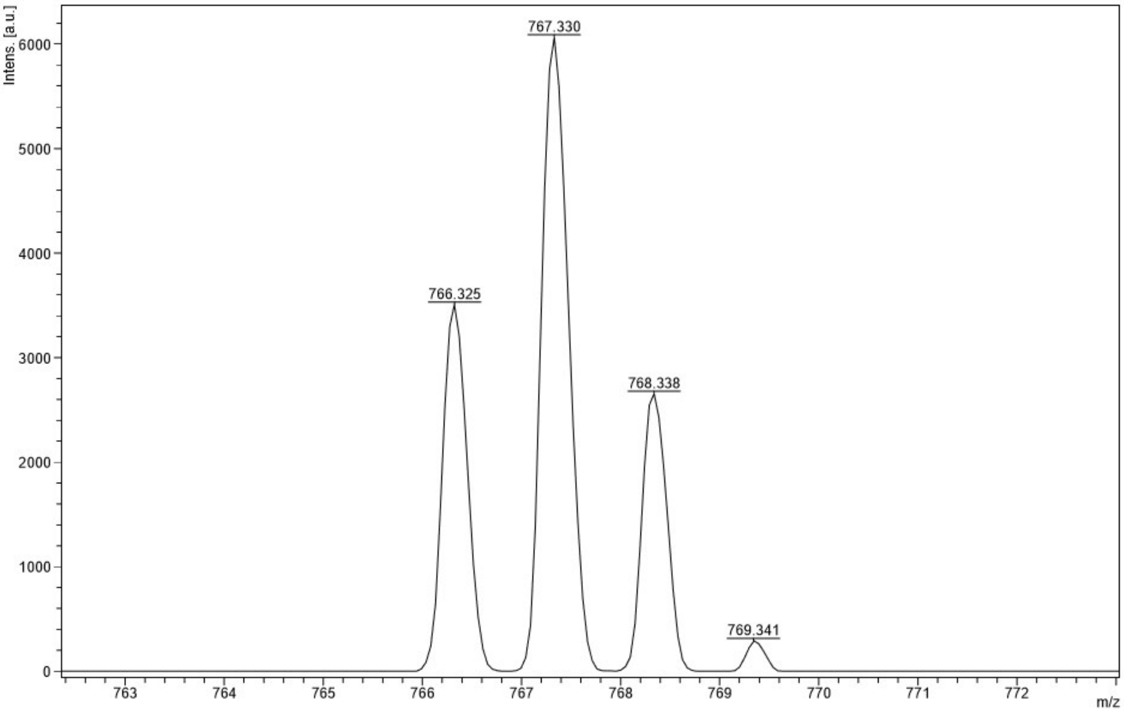
Crystal data for **1**: formula $C_{50}H_{54}N_4Si_2$, M = 767.18, F(000) = 820, purple block, size 0.100 ◊ 0.100 ◊ 0.150 mm^3, triclinic, space group P -1 , Z = 2, a = 10.1051(6) Å, b = 15.0628(8) Å, c = 15.6570(9) Å, α = 71.6998(19) °, β = 78.9052(19) °, γ = 77.5688(19) °, V = 2189.5(2) Å3, Dcalc. = 1.164 g cm^{-3}. The crystal was measured on a Bruker Kappa Apex2 diffractometer at 123K using graphite-monochromated Cu Kα-radiation with λ = 1.54178 Å, Θmax = 70.220 °. Minimal/maximal transmission 0.79/0.90, µ = 1.020 mm-1. The Apex2 suite has been used for datacollection and integration. From a total of 22699 reflections, 7968 were independent (merging r = 0.023). From these, 7930 were considered as observed (I>2.0σ(I)) and were used to refine 513 parameters. The structure was solved by other methods using the program Superflip. Least-squares refinement against Fsqd was carried out on all non-hydrogen atoms using the program CRYSTALS. R = 0.0541 (observed data), wR = 0.1127 (all data), GOF = 0.9088. Minimal/maximal residual electron density = -0.60/0.90 e Å-3. Chebychev polynomial weights were used to complete the refinement. Plots were produced using CAMERON. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Center, the deposition number is 1910504. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].



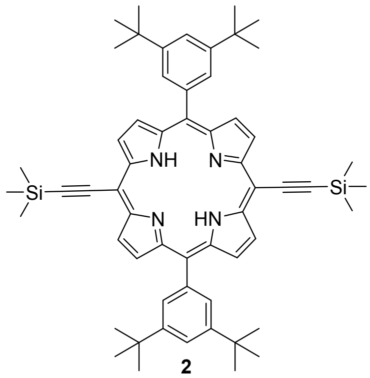
S 2: **^{1}H-NMR (500 MHz, THF-d_8, 298 K)** spectrum of **1.**



S 3: **MALDI-ToF** spectrum of **1**.



S 4: **Magnification** of S 3.



2

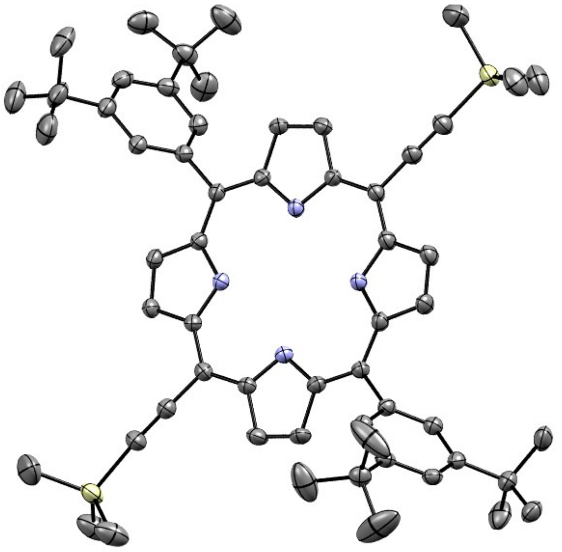
5,15-bis(3,5-di-*tert*-butylphenyl)-10,20-bis((trimethylsilyl)ethynyl)-porphyrin (2)[3]: A solution of 3-(trimethylsilyl)propiolaldehyde (0.52 mL, 3.50 mmol, 1.0 eq) and 2,2'-((3,5-di-*tert*-butylphenyl)methylene)bis(1*H*-pyrrole)[2] (1.17 g, 3.50 mmol, 1.0 eq.) in CH_2Cl_2 (500 mL) was purged with argon for 20 min at 0 °C. Trifluoroborate diethyl etherate (53 µL, 350 µmol, 0.1 eq.) was added and the reaction mixture was stirred for 5 min at 0 °C. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (874 mg, 3.85 mmol, 1.1 eq.) was added and the mixture was stirred for 1 h at rt. The reaction mixture was filtered over a plug of silica eluted with CH_2Cl_2 and was concentrated under reduced pressure. Crystallisation from CH_2Cl_2/CH_3OH gave the title compound **2**[3] (412 mg, 469 µmol, 27%) as a microcrystalline purple solid.

TLC (SiO_2, CH_2Cl_2/cyclohexane (1:2)): R_f = 0.61.

MP: >300 °C

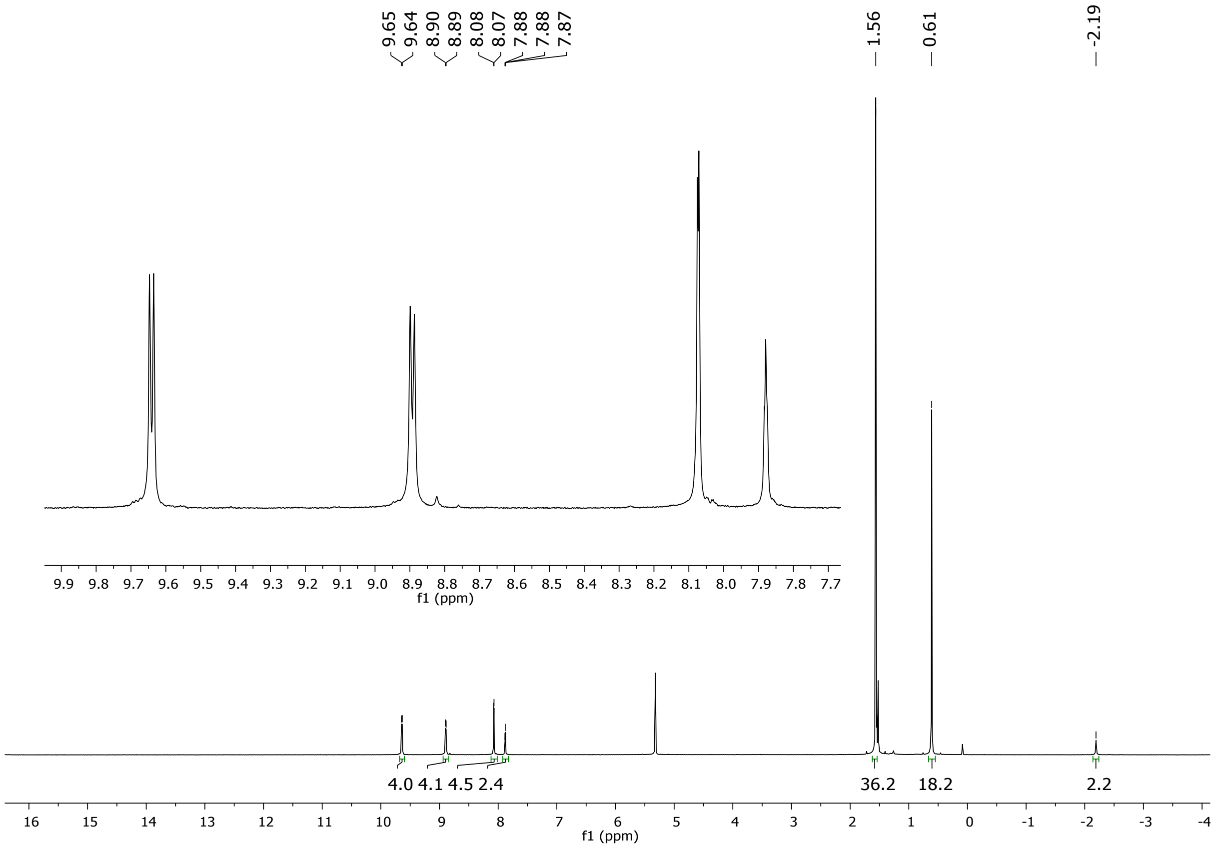
^{1}H-NMR (400 MHz, CD_2Cl_2, 298 K, δ/ppm): 9.64 (d, $^3J_{HH}$ = 4.7 Hz, 4H, H_β), 8.89 (d, $^3J_{HH}$ = 4.8 Hz, 4H, H_β), 8.07 (d, $^4J_{HH}$ = 1.8 Hz, 4H, H_{oPh}), 7.88 (t, $^4J_{HH}$ = 1.8 Hz, 2H, H_{pPh}), 1.56 (s, 36H, H_{tBu}), 0.61 (s, 18H, H_{TMS}), -2.19 (s, 2H, H_{NH}).

MALDI-TOF *m/z* (%) = 878 [M^+].

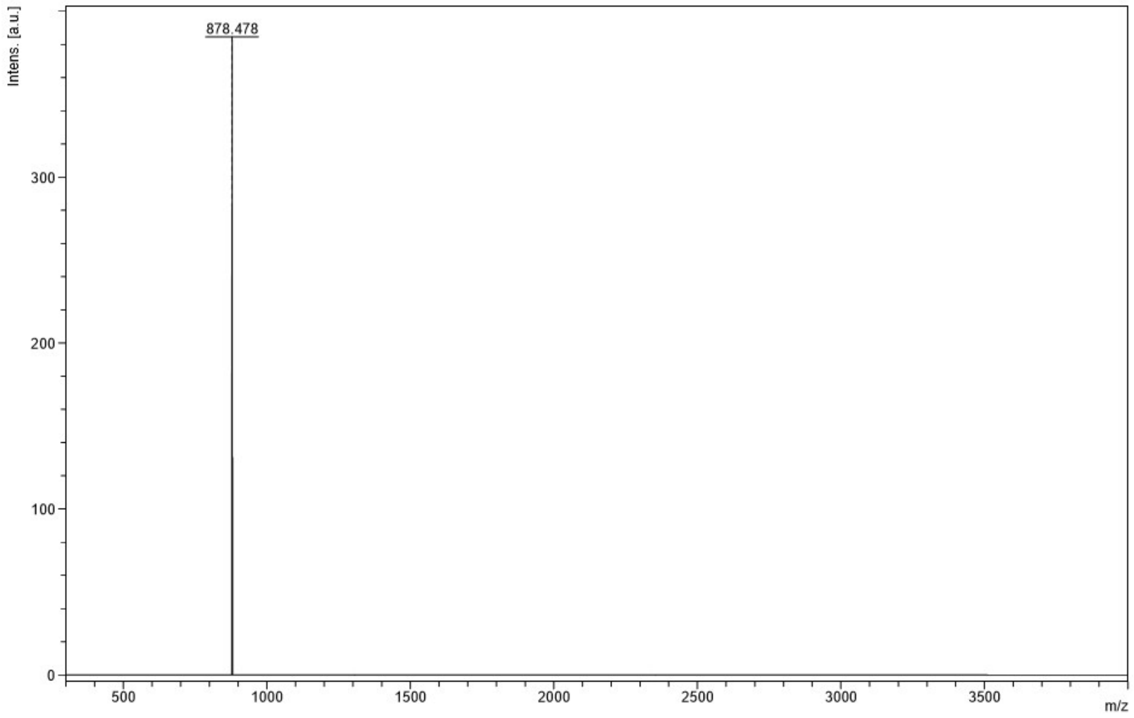


S 5 **ORTEP-representation of the solid state structure of 2.** Thermal ellipsoids are plotted on a 50% probability level. Protons and solvent molecules are omitted for clarity.

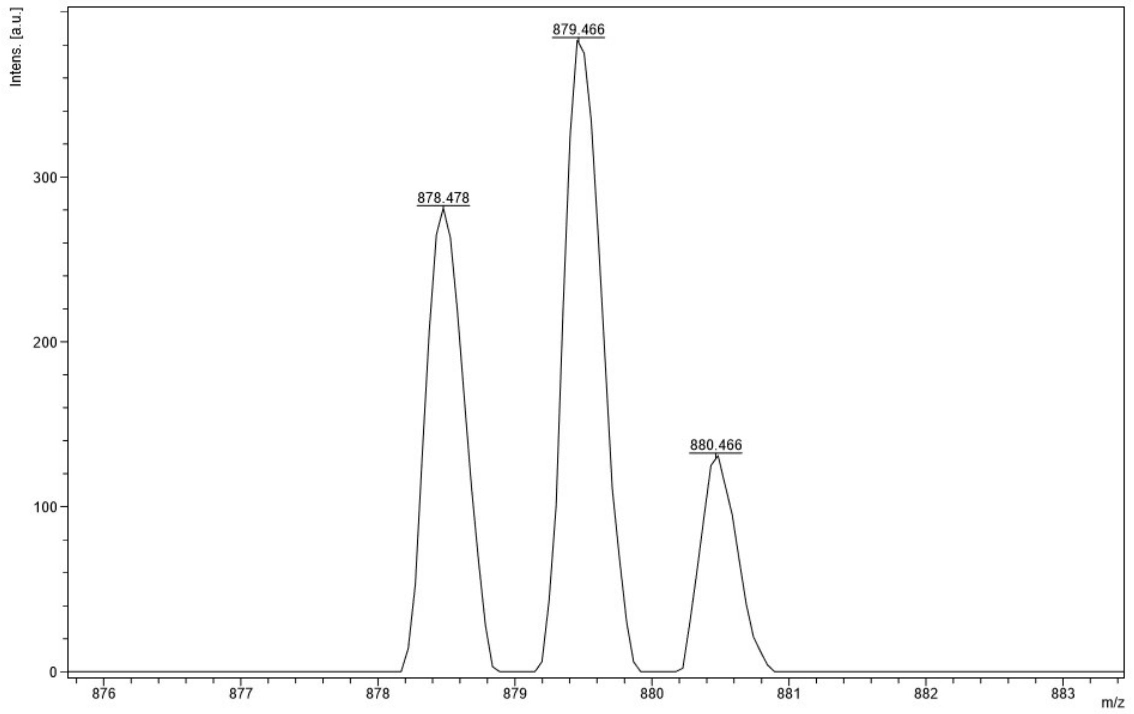
Crystal data for **2**: formula $C_{62}H_{78}N_4O_1Si_2$, M = 951.50, F(000) = 2056, red plate, size 0.040 ◊ 0.130 ◊ 0.140 mm^3, orthorhombic, space group P n a 21 , Z = 4, a = 31.3225(13) Å, b = 12.3379(5) Å, c = 14.6291(6) Å, α = 90 °, β = 90 °, γ = 90 °, V = 5653.5(4) Å^3, Dcalc. = 1.118 g cm^{-3}. The crystal was measured on a Bruker Kappa Apex2 diffractometer at 123K using graphite-monochromated Cu Kα-radiation with λ = 1.54180 Å, Θmax = 70.339 °. Minimal/maximal transmission 0.88/0.97, μ = 0.889 mm-1. The Apex2 suite has been used for datacollection and integration. From a total of 60949 reflections, 9480 were independent (merging r = 0.060). From these, 9436 were considered as observed (I>2.0σ(I)) and were used to refine 631 parameters. The structure was solved by other methods using the program Superflip. Least-squares refinement against Fsqd was carried out on all non-hydrogen atoms using the program CRYSTALS. R = 0.0568 (observed data), wR = 0.1460 (all data), GOF = 0.9893. Minimal/maximal residual electron density = -0.33/0.39 e Å-3. Chebychev polynomial weights were used to complete the refinement. Plots were produced using CAMERON. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Center, the deposition number is 1910502. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].



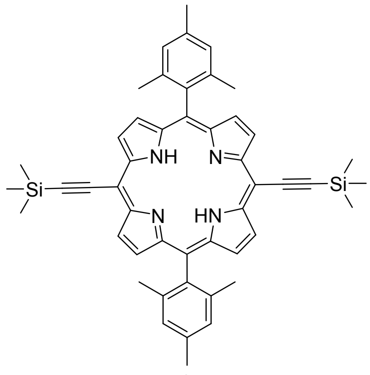
S 6: **^{1}H-NMR (400 MHz, CD_2Cl_2, 298 K**) spectrum of **2**.



S 7: **MALDI-ToF** spectrum of **2**.



S 8: **Magnification** of S 7.



3

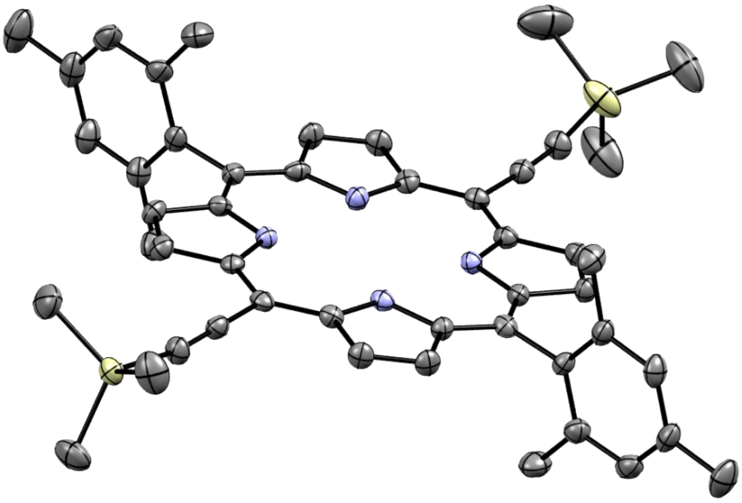
5,15-dimesityl-10,20-bis((trimethylsilyl)ethynyl)porphyrin (3): A solution of 3-(trimethylsilyl)propiolaldehyde (0.74 mL, 5.00 mmol, 1.0 eq) and 2,2'-(mesitylmethylene)bis(1*H*-pyrrole)[4] (1.32 g, 5.00 mmol, 1.0 eq.) in CH_2Cl_2 (500 mL) was purged with argon for 20 min at 0 °C. Trifluoroborate diethyl etherate (62 µL, 500 µmol, 0.1 eq.) was added and the reaction mixture was stirred for 5 min at 0 °C. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (1.25 g, 5.50 mmol, 1.1 eq.) was added and the mixture was stirred for 1 h at rt. The reaction mixture was filtered over a plug of silica eluted with CH_2Cl_2 and was concentrated under reduced pressure. Crystallisation from CH_2Cl_2/CH_3OH gave the title compound **3** (567 mg, 767 µmol, 31%) as a microcrystalline purple solid.

TLC (SiO_2, CH_2Cl_2/cyclohexane (1:2)): $R_f = 0.55$.

MP: > 300 °C

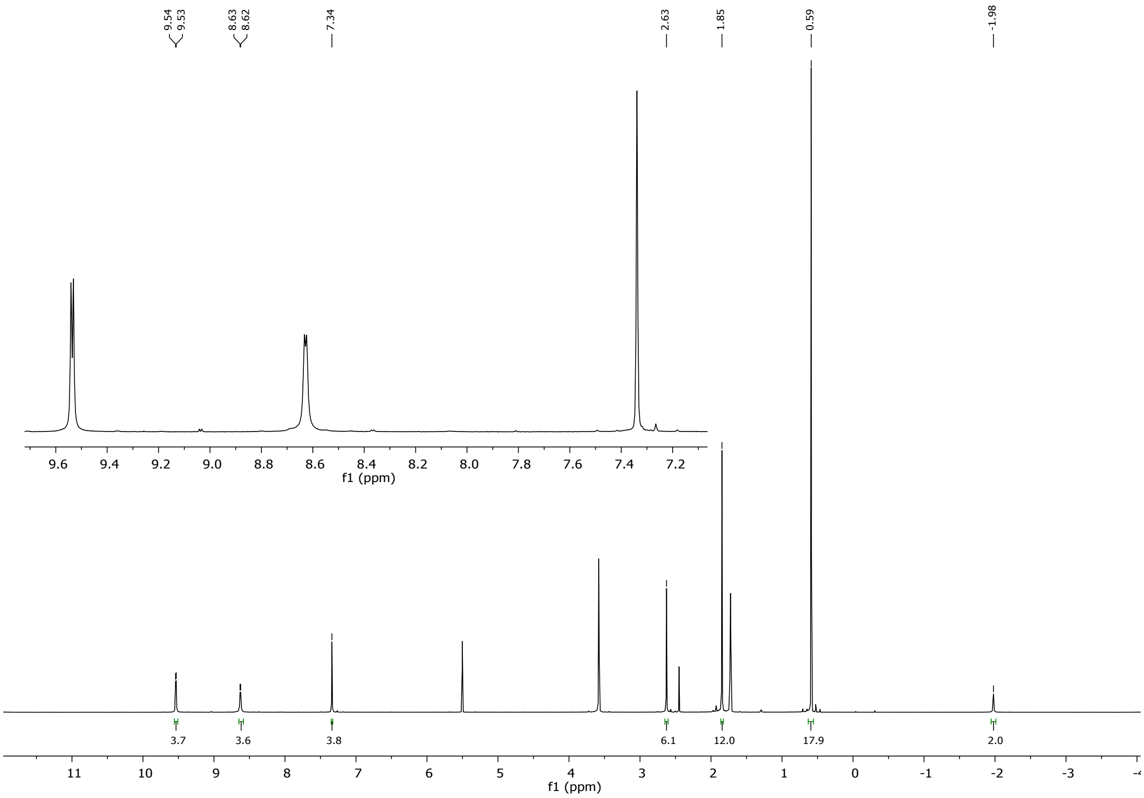
^{1}H-NMR (500 MHz, THF-d_8, 298 K, δ/ppm): 9.54 (d, $^3J_{HH}$ = 4.6 Hz, 4H, H_β), 8.63 (d, $^3J_{HH}$ = 4.1 Hz, 4H, H_β), 7.34 (s, 4H, H_{Ph}), 2.63 (s, 6H, H_{pMe}), 1.85 (s, 12H, H_{oMe}), 0.59 (s, 18H, H_{tBu}), -1.98 (s, 2H, H_{NH}).

MALDI-TOF *m/z* (%) = 739 [M$^+$].

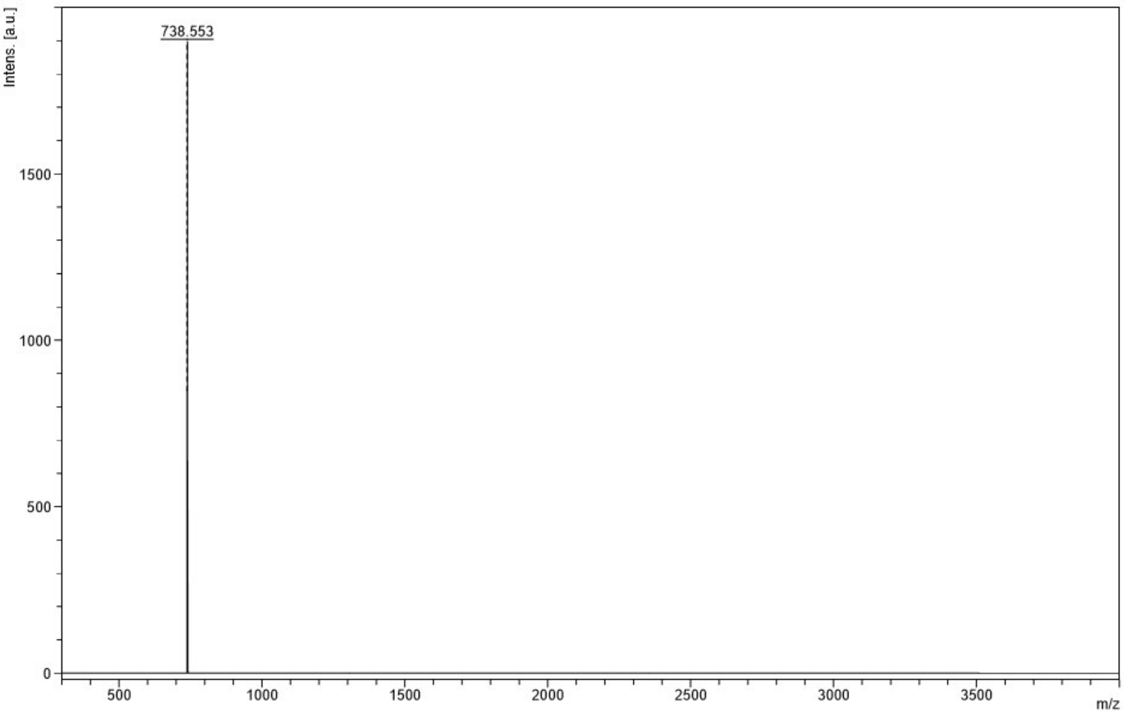


S 9 **ORTEP-representation of the solid state structure of** 3**.** Thermal ellipsoids are plotted on a 50% probability level. Protons and solvent molecules are omitted for clarity.

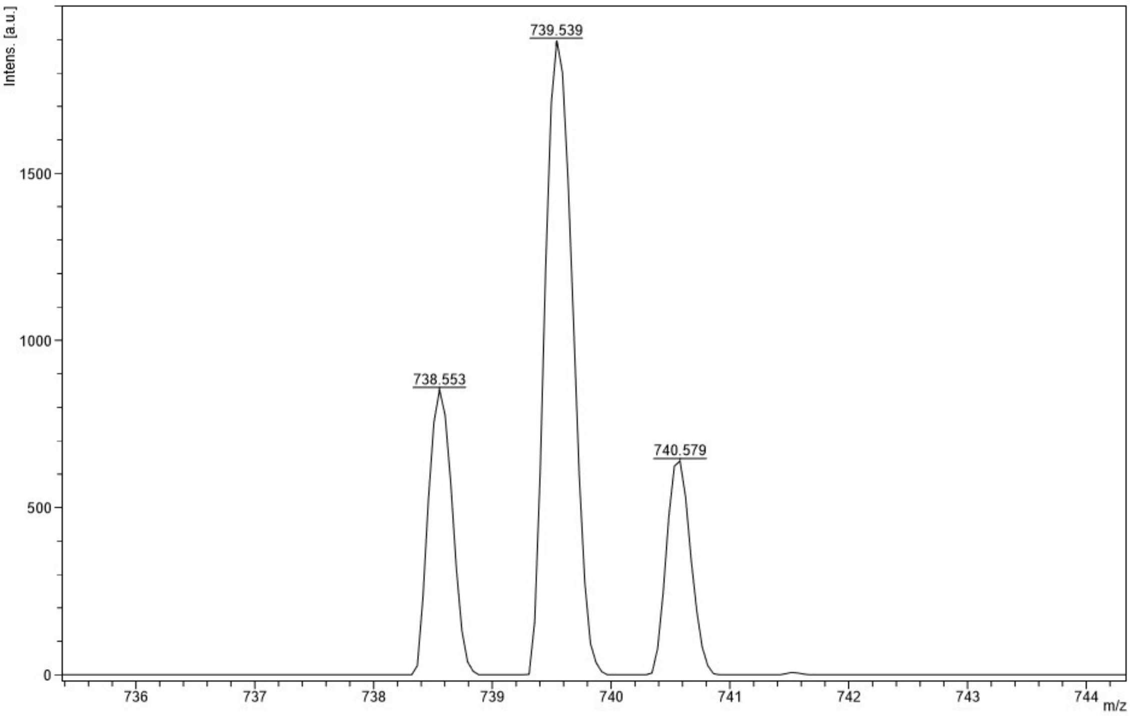
Crystal data for **3**: formula $C_{52}H_{58}N_5Si_2$, M = 809.24, F(000) = 866, purple block, size 0.050 ◊ 0.080 ◊ 0.100 mm^3, monoclinic, space group P 21 , Z = 2, a = 11.2455(5) Å, b = 14.4419(6) Å, c = 14.4390(6) Å, α = 90 °, β = 99.887(3) °, γ = 90 °, V = 2310.16(17) Å^3, Dcalc. = 1.163 g cm^{-3}. The crystal was measured on a Bruker Kappa Apex2 diffractometer at 123K using graphite-monochromated Cu Kα-radiation with λ = 1.54178 Å, Θmax = 67.680 °. Minimal/maximal transmission 0.79/0.95, μ = 0.997 mm-1. The Apex2 suite has been used for datacollection and integration. From a total of 11091 reflections, 6115 were independent (merging r = 0.028). From these, 6075 were considered as observed (I>2.0σ(I)) and were used to refine 541 parameters. The structure was solved by other methods using the program Superflip. Least-squares refinement against Fsqd was carried out on all non-hydrogen atoms using the program CRYSTALS. R = 0.0590 (observed data), wR = 0.1446 (all data), GOF = 0.9484. Minimal/maximal residual electron density = -0.47/1.10 e Å-3. Chebychev polynomial weights were used to complete the refinement. Plots were produced using CAMERON. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Center, the deposition number is 1910503. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].



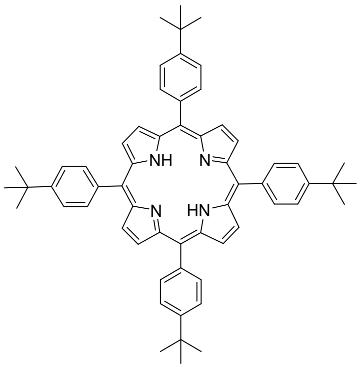
S 10: **^{1}H-NMR** (**500 MHz, THF-d_8, 298 K)** spectrum of **3**.



S 11: **MALDI-ToF** spectrum of **3**.



S 12: **Magnification** of S 11.



R2

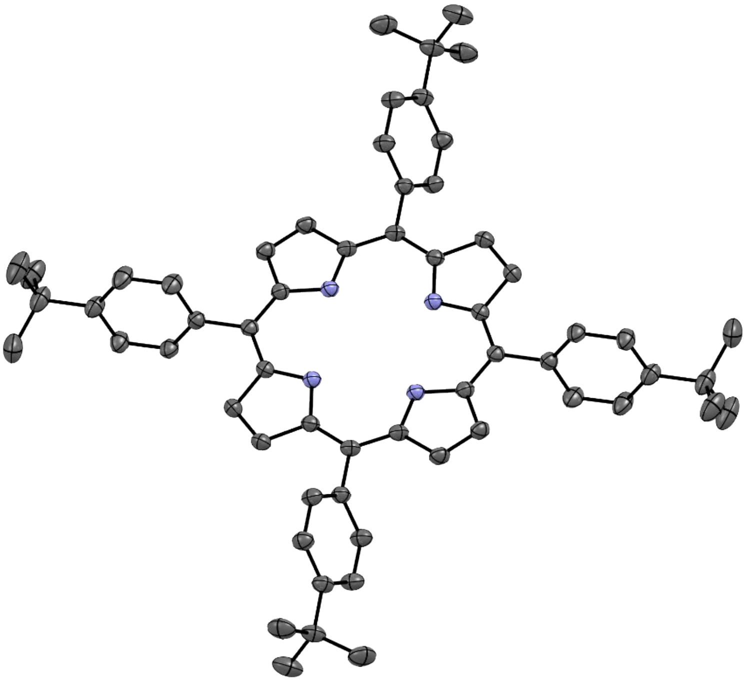
5,10,15,20-tetrakis-(4-(*tert*-butyl)phenyl) porphyrin (R2): A solution of 4-*tert*-butylbenzaldehyde (277 mg, 1.71 mmol, 1.0 eq) and ((4-*tert*-butylphenyl)methylene)bis(1*H*-pyrrole)[1] (467 mg, 1.71 mmol, 1.0 eq.) in CH_2Cl_2 (100 mL) was purged with argon for 20 min at rt. Trifluoroborate diethyl etherate (69 µL, 564 µmol, 0.33 eq.) was added and the reaction mixture was stirred for 45 min at rt. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (582 mg, 2.57 mmol, 1.5 eq.) was added and the mixture was stirred for 1 h at rt. The reaction mixture was filtered over a plug of silica eluted with with CH_2Cl_2 and was concentrated under reduced pressure. Crystallisation from CH_2Cl_2/CH_3OH gave the title compound **R2** (182 mg, 217 µmol, 25%) as a microcrystalline purple solid.

TLC (SiO_2, CH_2Cl_2/cyclohexane (1:1)): R_f = 0.58.

