Fullerene Templated Synthesis of a Cyclic Porphyrin Trimer Using Olefin Metathesis

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Supporting Information

Contents

Supplementary Material (ESI) for Chemical Communications

1. General procedures

Analytical thin layer chromatography (TLC) was carried out on aluminium plates precoated with Merck Silica Gel 60 F_{254}. Detection of compounds was achieved visually in ordinary visible light or by exposure to a short wavelength (254 nm) UV light source. Column chromatography was performed using Davisil LC60A 40-63 µm mesh silica and the specified eluent mixture, expressed as volume to volume (*v/v*) ratios.

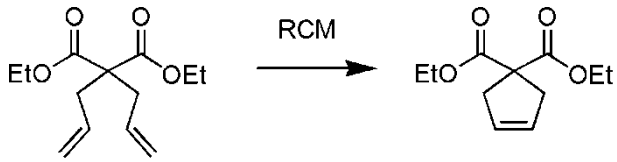
Low resolution electrospray ionisation (ESI) spectra were recorded on a Micromass Platform (QMS-quadrupole mass electrospray) or a Micromass ZMD mass spectrometer. High resolution ESI spectra were recorded on an Agilent Technologies 6220 Accurate-Mass TOF LC/MS spectrometer. Samples for MALDI-TOF mass spectral analysis were dissolved in dichloromethane and co-spotted onto the MALDI target plate with a matrix solution comprised of 10mg/ml α-cyano-4-hydroxycinnamic acid or sinapinic acid (Laser BioLabs, Sophia-Antipolis, France) in 50% Acetonitrile/0.1% TFA. The samples were analysed on an Applied Biosystems (Foster City, CA, USA) 4700 Proteomics Analyser MALDI-TOF/TOF in reflectron mode with a mass range of 800 to 3500Da, focus mass of 1400Da at 1500 shots per spectra.

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded using a Brüker DRX 400 MHz spectrometer (400 MHz ^{1}H, 100 MHz ^{13}C) or Brüker DPX 300 MHz spectrometer (300 MHz ^{1}H, 75 MHz ^{13}C), as solutions in the deuterated solvents specified. Chemical shifts (δ) were calibrated against the residual solvent peak. Each proton resonance is assigned according to the following convention: (operating frequency of spectrometer, solvent): chemical shift, multiplicity, number of protons, coupling constants (*J*, Hz), and peak assignment. Multiplicities are denoted as singlet (s), broad singlet (bs), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), or multiplet (m). ^{13}C NMR spectra were recorded using the JMOD pulse sequence or proton decoupled pulse sequence.

All reagents used were commercial grade, except in cases of multi-step syntheses or where otherwise stated. All solvents used were reagant or HPLC grade. Dichloromethane (DCM) was pre-dried with calcium hydride before distilling from calcium hydride. If required, DCM was degassed by bubbling through nitrogen for 30 min.

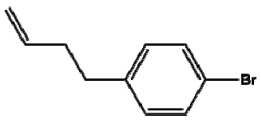
2. Synthetic Procedures

2.a. General procedure for ring closure metathesis (RCM) reactions in the presence of fullerenes



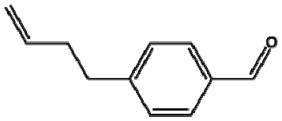
Diethyl diallylmalonate (50 mg, 0.208 mmol), 1st generation Grubbs' catalyst (9.3 mg, 10.4 µmol) and C_{60} (0.25 mol equivalents to diethyl diallylmalonate) were combined under an Ar environment. Degassed dichloromethane (20 mL) was added *via* syringe and the mixture was left to stir at room temperature for 2 d in darkness. The conversion was determined spectroscopically to be 100 %. Futhermore, no other metathesis products were observed indicating the C_{60} was not reactive towards the catalyst system.

2.b. Preparation of 4-(4-bromophenyl)-1-butene



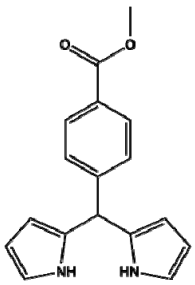
Synthesis conducted using the procedure of Kabalka *et al.*[1] 4-Bromobenzyl bromide (20 g, 80 mmol) was dissolved in anhydrous Et_2O (150 mL) under an Ar environment. Allyl magnesium bromide (96 mmol, 96 mL of a 1 M solution in ether) was added to the solution *via* a dropping funnel over a period of 30 min, and the reaction mixture was allowed to stir at room temperature for 2 h. The solution was refluxed for a further 3 h, with reaction progress monitored by TLC. After this time the reaction mixture was quenched with water (100 mL) and transferred to a separating funnel. The organic layer was washed water (3 × 50 mL), then with brine (1 × 50 mL), dried ($MgSO_4$) and the solvent removed by rotary evaporation. After thorough drying on a high vacuum pump, the crude bromophenyl alkene was purified by Kügelrohr distillation (150°C at 15 mmHg) to give the title compound (13.4 g, 80%) as a colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (ABq, *J* 8.2 Hz, 2 H, ArH); 7.06 (ABq, *J* 8.2 Hz, 2 H, ArH); 5.61 (m, 1 H, Alkene H); 5.06 (m, 2 H, Alkene H); 2.67 (t, *J* 8.2 Hz, 2 H, CH_2); 2.35 (Apparent q, 2 H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.7; 137.5; 131.3; 130.2; 119.5; 115.2; 35.2; 34.7. MS (ESI, +ve): $C_{10}H_{12}Br$ requires *m/z* 211.0, found *m/z* 210.9 $[M+H]^+$.

2.c. Preparation of 4-(3-butenyl)benzaldehyde



Synthesis conducted using a similar method to that of Wilcox *et al*.[2] A solution of 4-(4-bromophenyl)-1-butene (**4**) (10 g, 47.4 mmol) in THF (100 mL) was cooled to –78°C and *n*-butyllithium (2.5 M solution in hexane, 20.4 mL, 52.2 mmol) was added slowly, maintaining a temperature below –70°C and the solution was stirred for 30 min. DMF (8.8 ml, 111.8 mmol) was added at –78°C and was stirred for a further 30 min. The solution was warmed to 0°C and quenched with water (150 mL). The solution was extracted with diethyl ether (3 × 100 mL), washed with water (3 × 100 mL), dried ($MgSO_4$), filtered and solvent removed under reduced pressure to give a crude yellow residue. The residue was chromatographed on silica (60-200 mesh, 8:1 hexane / ethyl acetate) to give the title compound (**3**) (5.23 g, 69%) as a colourless liquid (stored under argon). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.95 (s, 1 H, CHO); 7.78 (ABq, *J* 8.4 Hz, 2 H, ArH); 7.32 (ABq, *J* 8.4 Hz, 2 H, ArH); 5.81 (m, 1 H, Alkene H); 5.00 (m, 2 H, Alkene H); 2.78 (t, *J* 8.2 Hz, 2 H, CH_2); 2.38 (Apparent q, 2 H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.0; 149.4; 137.4; 134.8; 130.0; 129.3; 115.6; 35.7; 35.1. MS (ESI, +ve): $C_{11}H_{13}O$ requires *m/z* 161.10, found *m/z* 160.9 $[M+H]^+$.

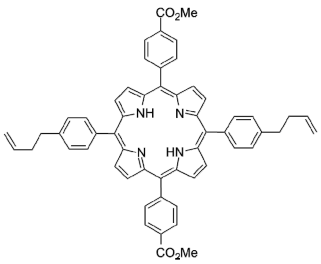
2.d. Preparation of methyl 4-(di(1*H*-pyrrol-2-yl)methyl)benzoate



Using the method of Zaida *et al*[3]*.*, a solution of pyrrole (3.043 g, 45.4 mmol) and methyl-4-formylbenzoate (372 mg, 2.27 mmol) was degassed for 20 min before adding TFA (20 µL) and stirring the reaction at RT, under nitrogen for 20 min, protected from light. The pyrrole was then removed under reduced pressure to yield a brown oil. This was subsequently purified on a short column of silica (40-63 µm) using DCM:MeOH:Et_3N (100:1:1) as the eluent, yielding a white solid (553 mg, 87%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.96-8.00 (m, 2H); 7.94 (bs, 2H); 7.28-7.30 (m, 2H); 6.71-6.73 (m, 2H); 6.15-6.18 (q, 2H, *J* 2.81 Hz); 5.89-5.90 (m, 2H); 3.91 (s, 3H); 5.53 (s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ

166.9; 147.3; 131.6; 129.9; 129.0; 128.4; 117.5; 108.6; 107.5; 52.1; 44.0. MS (ESI, -ve) $C_{17}H_{15}N_2O_2$ requires *m/z* 279.1, found *m/z* 279.0 $[M-H]^-$.

2.e. Preparation of 5,15-bis-(4-(3-butenyl)-phenyl)-10,20-bis-(4-methoxycarbonylphenyl)porphyrin

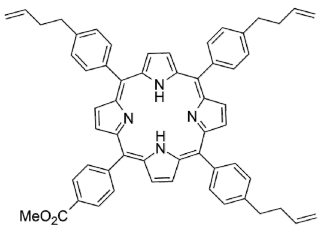


Methyl 4-(di(1*H*-pyrrol-2-yl)methyl)benzoate (140 mg, 0.497 mmol) and 4-(butenyl)benzaldehyde (79.7 mg, 0.497 mmol) were combined in DCM (90 ml) and the mixture was degassed for 20 min before adding TFA (27 µL) and stirring at room temperature, in the dark, under N_2 for 6 h. DDQ (124 mg, 0.547 mmol) was then added and the reaction stirred for a further hour before adding triethylamine (2 ml) and removing the solvent in vacuo. The crude black material was then passed through a silica plug before separating the porphyrinic material using silica gel chromatography (40-63 µm), 1 % Et_3N in DCM, two columns. The target porphyrin was isolated in 22 % yield (46.1 mg).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.93-8.92 (d, 4H, ^3J 4.8 Hz, β-pyrrolic H); 8.83-8.82 (d, 4H, ^3J 4.8 Hz, β-pyrrolic H); 8.48-8.46 (d, 4H, ^3J 8.2 Hz, Ar-H); 8.35-8.33 (d, 4H, ^3J 8.2 Hz, Ar-H); 8.14-8.12 (d, 4H, ^3J 8.0 Hz, Ar-H); 7.58-7.56 (d, 4H, ^3J 8.0 Hz, Ar-H); 6.15-6.05 (ddt, 2H ^3J 6.8, 10.4, 17.2 Hz, olefinic H); 5.29-5.16 (m, 4H, olefinic H); 4.14 (s, 6H, methyl ester); 3.10-3.06 (t, 4H, ^3J 8.2 Hz, methylene H); 2.73-2.67 (apparent-q, 4H, methlene H); -2.70 (bs, 2H, pyrrolenic H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 167.6; 147.3; 141.7; 139.6; 138.4; 134.8; 129.9; 128.1; 127.1; 120.9; 119.1; 115.5; 52.6; 35.9; 35.6. λ_{max} (toluene): 421 (log ε, 5.54); 516 (4.15); 551 (3.86); 592 (3.63); 648 nm (3.52). MS (ESI, +ve) $C_{56}H_{47}N_4O_4$ requires *m/z* 839.3592, found *m/z* 839.3591 $[M+H]^+$.