MP: >300 °C

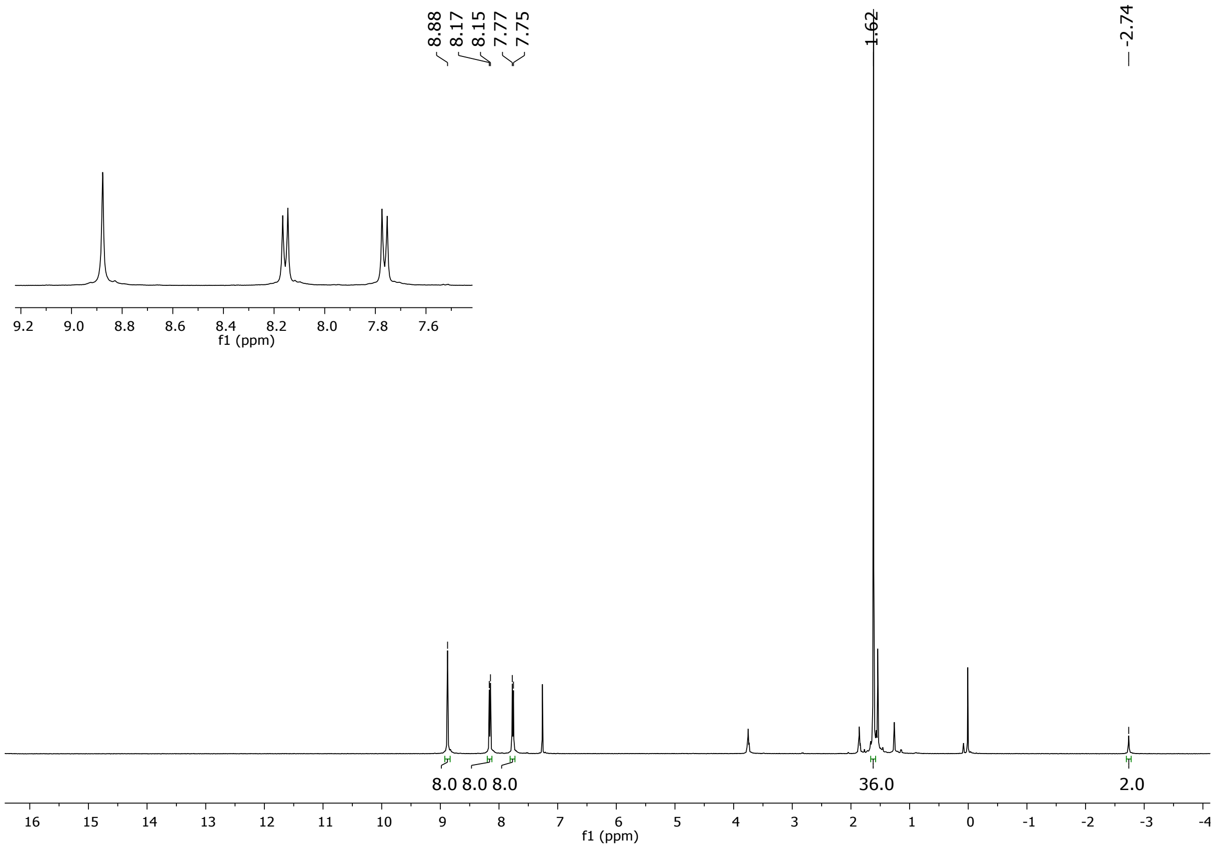
^{1}H-NMR (400 MHz, $CDCl_3$, 298 K, δ/ppm): 8.88 (s, 8H, H_β), 8.18 – 8.12 (m, 8H, H_{Ph}), 7.80 – 7.73 (m, 8H, H_{Ph}), 1.62 (s, 36H, H_{tBu}), -2.74 (s, 2H, H_{NH}).

MALDI-TOF *m/z* (%) = 839 [M^+].

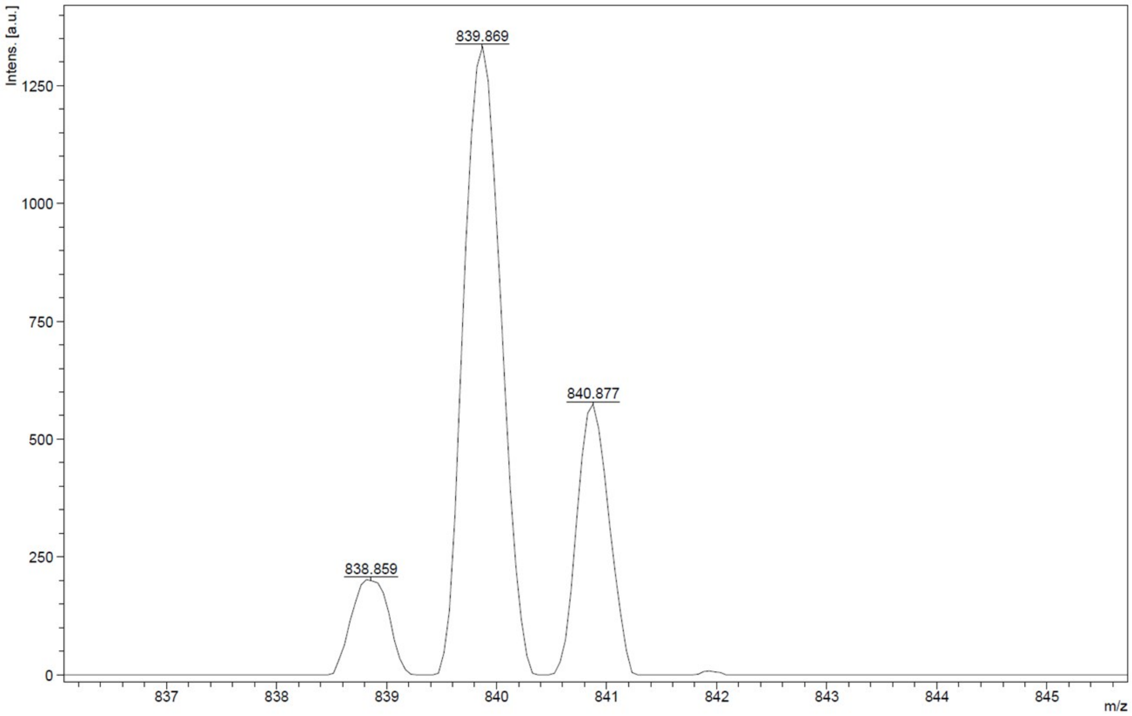


S 13: **ORTEP-representation of the solid state structure of R2.** Thermal ellipsoids are plotted on a 50% probability level. Protons and solvent molecules are omitted for clarity.

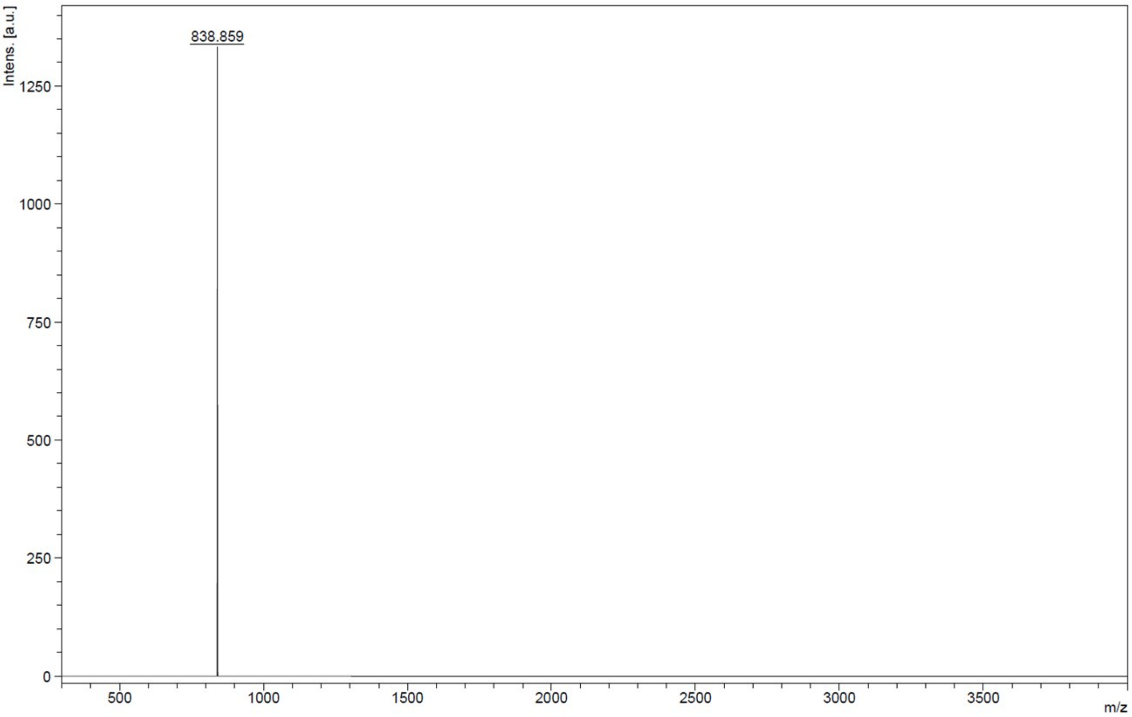
Crystal data for **R2**: formula $C_{60}H_{62}N_4$, M = 839.18, F(000) = 900, purple plate, size 0.050 ◊ 0.200 ◊ 0.250 mm^3, monoclinic, space group P 2_1/n , Z = 2, a = 13.6207(3) Å, b = 16.2758(3) Å, c = 15.1875(3) Å, α = 90 °, β = 133.4200(10) °, γ = 90 °, V = 2445.48(9) $Å^3$, $D_{calc.}$ = 1.140 g cm^{-3}. The crystal was measured on a Stoe StadiVari diffractometer at 130K using Graded multilayer mirror-monochromated GaK_α-radiation with λ = 1.34143 Å, Θ_{max} = 57.187 °. Minimal/maximal transmission 0.9808/0.9934, μ = 0.319 mm^{-1}. The X-Area Pilatus3_SV 1.31.150.0 suite has been used for datacollection and integration. From a total of 38050 reflections, 4955 were independent (merging r = 0.028). From these, 4935 were considered as observed (I>2.0σ(I)) and were used to refine 293 parameters. The structure was solved by other methods using the program Superflip. Least-squares refinement against Fsqd was carried out on all non-hydrogen atoms using the program CRYSTALS. R = 0.0433 (observed data), wR = 0.1115 (all data), GOF = 0.9103. Minimal/maximal residual electron density = -0.22/0.23 e $Å^{-3}$. Chebychev polynomial weights were used to complete the refinement. Plots were produced using CAMERON. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Center, the deposition number is 1910501. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].



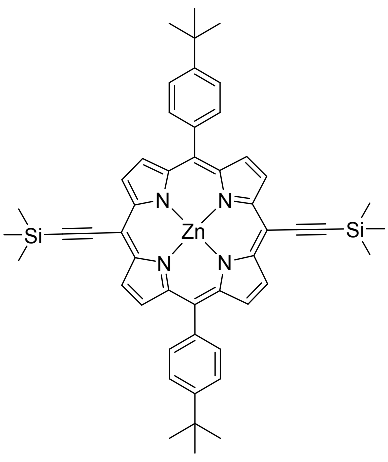
S 14: **^{1}H-NMR (400 MHz, $CDCl_3$, 298 K)** spectrum of **R2**.



S 15: **MALDI-ToF** spectrum of **R2**.



S 16: **Magnification** of S 15.



4

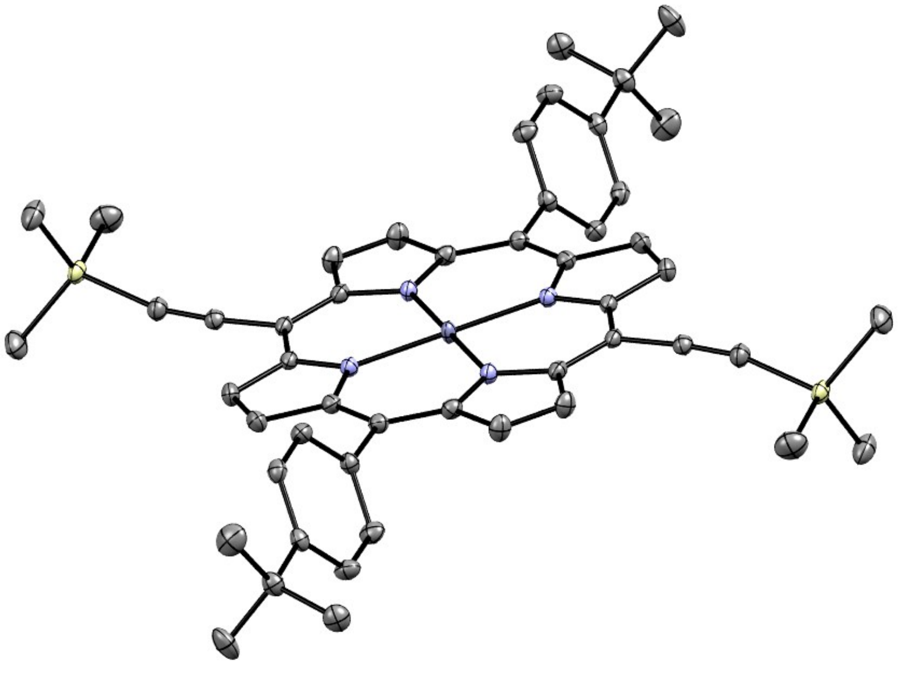
[5,15-bis(4-(*tert*-butyl)phenyl)-10,20-bis((trimethylsilyl)ethynyl)-porphyrinato]zinc(II) (4): A solution of 5,15-bis(4-(*tert*-butyl)phenyl)-10,20-bis((trimethylsilyl)ethynyl)porphyrin (**1**) (133 mg, 173 µmol, 1.0 eg.) and Zn(OAc)$_2$ (159 mg, 865 µmol, 5.0 eg.) in CH_2Cl_2/CH_3OH (100 mL, 5:1) was stirred for 1 h at rt. The mixture was dilluted with CH_2Cl_2 and successively washed with water. The organic phase was dried over anhydrous Na_2SO_4, filtered over a plug of silica eluted with CH_2Cl_2 and evaporated to dryness yielding the title compound **4** (144 mg, 173 µmol, 100%) as a microcrystalline purple solid.

TLC (SiO_2, CH_2Cl_2/cyclohexane (1:1)): $R_f = 0.32$.

MP: >300 °C

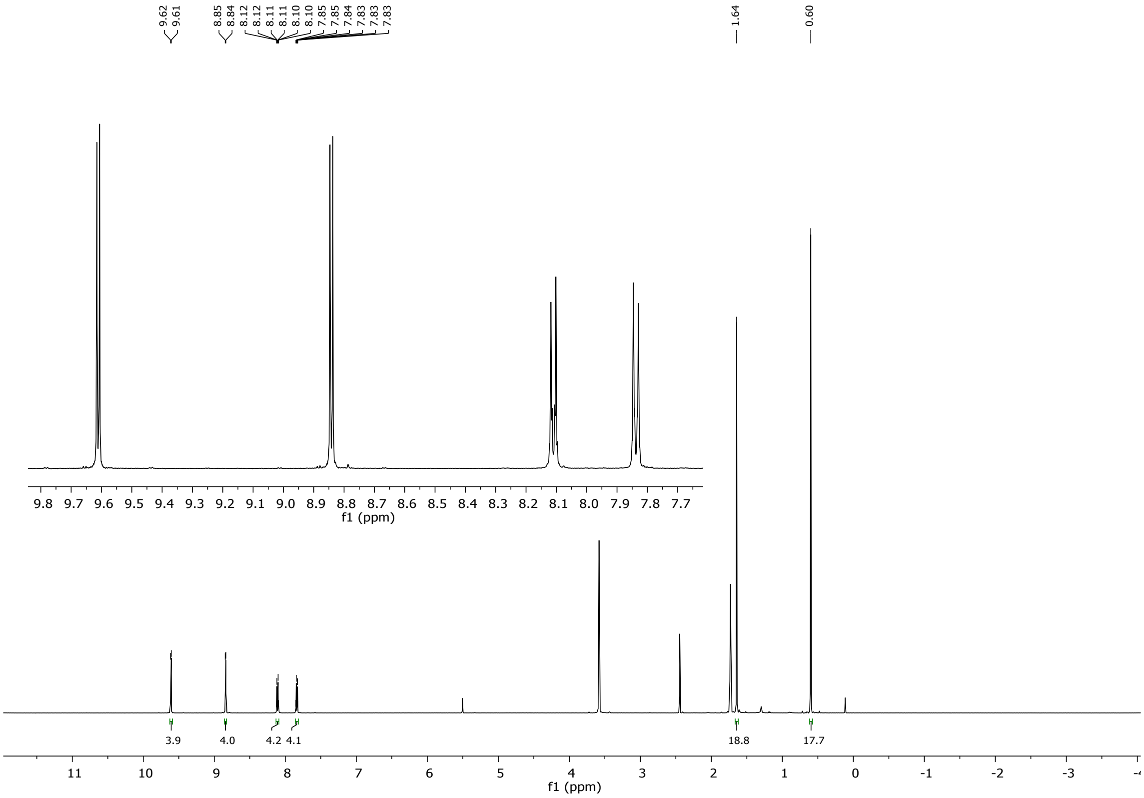
^{1}H-NMR (500 MHz, THF-d_8, 298 K, δ/ppm): 9.61 (d, $^3J_{HH} = 4.5$ Hz, 4H, H_β), 8.84 (d, $^3J_{HH} = 4.5$ Hz, 4H, H_β), 8.13 – 8.08 (m, 4H, H_{Ph}), 7.86 – 7.79 (m, 4H, H_{Ph}), 1.64 (s, 18H, H_{tBu}), 0.60 (s, 18H, H_{TMS}).

MALDI-TOF *m/z* (%) = 828 [M^+].

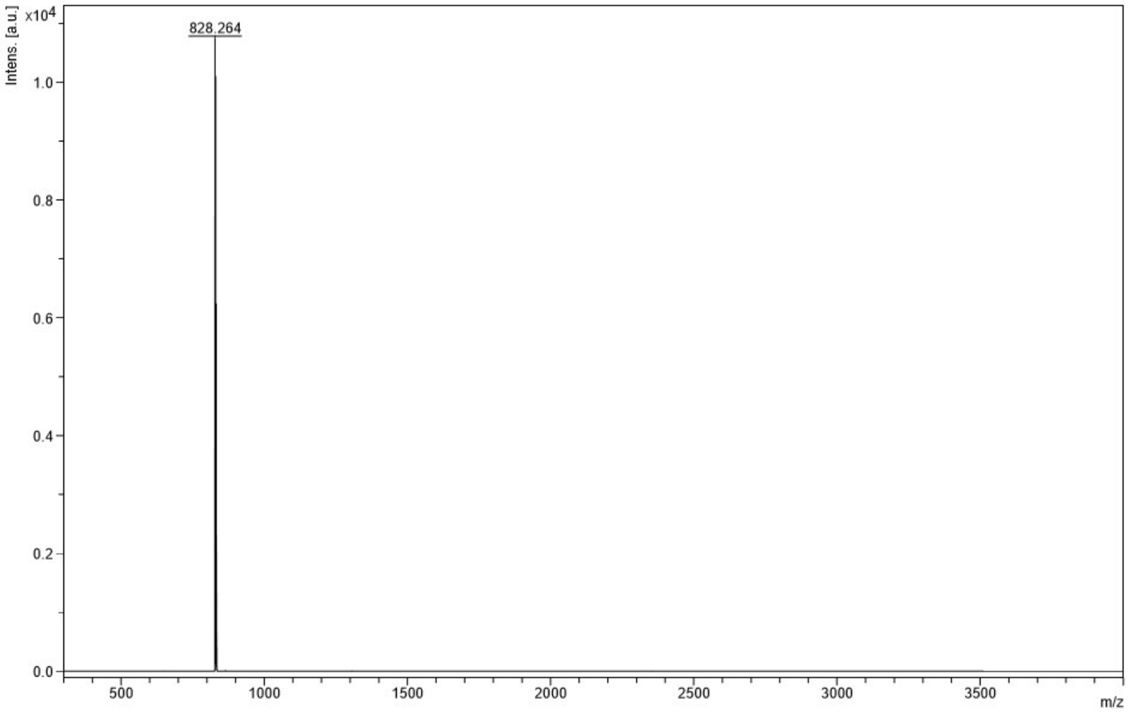


S 17: **ORTEP-representation of the solid state structure of 4.** Thermal ellipsoids are plotted on a 50% probability level. Protons and solvent molecules are omitted for clarity.

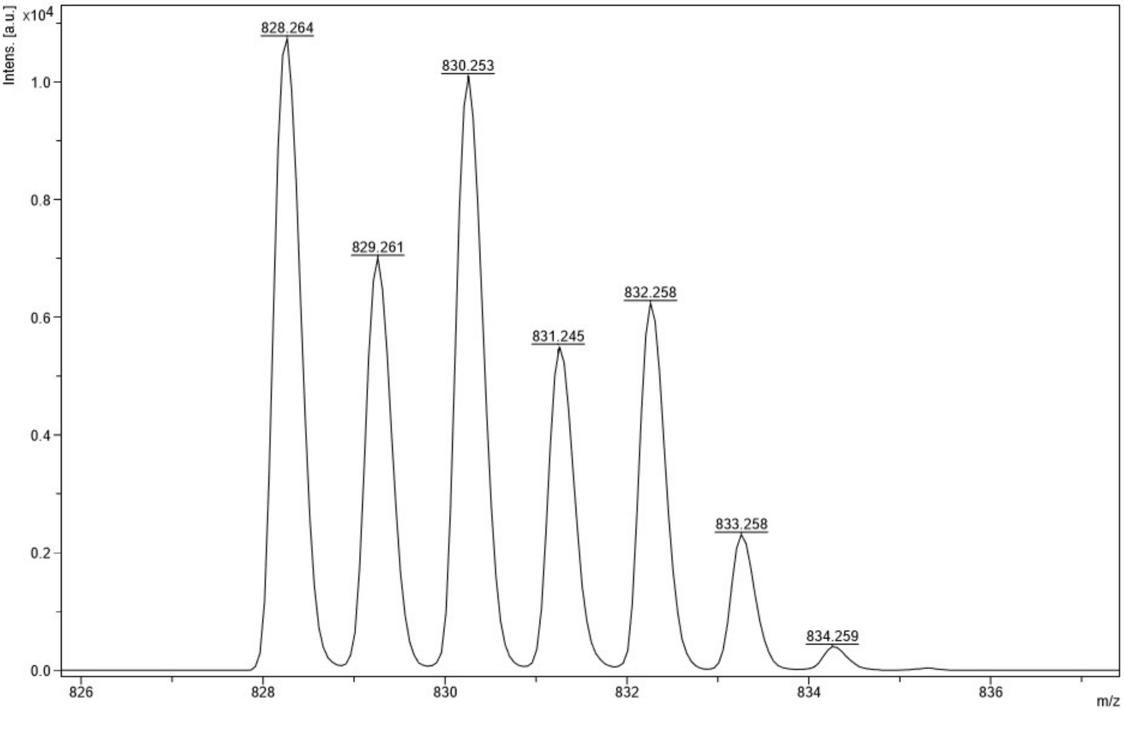
Crystal data for **4**: formula $C_{58}H_{68}N_4O_2Si_2Zn_1$, M = 974.76, F(000) = 518, green plate, size 0.040 ◊ 0.110 ◊ 0.130 mm^3, triclinic, space group P -1 , Z = 1, a = 9.3697(7) Å, b = 10.2821(8) Å, c = 14.2974(11) Å, α = 106.979(3) °, β = 98.215(3) °, γ = 92.569(3) °, V = 1298.39(17) Å^3, Dcalc. = 1.247 g cm^{-3}. The crystal was measured on a Bruker Kappa Apex2 diffractometer at 123K using graphite-monochromated Cu Kα-radiation with λ = 1.54180 Å, Θmax = 70.107 °. Minimal/maximal transmission 0.88/0.94, μ = 1.447 mm-1. The Apex2 suite has been used for datacollection and integration. From a total of 10943 reflections, 4680 were independent (merging r = 0.022). From these, 4658 were considered as observed (I>2.0σ(I)) and were used to refine 304 parameters. The structure was solved by other methods using the program Superflip. Least-squares refinement against Fsqd was carried out on all non-hydrogen atoms using the program CRYSTALS. R = 0.0292 (observed data), wR = 0.0710 (all data), GOF = 0.9668. Minimal/maximal residual electron density = -0.28/0.33 e Å-3. Chebychev polynomial weights were used to complete the refinement. Plots were produced using CAMERON. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Center, the deposition number is 1910506. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].



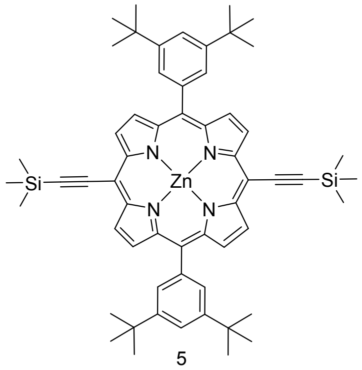
S 18: **^{1}H-NMR (500 MHz, THF-d$_8$, 298 K**) spectrum of **4**.



S 19: **MALDI-ToF** spectrum of **4**.



S 20: **Magnification** of S 19.



5

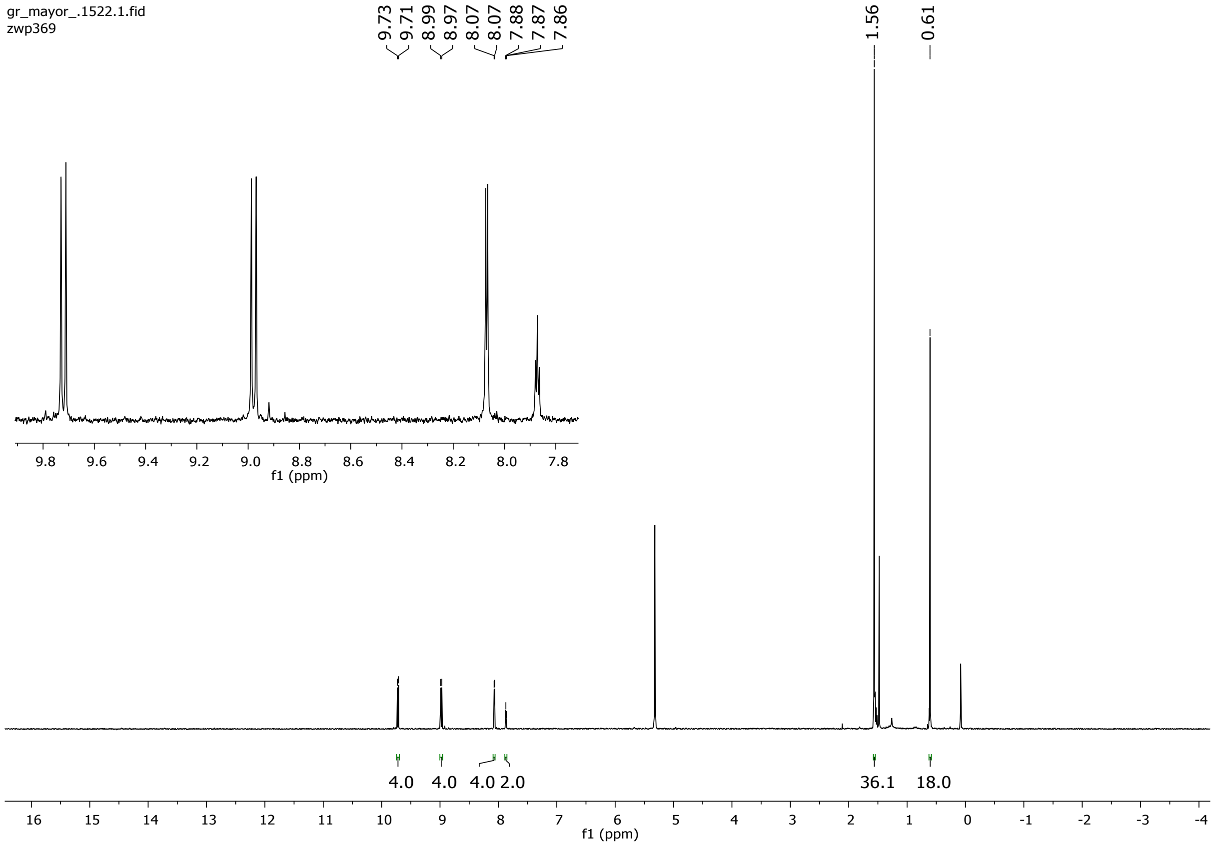
[5,15-bis(3,5-di-*tert*-butylphenyl)-10,20-bis((trimethylsilyl)ethynyl)-porphyrinato]zinc(II) (5): A solution of 5,15-bis(3,5-di-tert-butylphenyl)-10,20-bis((trimethylsilyl)ethynyl)-porphyrin (**2**)[3] (114 mg, 130 µmol, 1.0 eg.) and $Zn(OAc)_2$ (119 mg, 650 µmol, 5.0 eg.) in CH_2Cl_2/CH_3OH (100 mL, 5:1) was stirred for 1 h at rt under an argon atmosphere. The mixture was dilluted with CH_2Cl_2 and successively washed with water. The organic phase was dried over anhydrous Na_2SO_4, filtered over a plug of silica eluted with CH_2Cl_2 and evaporated to dryness yielding the title compound **5** (120 mg, 127 µmol, 98%) as a microcrystalline purple solid.

TLC (SiO_2, CH_2Cl_2/cyclohexane (1:1)): $R_f = 0.43$.

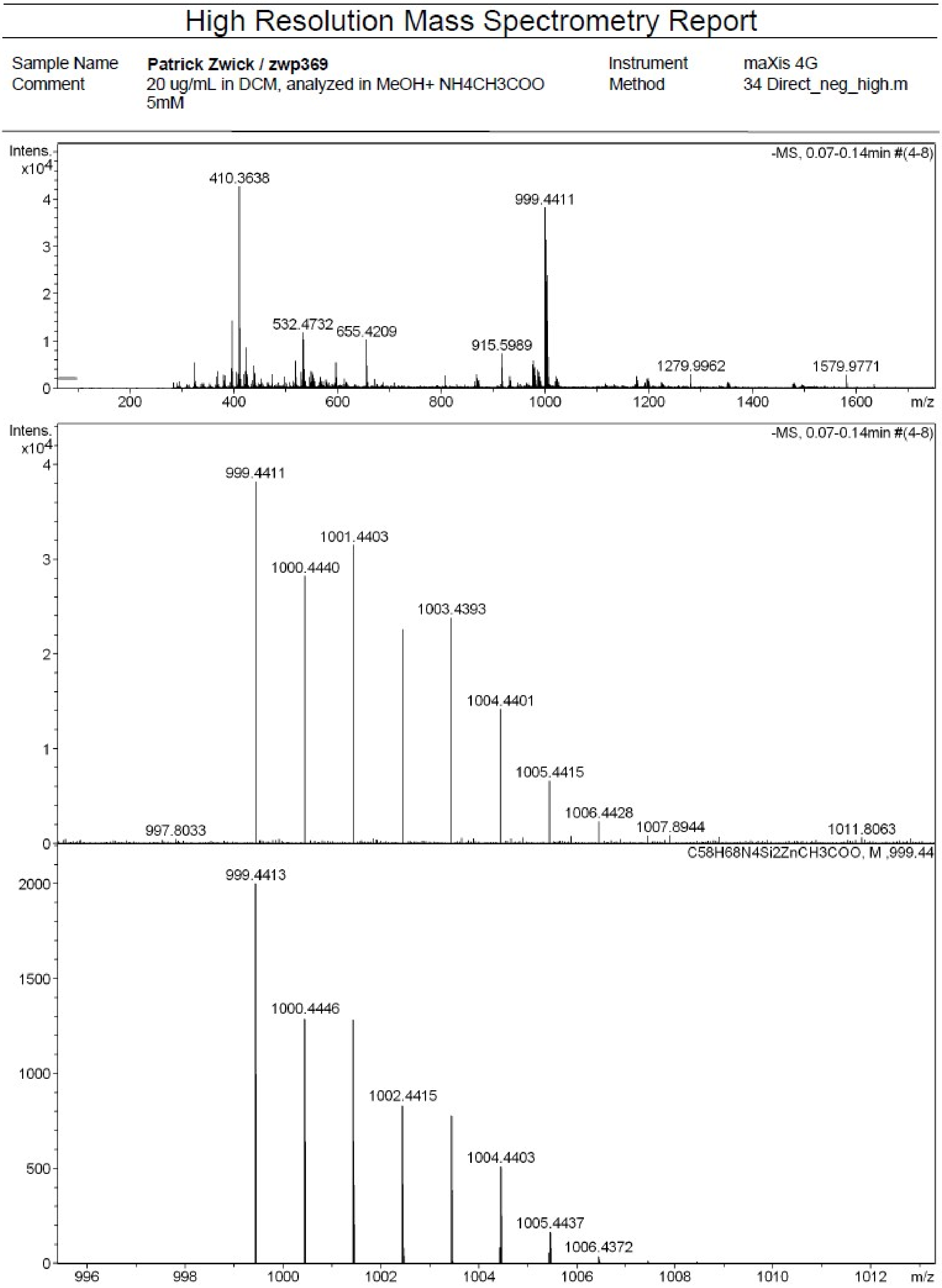
MP: >300 °C

^{1}H-NMR (250 MHz, CD_2Cl_2, 298 K, δ/ppm): 9.72 (d, $^3J_{HH} = 4.7$ Hz, 4H, H_β), 8.89 (d, $^3J_{HH} = 4.6$ Hz, 4H, H_β), 8.07 (d, $^4J_{HH} = 1.8$ Hz, 4H, H_{oPh}), 7.87 (t, $^4J_{HH} = 1.8$ Hz, 2H, H_{pPh}), 1.56 (s, 36H, H_{tBu}), 0.61 (s, 18H, H_{TMS}).

HRMS (ESI, -): *m/z* calcd. for $C_{58}H_{68}N_4Si_2ZnCH_3COO$ $[M+CH_3COO]^-$: 999.4413, found: 999.4411.



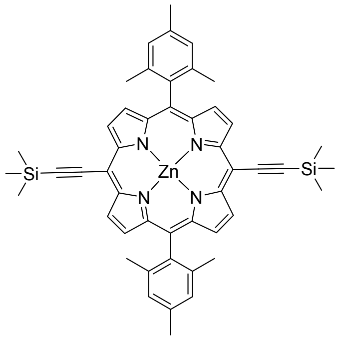
S 21: **^{1}H-NMR (250 MHz, CD_2Cl_2, 298 K)** spectrum of **5**.



High Resolution Mass Spectrometry Report

Sample Name	**Patrick Zwick / zwp369**	Instrument	maXis 4G
Comment	20 ug/mL in DCM, analyzed in MeOH+ NH4CH3COO 5mM	Method	34 Direct_neg_high.m

S 22: **HR-ESI MS** of **5**.



6

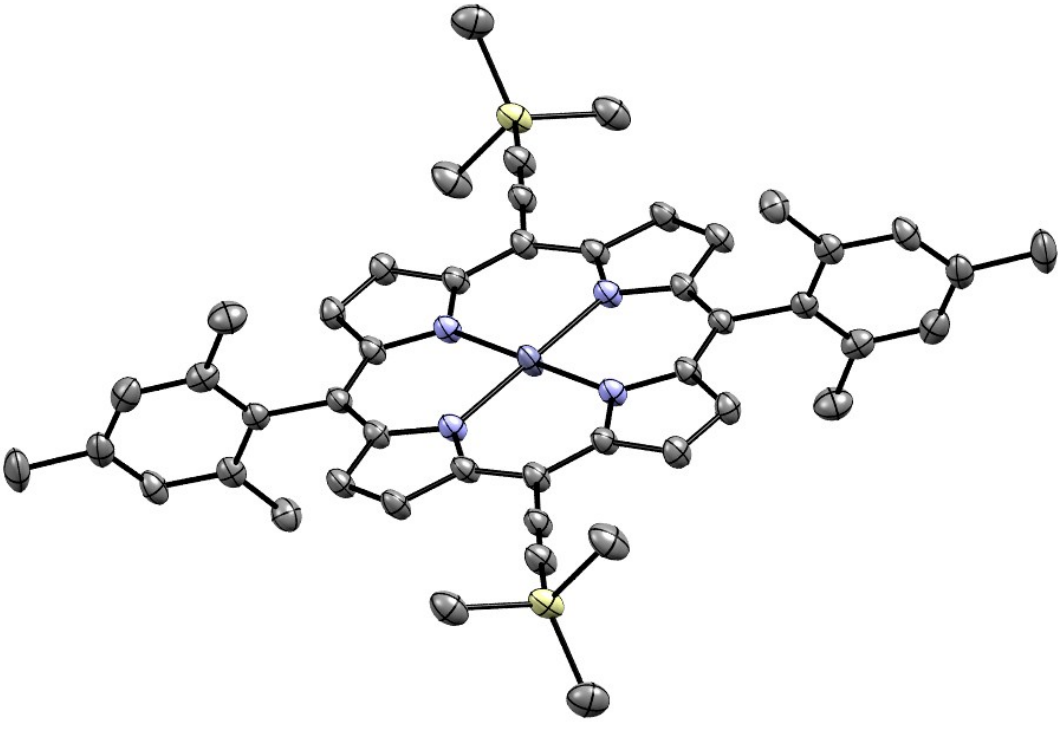
[5,15-dimesityl-10,20-bis((trimethylsilyl)ethynyl)porphyrinato]zinc(II) (6): A solution of 5,15-dimesityl-10,20-bis((trimethylsilyl)ethynyl)porphyrin (**3**) (122 mg, 165 µmol, 1.0 eg.) and $Zn(OAc)_2$ (151 mg, 825 µmol, 5.0 eg.) in CH_2Cl_2/CH_3OH (100 mL, 5:1) was stirred for 3 d at rt under an argon atmosphere. The mixture was dilluted with CH_2Cl_2 and successively washed with water. The organic phase was dried over anhydrous Na_2SO_4, filtered over a plug of silica eluted with CH_2Cl_2 and evaporated to dryness yielding the title compound **6** (130 mg, 162 µmol, 98%) as a microcrystalline purple solid.

TLC (SiO_2, CH_2Cl_2/cyclohexane (1:2)): $R_f = 0.18$.

MP: >300 °C

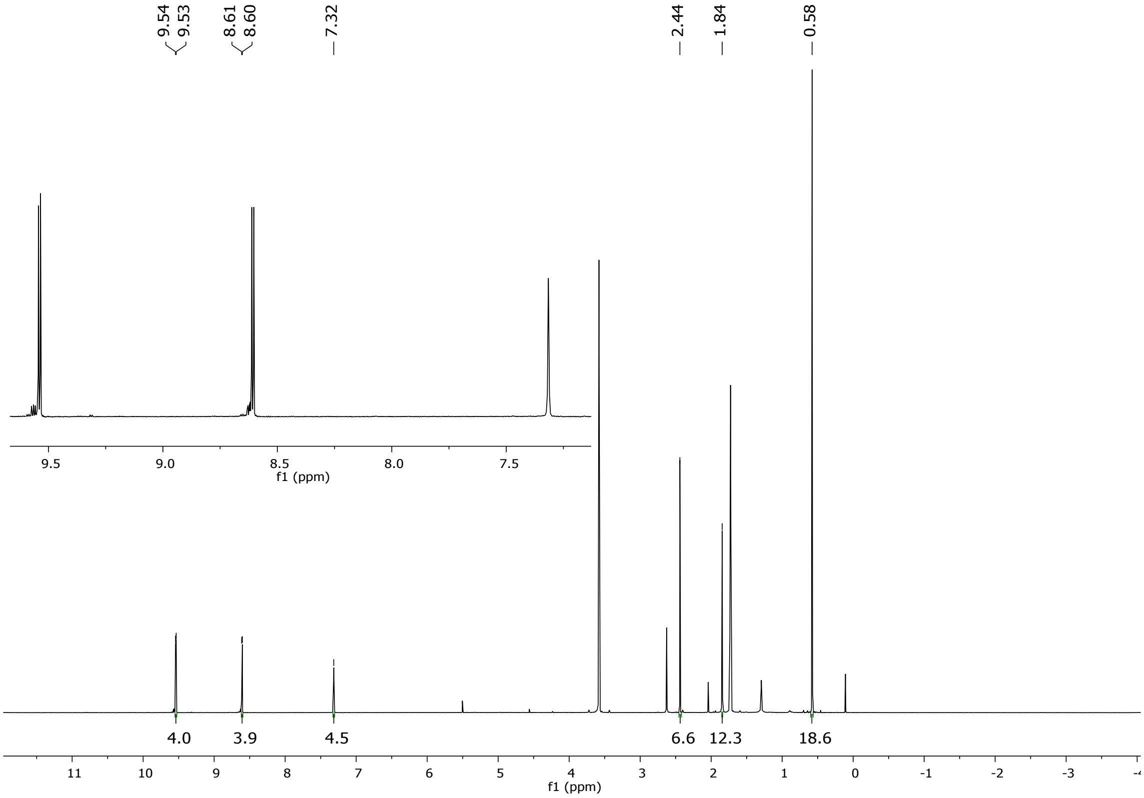
^{1}H-NMR (500 MHz, THF-d_8, 298 K, δ/ppm): 9.54 (d, $^3J_{HH} = 4.5$ Hz, 4H, H_β), 8.61 (d, $^3J_{HH} = 4.4$ Hz, 4H, H_β), 7.32 (s, 4H, H_{Ph}), 2.44 (s, 6H, H_{pMe}), 1.84 (s, 12H, H_{oMe}), 0.58 (s, 18H, H_{TMS}).

MALDI-TOF *m/z* (%) = 800 [M^+].

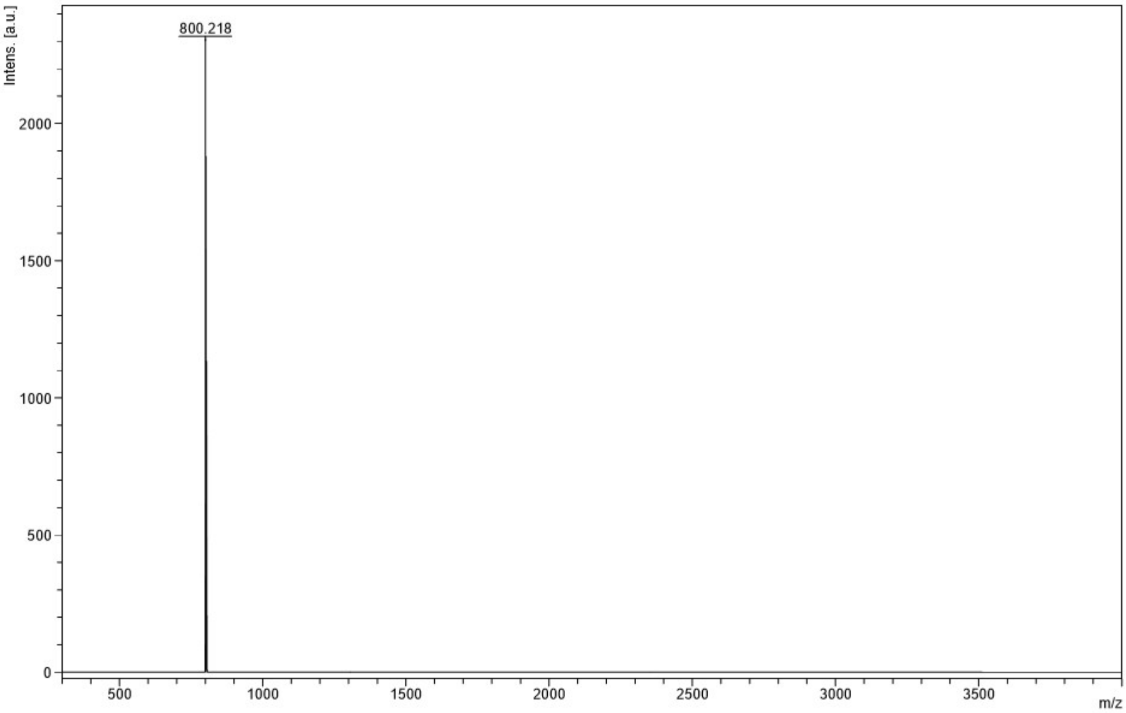


S 23: **ORTEP-representation of the solid state structure of 6.** Thermal ellipsoids are plotted on a 50% probability level. Protons and solvent molecules are omitted for clarity.

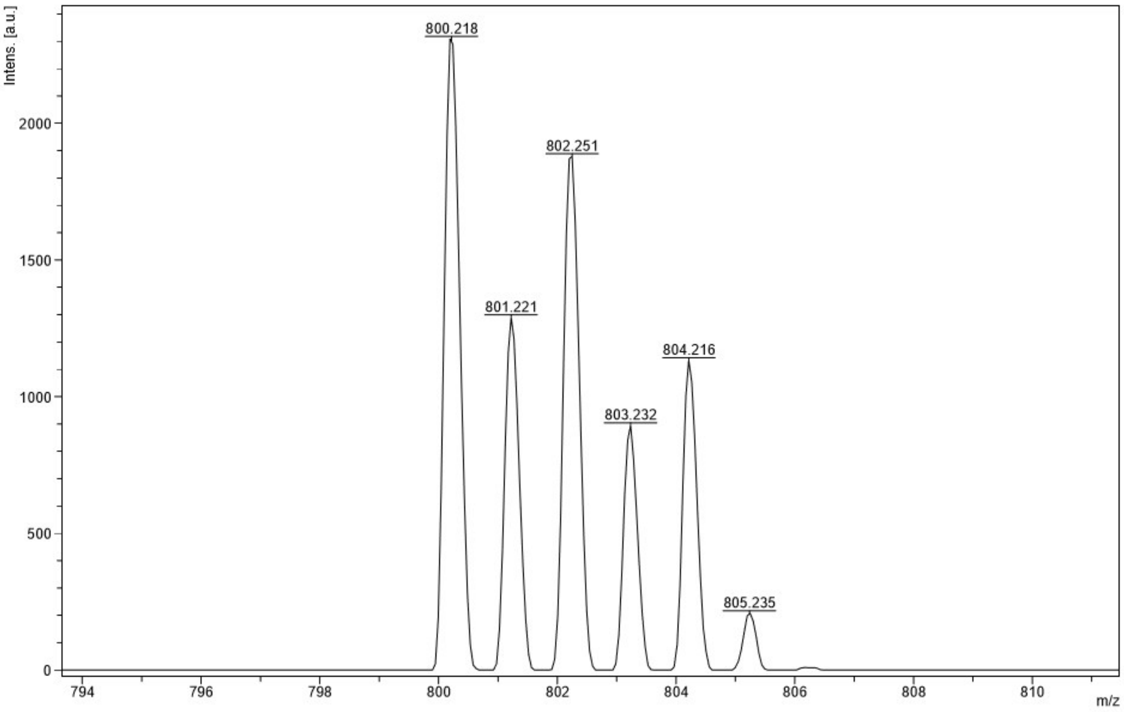
Crystal data for **6**: formula $C_{68}H_{88}N_4O_5Si_2Zn_1$, M = 1163.02, F(000) = 622, violet plate, size 0.030 ◊ 0.120 ◊ 0.130 mm^3, triclinic, space group P -1 , Z = 1, a = 10.0930(6) Å, b = 12.9691(8) Å, c = 13.7220(8) Å, α = 111.916(3) °, β = 107.689(3) °, γ = 94.609(3) °, V = 1548.96(17) Å^3, Dcalc. = 1.247 g cm^{-3}. The crystal was measured on a Bruker Kappa Apex2 diffractometer at 123K using graphite-monochromated Cu Kα-radiation with λ = 1.54180 Å, Θmax = 70.441 °. Minimal/maximal transmission 0.71/0.96, μ = 1.331 mm-1. The Apex2 suite has been used for datacollection and integration. From a total of 16711 reflections, 5605 were independent (merging r = 0.064). From these, 5571 were considered as observed (I>2.0σ(I)) and were used to refine 331 parameters. The structure was solved by other methods using the program Superflip. Least-squares refinement against Fsqd was carried out on all non-hydrogen atoms using the program CRYSTALS. R = 0.0841 (observed data), wR = 0.2288 (all data), GOF = 0.9320. Minimal/maximal residual electron density = -0.96/1.13 e Å-3. Chebychev polynomial weights were used to complete the refinement. Plots were produced using CAMERON. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Center, the deposition number is 1910505. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].



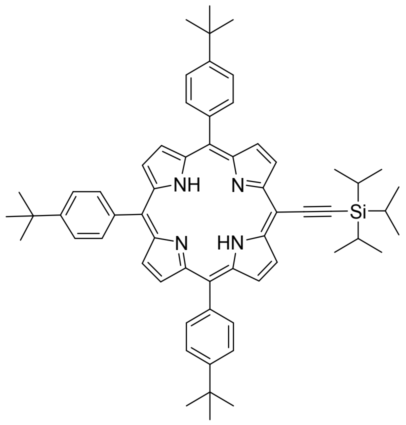
S 24: **^{1}H-NMR** spectrum of **6** measured in THF-d_8 at 298 K.



S 25: **MALDI-ToF** spectrum of **6**.



S 26: **Magnification** of S 25.



7

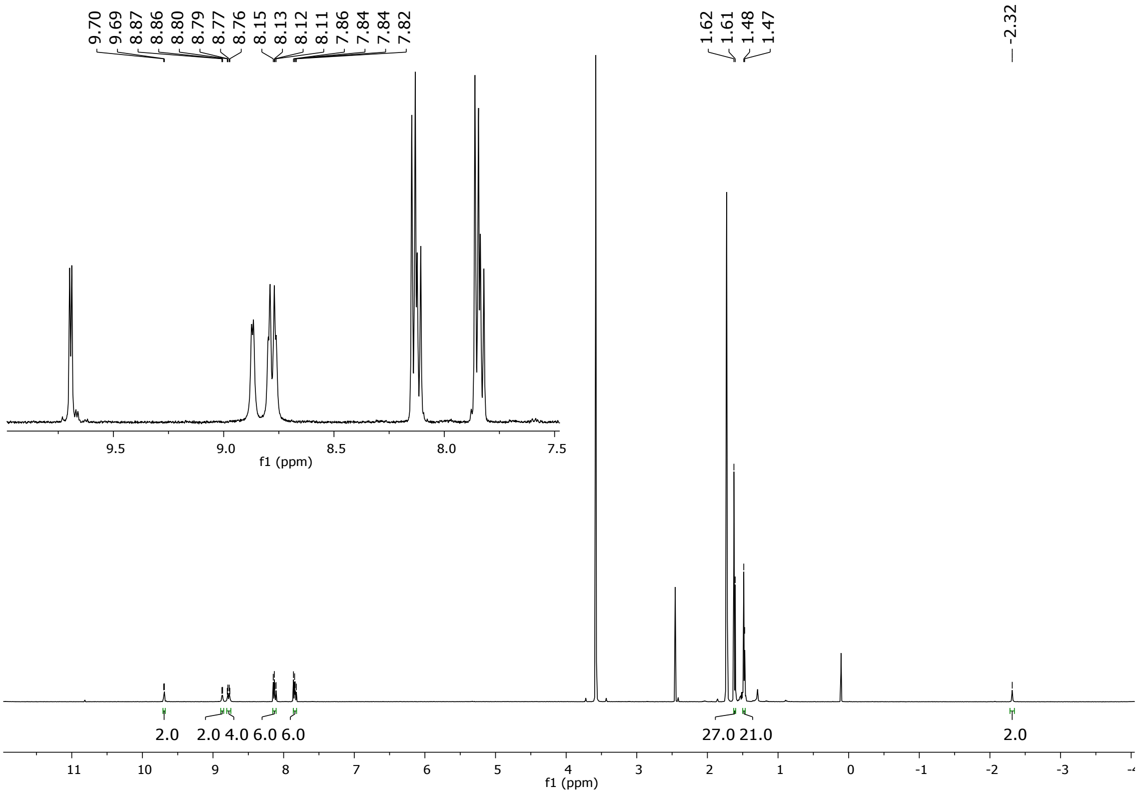
5,10,15-tris(4-(*tert*-butyl)phenyl)-20-((triisopropylsilyl) ethynyl)porphyrin (7): A solution of 3-(triisopropylsilyl)propiolaldehyde[5] (1.17 mL, 4.75 mmol, 1.0 eq), 4-*tert*-butylbenzaldehyde (504 mg, 4.75 mmol, 1.0 eq.) and ((4-*tert*-butylphenyl)methylene)bis(1*H*-pyrrole)[1] (2.65 g, 9.50 mmol, 2.0 eq.) in CH_2Cl_2 (1000 mL) was purged with argon for 20 min at rt. Trifluoroborate diethyl etherate (199 µL, 1.57 mmol, 0.33 eq.) was added and the reaction mixture was stirred for 5 min at rt. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (1.62 g, 7.12 mmol, 1.5 eq.) was added and the mixture was stirred for 1 h at rt. The reaction mixture was filtered over a plug of silica eluted with CH_2Cl_2 and was concentrated under reduced pressure. The crude product was subjected to flash column chromatography (SiO_2, CH_2Cl_2/cyclohexane (1:2)) followed by crystallisation from CH_2Cl_2/MeOH yielding the title compound **7** (378 mg, 426 µmol, 8.9%) as a microcrystalline purple solid.

TLC (SiO_2, CH_2Cl_2/cyclohexane (1:1)): $R_f = 0.79$.

MP: >300 °C

^{1}H-NMR (500 MHz, THF-d_8, 298 K, δ/ppm): 9.69 (d, $^3J_{HH} = 4.7$ Hz, 2H, H_β), 8.87 (d, $^3J_{HH} = 4.7$ Hz, 2H, H_β), 8.80 – 8.76 (m, 4H, H_β), 8.15 – 8.13 (m, 4H, $H_{10,20\text{-Ph}}$), 8.13 – 8.10 (m, 2H, $H_{5\text{-Ph}}$), 7.86 – 7.84 (m, 4H, $H_{10,20\text{-Ph}}$), 7.84 – 7.82 (m, 2H, $H_{5\text{-Ph}}$), 1.62 (s, 18H, $H_{10,20\text{-tBuPh}}$), 1.61 (s, 9H, $H_{5\text{-tBuPh}}$), 1.50 – 1.46 (m, 21H, H_{TIPS}), -2.32 (s, 2H, H_{NH}).

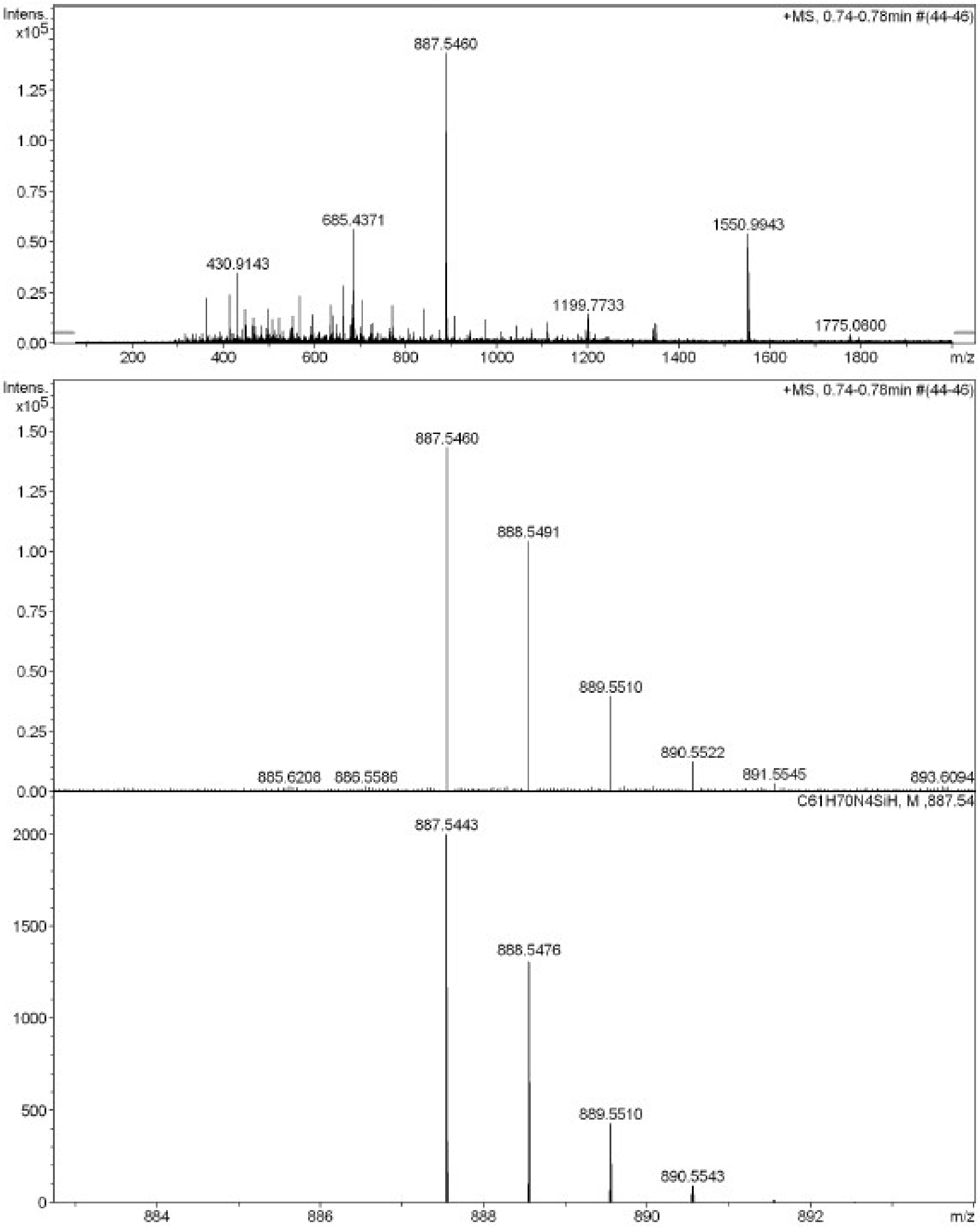
HRMS (ESI, +): *m/z* calcd. for $C_{61}H_{70}N_4SiH$ $[M+H]^+$: 887.5443, found: 887.5460.



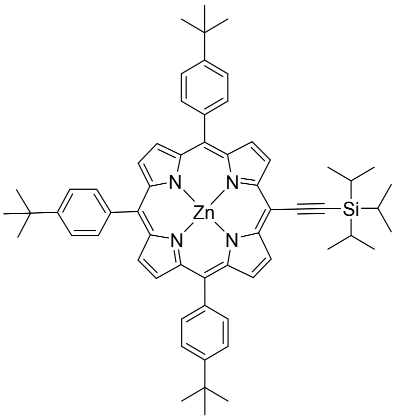
S 27: **^{1}H-NMR (500 MHz, THF-d_8, 298 K)** spectrum of **7**.

High Resolution Mass Spectrometry Report

Sample Name	**Patrick Zwick / zwp516**	Instrument	maXis 4G
Comment	10 ug/mL in DCM, analyzed in MeOH+0.1% HCOOH	Method	24 Direct_pos_high.m



S 28: **HR-ESI MS** of **7**.



8

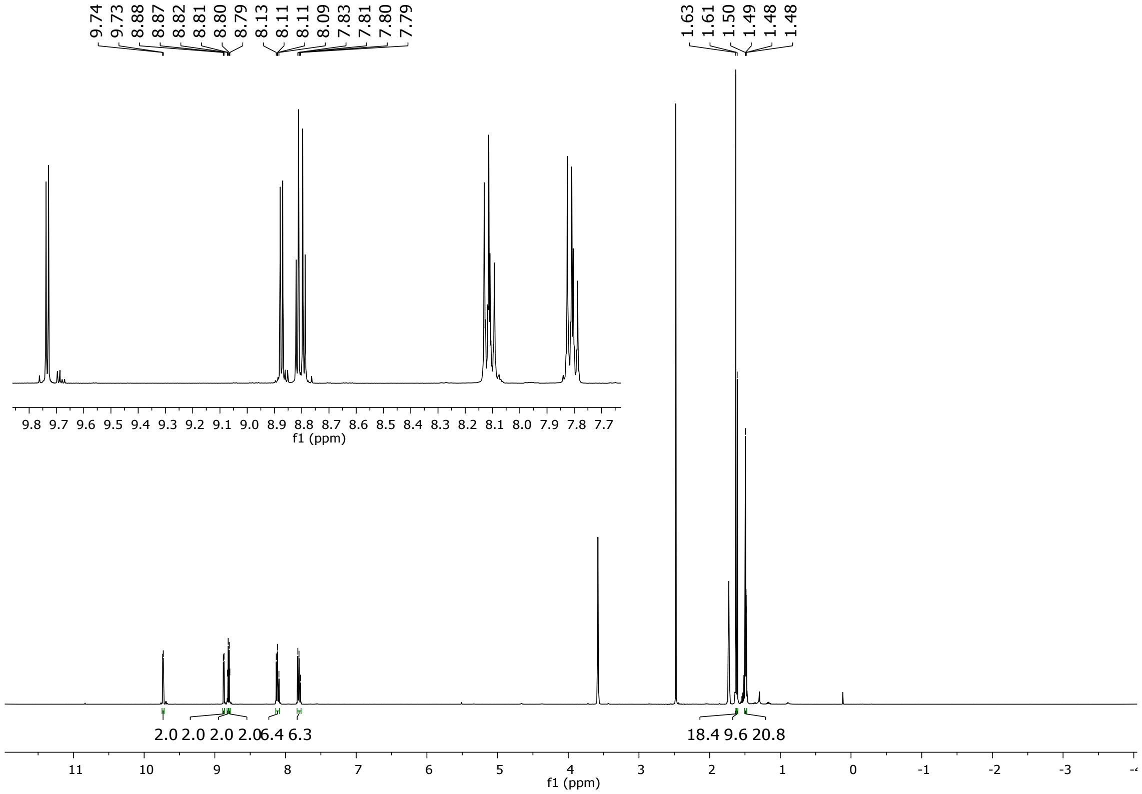
[5,10,15-tris(4-(tert-butyl)phenyl)-20-((triisopropylsilyl)ethynyl)porphyrinato]zinc(II) (8): A solution of **7** (130 mg, 147 µmol, 1.0 eg.) and $Zn(OAc)_2$ (135 mg, 735 µmol, 5.0 eg.) in CH_2Cl_2/MeOH (100 mL, 5:1) was stirred for 1 h at rt. The mixture was dilluted with CH_2Cl_2 and successively washed with water. The organic phase was dried over anhydrous Na_2SO_4, filtered over a plug of silica eluted with CH_2Cl_2 and evaporated to dryness yielding the title compound **8** (138 mg, 145 µmol, 99%) as a microcrystalline purple solid.

TLC (SiO_2, CH_2Cl_2/cyclohexane (1:1)): $R_f = 0.67$.

MP: >300 °C

^{1}H-NMR (500 MHz, THF-d_8, 298 K, δ/ppm): 9.73 (d, $^3J_{HH}$ = 4.6 Hz, 2H, H_β), 8.87 (d, $^3J_{HH}$ = 4.5 Hz, 2H, H_β), 8.82 (d, $^3J_{HH}$ = 4.5 Hz, 2H, H_β), 8.79 (d, $^3J_{HH}$ = 4.6 Hz, 2H, H_β), 8.13 – 8.11 (m, 4H, $H_{10,20\text{-}Ph}$), 8.11 – 8.09 (m, 2H, $H_{5\text{-}Ph}$), 7.83 – 7.81 (m, 4H, $H_{10,20\text{-}Ph}$), 7.81 – 7.78 (m, 2H, $H_{5\text{-}Ph}$), 1.63 (s, 18H, $H_{10,20\text{-}tBuPh}$), 1.61 (s, 9H, $H_{5\text{-}tBuPh}$), 1.50 – 1.48 (m, 21H, H_{TIPS}).

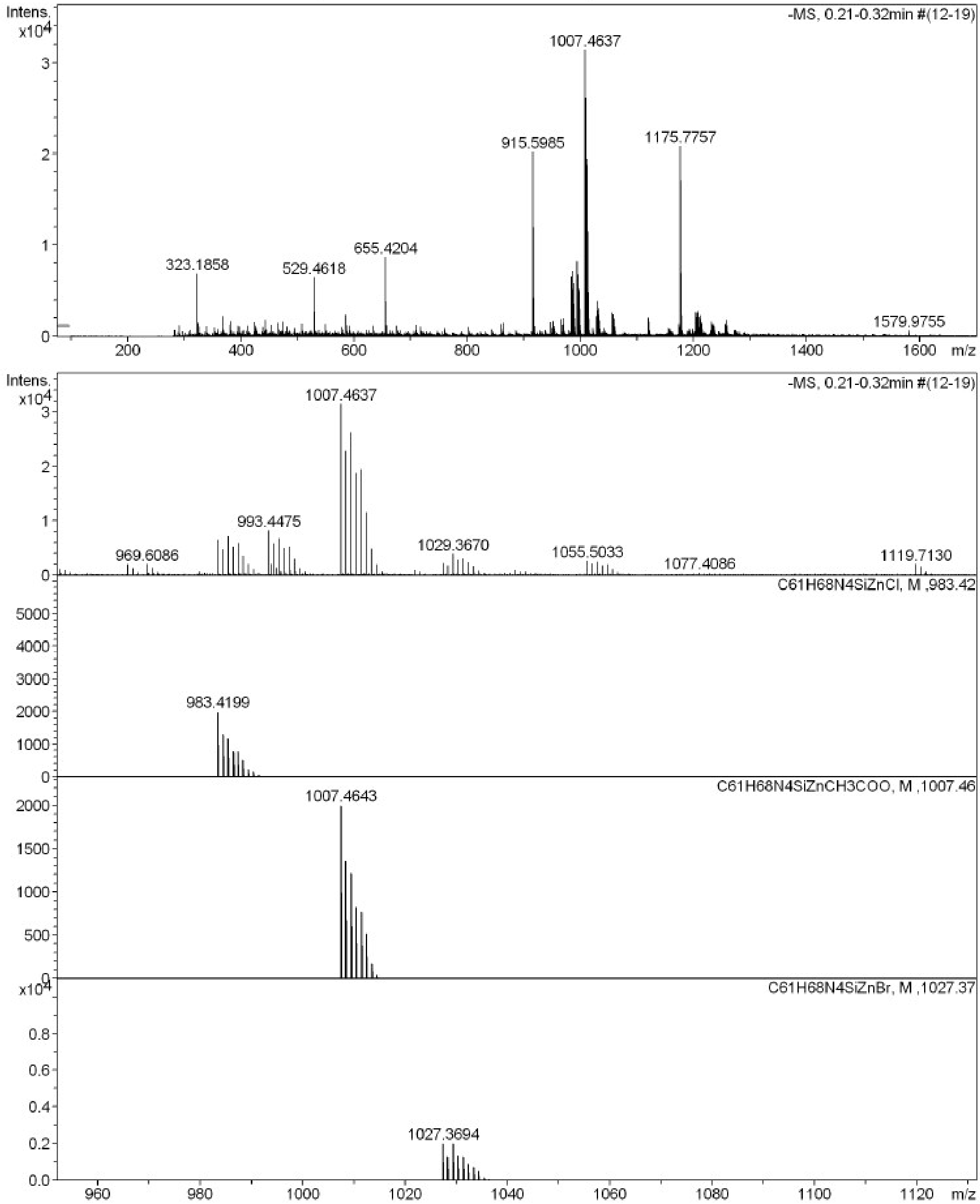
HRMS (ESI, +): *m/z* calcd. for $C_{61}H_{68}N_4SiZnCl$ $[M+Cl]^-$: 983.4199, found: 983.4190.



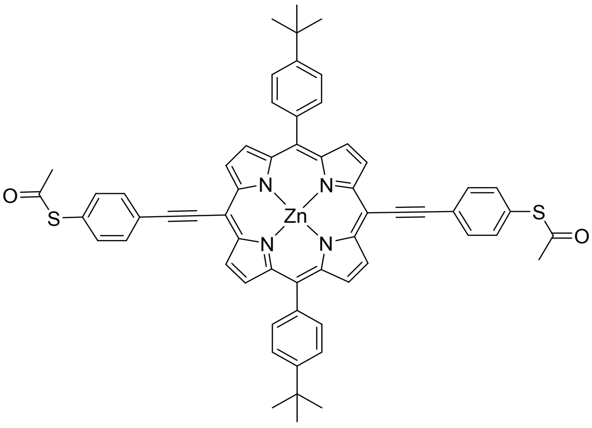
S 29: **^{1}H-NMR (500 MHz, THF-d_8, 298 K**) spectrum of **8**..