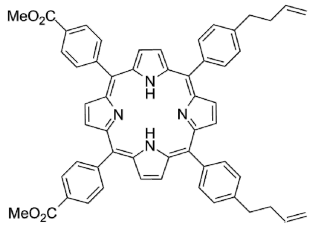
Major by-products isolated from this reaction:

5,10,15-tris-(4-(3-butenyl)-phenyl)-20-mono-(4-methoxycarbonylphenyl)porphyrin:



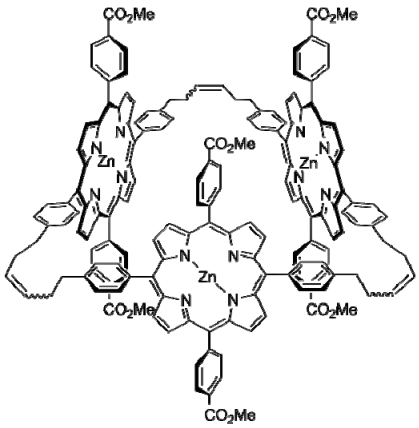
^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.89-8.87 (d, 2H, ^3J 4.8 Hz, β-pyrrolic H); 8.86 (s, 4H, β-pyrrolic H); 8.78-8.77 (d, 2H, ^3J 4.8 Hz, β-pyrrolic H); 8.45-8.43 (d, 2H, ^3J 8.3 Hz, Ar-H); 8.32-8.29 (d, 2H, ^3J 8.3 Hz, Ar-H); 8.14-8.11 (d, 6H, ^3J 8.0 Hz, Ar-H); 7.58-7.56 (d, 6H, ^3J 8.0 Hz, Ar-H); 6.13-6.02 (ddt, 3H ^3J 6.8, 10.4, 17.2 Hz, olefinic H); 5.26-5.12 (m, 6H, olefinic H); 4.12 (s, 3H, methyl ester); 3.09-3.04 (t, 6H, ^3J 8.2 Hz, methylene H); 2.73-2.65 (apparent-q, 6H, methylene H); -2.75 (bs, 2H, pyrrolenic H). MS (ESI, +ve) $C_{58}H_{51}N_4O_2$ requires *m/z* 835.4, found *m/z* 835.2 $[M+H]^+$.

5,10-bis-(4-(3-butenyl)-phenyl)-15,20-bis-(4-methoxycarbonylphenyl)porphyrin:



^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.89-8.88 (d, 2H, ^3J 4.9 Hz, β-pyrrolic H); 8.87 (s, 2H, β-pyrrolic H); 8.80 (s, 2H, β-pyrrolic H); 8.79-8.77 (d, 2H, ^3J 4.9 Hz, β-pyrrolic H); 8.46-8.43 (d, 4H, ^3J 8.3 Hz, Ar-H); 8.31-8.29 (d, 4H, ^3J 8.3 Hz, Ar-H); 8.13-8.11 (d, 4H, ^3J 8.0 Hz, Ar-H); 7.59-7.56 (d, 4H, ^3J 8.0 Hz, Ar-H); 6.13-6.04 (ddt, 2H ^{3}J *J* 6.8, 10.4, 17.2 Hz, olefinic H); 5.26-5.12 (m, 4H, olefinic H); 4.11 (s, 6H, methyl ester); 3.10-3.05 (t, 4H, ^3J 8.2 Hz, methylene H); 2.73-2.67 (apparent-q, 4H, methylene H); -2.76 (bs, 2H, pyrrolenic H). MS (ESI, +ve) $C_{56}H_{47}N_4O_4$ requires *m/z* 839.4, found *m/z* 839.2 $[M+H]^+$.

2.f. General procedure for the preparation of the cyclic porphyrin trimer



5,15-Bis-(4-(3-butenyl)-phenyl)-10,20-bis-(4-methoxycarbonylphenyl)porphyrin (1 eq.) and the template (either C_{60} or C_{70}, 0.33 eq.) were combined under an argon environment and freshly distilled/degassed DCM (2.55 ml/mg porphyrin) was added *via* syringe. Grubbs' catalyst gen. I (20

mol %) was added and the reaction stirred at RT, under argon, for 48 h. The solvent was then removed and the crude material loaded onto a short silica column, eluting first with DCM:toluene 1:1 to remove the template (for C_{60} and C_{70}), followed by $CHCl_3$: acetone 20:1 to elute the porphyrinic material. The second band collected was a mixture of the isomers of the cyclic porphyrin trimer containing trace amounts of a cyclic porphyrin dimer. After evaporating the solvent *in vacuo* the trimeric mixture was taken up in $CHCl_3$: saturated $Zn(OAc)_2$ in MeOH (2:1) and heated at reflux for 1 h before cooling to RT. The reaction mixture was transferred to a separating funnel, washed 3 x with water, dried (Na_2SO_4), filtered and the solvent removed *in vacuo*. The trimeric material was then further purified by several rounds of column chromatography: first column (SiO_2, DCM:EtOAc 25:1 → DCM:acetone 5:1), then (SiO_2, DCM:EtOAc 30:1) until individual isomers of acceptable purity were obtained.

C_{60} templation: 5,15-Bis-(4-(3-butenyl)-phenyl)-10,20-bis-(4-methoxycarbonylphenyl)porphyrin (29.6 mg, 35.3 µmol), Grubbs' gen. I (5.79 mg, 7.06 µmol), C_{60} (8.47 mg, 11.8 µmol), DCM (75 ml), yielded 16.8 mg of the free-base cyclic porphyrin trimer (6.90 µmol, 59 %); 1.17 mg of the free-base cyclic porphyrin dimer (0.72 µmol, 4 %).

C_{70} templation: 5,15-Bis-(4-(3-butenyl)-phenyl)-10,20-bis-(4-methoxycarbonylphenyl)porphyrin (17.6 mg, 20.9 µmol), Grubbs' gen. I (3.43 mg, 4.18 µmol), C_{70} (5.86 mg, 6.97 µmol), DCM (45 ml), yielded 8.66 mg of the free-base porphyrin trimer (3.56 µmol, 51 %); 3.24 mg of the free-base cyclic porphyrin dimer (2.00 µmol, 19 %).

Spectral data:

1st band: *cis-cis-trans* cyclic metalloporphyrin trimer

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.95-8.89 (m, 12H, β-pyrrolic H); 8.74-8.66 (m, 12H, β-pyrrolic H); 8.15-8.00 (m, 24H, Ar-H); 7.64-7.50 (m, 20H, Ar-H); 7.24-7.23 (m, 4H, Ar-H); 5.79-5.76 (m, 4H, olefinic H); 5.73-5.71 (m, 2H, olefinic H); 3.14-3.09 (m, 14H, overlapping methyl ester, methylene-H); 3.04-2.93 (m, 10H, overlapping methyl ester, methylene H); 2.89 (s, 6H, methyl ester); 2.70-2.65 (m, 12H, methylene H). λ_{max} (toluene): 430 (log ε, 6.02); 553 (4.81); 594 nm (4.24). MS (MALDI-TOF, SINAPINIC ACID) $C_{162}H_{121}N_{12}O_{12}Zn_3$ requires *m/z* 2623 , found *m/z* 2622 $[M+H]^+$.

2nd band: *trans-trans-cis* cyclic metalloporphyrin trimer

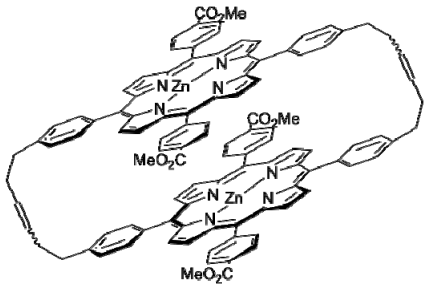
^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.94-8.89 (m, 12H, β-pyrrolic H); 8.75-8.68 (m, 12H, β-pyrrolic H); 8.10-8.02 (m, 24H, Ar-H); 7.71-7.70 (d, 4H, ^3J 8.4 Hz, Ar-H); 7.63-7.61 (d, 4H, ^3J 8.0 Hz, Ar-H); 7.56-

7.54 (apparent-dd, 9H, Ar-H); 7.48-7.46 (d, 7H, ^3J 8.4 Hz, Ar-H); 5.79-5.77 (t, 2H, ^3J 4.8 Hz, olefinic H); 5.72-5.69 (m, 4H, olefinic H); 3.32 (s, 5H, methyl ester); 3.13-3.06 (m, 20H, overlapping methyl ester, methylene H); 2.99-2.96 (t, 5H, ^3J 7.2 Hz, methylene H); 2.70-2.65 (m, 12H, methylene H). λ_{max} (toluene): 429 (log ε, 5.79); 553 (4.59); 594 nm (4.01). MS (MALDI-TOF, α-CYANO-4-HYDROXYCINNAMIC ACID) $C_{162}H_{121}N_{12}O_{12}Zn_3$ requires *m/z* 2623, found *m/z* 2622 $[M+H]^+$; $C_{162}H_{123}N_{12}O_{12}Zn_2$ requires *m/z* 2559, found *m/z* 2559 $[M+3H-Zn]^+$; $C_{162}H_{125}N_{12}O_{12}Zn$ requires *m/z* 2495, found *m/z* 2496 $[M+5H-2Zn]^+$; $C_{162}H_{127}N_{12}O_{12}$ requires *m/z* 2432, found *m/z* 2434 $[M+7H-3Zn]^+$.