High Resolution Mass Spectrometry Report

Sample Name	**Patrick Zwick / zwp517**	Instrument	maXis 4G
Comment	10 ug/mL in DCM, analyzed in MeOH + ammonium acetate (5mM)	Method	34 Direct_neg_high.m



S 30: **HR-ESI MS** of **8**.



ZnP1

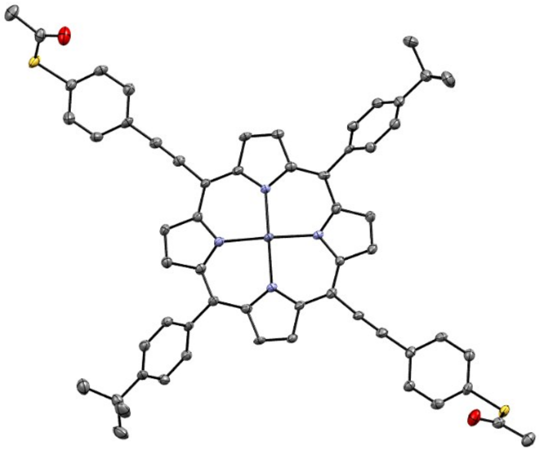
[*S,S'*-(((10,20-bis(4-(*tert*-butyl)phenyl)porphyrinato-5,15-diyl)bis(ethyne-2,1-diyl))bis(4,1-phenylene)) diethanethioate]zinc(II) (ZnP1):

A degassed solution of **4** (29 mg, 35.0 µmol, 1.0 eq.) in 2-MeTHF (10 mL) was treated with a solution of tetrabutylammonium fluoride (TBAF) in THF (1M, 175 µL, 175 umol, 5.0 eq.). The resulting mixture was stirred for 1 h at rt, when TLC monitoring indicated completion. The mixture was succesively washed with water, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was re-dissolved in dry and degassed THF (6.0 mL) and was subsequently transferred to a degassed solution of *S*-(4-iodophenyl)ethanethioate (29.2 mg, 105 µmol, 3.0 eq.), $Pd(PPh_3)_4$ (2.02 mg, 1.75 µmol, 0.05 eq.) and CuI (408 µg, 2.10 µmol, 0.06 eq.) in dry THF/NEt_3 (1:1, 6.0 mL) in a flame dried Schlenk tube under argon atmosphere via syringe. The mixture was further degassed by purging with argon for 5 min and was stirred for 16 h at rt. The mixture was evaporated, re-dissolved in CH_2Cl_2 and filtered over a plug of silica eluted with CH_2Cl_2. The crude product was subjected to flash column chromatography (SiO_2, CH_2Cl_2 4:1 cyclohexane) yielding the title compound **ZnP1** (10 mg, 9.86 µmol, 29%) as a purple solid.

TLC (SiO_2, CH_2Cl_2/cyclohexane (4:1)): $R_f = 0.31$.

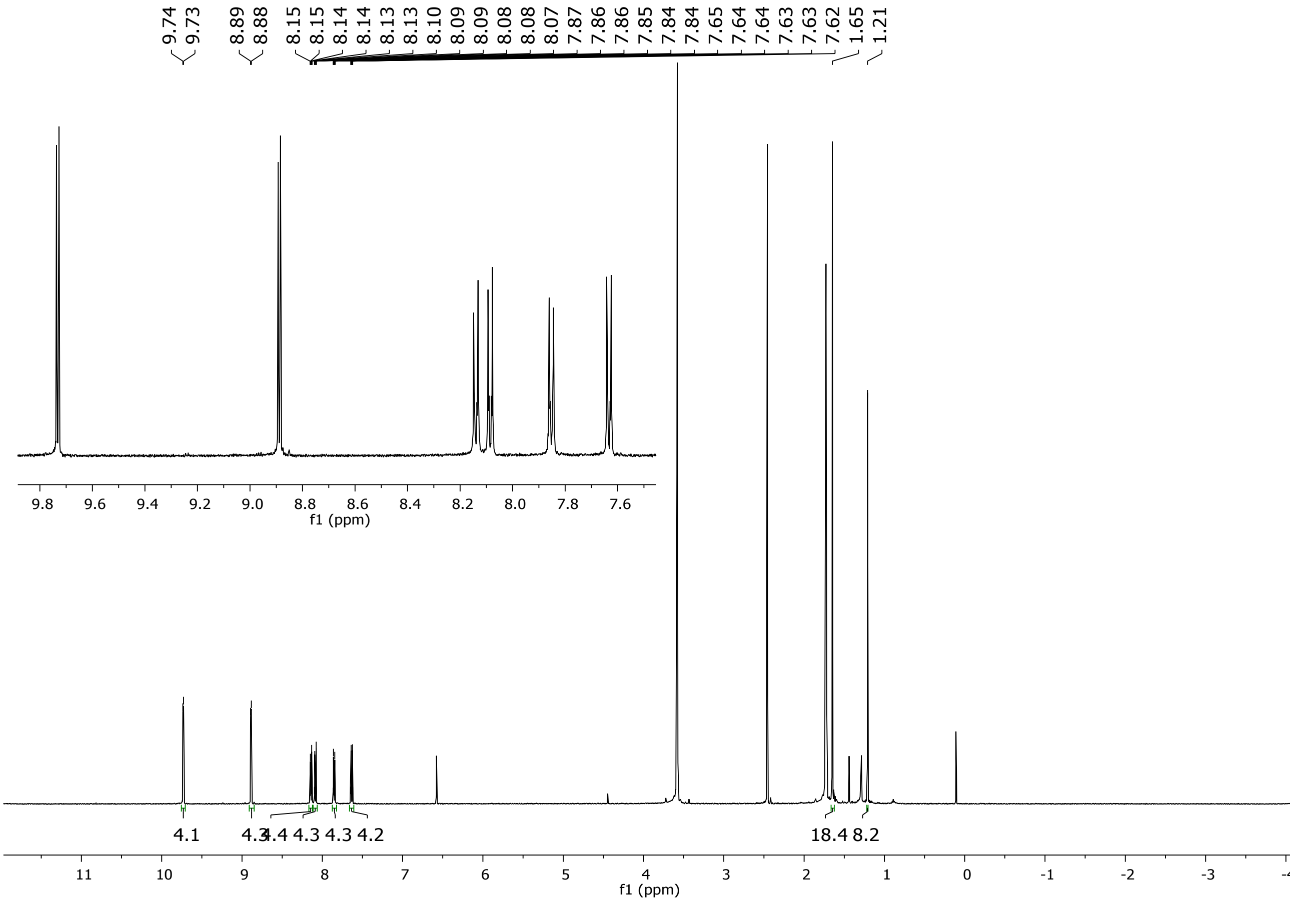
^{1}H-NMR (500 MHz, THF-d_8, 298 K, δ/ppm): 9.73 (d,$^3J_{HH}$ = 4.5 Hz, 4H, H_β), 8.89 (d, $^3J_{HH}$ = 4.5 Hz, 4H, H_β), 8.15 – 8.13 (m, 4H, H_{Ph}), 8.10 – 8.07 (m, 4H, H_{Ph}), 7.87 – 7.84 (m, 4H, H_{Ph}), 7.65 - 7.62 (m, 4H, H_{Ph}), 1.65 (s, 18H, H_{tBu}), 1.21 (s, 6H, H_{Sac} [slightly overlaps with H_2O signal]).

MALDI-TOF *m/z* (%) = 984 (100) [M^+].

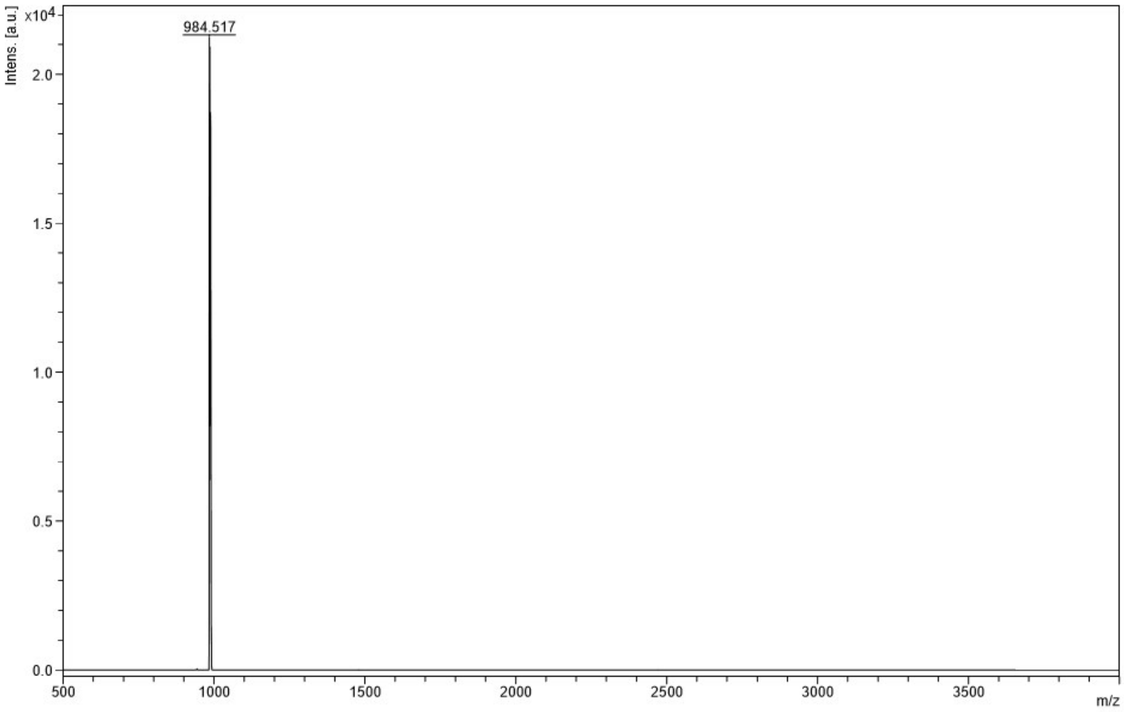


S 31: **ORTEP-representation of the solid state structure of ZnP1.** Thermal ellipsoids are plotted on a 50% probability level. Protons and solvent molecules are omitted for clarity.

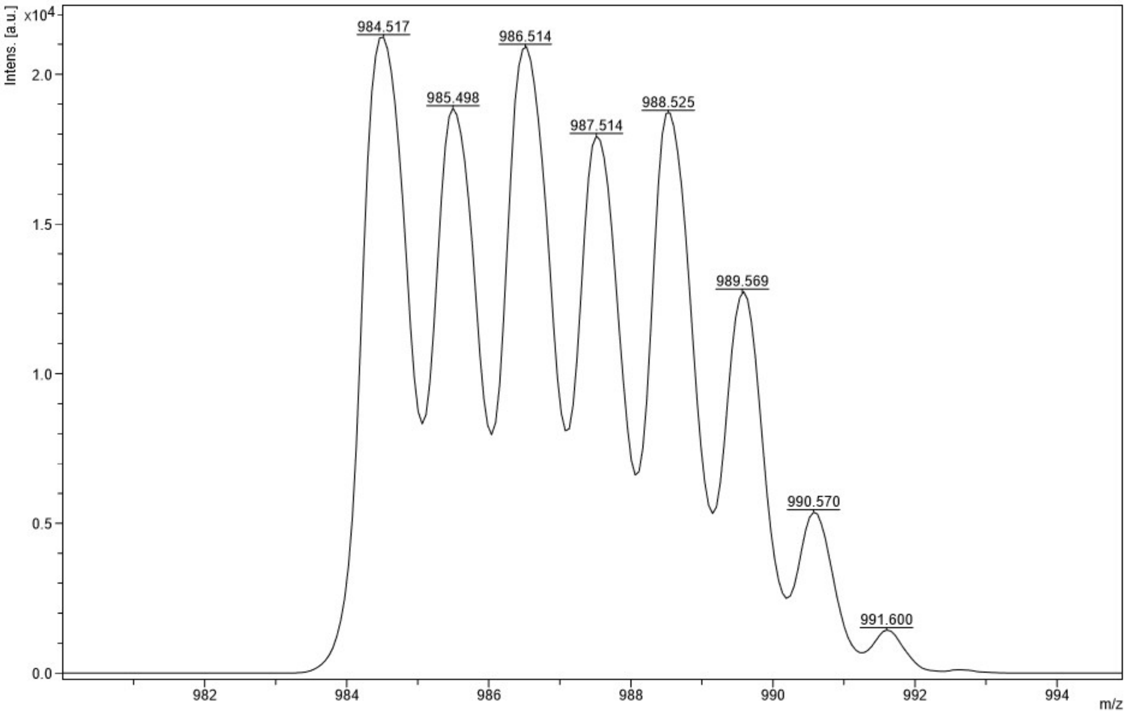
Crystal data for **ZnP1**: formula $C_{64}H_{56}N_4O_3S_2Zn_1$, M = 1058.68, F(000) = 1108, green block, size 0.080 ◊ 0.100 ◊ 0.120 mm^3, monoclinic, space group P 1 21 1 , Z = 2, a = 10.5687(6) Å, b = 17.5433(9) Å, c = 14.2726(8) Å, α = 90 °, β = 90.077(3) °, γ = 90 °, V = 2646.3(3) Å^3, Dcalc. = 1.329 g cm^{-3}. The crystal was measured on a Bruker Kappa Apex2 diffractometer at 123K using graphite-monochromated Cu Kα-radiation with λ = 1.54178 Å, Θmax = 70.323 °. Minimal/maximal transmission 0.79/0.87, μ = 1.785 mm-1. The Apex2 suite has been used for datacollection and integration. From a total of 13644 reflections, 7406 were independent (merging r = 0.027). From these, 7367 were considered as observed (I>2.0σ(I)) and were used to refine 668 parameters. The structure was solved by other methods using the program Superflip. Least-squares refinement against Fsqd was carried out on all non-hydrogen atoms using the program CRYSTALS. R = 0.0439 (observed data), wR = 0.1170 (all data), GOF = 0.8466. Minimal/maximal residual electron density = -0.67/0.37 e Å-3. Chebychev polynomial weights were used to complete the refinement. Plots were produced using CAMERON. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Center, the deposition number is 1910507. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].



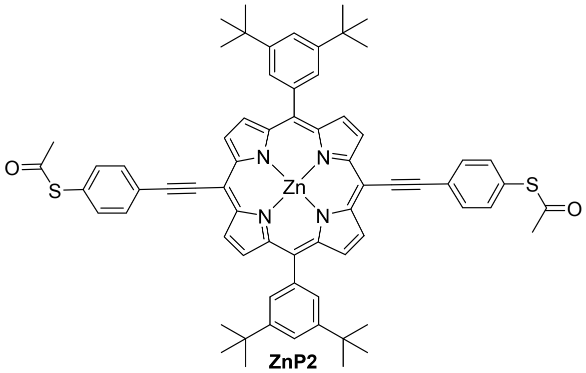
S 32: **^{1}H-NMR (500 MHz, THF-d_8, 298 K)** spectrum of **ZnP1**.



S 33: **MALDI-ToF** spectrum of **ZnP1**.



S 34: **Magnification** of S 33.



ZnP2

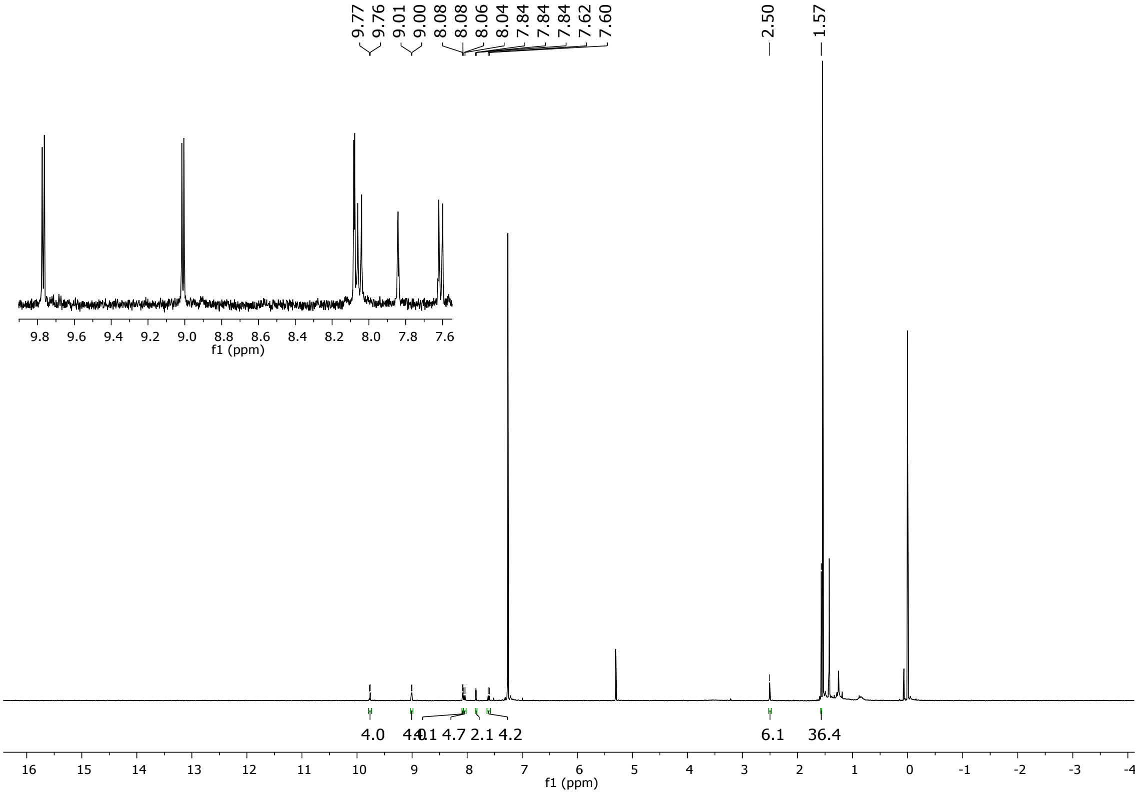
[*S,S'*-(((10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinato-5,15-diyl)bis(ethyne-2,1-diyl))bis(4,1-phenylene)) diethanethioate]zinc(II) (ZnP2):

A degassed solution of **5** (42 mg, 44.5 µmol, 1.0 eq.) in 2-MeTHF (10 mL)was treated with a solution of tetrabutylammonium fluoride (TBAF) in THF (1M, 222 µL, 222 µmol, 5.0 eq.). The resulting mixture was stirred for 1 h at rt, when TLC monitoring indicated completion. The mixture was succesively washed with water, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was re-dissolved in dry and degassed THF (6.0 mL) and was subsequently transferred to a degassed solution of *S*-(4-iodophenyl)ethanethioate (37.1 mg, 133 µmol, 3.0 eq.), $Pd(PPh_3)_4$ (2.57 mg, 2.23 µmol, 0.05 eq.) and CuI (519 µg, 2.67 µmol, 0.06 eq.) in dry THF/NEt_3 (1:1, 6 mL) in a flame dried Schlenk tube under argon atmosphere via syringe. The mixture was further degassed by purging with argon for 5 min and was stirred for 16 h at rt. The mixture was evaporated, re-dissolved in CH_2Cl_2 and filtered over a plug of silica eluted with CH_2Cl_2. The crude product was subjected to flash column chromatography (SiO_2, CH_2Cl_2 2:1 cyclohexane) yielding the title compound **ZnP2** (7.5 mg, 7.0 µmol, 15%) as a purple solid.

TLC (SiO_2, CH_2Cl_2/cyclohexane (2:1)): $R_f = 0.40$.

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K, δ/ppm): 9.77 (d, $^3J_{HH} = 4.6$ Hz, 4H, H_β), 9.01 (d, $^3J_{HH} = 4.6$ Hz, 4H, H_β), 8.08 (d, $^4J_{HH} = 1.8$ Hz, 4H, H_{oPh}), 8.07 – 8.03 (m, 4H, H_{SAcPh}), 7.84 (t, $^4J_{HH} = 1.8$ Hz, 2H, H_{pPh}), 7.64 – 7.59 (m, 4H, H_{SAcPh}), 2.50 (s, 6H, H_{SAc}), 1.57 (s, 36H, H_{tBu}).

HR-MALDI-TOF *m/z* = 1096.3761 ($[M]^+$ requires 1096.3757).



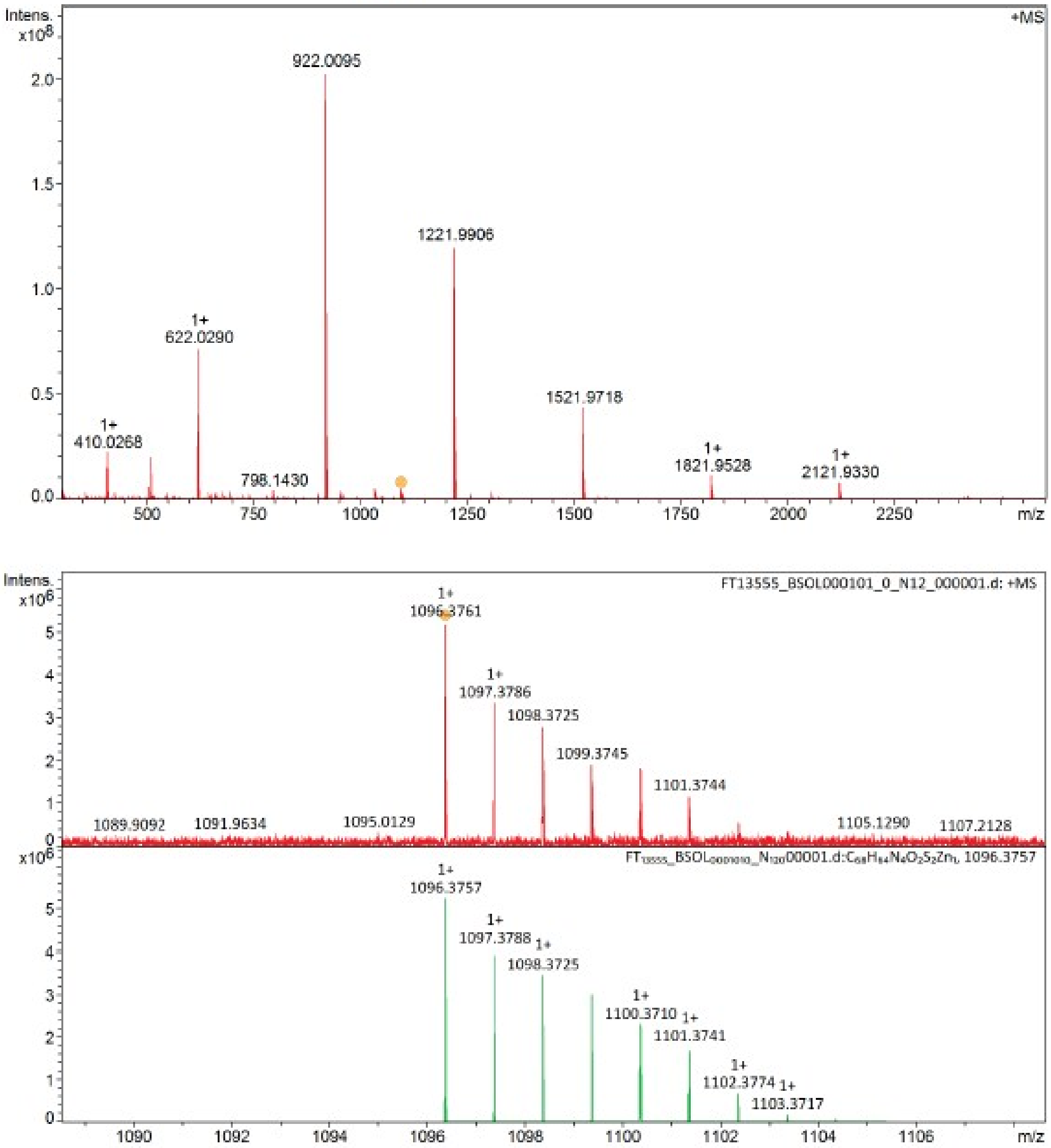
S 37: **^{1}H-NMR (400 MHz, CDCl$_3$, 298 K**) spectrum of **ZnP2**.

FT13555_BSOL000101 Patrick Zwick/ - ZnP2 - DCM - DHB 1:10

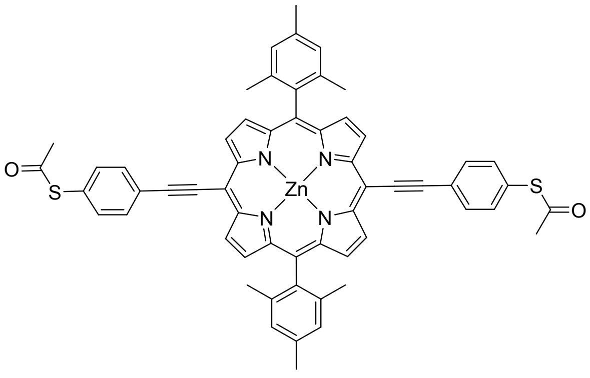
ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Acquisition Parameter

Method:	MALDI_MS_POS_300-2600_2M_16AvScans			Acquisition Date:	27.11.2018 15:16:53
File Name:	D:\ETH\Data\FT135xx\FT13555_BSOL000101_0_N12_000001.d			Operator:	Daniel Wirz
Source	Dual (MALDI/ESI)	Polarity	Positive	Nebulizer Gas	1.3 bar
Broadband Low Mass	303.1 m/z	n/a	n/a	Drying Gas Flow Rate	3.7 L/min
Broadband High Mass	2600.0 m/z	Laser Power	56.4 lp	Capillary	3000.0 V
No. of Cell Fills	1	n/a	n/a	Drying Gas Temperature	200.0 °C
Apodization	Full-Sine	Time of Flight to Detector	0.001 sec		



S 38: **HR-MALDI-ToF MS** of **ZnP2**.



ZnP3

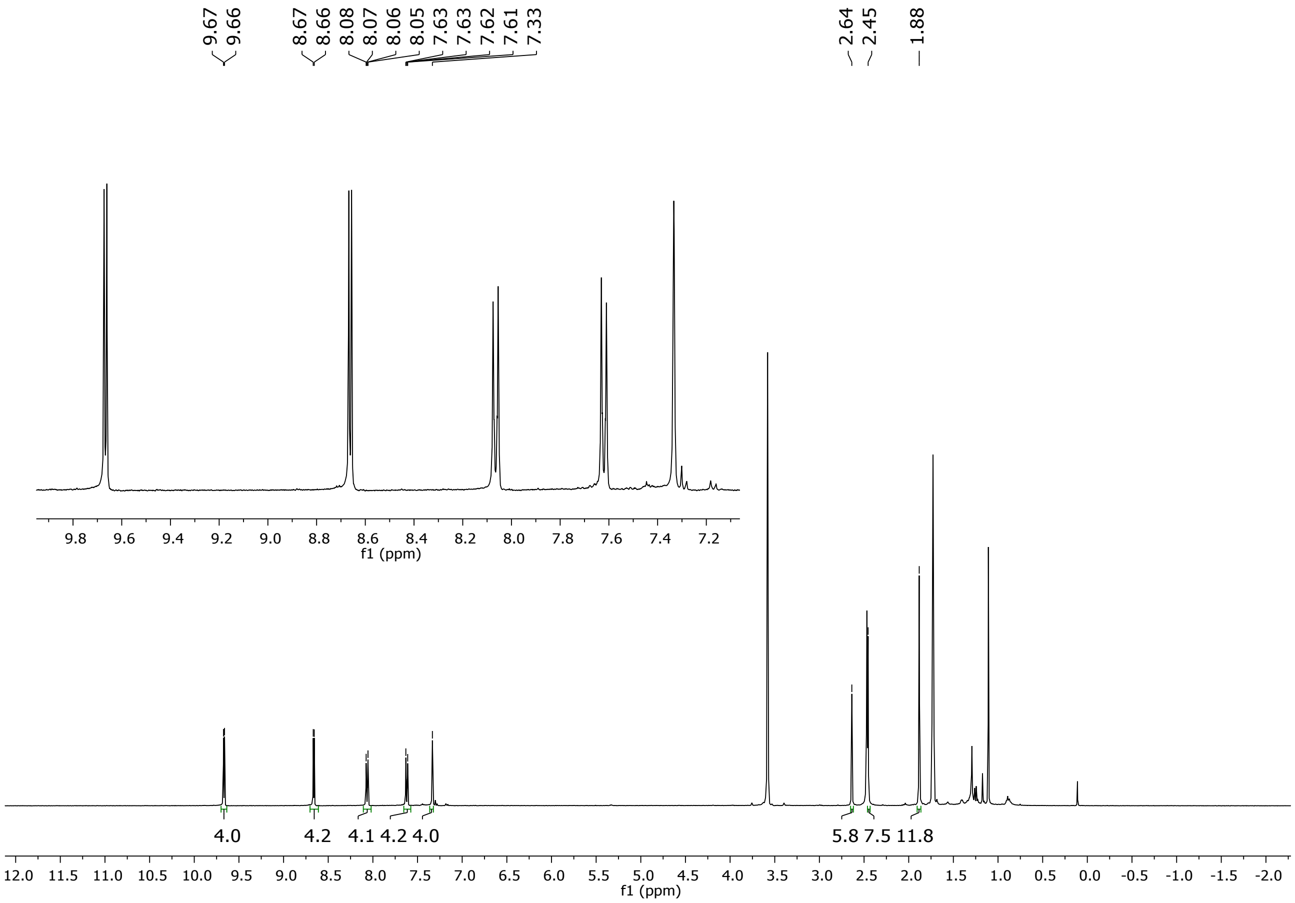
[*S,S'*-(((10,20-dimesitylporphyrinato-5,15-diyl)bis(ethyne-2,1-diyl))bis(4,1-phenylene)) diethanethioate]zinc(II) (ZnP3):

A degassed solution of **6** (31 mg, 38.0 µmol, 1.0 eq.) in 2-MeTHF (10 mL) was treated with a solution of tetrabutylammonium fluoride (TBAF) in THF (1M, 190 µL, 190 µmol, 5.0 eq.). The resulting mixture was stirred for 1 h at rt, when TLC monitoring indicated completion. The mixture was succesively washed with water, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was re-dissolved in dry and degassed THF (6.0 mL) and was subsequently transferred to a degassed solution of *S*-(4-iodophenyl)ethanethioate (31.7 mg, 114 µmol, 3.0 eq.), $Pd(PPh_3)_4$ (2.20 mg, 1.90 µmol, 0.05 eq.) and CuI (443 µg, 2.28 µmol, 0.06 eq.) in dry THF/NEt_3 (1:1, 6 mL) in a flame dried Schlenk tube under argon atmosphere via syringe. The mixture was further degassed by purging with argon for 5 min and was stirred for 16 h at rt. The mixture was evaporated, re-dissolved in CH_2Cl_2 and filtered over a plug of silica eluted with CH_2Cl_2. The crude product was subjected to flash column chromatography (SiO_2, CH_2Cl_2 4:1 cyclohexane) yielding the title compound **ZnP3** (11 mg, 11.0 µmol, 30%) as a purple solid.

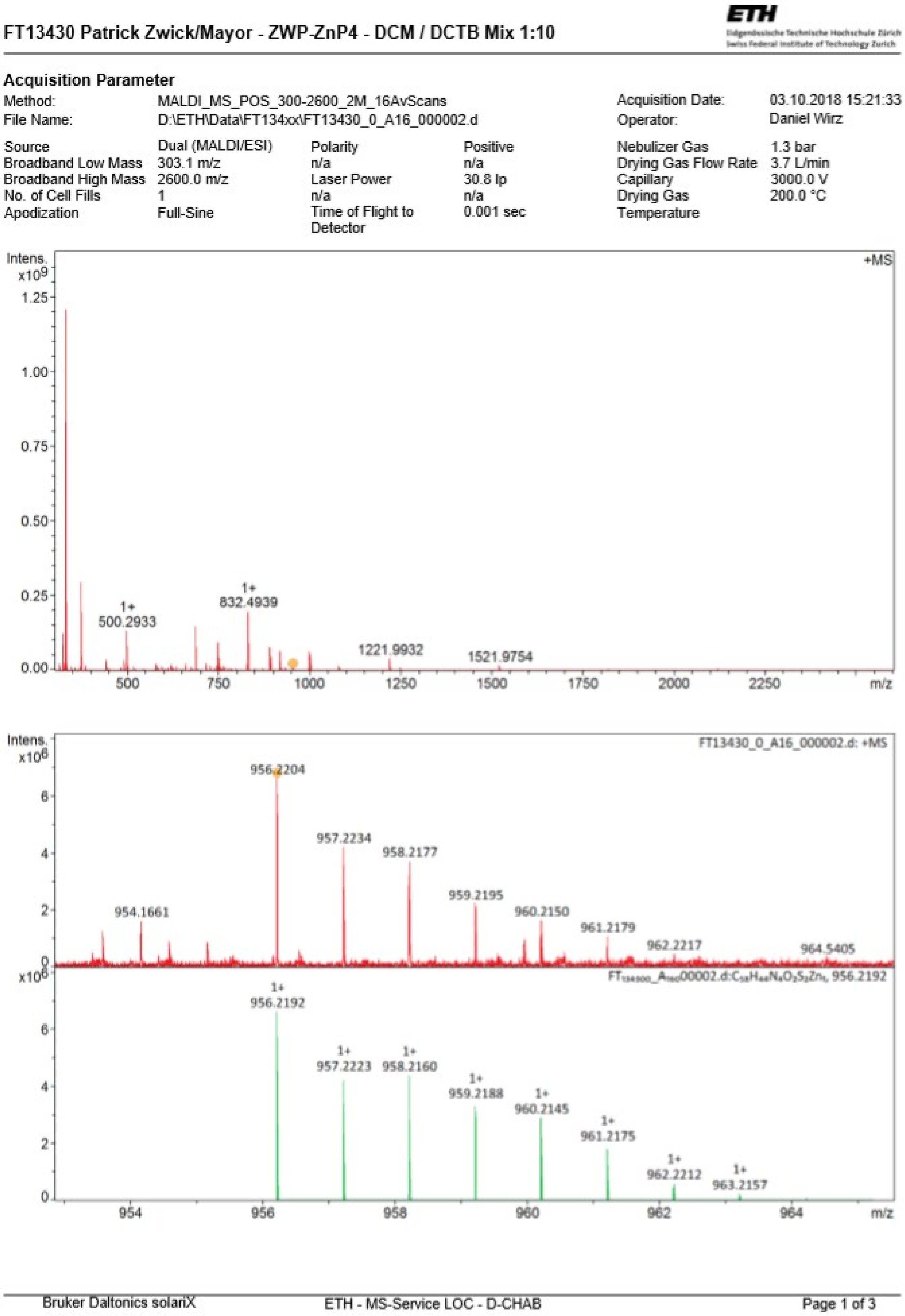
TLC (SiO_2, CH_2Cl_2/cyclohexane (4:1)): $R_f = 0.47$.

^{1}H-NMR (400 MHz, THF-d_8, 298 K, δ/ppm): 9.67 (d, $^3J_{HH} = 4.5$ Hz, 4H, H_β), 8.66 (d, $^3J_{HH} = 4.5$ Hz, 4H, H_β), 8.09 – 8.04 (m, 4H, H_{Ph}), 7.65 – 7.58 (m, 4H, H_{Ph}), 7.33 (s, 4H, H_{Ph}), 2.64 (s, 6H, H_{pMe}), 2.45 (s, 6H, H_{Sac} [slightly overlaps with H_2O signal]), 1.88 (s, 12H, H_{oMe}).

HR-MALDI-TOF *m/z* = 956.2204 ($[M]^+$ requires 956.192).



S 35: **^{1}H-NMR (400 MHz, THF-d_8, 298 K**) spectrum of **ZnP3**.



FT13430 Patrick Zwick/Mayor - ZWP-ZnP4 - DCM / DCTB Mix 1:10

ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Acquisition Parameter

Method:	MALDI_MS_POS_300-2600_2M_16AvScans			Acquisition Date:	03.10.2018 15:21:33
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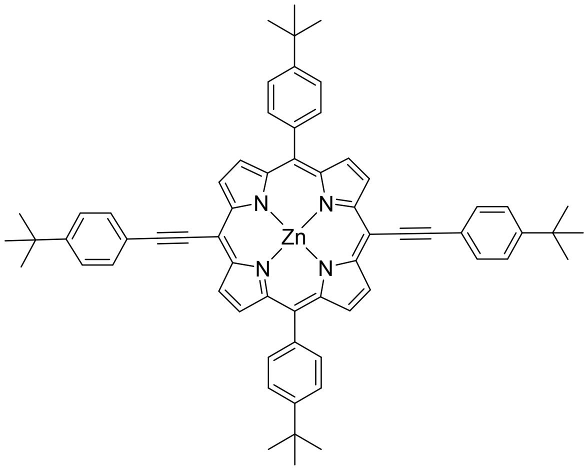
Broadband Low Mass	303.1 m/z	n/a	n/a	Drying Gas Flow Rate	3.7 L/min
Broadband High Mass	2600.0 m/z	Laser Power	30.8 lp	Capillary	3000.0 V
No. of Cell Fills	1	n/a	n/a	Drying Gas Temperature	200.0 °C
Apodization	Full-Sine	Time of Flight to Detector	0.001 sec		

Bruker Daltonics solariX ETH - MS-Service LOC - D-CHAB Page 1 of 3

S 36: **HR-MALDI-ToF MS** of **ZnP3**.



ZnR3

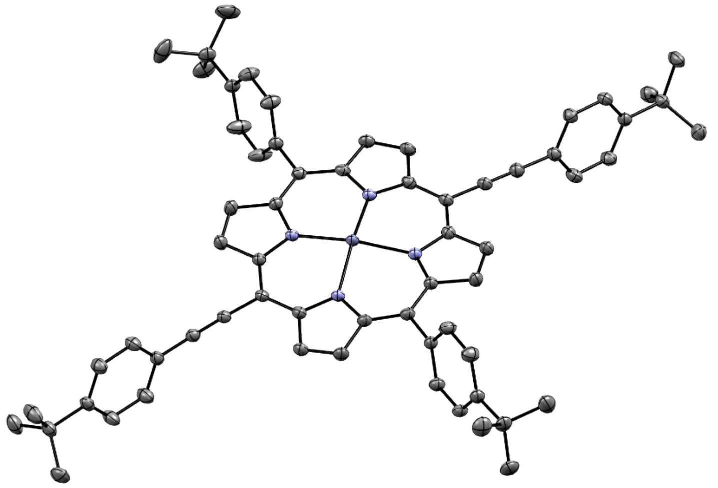
[5,15-bis(4-(*tert*-butyl)phenyl)-10,20-bis((4-(*tert*-butyl)phenyl)ethynyl)porphyrinato]zinc(II) (ZnR3):

A degassed solution of **4** (30.5 mg, 36.7 µmol, 1.0 eq.) in THF (6 mL) was treated with a solution of tetrabutylammonium fluoride (TBAF) in THF (1M, 184 µL, 184 µmol, 5.0 eq.). The resulting mixture was stirred for 1 h at rt, when TLC monitoring indicated completion. The mixture was transferred to a degassed solution of 4-*tert*-butyl-iodo-benzene (28.6 mg, 110 µmol, 3.0 eq.), $Pd(PPh_3)_4$ (2.12 mg, 1.84 µmol, 0.05 eq.) and CuI (428 µg, 2.20 µmol, 0.06 eq.) in THF/NEt_3 (1:1, 6.0 mL) in a Schlenk tube under argon atmosphere via syringe. The mixture was further degassed by purging with argon for 5 min and was stirred for 16 h at rt. The mixture was evaporated, re-dissolved in CH_2Cl_2 and filtered over a plug of silica eluted with CH_2Cl_2. The crude product was subjected to flash column chromatography (SiO_2, CH_2Cl_2 1:2 cyclohexane) yielding the title compound **ZnR3** (12 mg, 13 µmol, 34%) as a purple solid.

TLC (SiO_2, CH_2Cl_2/cyclohexane (1:2)): $R_f = 0.19$.

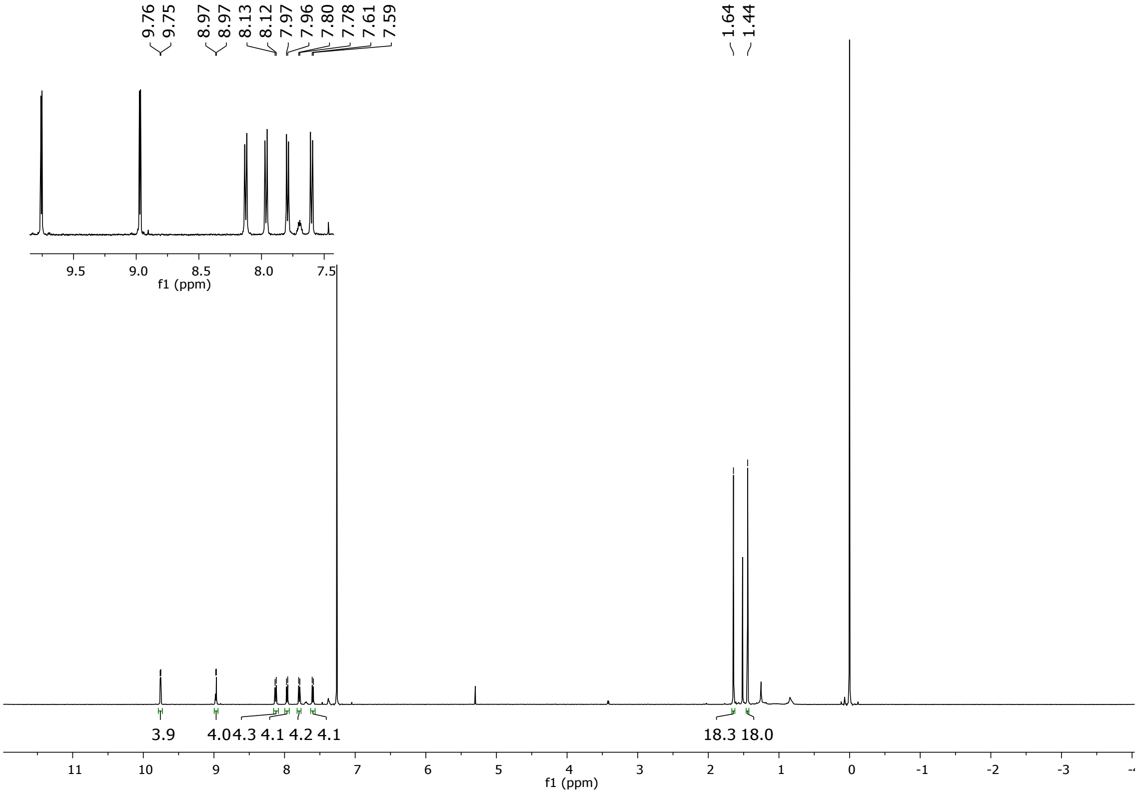
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K, δ/ppm): 9.76 (d, $^3J_{HH} = 4.6$ Hz, 4H, H_β), 8.97 (d, $^3J_{HH} = 4.6$ Hz, 4H, H_β), 8.15 – 8.09 (m, 4H, H_{Ph}), 7.99 – 7.92 (m, 4H, H_{Ph}), 7.82 – 7.77 (m, 4H, H_{Ph}), 7.63 – 7.57 (m, 4H, H_{Ph}), 1.64 (s, 18H, H_{tBu}), 1.44 (s, 18H, H_{tBu}).

HR-MALDI-TOF *m/z* = 948.4105 ($[M]^+$ requires 948.4104).

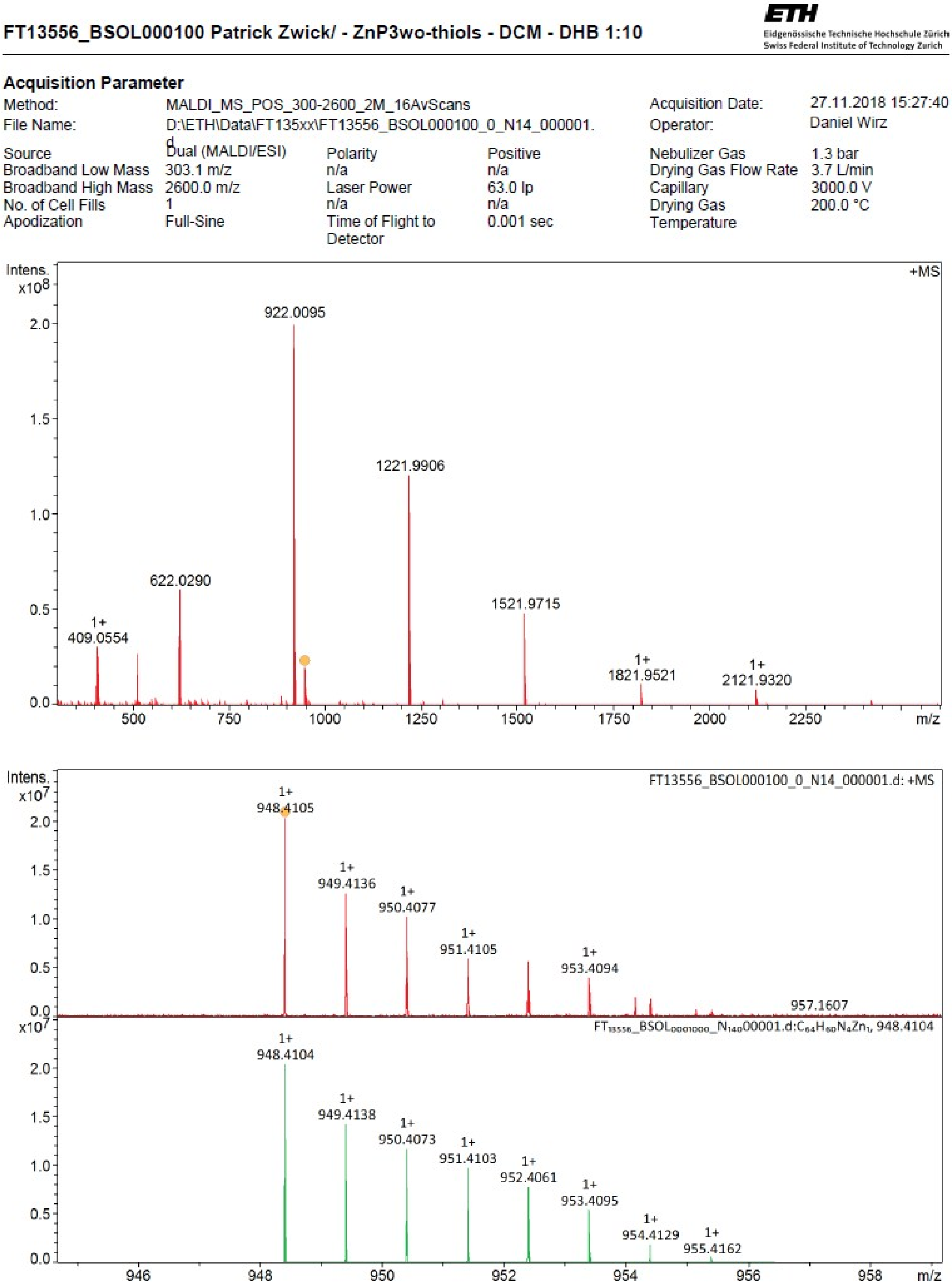


S 39: **ORTEP-representation of the solid state structure of ZnR3.** Thermal ellipsoids are plotted on a 50% probability level. Protons and solvent molecules are omitted for clarity.

Crystal data for **ZnR3**: formula $C_{72}H_{76}N_4O_2Zn$, M = 1094.73, F(000) = 1164, violet block, size 0.17 ◊ 0.21 ◊ 0.23 mm^3, triclinic, space group P-1, Z = 2, a = 14.3919(7) Å, b = 15.0704(7) Å, c = 15.2655(8) Å, α = 96.327(2)º, β = 113.100(2)º, γ = 102.726(2)º, V = 2898.5(3) Å^3, $D_{calc.}$ = 1.254 g cm^{-3}. The crystal was measured on a Bruker APEX-II CCD diffractometer at 130K using graphite-monochromated CuK_α-radiation with λ = 1.54178 Å, Θ_{max} = 70.273 º. Minimal/maximal transmission 0.6563/0.7533, μ = 0.974 mm^{-1}. The Apex2 suite has been used for datacollection and integration. From a total of 36414 reflections, 10700 were independent (merging r = 0.0378). From these, 10700 were considered as observed (I > 2σ(I)) and were used to refine 733 parameters. The structure was solved by dual methods using the program SHELXT 2014/5. Least-squares refinement against Fsqd was carried out on all non-hydrogen atoms using the program ShelXL. R = 0.0625 (observed data), wR = 0.1997 (all data), GOF = 1.054. Minimal/maximal residual electron density = -1.730/0.670 e Å^{-3}. Chebychev polynomial weights were used to complete the refinement. Plots were produced using Olex2. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Center, the deposition number is 1910499. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].



S 40: **^{1}H-NMR (500 MHz, CDCl$_3$, 298 K)** spectrum of **ZnR3**.



FT13556_BSOL000100 Patrick Zwick/ - ZnP3wo-thiols - DCM - DHB 1:10

ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Acquisition Parameter

Method:	MALDI_MS_POS_300-2600_2M_16AvScans			Acquisition Date:	27.11.2018 15:27:40
File Name:	D:\ETH\Data\FT135xx\FT13556_BSOL000100_0_N14_000001.d			Operator:	Daniel Wirz
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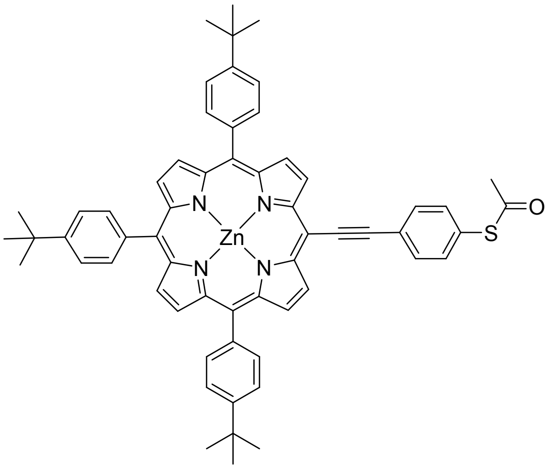
Broadband High Mass	2600.0 m/z	Laser Power	63.0 lp	Capillary	3000.0 V
No. of Cell Fills	1	n/a	n/a	Drying Gas Temperature	200.0 °C
Apodization	Full-Sine	Time of Flight to Detector	0.001 sec		

S 41: **HR-MALDI-ToF MS** of **ZnR3**.



ZnR1

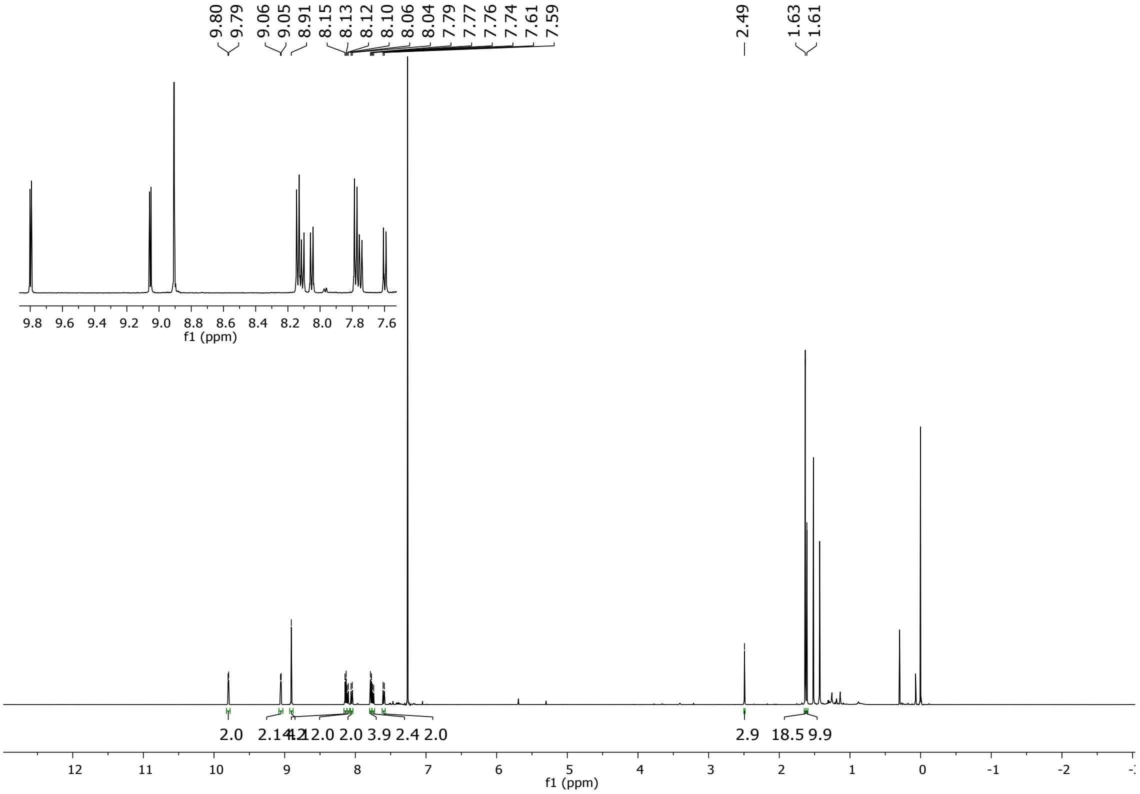
[*S*-(4-((10,15,20-tris(4-(*tert*-butyl)phenyl)porphyrinato-5-yl)ethynyl)phenyl) ethanethioate]zinc(II) (ZnR1):

A degassed solution of **8** (22.7 mg, 23.9 µmol, 1.0 eq.) in 2-MeTHF (10 mL)was treated with a solution of tetrabutylammonium fluoride (TBAF) in THF (1M, 59 µL, 59 µmol, 2.5 eq.). The resulting mixture was stirred for 1 h at rt, when TLC monitoring indicated completion. The mixture was succesively washed with water, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was re-dissolved in dry and degassed THF (6.0 mL) and was subsequently transferred to a degassed solution of *S*-(4-iodophenyl)ethanethioate (13.3 mg, 47.8 µmol, 2.0 eq.), $Pd(PPh_3)_4$ (1.38 mg, 1.20 µmol, 0.05 eq.) and CuI (279 µg, 1.43 µmol, 0.06 eq.) in dry THF/NEt_3 (1:1, 6 mL) in a flame dried Schlenk tube under argon atmosphere via syringe. The mixture was further degassed by purging with argon for 5 min and was stirred for 16 h at rt. The mixture was evaporated, re-dissolved in CH_2Cl_2 and filtered over a plug of silica eluted with CH_2Cl_2. The crude product was subjected to flash column chromatography (SiO_2, CH_2Cl_2 2:1 cyclohexane) yielding the title compound **ZnR1** (8 mg, 9.00 µmol, 37%) as a purple solid.

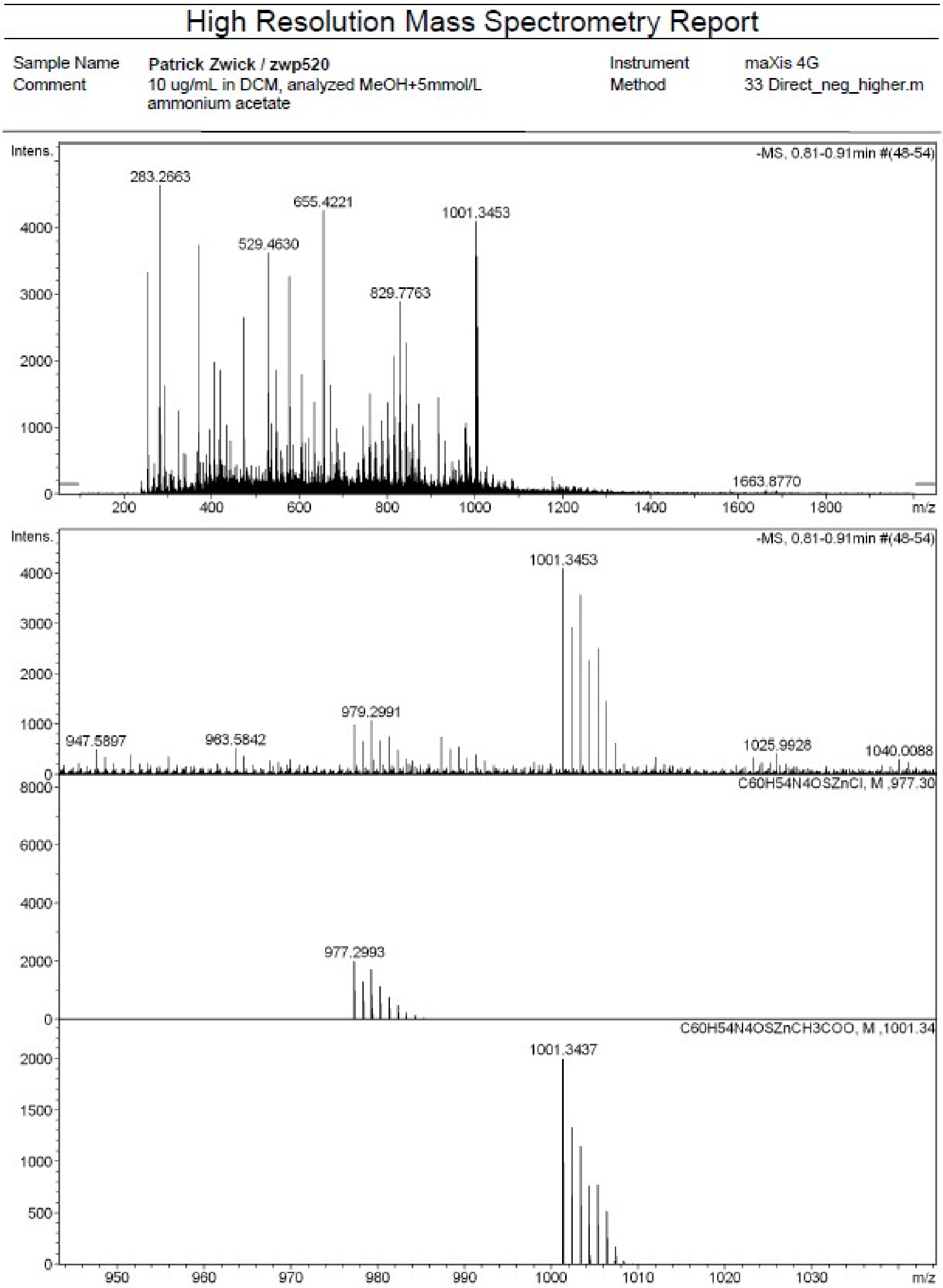
TLC (SiO_2, CH_2Cl_2/cyclohexane (2:1)): $R_f = 0.49$.

^{1}H-NMR (500 MHz, $CDCl_3$, 298 K, δ/ppm): 9.80 (d, $^3J_{HH} = 4.6$ Hz, 2H, H_β), 9.05 (d, $^3J_{HH} = 4.6$ Hz, 2H, H_β), 8.91 (s, 4H, H_β), 8.15 – 8.12 (m, 4H, H_{Ph}), 8.12 – 8.09 (m, 2H, H_{Ph}), 8.07 – 8.04 (m, 2H, H_{Ph}), 7.79 – 7.76 (m, 4H, H_{Ph}), 7.76 – 7.73 (m, 2H, H_{Ph}), 7.63 – 7.58 (m, 2H, H_{Ph}), 2.49 (s, 3H, H_{SAc}), 1.63 (s, 18H, H_{tBu}), 1.61 (s, 9H, H_{tBu}).

HRMS (ESI, -): *m/z* calcd. for $C_{60}H_{54}N_4OSZnCH_3COO$ $[M+CH_3COO]^-$: 1001.3448, found: 1001.3453.



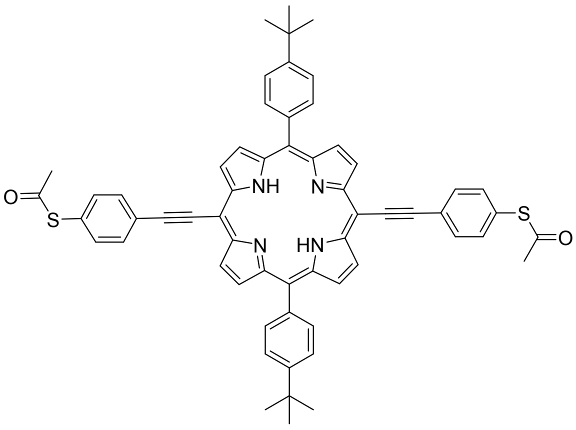
S 42: **^{1}H-NMR (500 MHz, CDCl$_3$, 298 K)** spectrum of **ZnR1**.



High Resolution Mass Spectrometry Report

Sample Name **Patrick Zwick / zwp520**
Comment 10 ug/mL in DCM, analyzed MeOH+5mmol/L ammonium acetate
Instrument maXis 4G
Method 33 Direct_neg_higher.m

S 43: **HR-ESI MS** of **ZnR1**.



P1

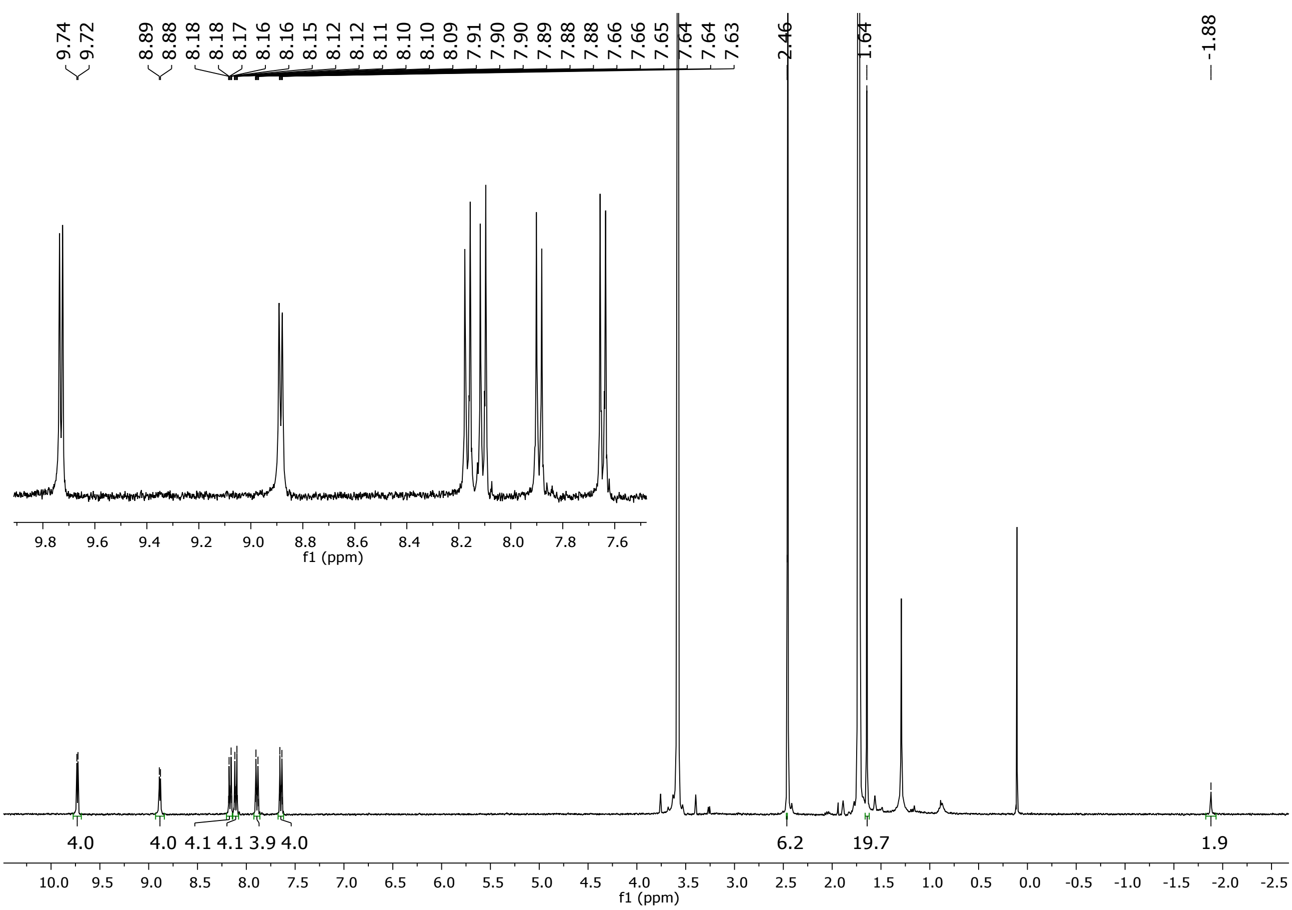
S,S'-(((10,20-bis(4-(*tert*-butyl)phenyl)porphyrin-5,15-diyl)bis(ethyne-2,1-diyl))bis(4,1-phenylene))diethanethioate (P1): from ZnP1

A solution of **ZnP1** (8 mg, 8.11 µmol, 1.0 eq.) in CH_2Cl_2 (5 mL) was treated with 5 drops of TFA. The mixture was stirred for 2 h at rt. Water was added, the organic phase was extracted with CH_2Cl_2 and washed with water twice. The solution was dried over anhydrous Na_2SO_4, filtered off and dried under high vacuum to yield the title compound **P1** (7 mg, 7.62 µmol, 94%) as a purple solid.

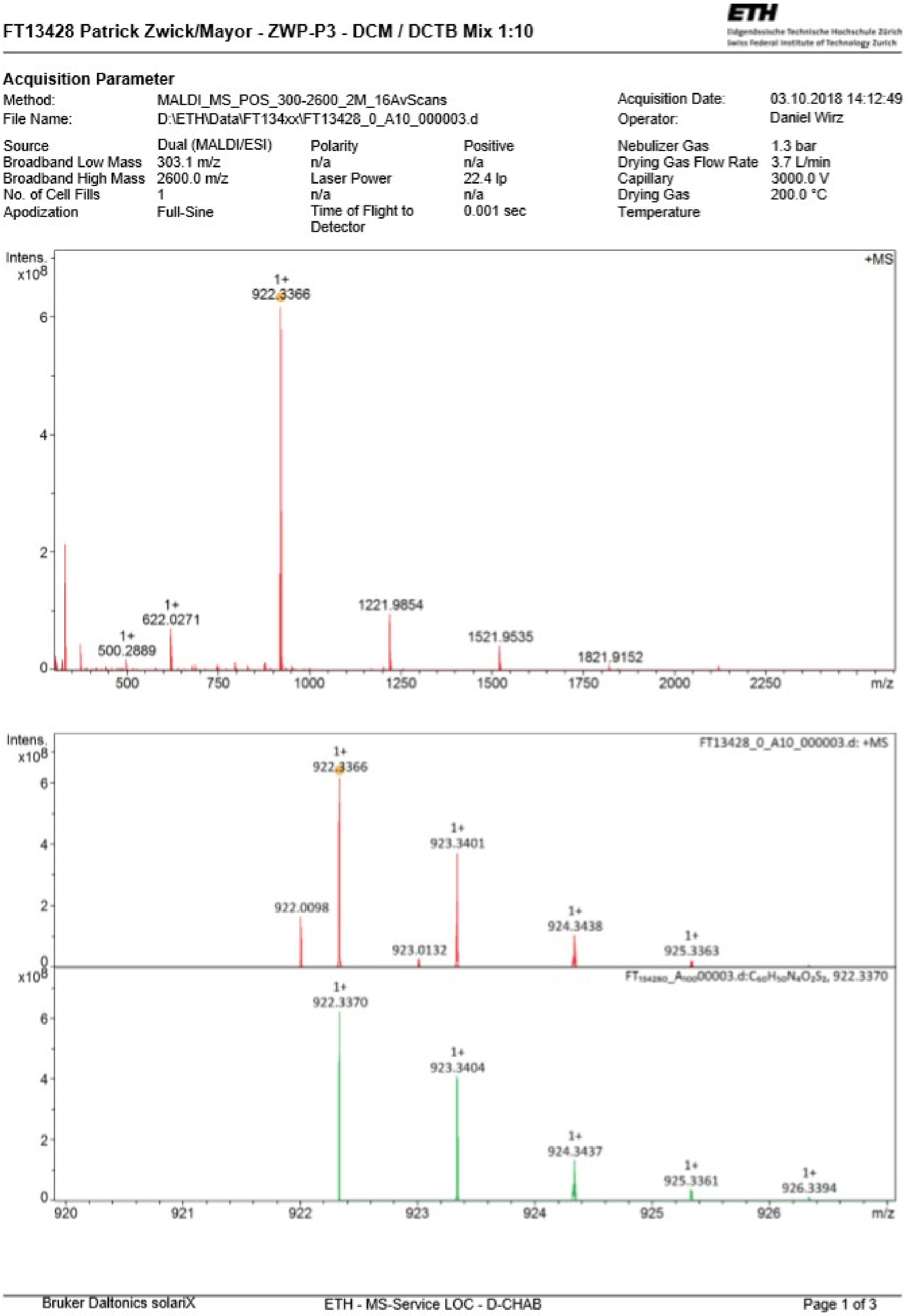
TLC (SiO_2, CH_2Cl_2/cyclohexane (4:1)): R_f = 0.72.