3rd band: *trans-trans-trans* cyclic metalloporphyrin trimer

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.92-8.91 (d, 12H, ^3J 4.8 Hz, β-pyrrolic H); 8.74-8.72 (d, 12H, ^3J 4.8 Hz, β-pyrrolic H); 8.08-8.04 (apparent-t, 24H, Ar-H); 7.74-7.72 (d, 12H, ^3J 8.0 Hz, Ar-H); 7.56-7.54 (d, 12H, ^3J 8.0 Hz, Ar-H); 5.72-5.71 (t, 6H, ^3J 3.6 Hz, olefinic H); 3.35 (s, 18H, methyl ester); 3.12-3.08 (t, 12H, ^3J 6.8 Hz, methylene H); 2.71-2.70 (m, 12H, methylene H). λ_{max} (toluene): 427 (log ε, 5.56); 554 (4.33); 595 nm (3.77). MS (MALDI-TOF, SINAPINIC ACID) $C_{162}H_{123}N_{12}O_{12}Zn_3$ requires *m/z* 2623, found *m/z* 2621 $[M+H]^+$.

2.g. Olefin metathesis of the porphyrin monomer in the absence of a fullerene template



To a solution of 5,15-bis-(4-(3-butenyl)-phenyl)-10,20-bis-(4-methoxycarbonylphenyl)porphyrin (5.00 mg, 5.96 µmol) in freshly distilled/degassed DCM (12 ml) was added Grubbs' catalyst gen. I (20 mol %, 1.19 µmol, 0.97 mg). The reaction was stirred at RT, under argon for 48 h. The solvent was then removed and the crude material loaded onto a silica plug, eluting with $CHCl_3$: acetone 20:1. The crude mixture was then zinc metallated by heating at reflux in a 2:1 mixture of $CHCl_3$:saturated $Zn(OAc)_2$ in MeOH for 2 h. After an aqueous work-up the organic layer was dried (Na_2SO_4) and the solvent removed in vacuo. Silica gel chromatography was then used to separate out the product mixture (40-63 µm SiO_2, DCM:EtOAc 30:1), isolating the cyclic metalloporphyrin dimer in 41 % yield (2.14 mg, 1.22 µmol). Furthermore, an unidentified compound (0.84 mg) which gave two major molecular ion peaks at *m/z* 883 and *m/z* 2015 was isolated, as well as another band which was identified as a 1:1 mixture (determined spectroscopically) of the cyclic metalloporphyrin dimer and

trimer (0.96 mg, 9 % yield of the cyclic metalloporphyrin dimer, 9 % yield of the cyclic metalloporphyrin trimer).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.01-8.84 (m, 6H, β-pyrrolic H); 8.53-8.48 (m, 4H, β-pyrrolic H); 8.45-8.29 (m, 4H, Ar-H); 8.25-8.05 (m, 8H, Ar-H); 7.92-7.82 (m, 8H, Ar-H); 7.77-7.56 (m, 14H, Ar-H); 7.50-7.46 (m, 4H, Ar-H); 5.93-5.90 (m, 2H, olefinic H); 5.87-5.85 (m, 2H, olefinic H); 4.14-6.09 (apparent-t, 9H, methyl ester); 3.73 (s, 3H, methyl ester); 3.24-3.05 (m, 8H, methylene H); 2.82-2.70 (m, 8H, methylene H). λ_{max} (toluene): 426 (log ε, 5.74); 553 (4.53); 593 nm (3.96). MS (MALDI-TOF, SINAPINIC ACID) $C_{108}H_{81}N_8O_8Zn_2$ requires *m/z* 1749, found *m/z* 1748 $[M+H]^+$; $C_{108}H_{85}N_8O_8$ requires *m/z* 1622, found *m/z* 1622 $[M+5H-2Zn]^+$.

3. Spectral Analysis

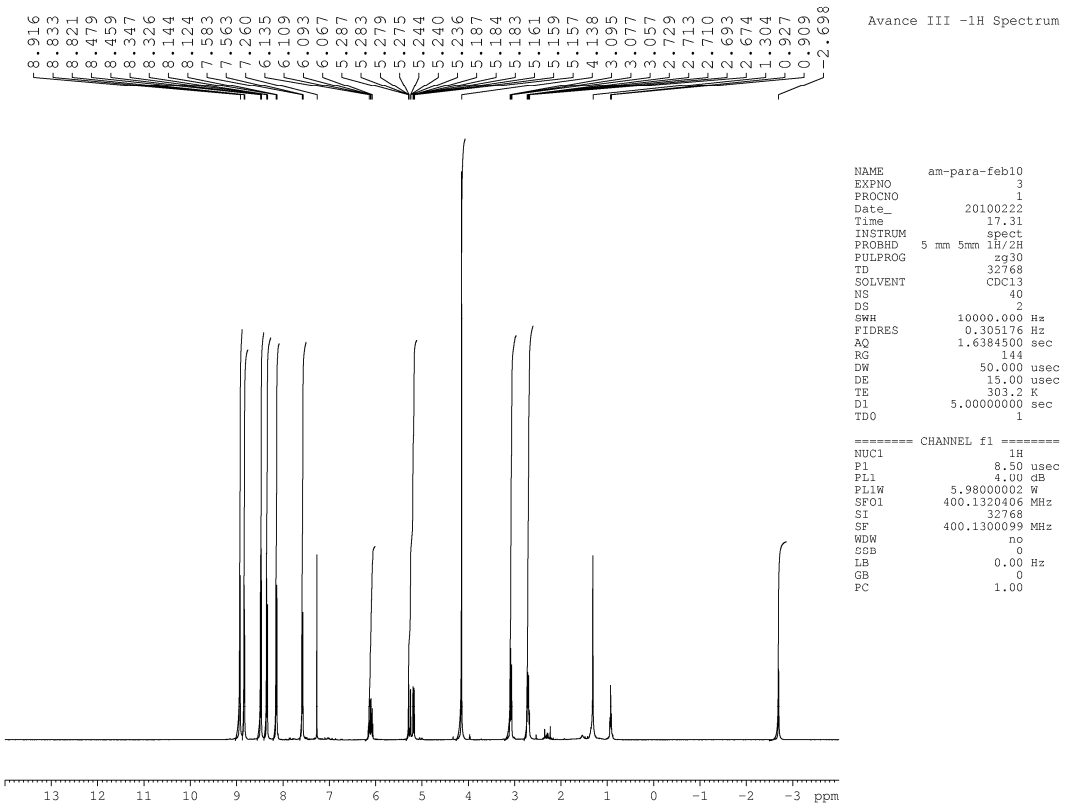


Figure 1. ^{1}H-NMR spectrum of 5,15-bis-(4-(3-butenyl)-phenyl)-10,20-bis-(4-methoxycarbonylphenyl)porphyrin **1**.

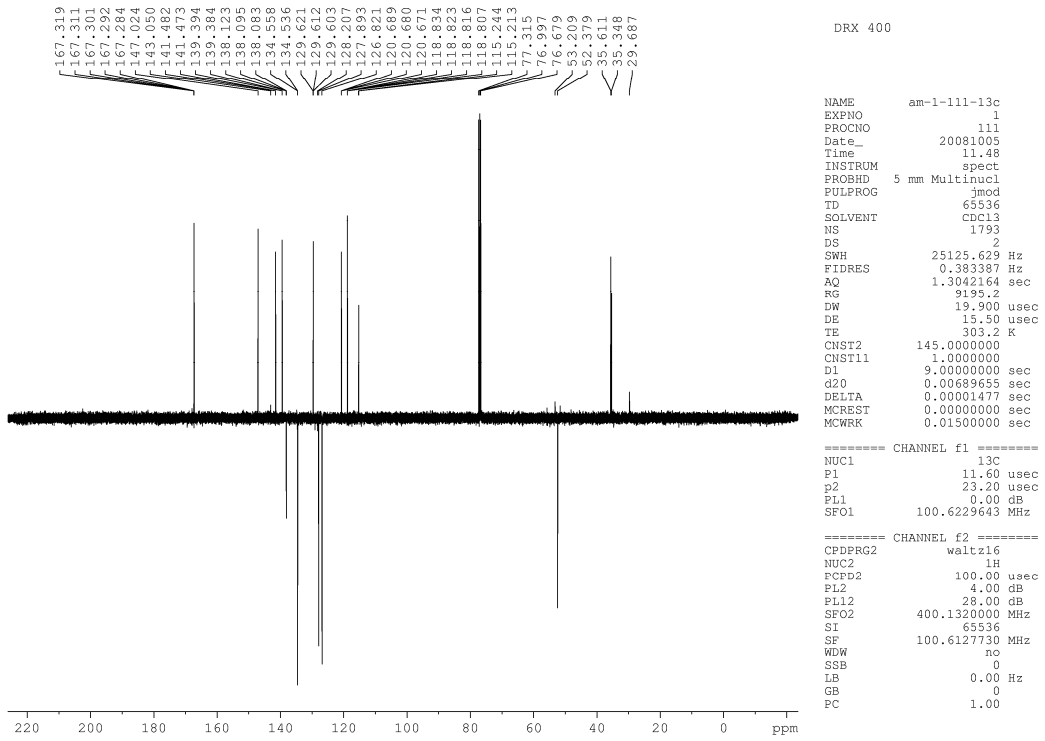


Figure 2. ^{13}C-NMR spectrum of 5,15-bis-(4-(3-butenyl)-phenyl)-10,20-bis-(4-methoxycarbonylphenyl)porphyrin **1**.