^{1}H-NMR (400 MHz, THF-*d*$_8$, 298 K, δ/ppm): 9.73 (d, $^3J_{HH}$ = 4.7 Hz, 4H, H_β), 8.89 (d, $^3J_{HH}$ = 4.8 Hz, 4H, H_β), 8.21 – 8.13 (m, 4H, H_{Ph}), 8.15 – 8.07 (m, 4H, H_{Ph}), 7.93 – 7.85 (m, 4H, H_{Ph}), 7.69 – 7.61 (m, 4H, H_{Ph}), 2.46 (s, 6H, H_{SAc} [slightly overlaps with H_2O signal]), 1.64 (s, 18H, H_{tBu}), -1.88 (s, 2H, H_{NH}).

HR-MALDI-TOF *m/z* = 922.3366 ([M]$^+$ requires 922.3370).



S 44: **^{1}H-NMR (400 MHz, THF-d_8, 298 K)** spectrum of **P1**.



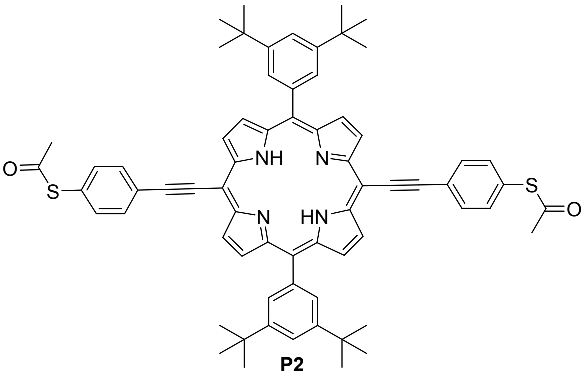
FT13428 Patrick Zwick/Mayor - ZWP-P3 - DCM / DCTB Mix 1:10

Acquisition Parameter

Method:	MALDI_MS_POS_300-2600_2M_16AvScans			Acquisition Date:	03.10.2018 14:12:49
File Name:	D:\ETH\Data\FT134xx\FT13428_0_A10_000003.d			Operator:	Daniel Wirz
Source	Dual (MALDI/ESI)	Polarity	Positive	Nebulizer Gas	1.3 bar
Broadband Low Mass	303.1 m/z	n/a	n/a	Drying Gas Flow Rate	3.7 L/min
Broadband High Mass	2600.0 m/z	Laser Power	22.4 lp	Capillary	3000.0 V
No. of Cell Fills	1	n/a	n/a	Drying Gas Temperature	200.0 °C
Apodization	Full-Sine	Time of Flight to Detector	0.001 sec		

Bruker Daltonics solariX | ETH - MS-Service LOC - D-CHAB | Page 1 of 3

S 45: **HR-MALDI-ToF MS** of **P1**.



P2

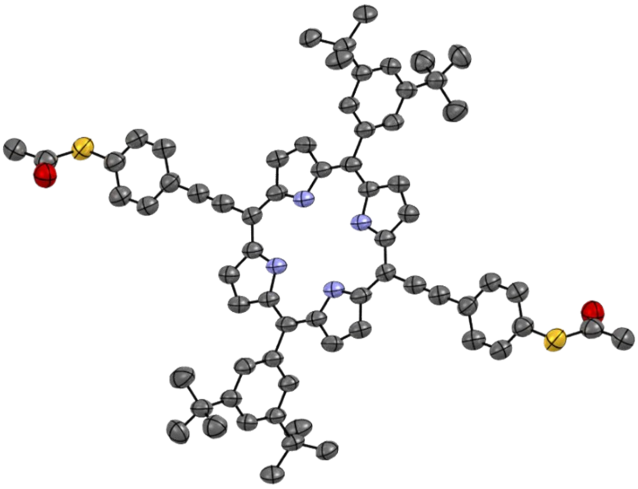
***S,S'*-(((10,20-bis(3,5-di-*tert*-butylphenyl)porphyrin-5,15-diyl)bis(ethyne-2,1-diyl))bis(4,1-phenylene))diethanethioate (P2):**

A solution of **ZnP2** (7 mg, 6.37 µmol, 1.0 eq.) in CH_2Cl_2 (5 mL) was treated with 5 drops of TFA. The mixture was stirred for 2 h at rt. Water was added, the organic phase was extracted with CH_2Cl_2 and washed with water twice. The solution was dried over anhydrous Na_2SO_4, filtered off and dried under high vacuum to yield the title compound **P2** (6.2 mg, 5.98 µmol, 94%) as a purple solid.

TLC (SiO_2, CH_2Cl_2/cyclohexane (4:1)): $R_f = 0.81$.

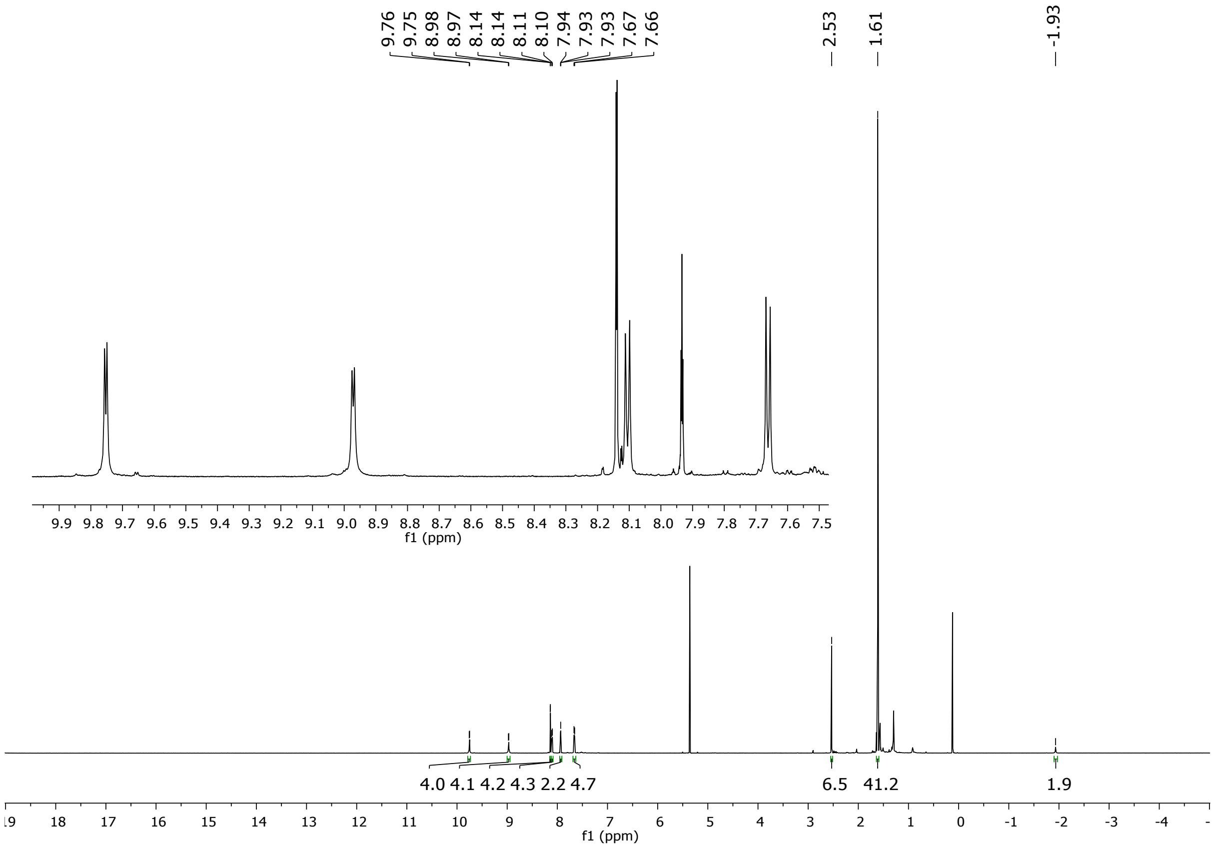
^{1}H-NMR (600 MHz, CD_2Cl_2, 298 K, δ/ppm): 9.75 (d, $^3J_{HH} = 4.7$ Hz, 4H), 8.97 (d, $^3J_{HH} = 4.6$ Hz, 4H), 8.14 (d, $^4J_{HH} = 1.8$ Hz, 4H, H_{oPh}), 8.12 – 8.09 (m, 4H, H_{Ph}), 7.93 (t, $^4J_{HH} = 1.8$ Hz, 2H, H_{pPh}), 7.68 – 7.64 (m, 4H, H_{Ph}), 2.53 (s, 6H, H_{SAc}), 1.61 (s, 36H, H_{tBu}), -1.93 (s, 2H, H_{NH}).

HR-MALDI-TOF *m/z* = 1034.4622 ([M]$^+$ requires 1034.4622).

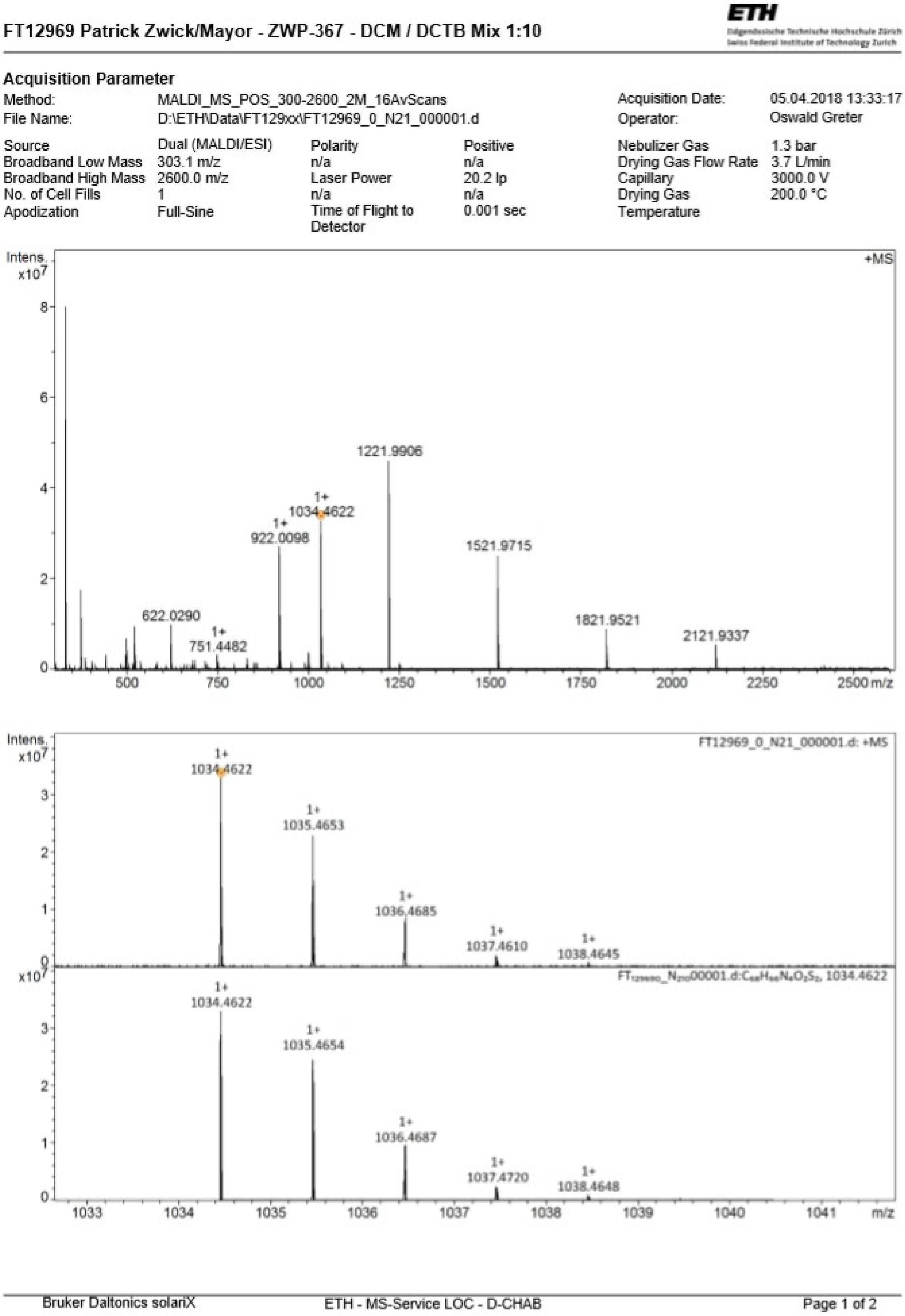


S 46: **ORTEP-representation of the solid state structure of P2.** Thermal ellipsoids are plotted on a 50% probability level. Protons and solvent molecules are omitted for clarity.

Crystal data for **P2**: formula $C_{68}H_{66}N_4O_2S_2$, M = 1035.43, F(000) = 1100, green plate, size 0.050 ◊ 0.153 ◊ 0.230 mm^3, triclinic, space group P -1 , Z = 2, a = 10.2458(5) Å, b = 16.2032(7) Å, c = 19.8087(9) Å, α = 72.034(3) °, β = 79.820(4) °, γ = 73.234(4) °, V = 2981.3(2) $Å^3$, $D_{calc.}$ = 1.153 g cm^{-3}. The crystal was measured on a Stoe StadiVari diffractometer at 130K using Graded multilayer mirror-monochromated GaK_α-radiation with λ = 1.34143 Å, Θ_{max} = 56.933 °. Minimal/maximal transmission 0.1321/0.9182, μ = 0.761 mm^{-1}. The X-Area Pilatus3_SV 1.31.150.0 suite has been used for datacollection and integration. From a total of 39162 reflections, 10597 were independent (merging r = 0.067). From these, 10545 were considered as observed ($I>2.0\sigma(I)$) and were used to refine 685 parameters. The structure was solved by other methods using the program Superflip. Least-squares refinement against Fsqd was carried out on all non-hydrogen atoms using the program CRYSTALS. R = 0.1045 (observed data), wR = 0.3578 (all data), GOF = 1.1616. Minimal/maximal residual electron density = -0.55/1.46 e $Å^{-3}$. Chebychev polynomial weights were used to complete the refinement. Plots were produced using CAMERON. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Center, the deposition number is 1910500. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].



S 47: **^{1}H-NMR (600 MHz, CD_2Cl_2, 298 K)** spectrum of **P2**.


FT12969 Patrick Zwick/Mayor - ZWP-367 - DCM / DCTB Mix 1:10

ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Acquisition Parameter

Method:	MALDI_MS_POS_300-2600_2M_16AvScans			Acquisition Date:	05.04.2018 13:33:17
File Name:	D:\ETH\Data\FT129xx\FT12969_0_N21_000001.d			Operator:	Oswald Greter
Source	Dual (MALDI/ESI)	Polarity	Positive	Nebulizer Gas	1.3 bar
Broadband Low Mass	303.1 m/z	n/a	n/a	Drying Gas Flow Rate	3.7 L/min
Broadband High Mass	2600.0 m/z	Laser Power	20.2 lp	Capillary	3000.0 V
No. of Cell Fills	1	n/a	n/a	Drying Gas Temperature	200.0 °C
Apodization	Full-Sine	Time of Flight to Detector	0.001 sec		

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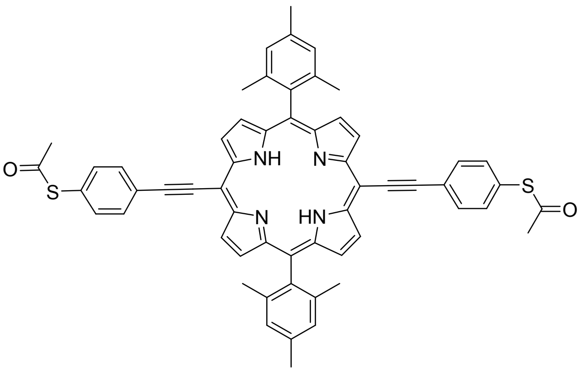
S 48: **HR-ESI MS** of **P2**.



P3

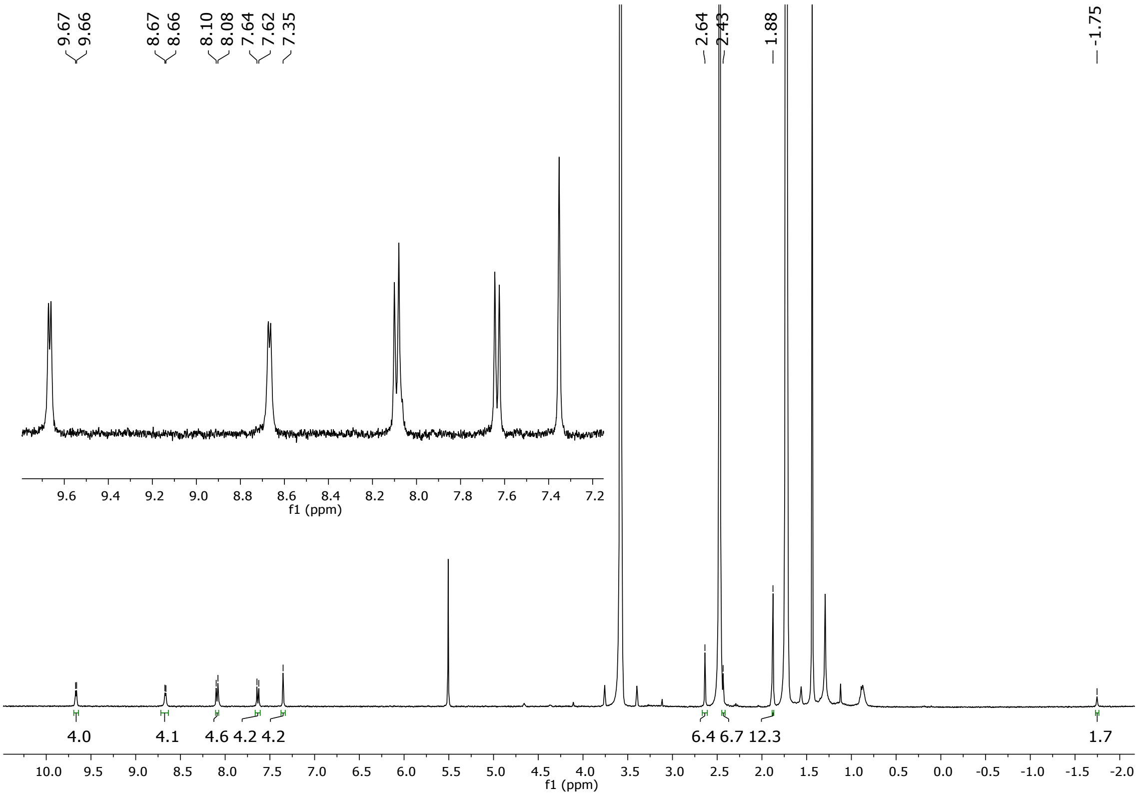
S,S'-(((10,20-dimesitylporphyrin-5,15-diyl)bis(ethyne-2,1-diyl))bis(4,1-phenylene))diethanethioate (P3):

A solution of **ZnP3** (11 mg, 11.5 µmol, 1.0 eq.) in CH_2Cl_2 (5 mL) was treated with 5 drops of TFA. The mixture was stirred for 2 h at rt. Water was added, the organic phase was extracted with CH_2Cl_2 and washed with water twice. The solution was dried over anhydrous Na_2SO_4, filtered off and dried under high vacuum to yield the title compound **P3** (10 mg, 11.0 µmol, 97%) as a purple solid.

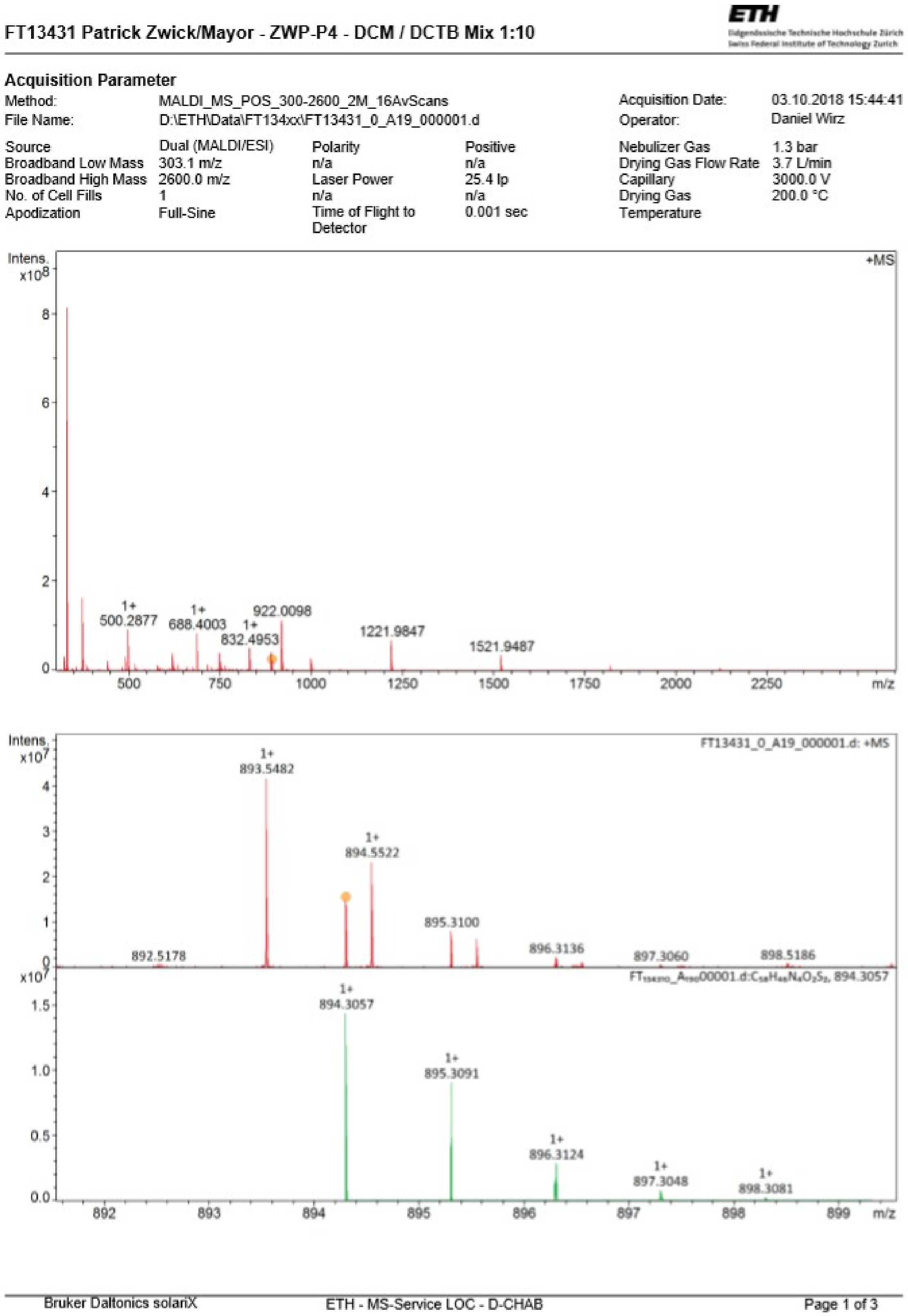
TLC (SiO_2, CH_2Cl_2/cyclohexane (4:1)): $R_f = 0.78$.

^{1}H-NMR (400 MHz, THF-d_8, 298 K, δ/ppm): 9.67 (d, $^3J_{HH} = 4.7$ Hz, 4H, $H_{\text{⍰}}$), 8.67 (d, $^3J_{HH} = 4.8$ Hz, 4H, $H_{\text{⍰}}$), 8.13 – 8.05 (m, 4H, H_{Ph}), 7.66 – 7.60 (m, 4H, H_{Ph}), 7.35 (s, 4H, H_{Ph}), 2.64 (s, 6H, $H_{p\mathrm{Me}}$), 2.43 (s, 6H, H_{Sac} [slightly overlaps with H_2O signal]), 1.88 (s, 12H, $H_{o\mathrm{Me}}$), -1.75 (s, 2H, H_{NH}).

HR-MALDI-TOF *m/z* = 894.3069 ($[M]^+$ requires 894.3057).



S 49: **^{1}H-NMR (400 MHz, THF-d_8, 298 K)** spectrum of **P3**.



FT13431 Patrick Zwick/Mayor - ZWP-P4 - DCM / DCTB Mix 1:10

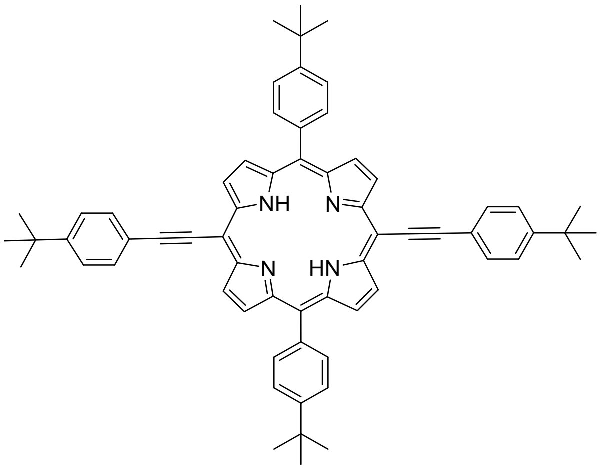
ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Acquisition Parameter

Method:	MALDI_MS_POS_300-2600_2M_16AvScans			Acquisition Date:	03.10.2018 15:44:41
File Name:	D:\ETH\Data\FT134xx\FT13431_0_A19_000001.d			Operator:	Daniel Wirz
Source	Dual (MALDI/ESI)	Polarity	Positive	Nebulizer Gas	1.3 bar
Broadband Low Mass	303.1 m/z	n/a	n/a	Drying Gas Flow Rate	3.7 L/min
Broadband High Mass	2600.0 m/z	Laser Power	25.4 lp	Capillary	3000.0 V
No. of Cell Fills	1	n/a	n/a	Drying Gas Temperature	200.0 °C
Apodization	Full-Sine	Time of Flight to Detector	0.001 sec		

Bruker Daltonics solariX ETH - MS-Service LOC - D-CHAB Page 1 of 3

S 50: **HR-MALDI-ToF MS** of **P3**.



R3

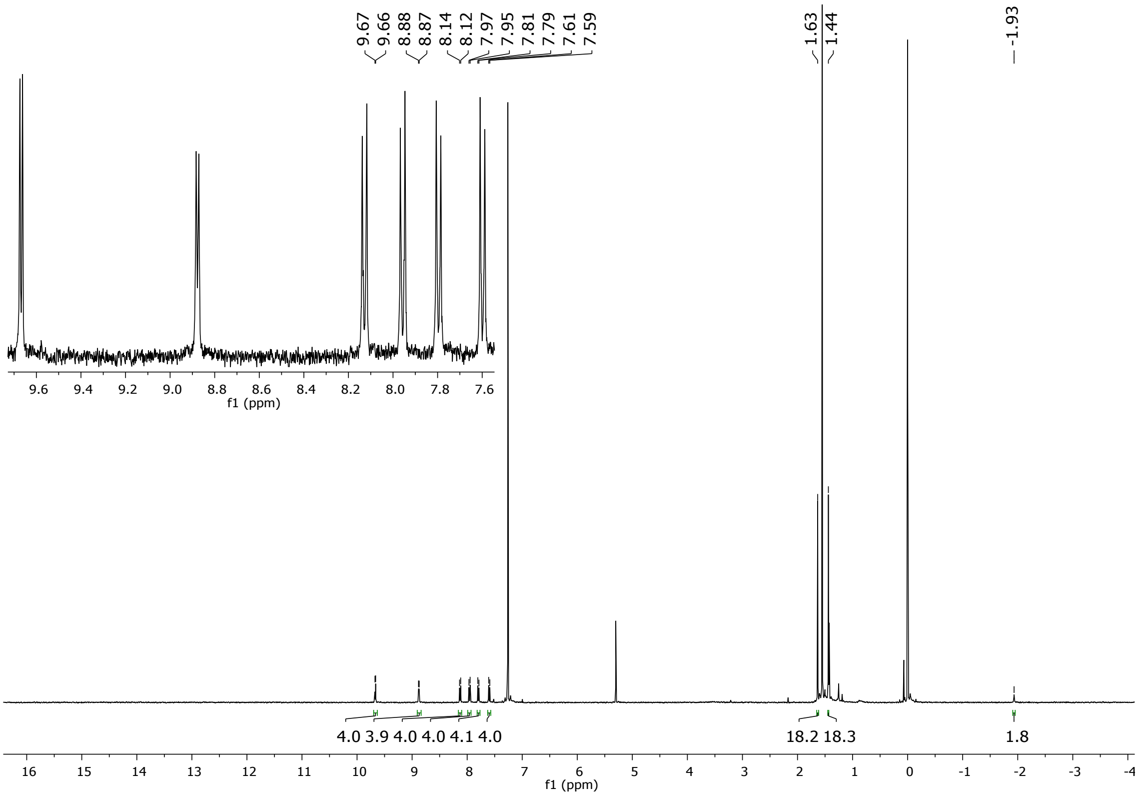
5,15-bis(4-(*tert*-butyl)phenyl)-10,20-bis((4-(*tert*-butyl)phenyl)ethynyl)porphyrin (R3):

A solution of **ZnR3** (10 mg, 10.5 µmol, 1.0 eq.) in CH_2Cl_2 (5 mL) was treated with 5 drops of TFA. The mixture was stirred for 2 h at rt. Water was added, the organic phase was extracted with CH_2Cl_2 and washed with water twice. The solution was dried over anhydrous Na_2SO_4, filtered off and dried under high vacuum to yield the title compound **R3** (9.2 mg, 10.4 µmol, 99%) as a purple solid.

TLC (SiO_2, CH_2Cl_2/cyclohexane (1:2)): R_f = 0.50.

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K, δ/ppm): 9.67 (d, $^3J_{HH}$ = 4.7 Hz, 4H, H_β), 8.88 (d, $^3J_{HH}$ = 4.8 Hz, 4H, H_β), 8.16 – 8.09 (m, 4H, H_{Ph}), 7.99 – 7.91 (m, 4H, H_{Ph}), 7.83 – 7.75 (m, 4H, H_{Ph}), 7.64 – 7.56 (m, 4H, H_{Ph}), 1.63 (s, 18H, H_{tBu}), 1.44 (s, 18H, H_{tBu}), -1.93 (s, 2H, H_{NH}).

HR-MALDI-TOF m/z = 887.5047 ($[M]^+$ requires 887.5047).



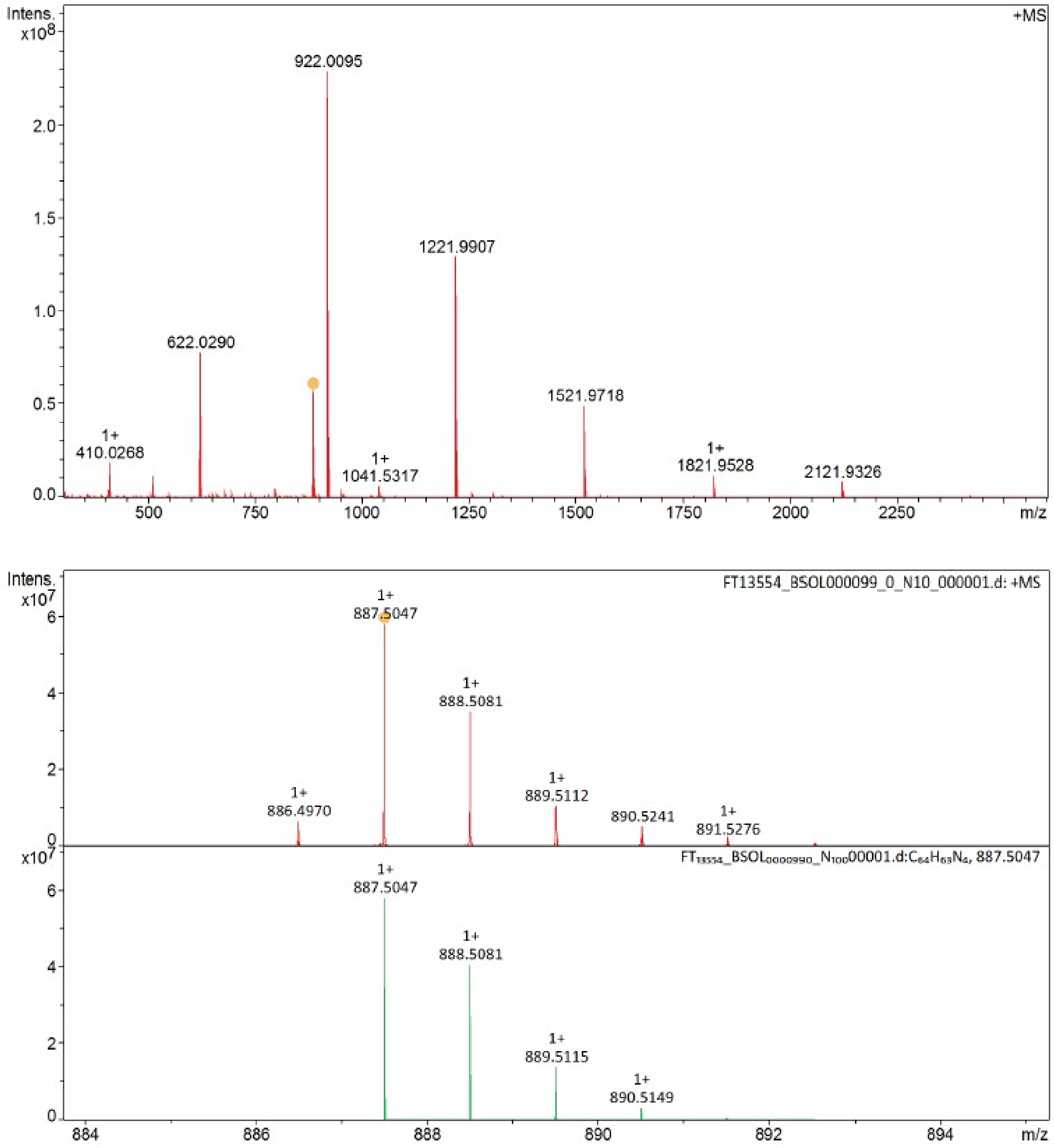
S 51: **^{1}H-NMR (400 MHz, $CDCl_3$, 298 K)** spectrum of **R3**.