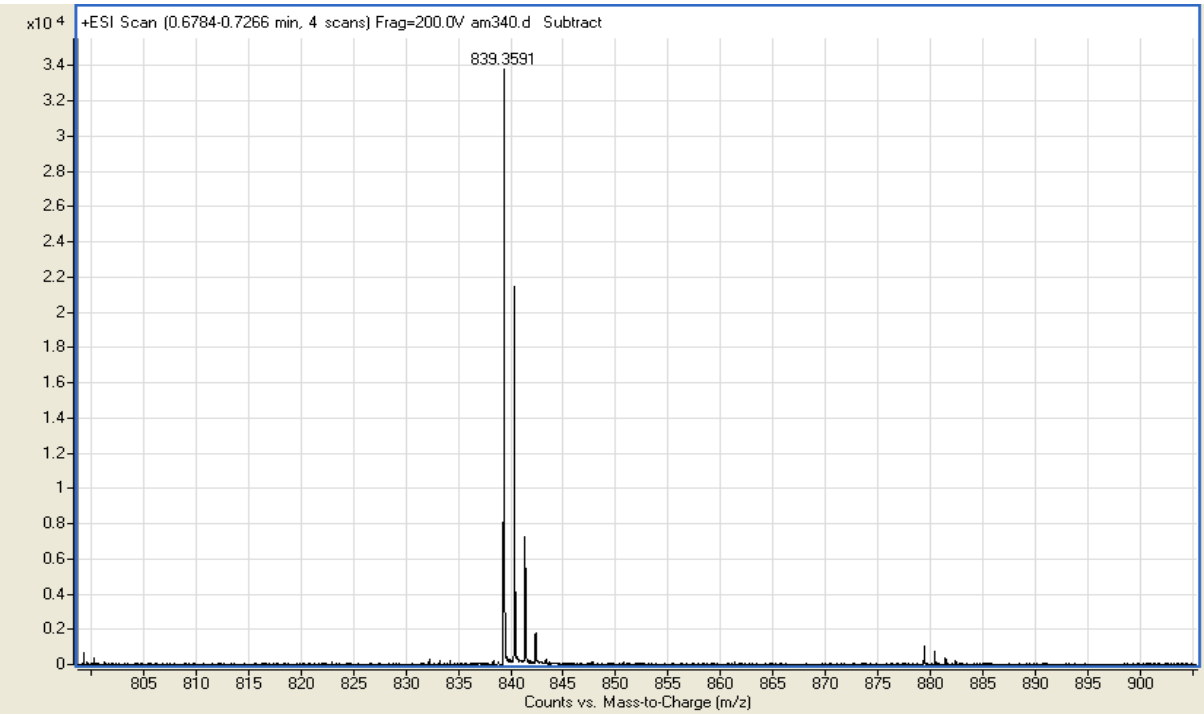


Figure 3. High resolution mass spectrum of 5,15-bis-(4-(3-butenyl)-phenyl)-10,20-bis-(4-methoxycarbonylphenyl)porphyrin **1**.

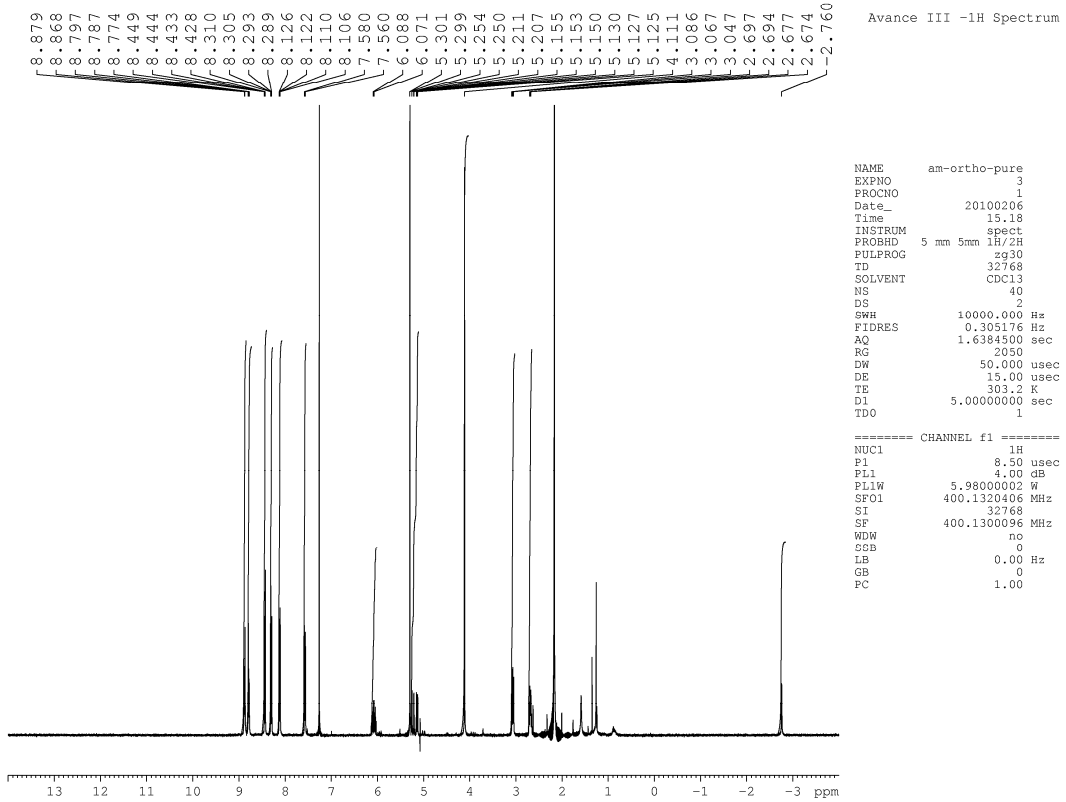


Figure 4. ^{1}H-NMR spectrum of 5,10-bis-(4-(3-butenyl)-phenyl)-15,20-bis-(4-methoxycarbonylphenyl)porphyrin.

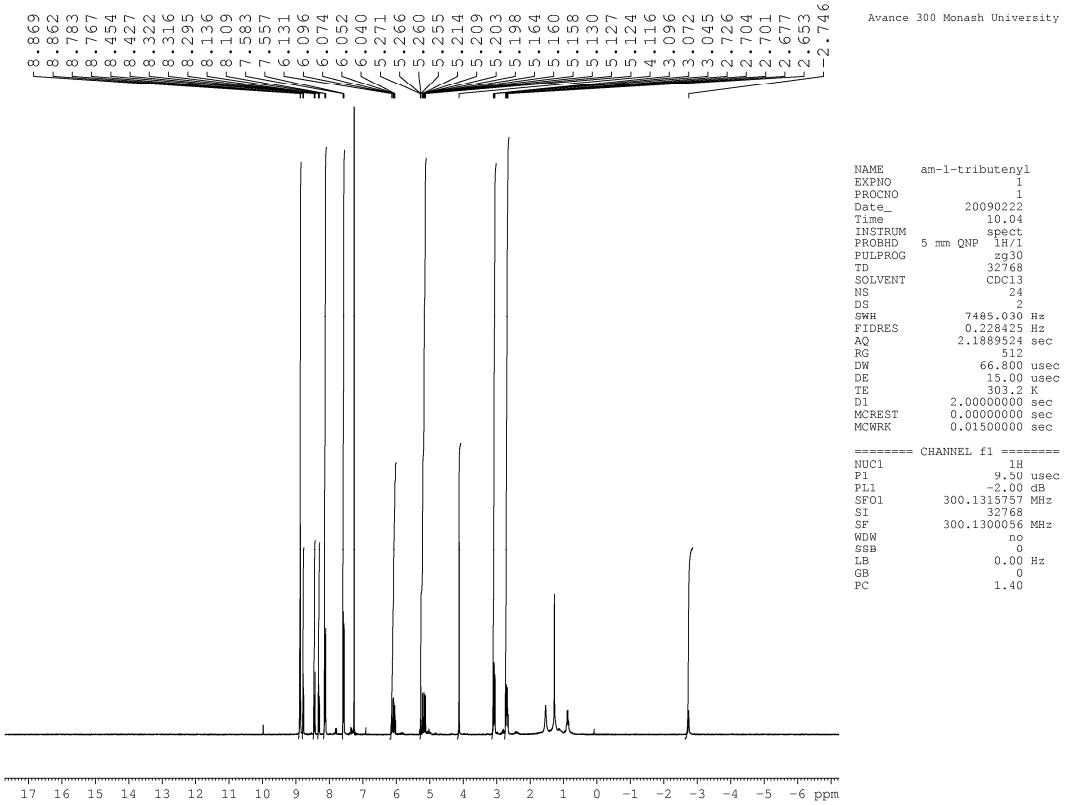


Figure 5. ^{1}H-NMR spectrum of 5,10,15-tris-(4-(3-butenyl)-phenyl)-20-(4-methoxycarbonylphenyl)porphyrin.

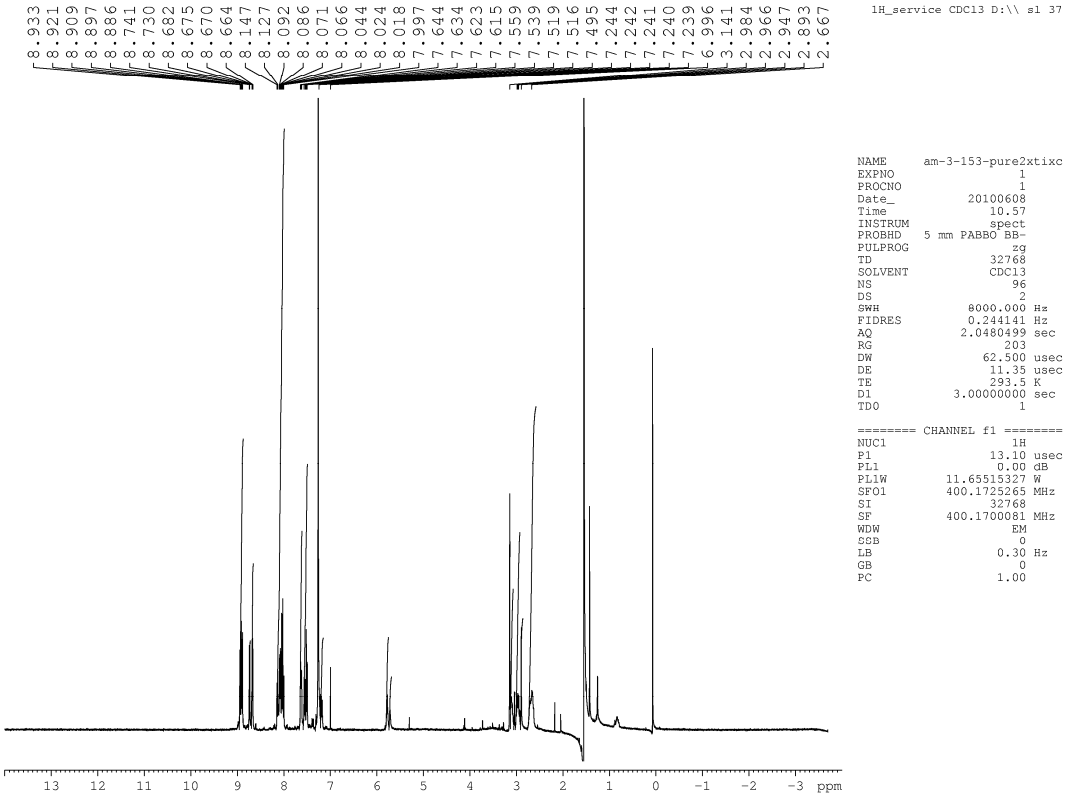


Figure 6. ^{1}H-NMR spectrum of the *cis*-*cis*-*trans*-cyclic porphyrin trimer **3**.

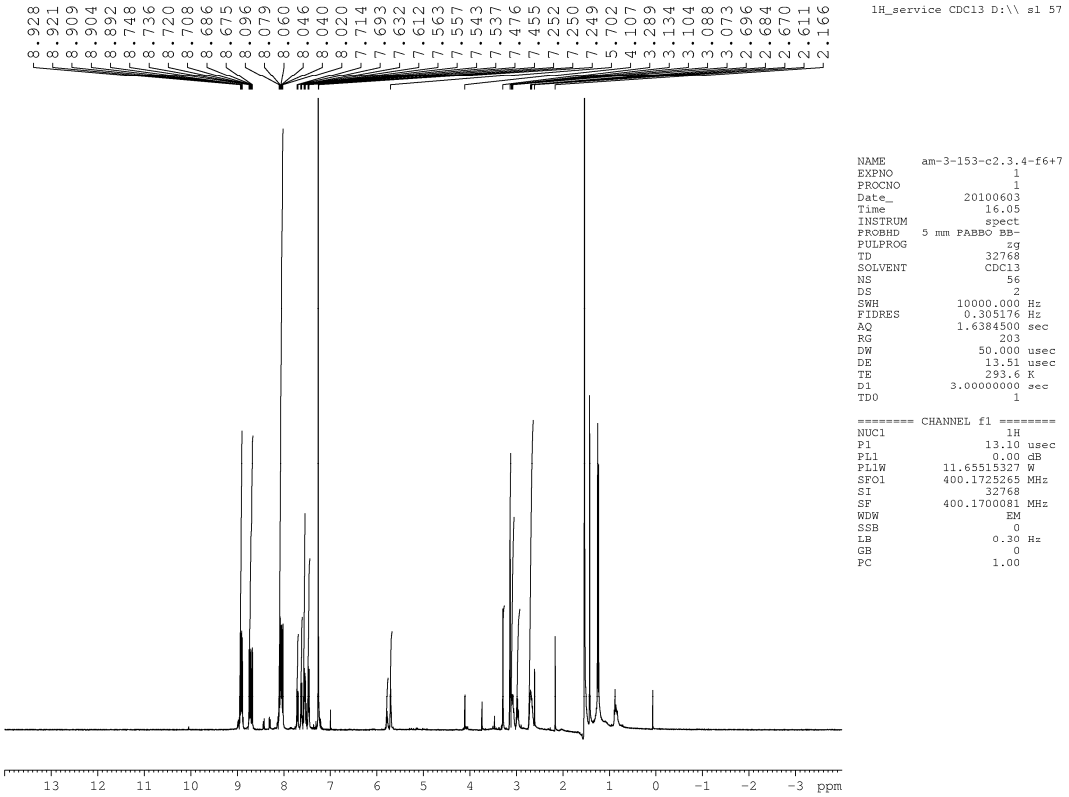


Figure 7. ^{1}H-NMR spectrum of the *trans-trans-cis*-cyclic porphyrin trimer **3**.

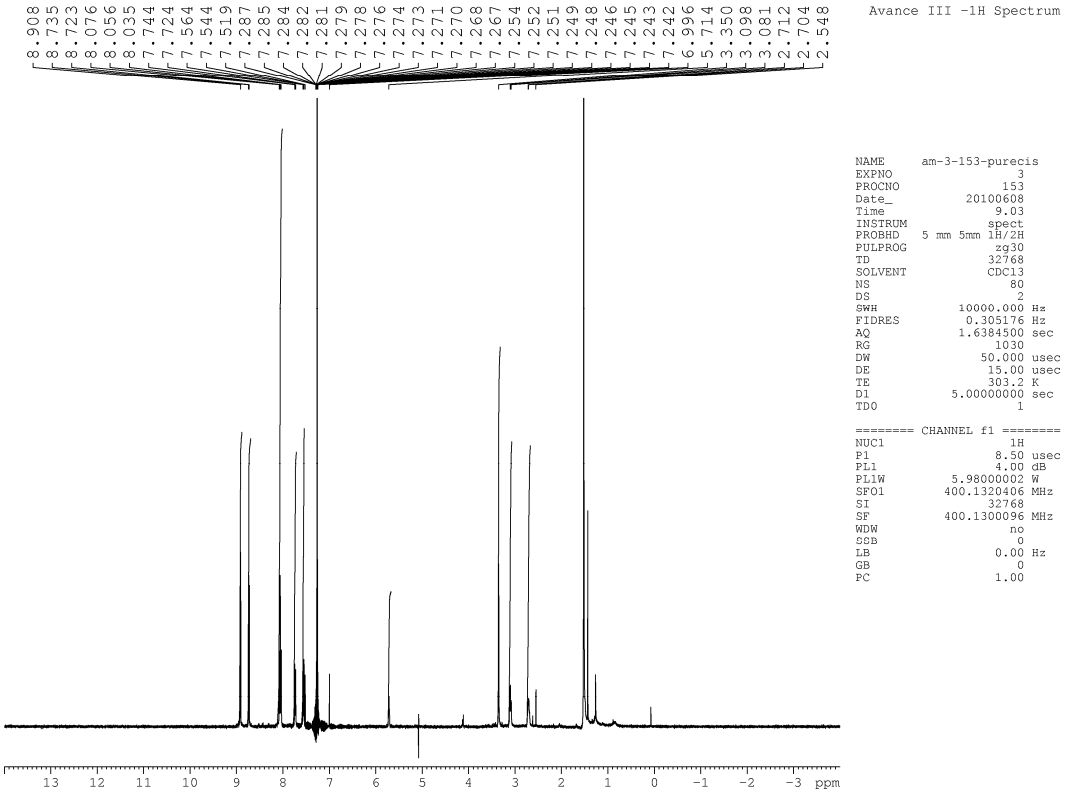


Figure 8. ^{1}H-NMR spectrum of the *trans-trans-trans*-cyclic porphyrin trimer **3**.

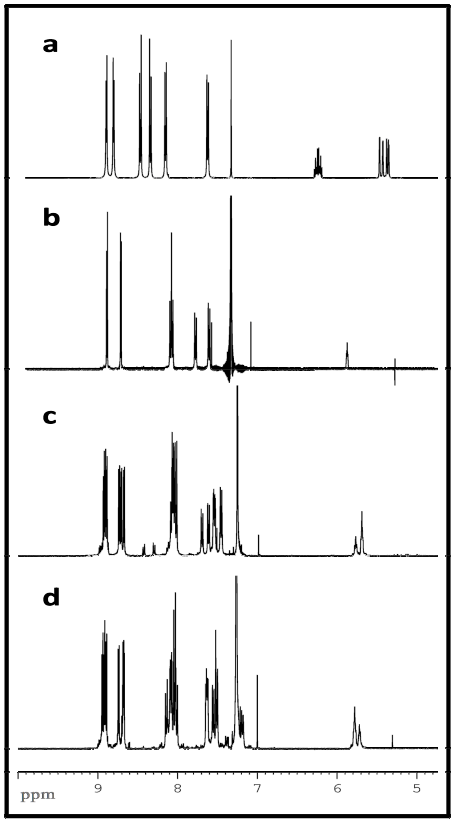


Figure 9. ^{1}H-NMR analysis of the starting porphyrin (a) and the three isomers of the cyclic system **3** (b- *trans-trans-trans*; c- *trans-trans-cis* and d- *trans-cis-cis*), isolated as the trizinc complexes. Spectra were obtained in $CDCl_3$ at an operating frequency of 400 MHz.

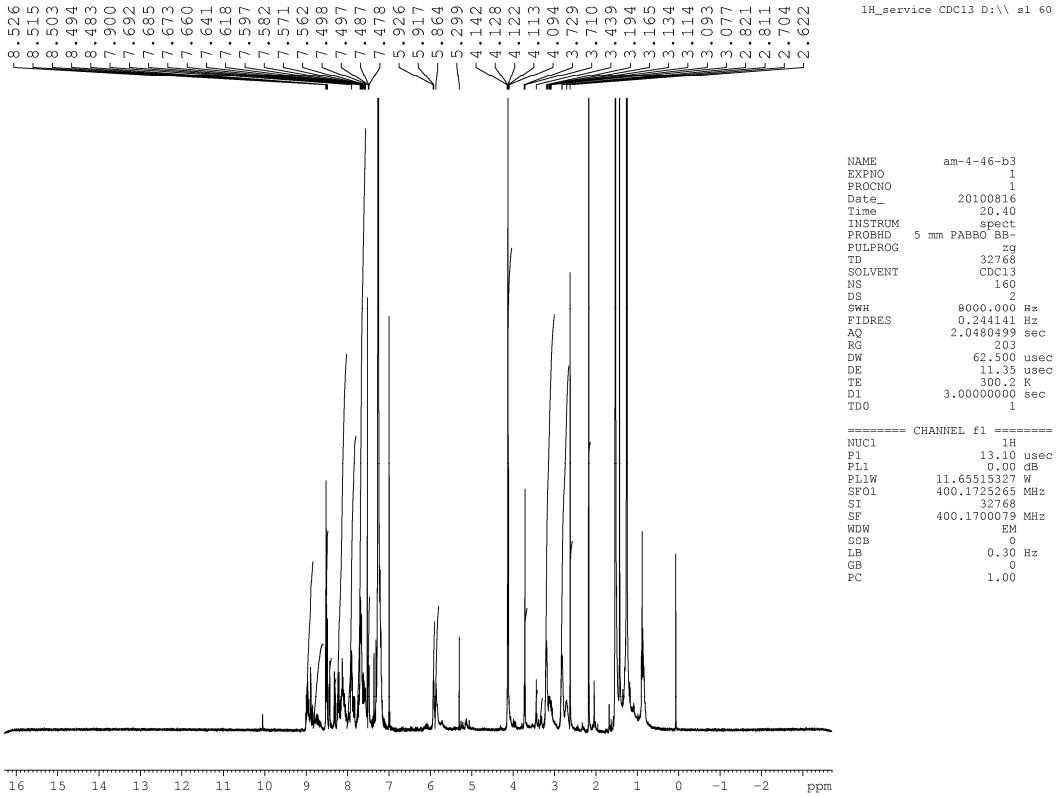


Figure 10. ^{1}H-NMR spectrum of the cyclic porphyrin dimer **4**.