FT13554_BSOL000099 Patrick Zwick/ - P3wo-thiols - DCM - DHB 1:10

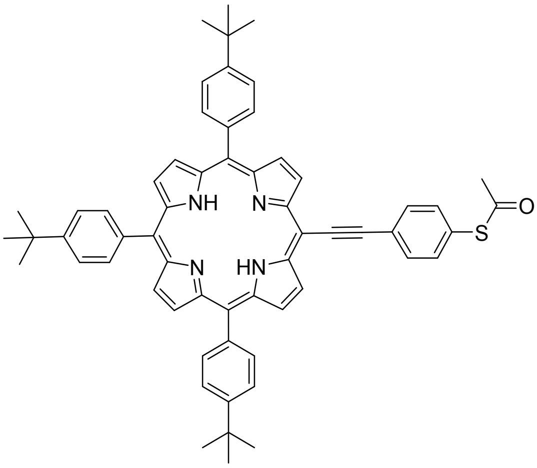
ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Acquisition Parameter

Method:	MALDI_MS_POS_300-2600_2M_16AvScans			Acquisition Date:	27.11.2018 15:04:55
File Name:	D:\ETH\Data\FT135xx\FT13554_BSOL000099_0_N10_000001.d			Operator:	Daniel Wirz
Source	Dual (MALDI/ESI)	Polarity	Positive	Nebulizer Gas	1.3 bar
Broadband Low Mass	303.1 m/z	n/a	n/a	Drying Gas Flow Rate	3.7 L/min
Broadband High Mass	2600.0 m/z	Laser Power	53.2 lp	Capillary	3000.0 V
No. of Cell Fills	1	n/a	n/a	Drying Gas Temperature	200.0 °C
Apodization	Full-Sine	Time of Flight to Detector	0.001 sec		



S 52: **HR-MALDI-ToF MS** of **R3**.



R1

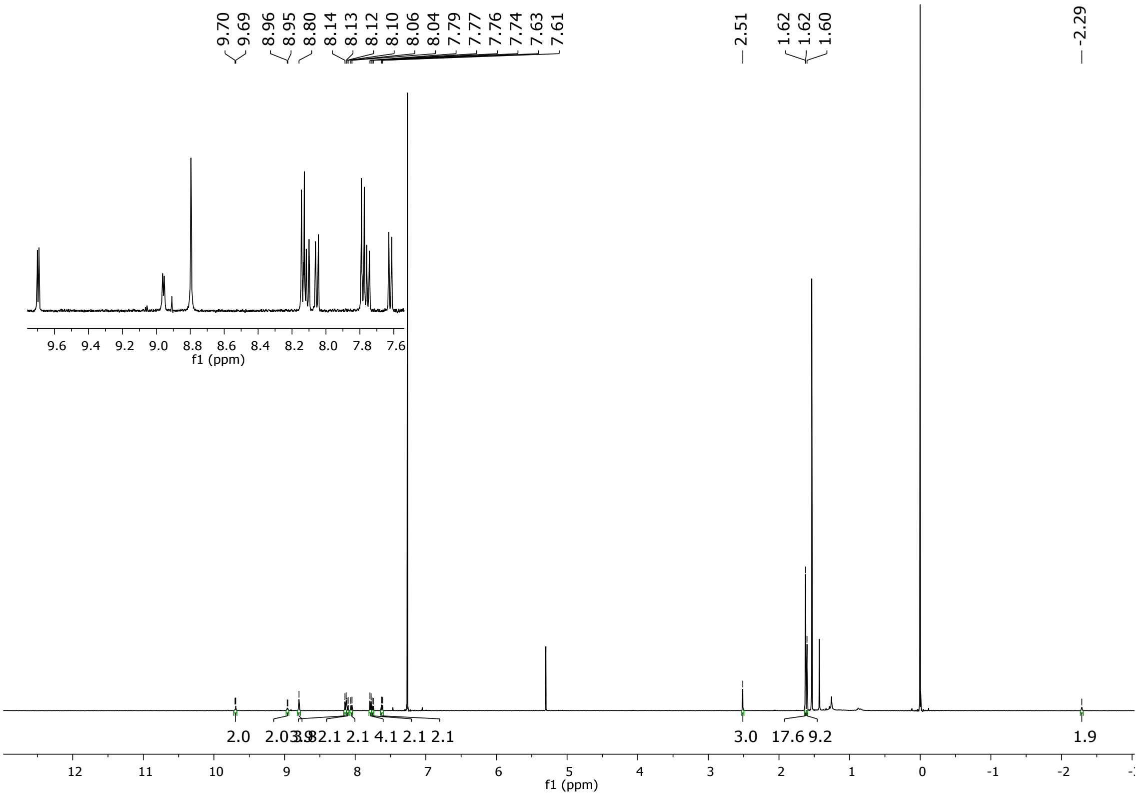
S-(4-((10,15,20-tris(4-(*tert*-butyl)phenyl)porphyrin-5-yl)ethynyl)phenyl)ethanethioate (R1):

A solution of **ZnR1** (7 mg, 7.41 µmol, 1.0 eq.) in CH_2Cl_2 (5 mL) was treated with 5 drops of TFA. The mixture was stirred for 2 h at rt. Water was added, the organic phase was extracted with CH_2Cl_2 and washed with water twice. The solution was dried over anhydrous Na_2SO_4, filtered off and dried under high vacuum to yield the title compound **R1** (6.3 mg, 7.11 µmol, 96%) as a purple solid.

TLC (SiO_2, CH_2Cl_2/cyclohexane (1:1)): $R_f = 0.20$.

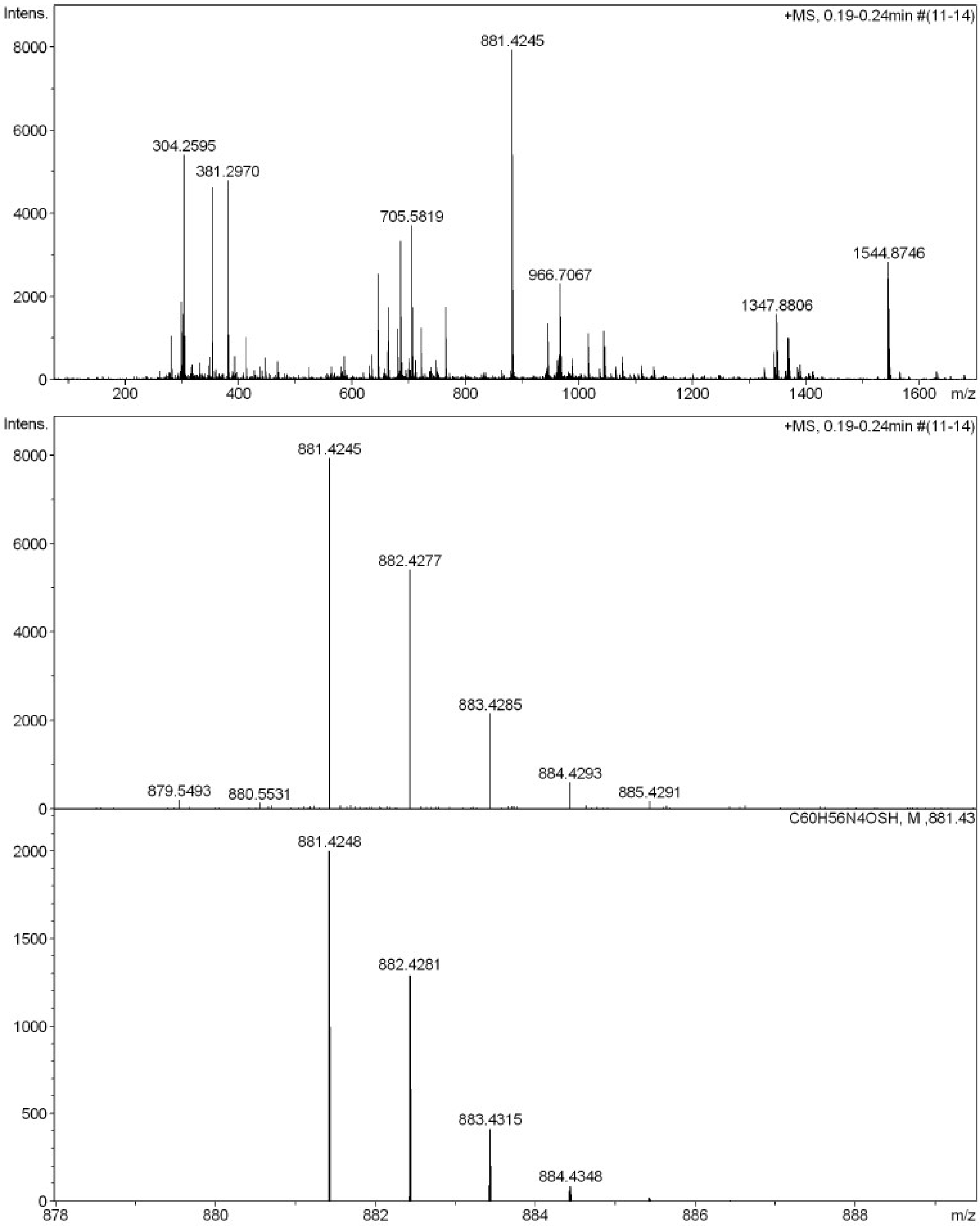
^{1}H-NMR (500 MHz, $CDCl_3$, 298 K, δ/ppm): 9.70 (d, $^3J_{HH} = 4.8$ Hz, 2H, H_β), 8.96 (d, $^3J_{HH} = 4.8$ Hz, 2H, H_β), 8.80 (s, 4H, H_β), 8.16 – 8.12 (m, 4H, H_{Ph}), 8.12 – 8.09 (m, 2H, H_{Ph}), 8.07 – 8.04 (m, 2H, H_{Ph}), 7.80 – 7.76 (m, 4H, H_{Ph}), 7.76 – 7.73 (m, 2H, H_{Ph}), 7.65 – 7.60 (m, 2H, H_{Ph}), 2.51 (s, 3H, H_{SAc}), 1.62 (s, 18H, H_{tBu}), 1.60 (s, 9H, H_{tBu}), -2.29 (s, 2H, H_{NH}).

HRMS (ESI, +): *m/z* calcd. for $C_{60}H_{56}N_4OSH$ $[M+H]^+$: 881.4248, found: 881.4245.



S 53: **^{1}H-NMR (500 MHz, $CDCl_3$, 298 K)** spectrum of **R1**.

Sample Name	**Patrick Zwick / zwpP3B3**	Instrument	maXis 4G
Comment	10 ug/mL in DCM, analyzed in MeOH	Method	23 Direct_pos_higher.m



S 54: **HR-ESI MS** of **R1**.

RAW DATA AND CLUSTER ANALYSIS

In figure S1 the 2D histogram of all the molecules measured in this study are presented. All the measurements consist in a 10 000 consecutive traces without any data selection. A flat plateau above 10^{-4} G_0 is present in the measurements of molecules P1, ZnP1, P2 and P3 whereas for molecules R1, R2 and R3 no clear plateau is observed.

In figures S2, S3 and S4 the complete classes sets are presented for molecules P1, R1 and R3 in order to compare the different classes obtained after the clustering analysis. Figure S2 presents the classes obtained after applying the cluster analysis to the measurements of molecule P1. Four classes corresponding to Class A, Class B, Class C and the tunnelling class are present. In figure S3, three classes are displayed for the case of molecule R1, attributed to Class B, Class C and the tunnelling class. Notice that Class B, although have a similar conductance peak as P1, is more slanted. Finally, in figure S4 the two classes corresponding to molecule R3 are shown. These classes are attributed to Class C and the tunnelling class. Molecule R2 presents only tunnelling traces.

In figure S5 and S6, we subdivide the clusters of P3 and R3 into two clusters. For both molecules and all the classes, the obtained classes are very similar to the initial cluster.

In figure S7, S8 and S9, we subdivide data set measured in the case of molecule R3 into 3, 4 and 5 classes. Only 3 classes (including the tunnelling class) are identified even after subdivision in a larger number of clusters.

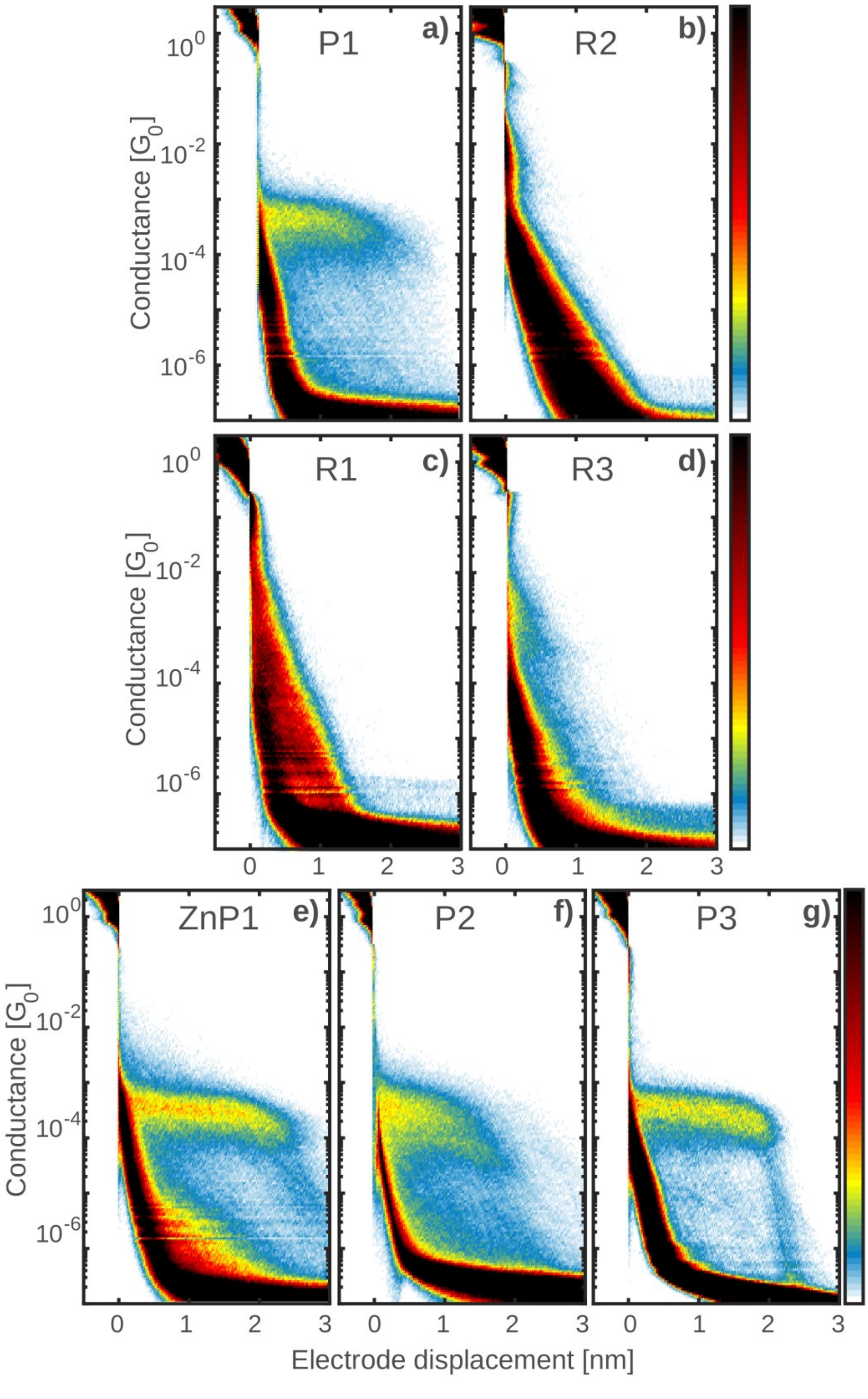


Fig S1. **a)-g)** Two-dimensional (2D) conductance versus displacement histograms built from 10 000 consecutive breaking traces of P1, R1, R2, R3, ZnP1, P2 and P3. No data selection was made. All measurements were performed with a bias of 100 mV and a bending speed of 6×10^4 nm/s at room temperature. The insets represent the chemical structure of each measurement.

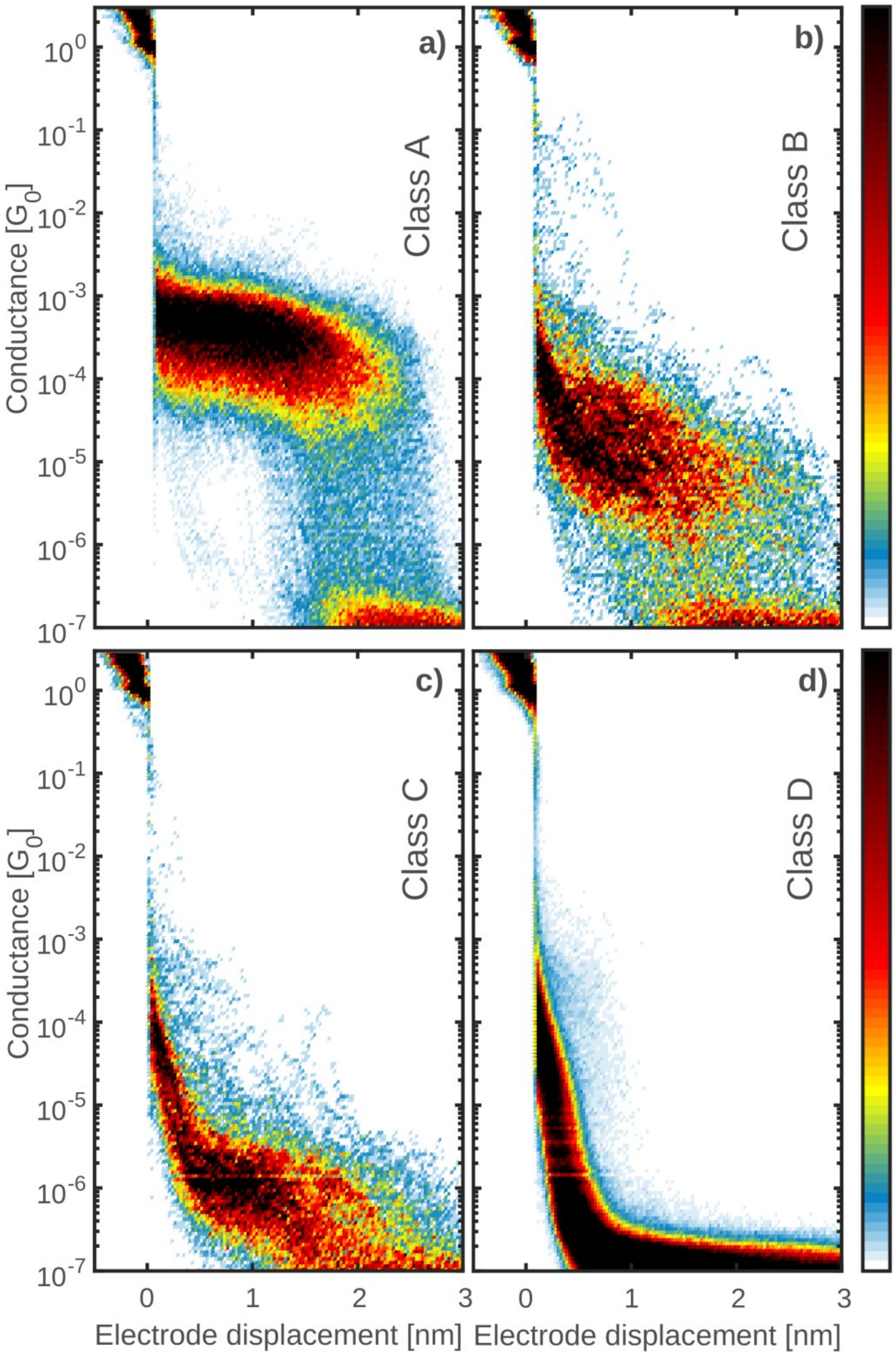


Fig S2. Two-dimensional histograms of the complete data from P1. Four different categories of breaking traces are shown corresponding to **a)** Class A (7.9%), **b)** class B (2.0%), **c)** class C (2.7%) and **d)** class D with no clear molecular signature (84.7%).

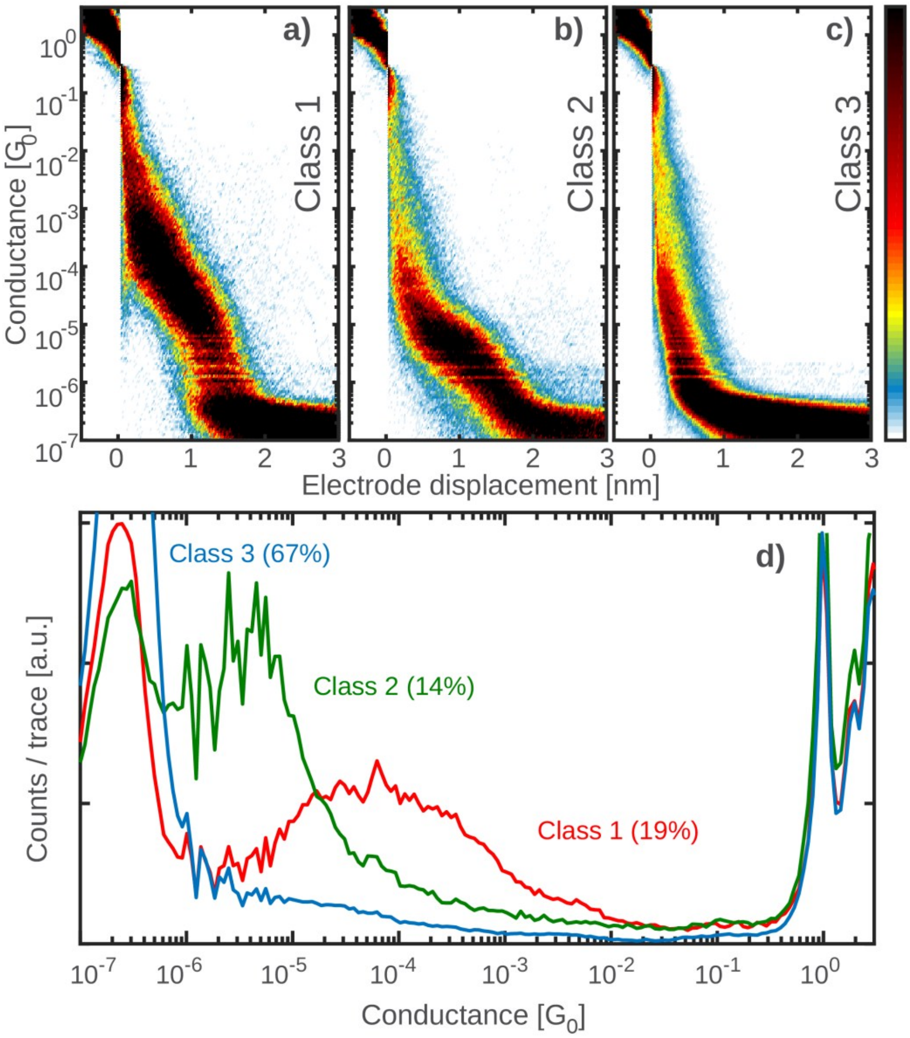


Fig S3. Two-dimensional histograms of the complete data from R1. Three different categories of breaking traces are shown corresponding to **a)** Class 1 (19%), **b)** class 2 (14%) and **c)** class 3 (67%) with no clear molecular signature. **d)** 1D conductance histogram for class 1, class 2 and class 3 .

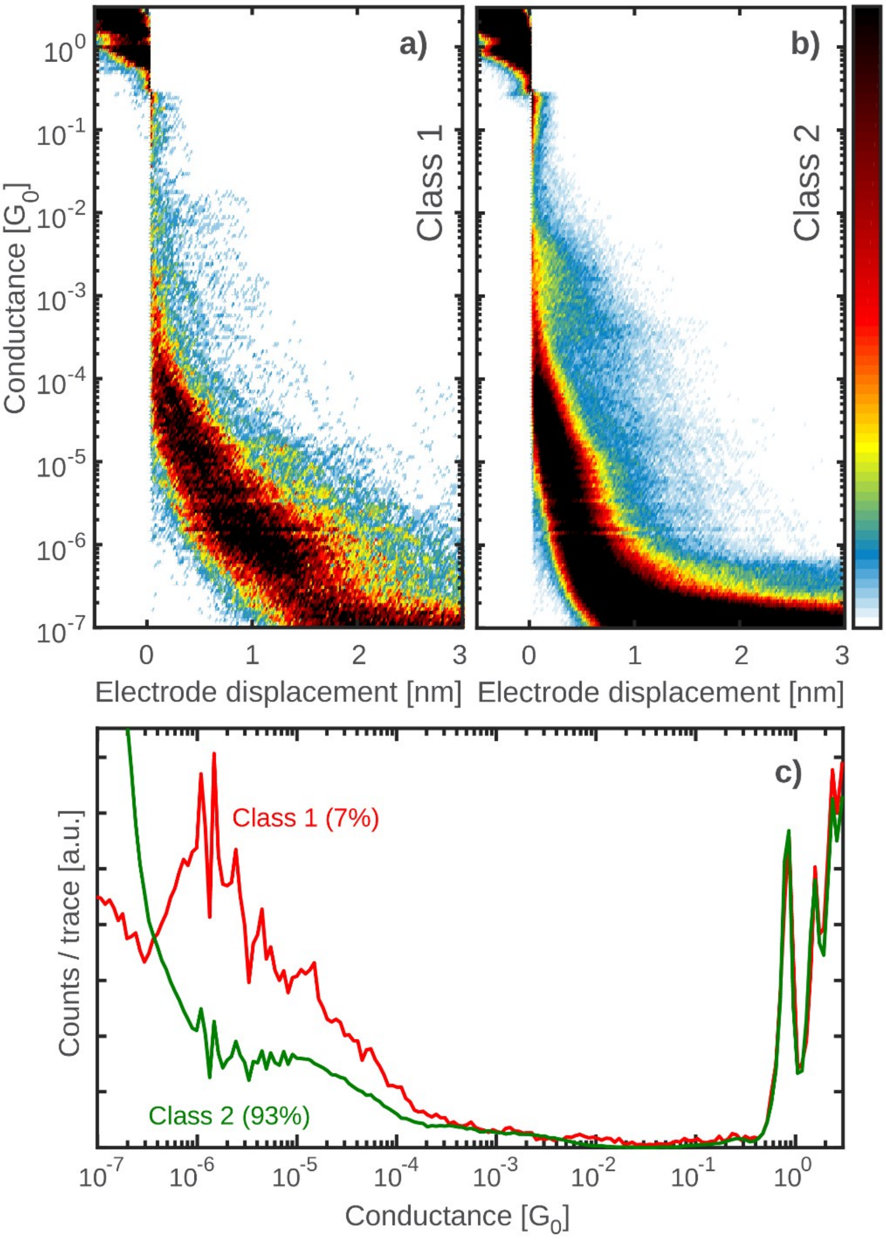


Fig S4. Two-dimensional histograms of the complete data from R3. Two different categories of breaking traces are shown corresponding to **a)** Class 1 (7%) and **b)** class 2 (93%) with no clear molecular signature. **d)** 1D conductance histogram for class 1 and 2.

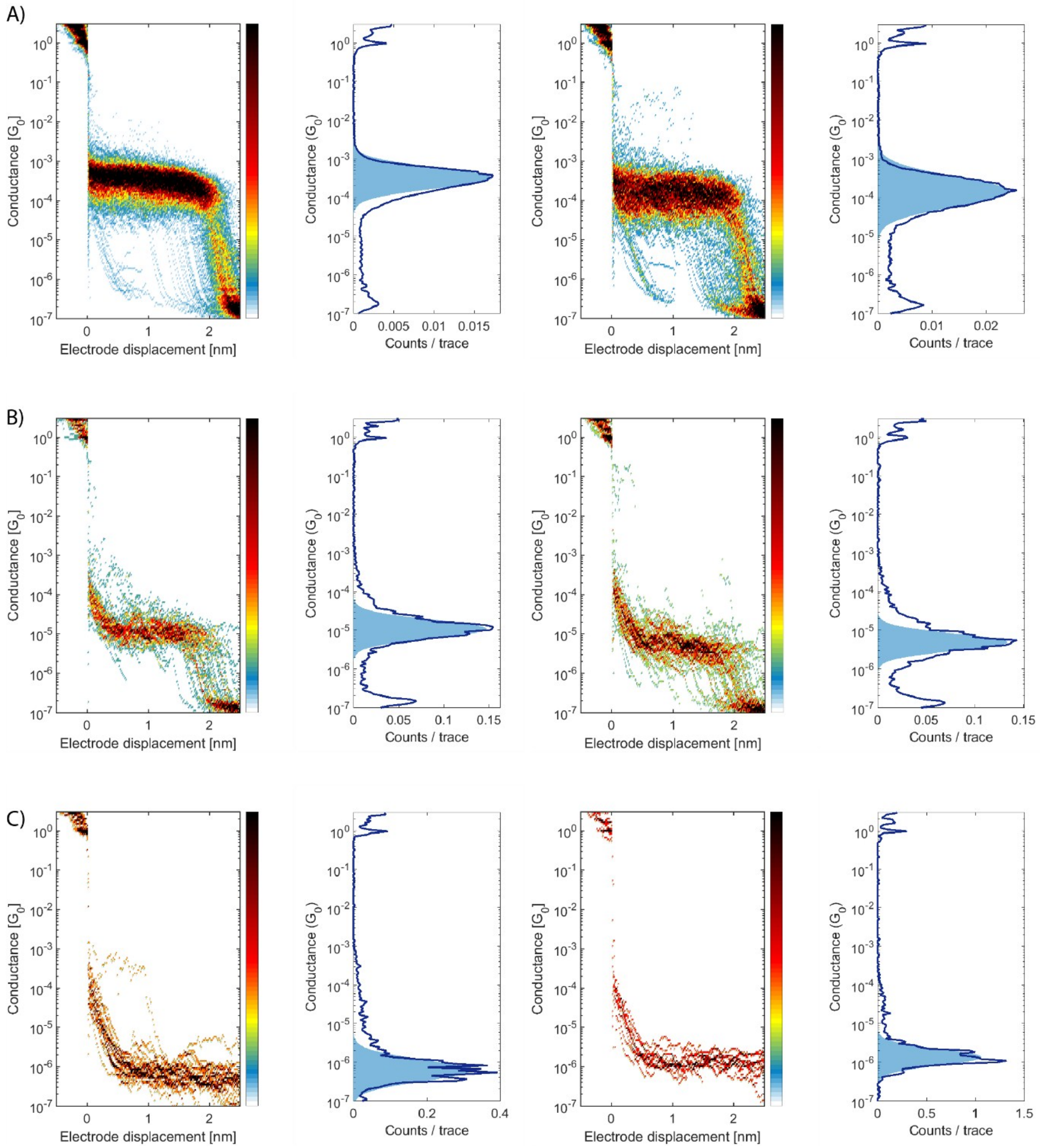


Fig S5. Two and one-dimensional histograms of the clusters obtained for P3 and clustered into two subclasses. A, B and C correspond respectively to Class A, B and C. The two sub-classes obtained for the three clusters are very similar.

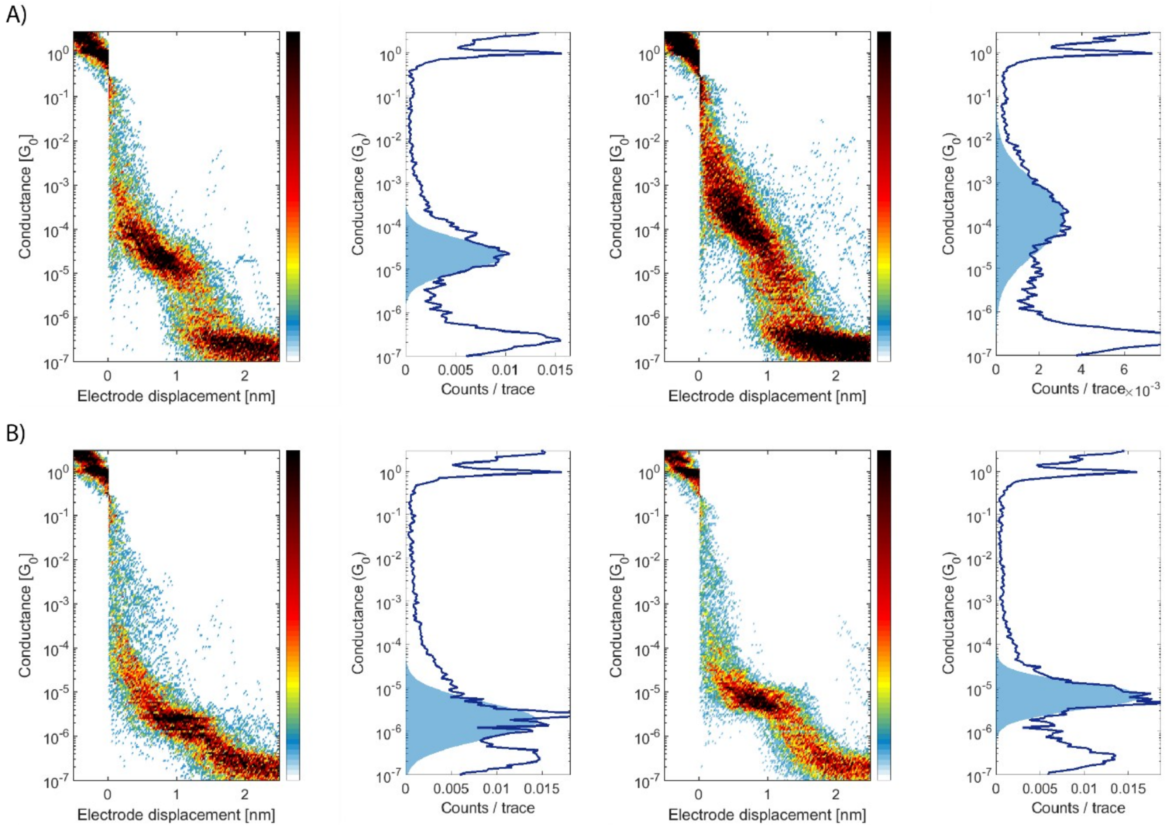


Fig S6. Two and one-dimensional histograms of the clusters obtained for R3 and clustered into two subclasses. A, and B correspond respectively to Class B and C. The two sub-classes obtained for the two clusters are very similar.