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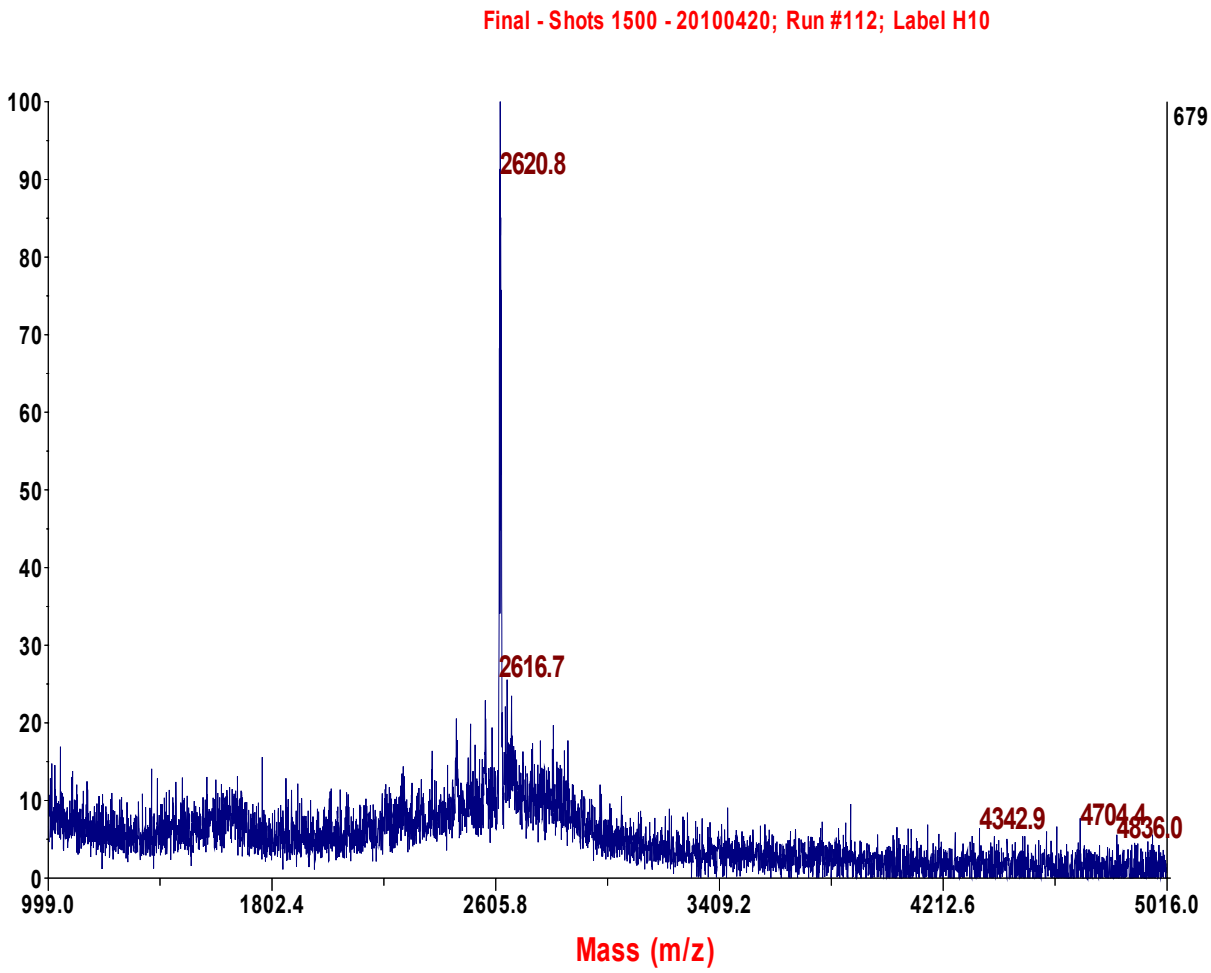

Figure 11. MALDI-TOF spectrum of the *trans*-*trans*-*trans*-cyclic porphyrin trimer **3**.

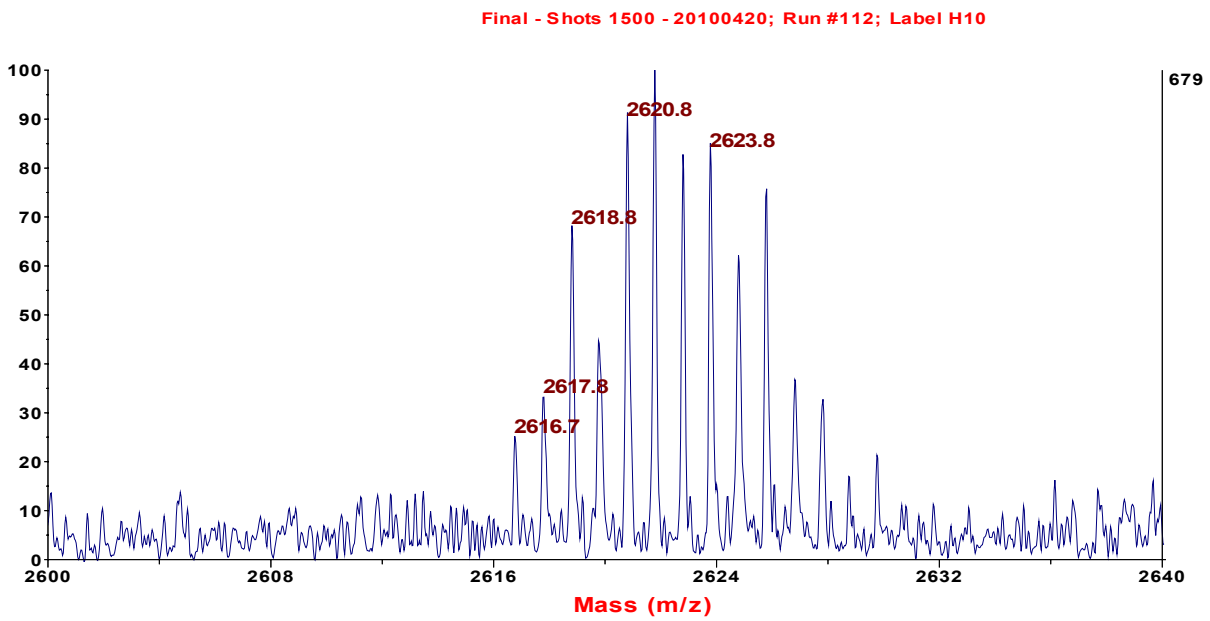

Figure 12. Expansion of the major molecular ion peak in the MALDI-TOF spectrum of the *trans-trans-trans*-cyclic porphyrin trimer **3**.

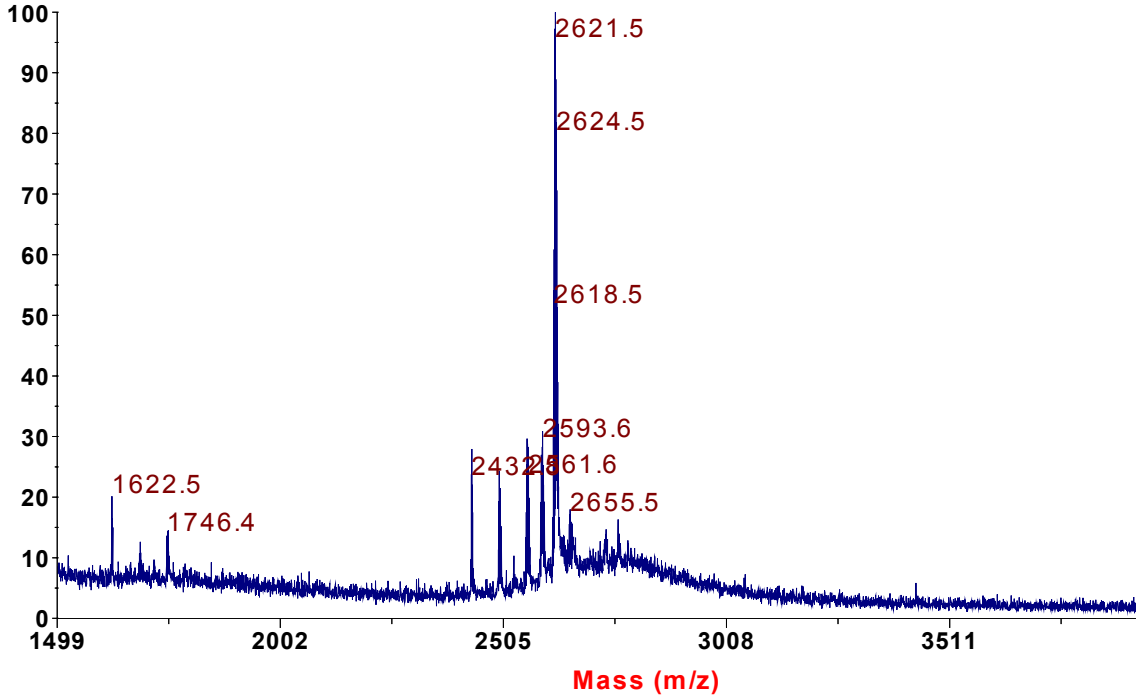

Figure 13. MALDI-TOF spectrum of the *trans-trans-cis*-cyclic porphyrin trimer **3**.