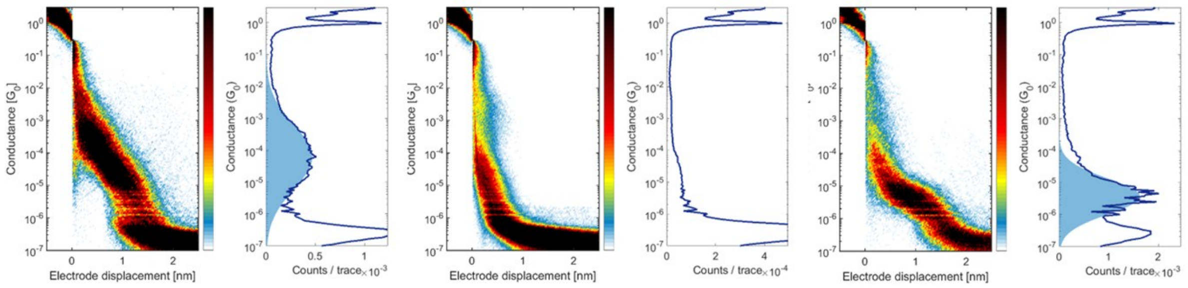


Fig S7. Two and one-dimensional histograms of the clusters obtained for R3 if the cluster number is fixed to 3.

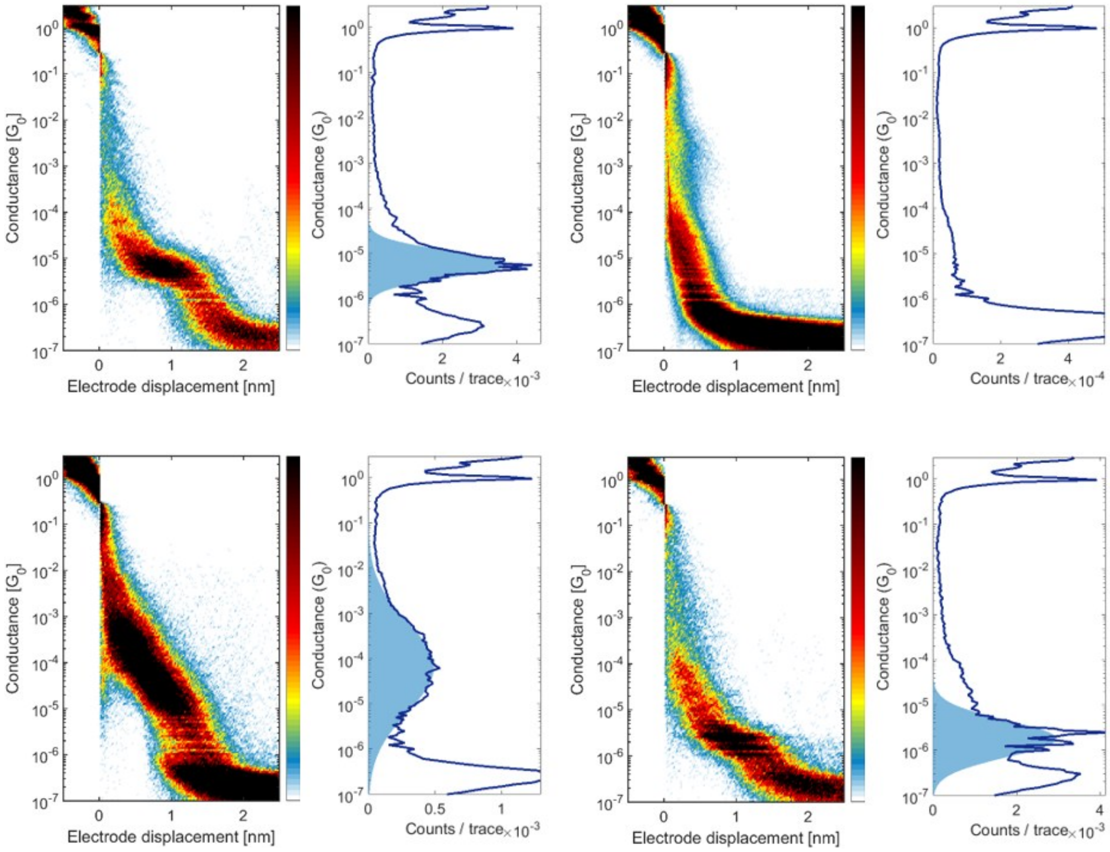


Fig S8. Two and one-dimensional histograms of the clusters obtained for R3 if the cluster number is fixed to 4.

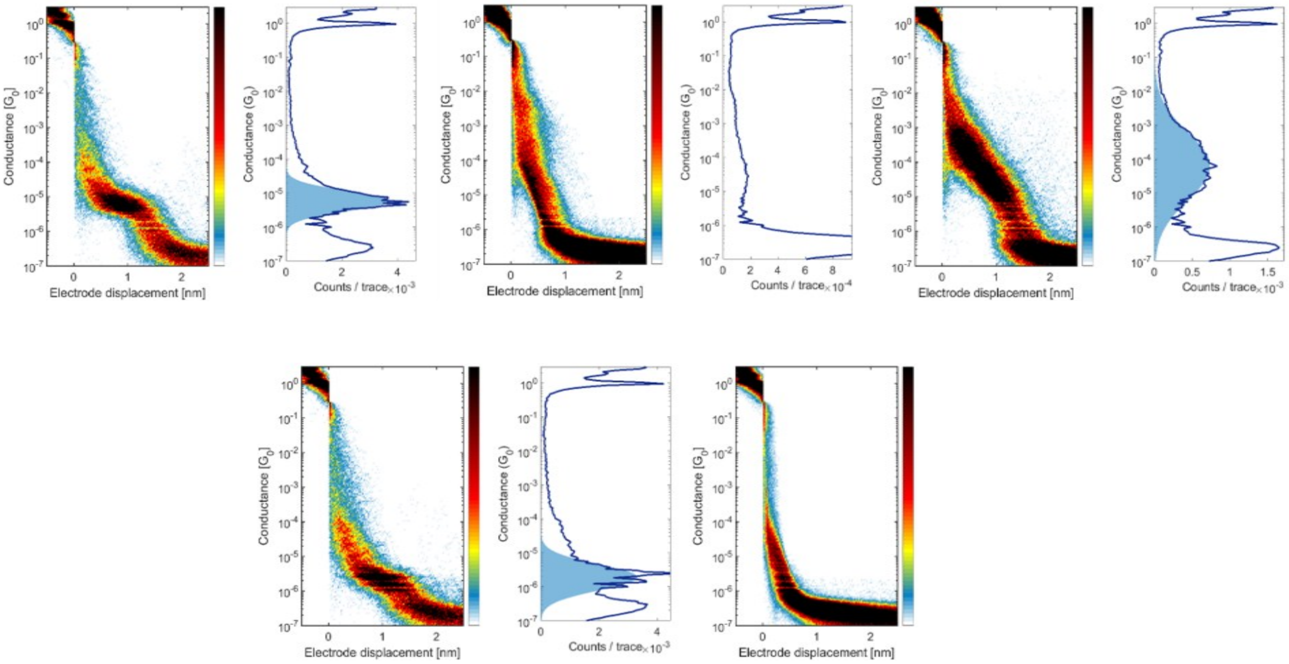


Fig S9. Two and one-dimensional histograms of the clusters obtained for R3 if the cluster number is fixed to 5. The first and fourth class contain traces that display similar behaviours.

TIME EVOLUTION

Figure S10, S11 and S12 show the evolution in time of the cluster probability (population). We can notice a slight increase of the molecular traces population until 4 000 traces in the case of protected P1 that can be attributed to a slow in-situ deprotection of the molecule at the gold surface. After the 4 000th event, the probabilities stabilize. We can also notice that the clusters events are fairly independent.

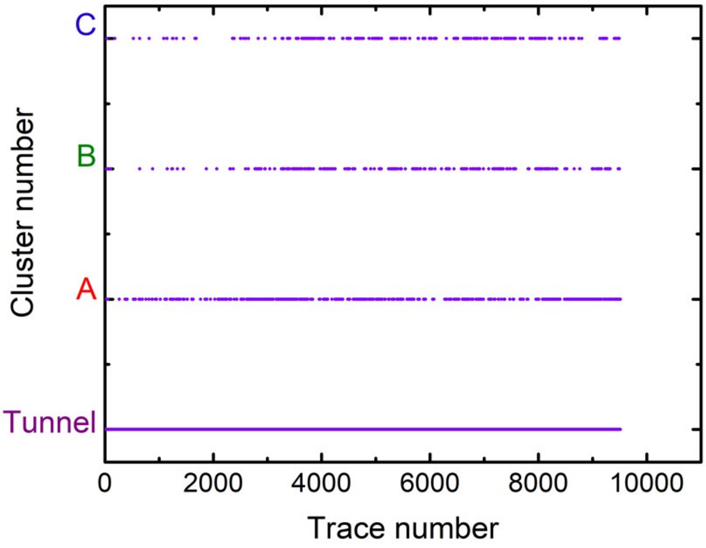


Fig S10. Cluster evolution of P1: evolution of the class attribution as a function of the trace number.

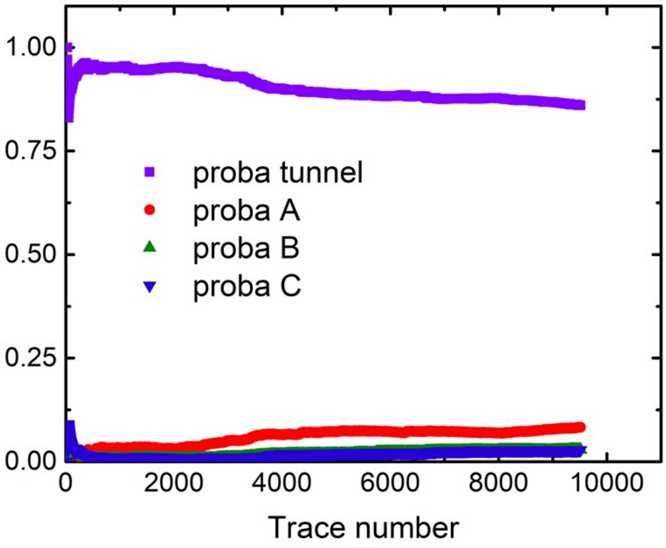


Fig S11. Evolution of the probability of the 4 identified classes of P1 as a function of time.

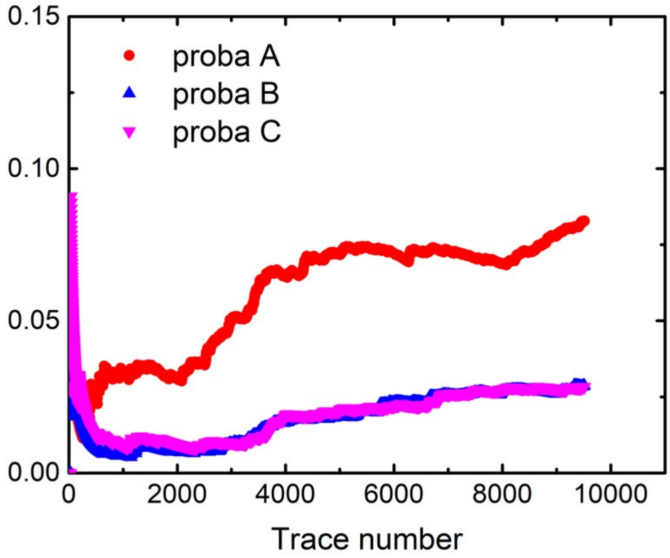


Fig S12. Evolution of the probability of the 3 identified molecular classes of P1 as a function of time.

MASTER TRACES AND PLATEAU LENGTH

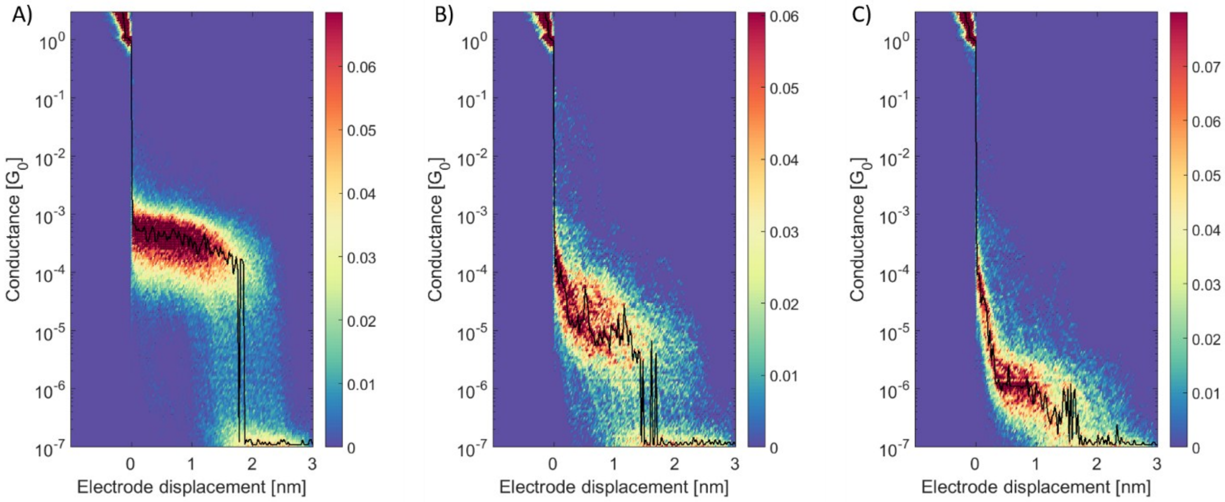


Fig S13. Two-dimensional histograms of the clusters obtained for P1 and the master trace calculated for each cluster. The length of the master traces are respectively : 1.7, 1.5 and 1.2 nm for class A, B and C.

EXPERIMENTAL: SELF-BREAKING AND CLASS COMPARISON

In Fig. S14, the self-breaking measurements of P1 are presented. The plateaus between 3×10^{-5} and 1×10^{-3} G_0 are the most stable, with a junction lifetime up to 5 minutes. The longest self-breaking traces can be mostly associated to Class A from the fast breaking. Note that the peak around 3×10^{-5} G_0 present in the 1D histograms is attributed to long traces (up to 300 seconds) corresponding to Class A.

In Fig. S15 and S16, Classe A and C are compared. In Fig. S15, the 1D histogram of Class A is presented for molecules P1, ZnP1, P2 and P3 in order to study the effect of the bulky groups and the metal ion in the core. As is explained in the main text, the differences in plateau conductance or length that are observed are within the variations typically found in MCBJ experiments when performed on the same molecule. In the case of Fig. S16 the 2D and 1D histograms of Class C are presented for molecules P1, R1 and R3. Here, the differences between the measurements are attributed to the role played by the Sulphur in mechanically stabilizing the molecular junction.

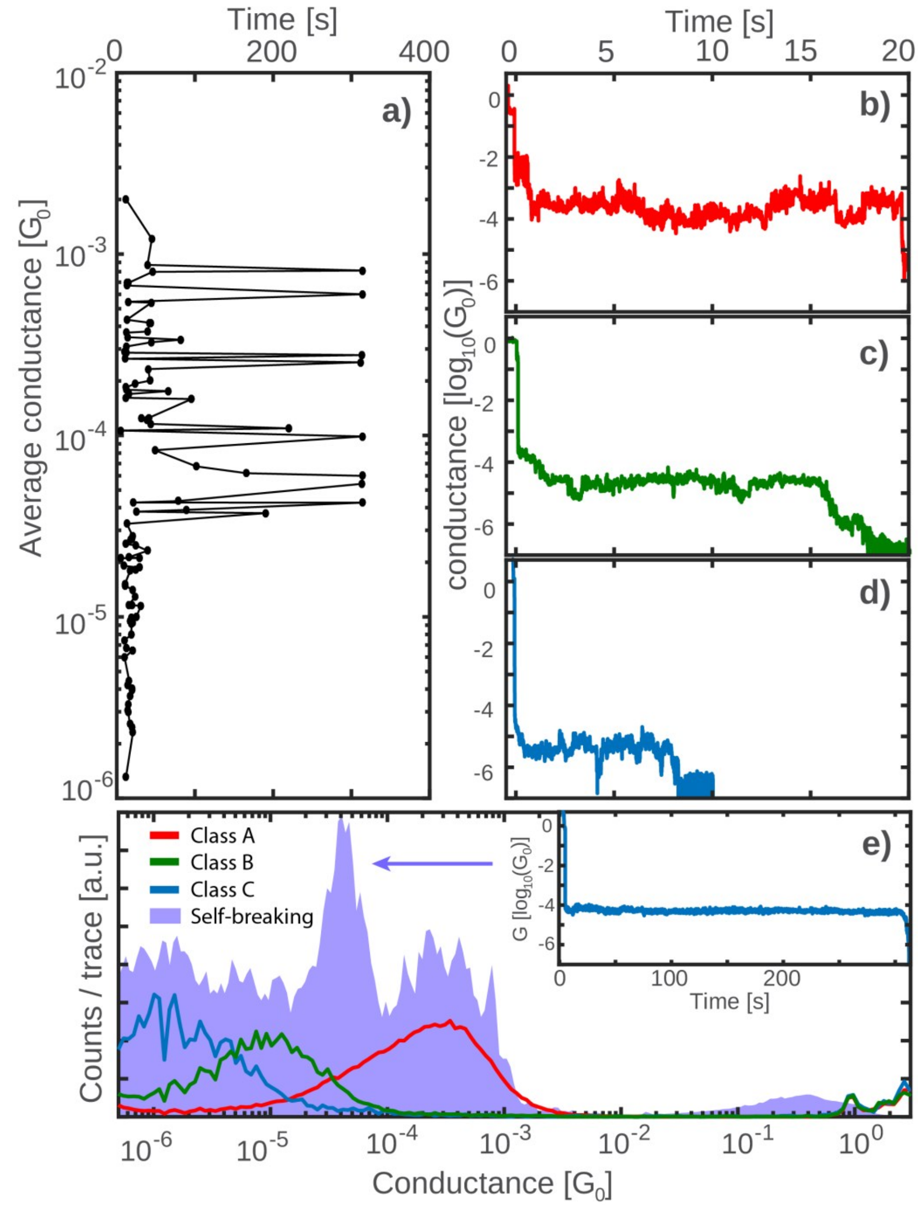


Fig S14. Self-breaking measurements for P1. **a)** Average conductance vs time of 384 self-breaking traces. The maximum recorded time was 300 seconds. **b)-c)** Examples of single traces corresponding to Class A (red), Class B (green) and Class C (blue). **e)** 1D histogram of self-breaking traces (purple area) and fast-breaking traces for each class (solid lines). The high peak at 3×10^{-5} G_0 is due to very long traces (300 seconds) corresponding to Class A (inset).

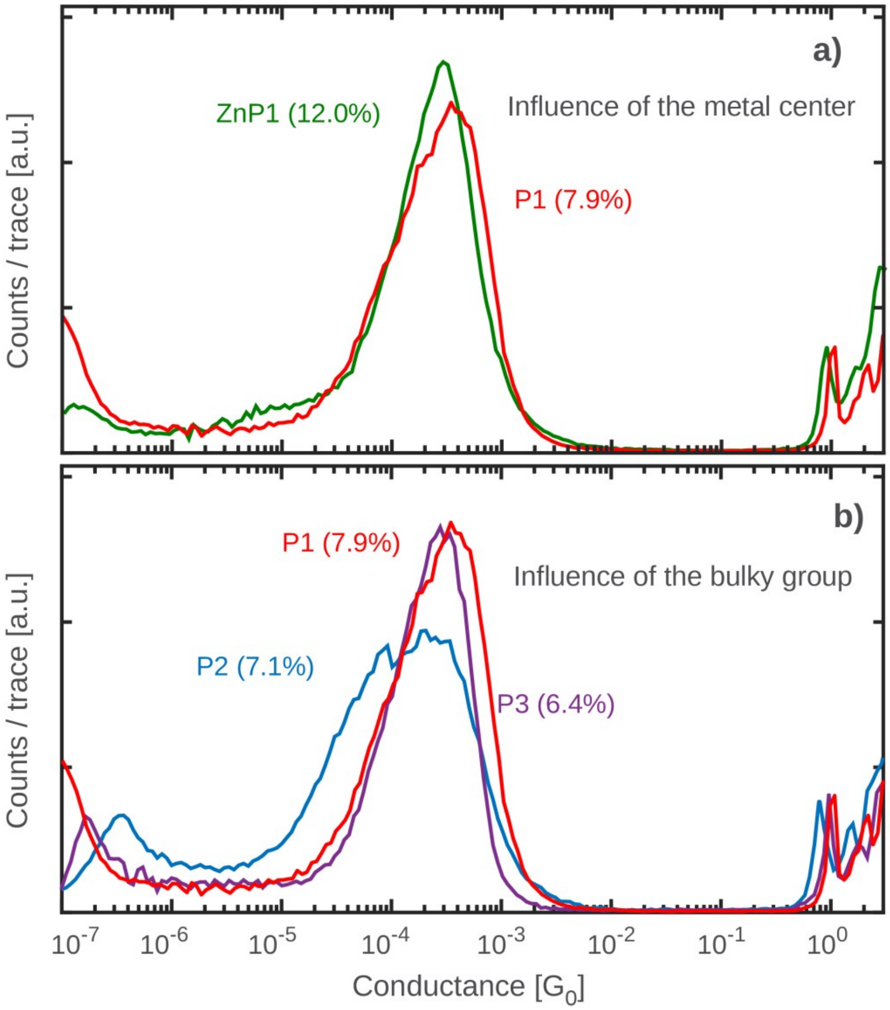


Fig S15. 1D conductance histograms of Class A from **a)** P1 (7.9%) and ZnP1 (12.0%) showing the influence of the metal center and **b)** P1, P2 (7.1%) and P3 (6.4%) comparing the different bulky groups.

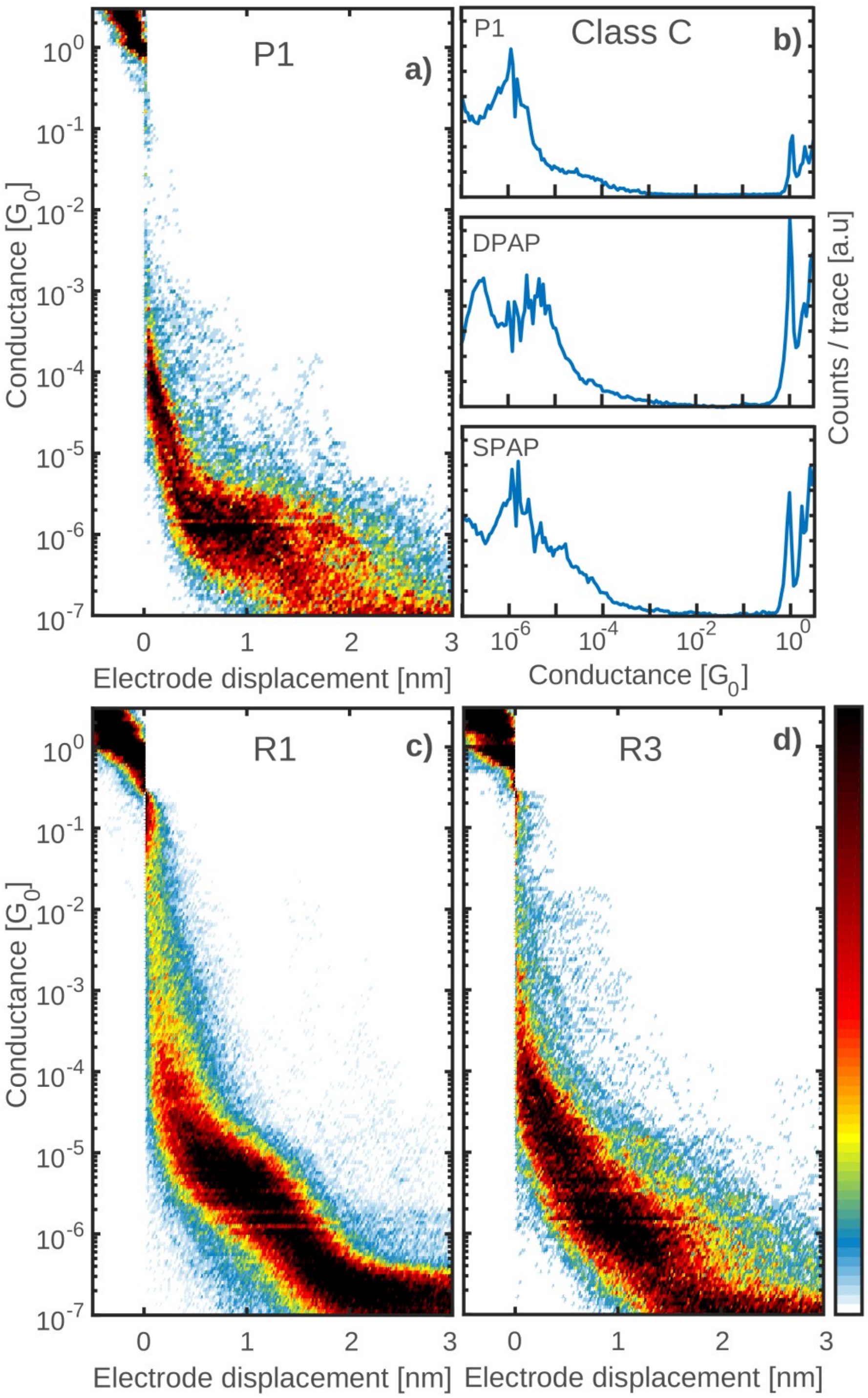


Fig S16. **a)** 2D conductance versus displacement histograms of class C (see Fig. 2). **b)** One-dimensional (1D) conductance histograms of class C and classes obtained from two control measurements (R1 and R3). **c)**, **d)** 2D histograms of classes from R1 and R3, respectively.

ELECTRONIC PATHS IDENTIFICATION

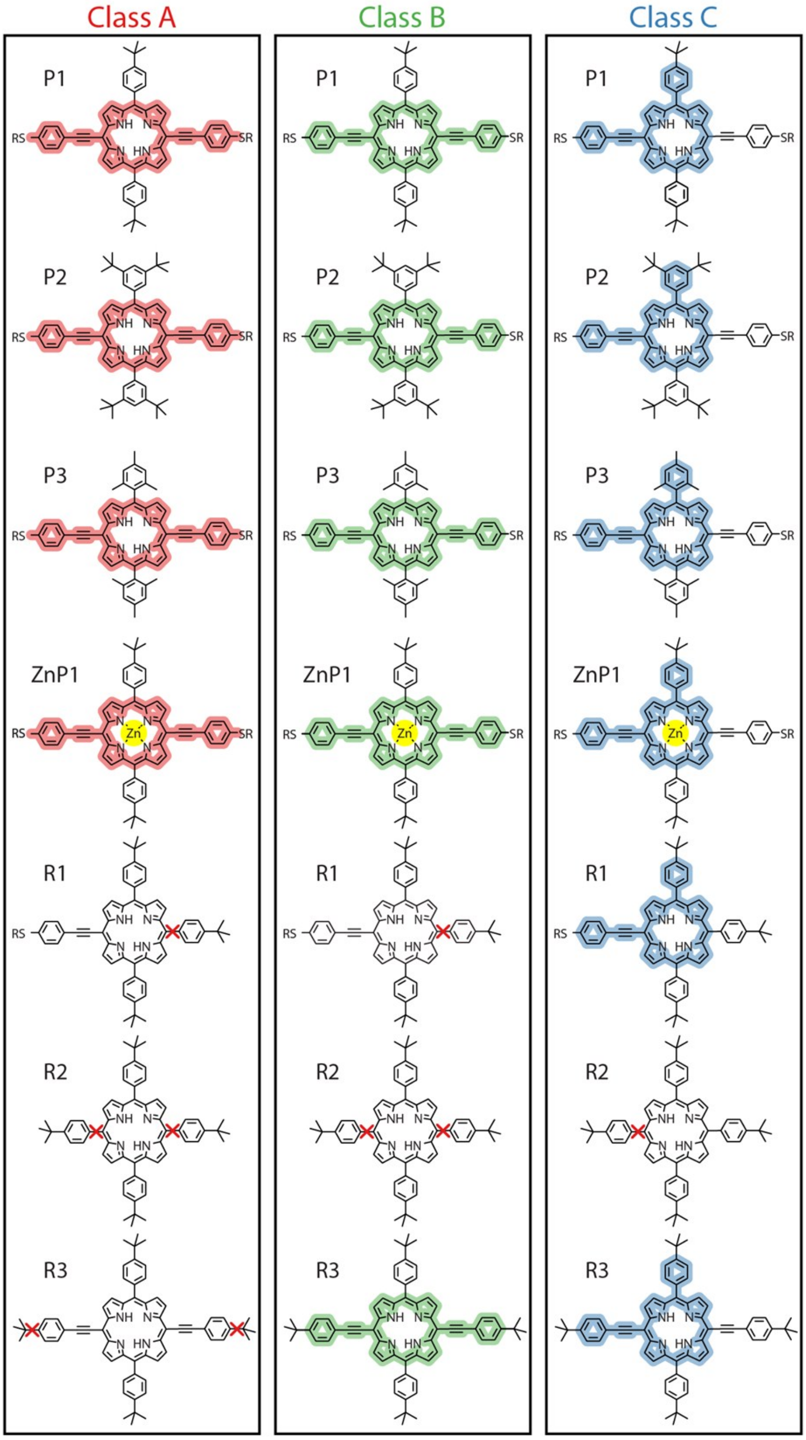


Fig S17. Identification of the electronic paths for Class A, B and C according to the common chemical structure of the molecules presenting the corresponding Class.

CONDUCTANCE VALUES AND MEASUREMENTS SUMMARY

Table S1 shows a summary of fitting of the conductance peak of the three different classes. The Full Width Half Maximum (FWHM), yield and length of every measured molecule attributed to each class is presented. Table S2 presents a summary of all the measurements performed in this study. In the table, the number of samples, junctions and traces is shown for different bias voltage and bending speed. Each sample has a maximum of 4 junctions.

	Class B								
	$G_M(G_0)$	FWHM	Yield	$G_M(G_0)$	FWHM	Yield	$G_M(G_0)$	FWHM	Yield
P1	2.8E-4	1.1	7.9%	1.1E-5	1.5	2.0%	1.0E-6	1.0	2.7%
R1	-	-	-	-	-	-	1.2E-6	2.0	7.0%
R2	-	-	-	-	-	-	-	-	-
R3	-	-	-	5.1E-5	2.4	19.0%	2.8E-6	1.6	14.0%
ZnP1	2.4E-4	1.8	12.0%	2.1E-5	1.7	4.1%	4.1E-6	1.9	16.2%
P2	1.9E-4	1.2	7.1%	4.0E-5	1.2	7.1%	1.7E-6	1.7	4.7%
P3	2.3E-4	0.8	6.4%	8.3E-6	0.9	1.0%	1.0E-6	0.6	0.3%

Table S1. Conductance peak, standard deviation, yield and length extracted from the clustering analysis and the 1D histogram fitting for each class on every molecule measured, related to each class (see Fig. 3).

Molecule	Sample	Junction	Bias (V)	Bending speed (nm/s)	Traces
P1	1	1	0.1	6×10^4	20 000
			0.1	6×10^4	5 000
		2	0.1	6×10^4	9 589
	2	1	0.1	6×10^4	10 000
		2	0.1	6×10^4	10 000
Total	**2**	**4**			**54 589**
R2	1	1	0.1	6×10^4	20 000
			0.2	6×10^4	10 000
Total	**1**	**1**			**30 000**
R1	1	1	0.1	6×10^4	10 000
			0.2	6×10^4	10 000
			0.3	6×10^4	10 000
Total	**1**	**1**			**30 000**
R3	1	1	0.1	6×10^4	4 994
		2	0.1	6×10^4	17 271
Total	**1**	**2**			**22 265**
ZnP1	1	1	0.1	6×10^4	5 000
			0.1	3×10^4	5 000
		2	0.1	6×10^4	20 000
			0.2	6×10^4	5 000
	2	1	0.1	6×10^4	20 000
			0.2	6×10^4	10 000
			0.3	6×10^4	8 280
Total	**1**	**2**			**73 280**
P2	1	1	0.1	6×10^4	8 376
		2	0.1	6×10^4	10 000
	2	1	0.1	3×10^4	3 083
	3	1	0.1	3×10^4	9 236
	4	1	0.1	3×10^4	14 835
	5	1	0.1	3×10^4	5 000
Total	**5**	**6**			**50 530**
P3	1	1	0.2	6×10^4	10 000
			0.1	6×10^4	20 000
	2	1	0.1	6×10^4	5 000
Total	**2**	**2**			**25 000**
Total of traces	**285 664**				

Table S2. Number of samples, junctions and traces measured with the different parameters (bias and bending speed) for the different molecules. All the comparisons presented in this paper are using 10 000 traces with a bias of 100 mV and a speed of 200 V/s.

REFERENCES

[1] Dogutan, D. K.; Zaidi, S. H. H.; Thamyongkit, P.; Lindsey, J. S., The Journal of organic chemistry 2007, 72, 7701-7714.

[2] Plater, M. J.; Aiken, S.; Bourhill, G., Tetrahedron 2002, 58, 2415_2422.

[3] Taylor, P. N.; Anderson, H. L., Journal of the American Chemical Society 1999, 121, 11538_11545.

[4] Cheng, K. F.; Drain, C. M.; Grohmann, K., Inorganic chemistry 2003, 42, 2075_2083.

[5] Robles, O.; McDonald, F. E., Organic letters 2008, 10, 1811_1814.