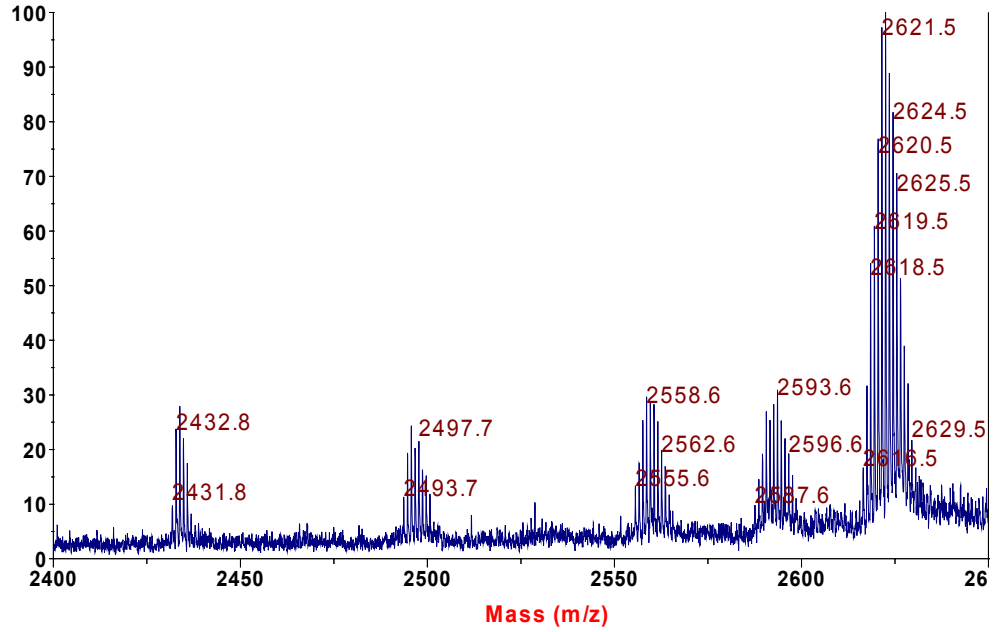

Figure 14. Expansion of the MALDI-TOF spectrum of the *trans-trans-cis*-cyclic porphyrin trimer **3**.

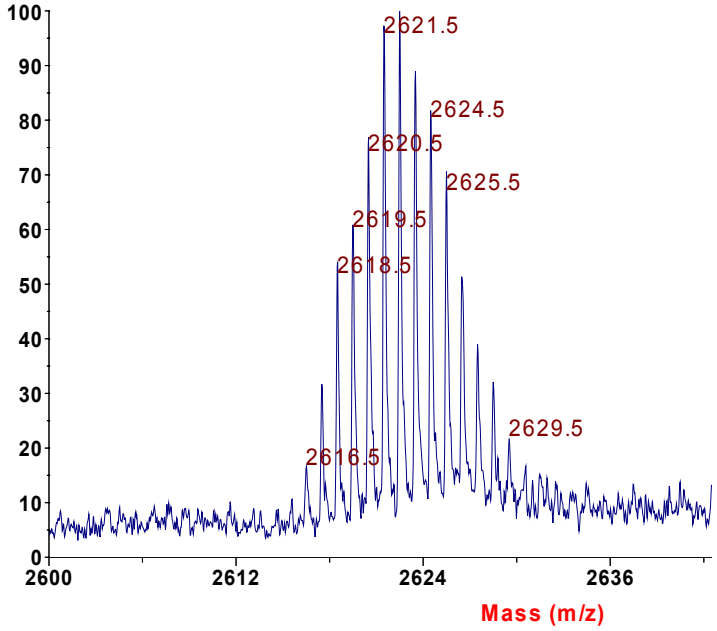

Figure 15. Expansion of the major molecular ion peak in the MALDI-TOF spectrum of the *trans-trans-cis*-cyclic porphyrin trimer **3**.

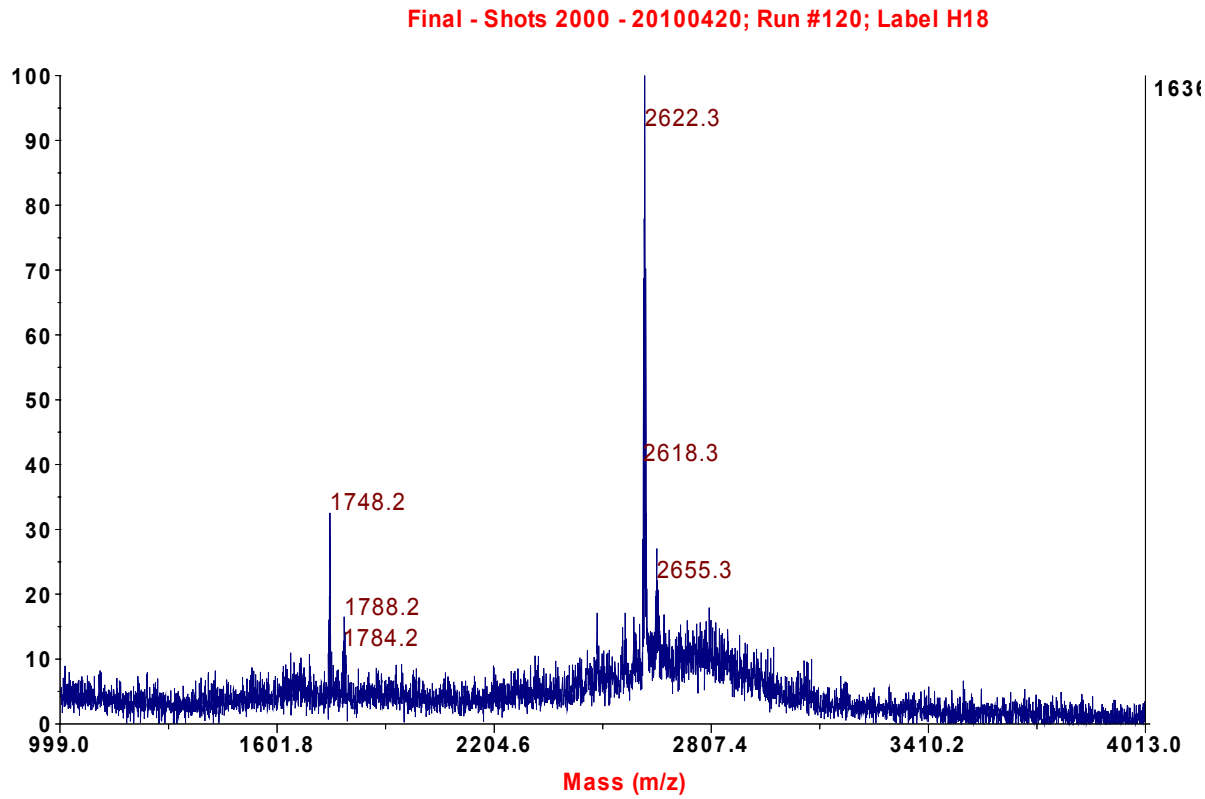

Figure 16. MALDI-TOF spectrum of the *trans-cis-cis*-cyclic porphyrin trimer **3**.

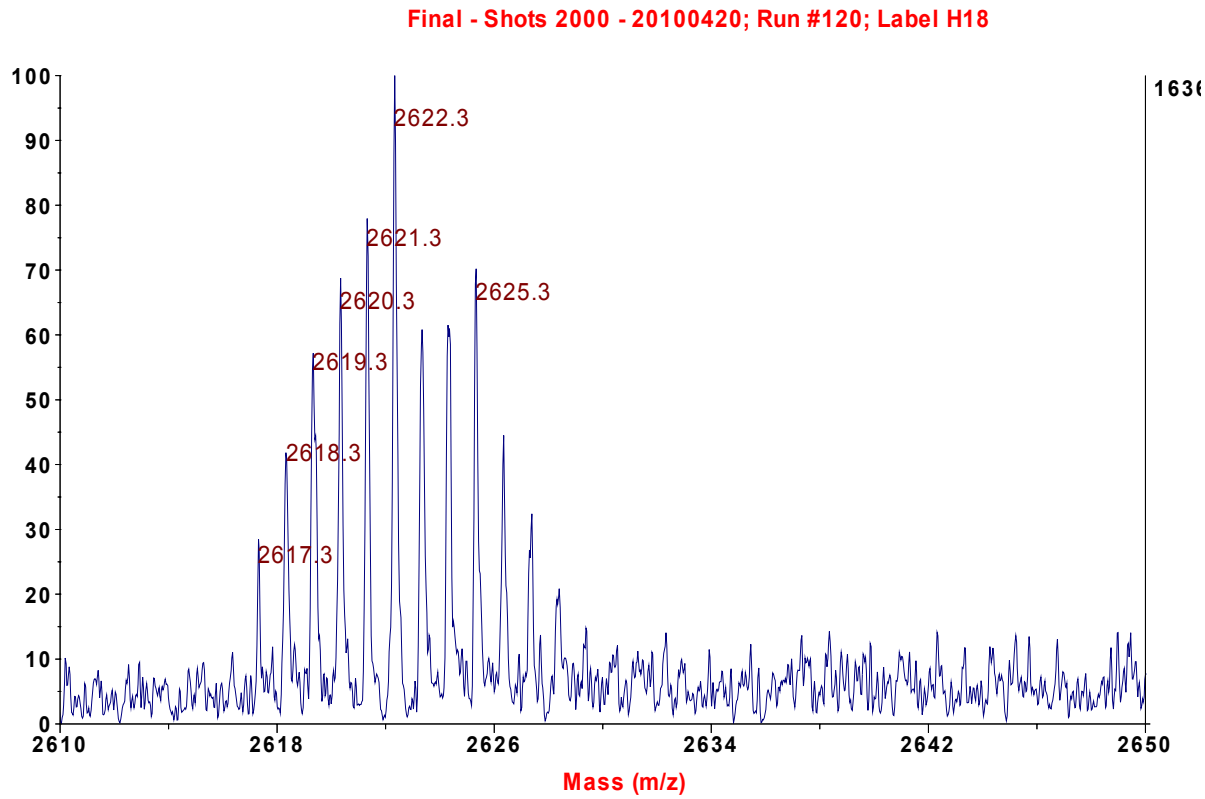

Figure 17. Expansion of the major molecular ion peak in the MALDI-TOF spectrum of the *trans-cis-cis*-cyclic porphyrin trimer **3**.

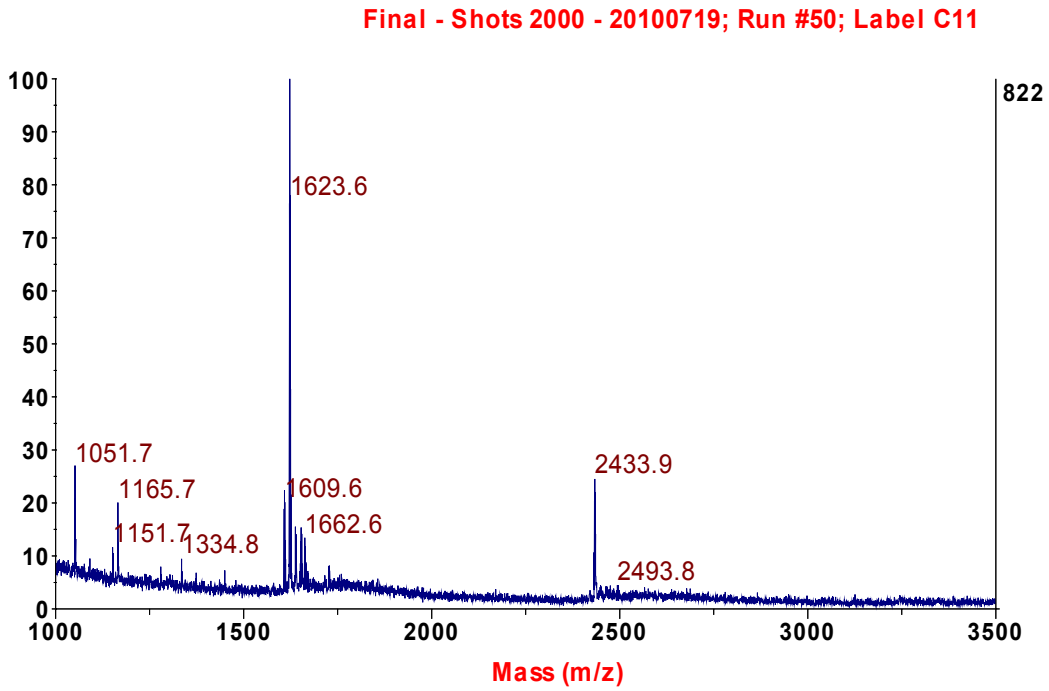

Figure 18. MALDI-TOF spectrum of the crude material following olefin metathesis in the absence of a template.

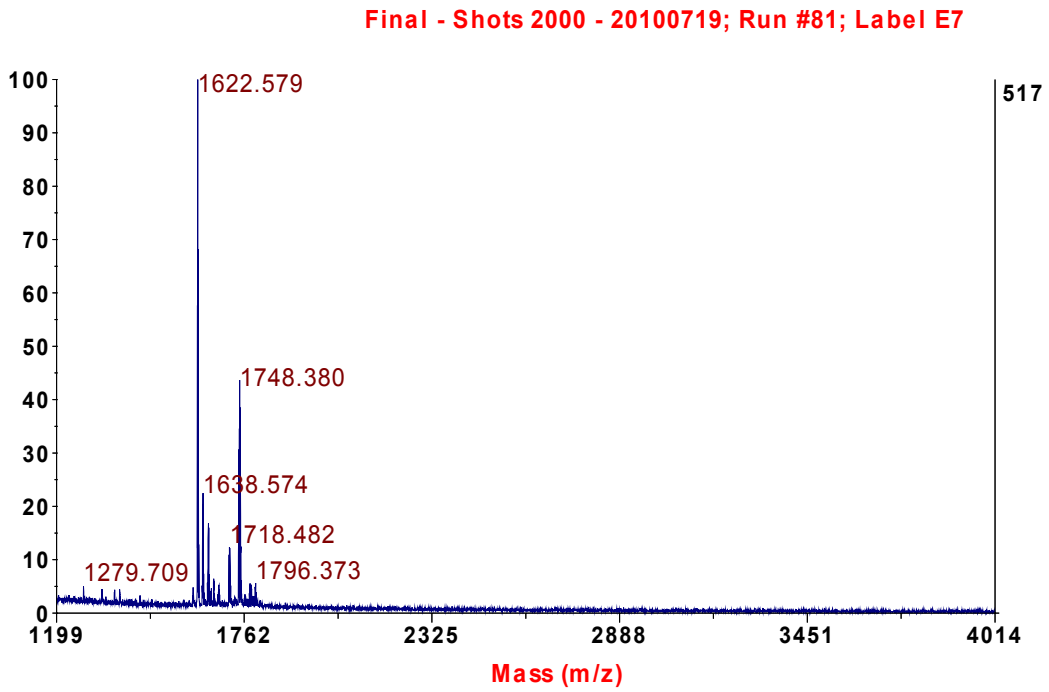

Figure 19. MALDI-TOF spectrum of the cyclic metalloporphyin dimer **4**.

4. Binding Studies

The UV-vis titrations were conducted on a Varian Cary 100 Bio UV-visible Spectrophotometer using matched 10 mm quartz cells. Fluorescence quenching experiments were conducted on a Varian Cary Eclipse Spectrophotometer using a quartz fluorescence cell of path length 10 mm. In a typical titration, a 1.10 x 10^{-6} M solution of the *trans-trans-cis* metalloporphyrin trimer **3** in toluene was used to make up a 5.06 x 10^{-4} M solution of C_{60} in toluene. To a quartz cuvette was added 2.00 ml of the *trans-cis-cis* metalloporphyrin trimer in chloroform, the trimer having a total concentration of 1.10 x 10^{-6} M. Aliquots of the C_{60} solution were then added to the cuvette and the UV-vis absorption/fluorescence emission spectrum recorded. The concentration of the porphyrin trimer remained constant throughout. Fluorescence quenching experiments were repeated in triplicate.

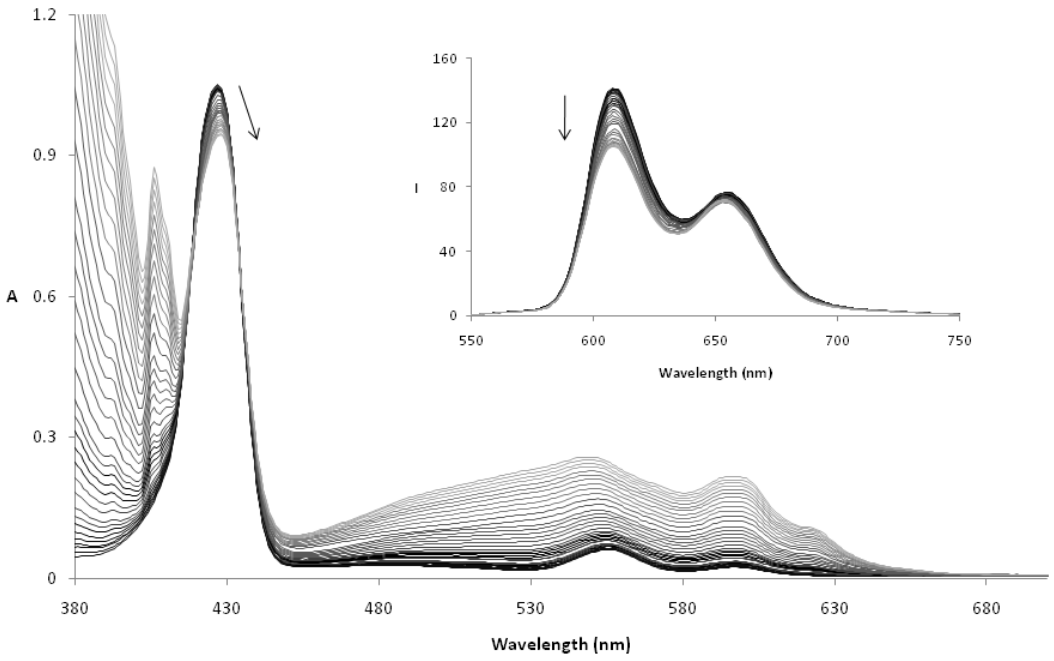

Figure 20. UV-vis spectrum of the *trans-cis-cis* metalloporphyrin trimer **3** upon titration with C_{60}; Inset: Fluorescence emission spectrum of the *trans-cis-cis* metalloporphyrin trimer **3** upon titration with C_{60}; [G]/[H] 0-212.

A Benesi-Hildebrand plot of the reciprocal of the change in fluorescence intensity (at 605 nm) as a function of the reciprocal of the concentration of the guest was used to determine the binding constant.[4] From this, the binding constant is estimated to be 2.65 x $10^{3}M^{-1}$ +/- 0.38.

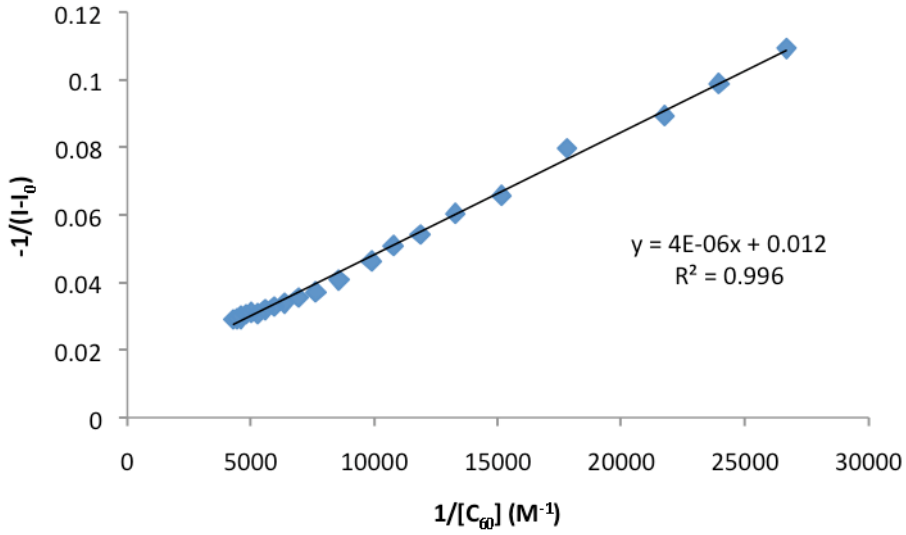

Figure 22. Representative Benesi-Hildebrand plot of the fluorescence quenching data.

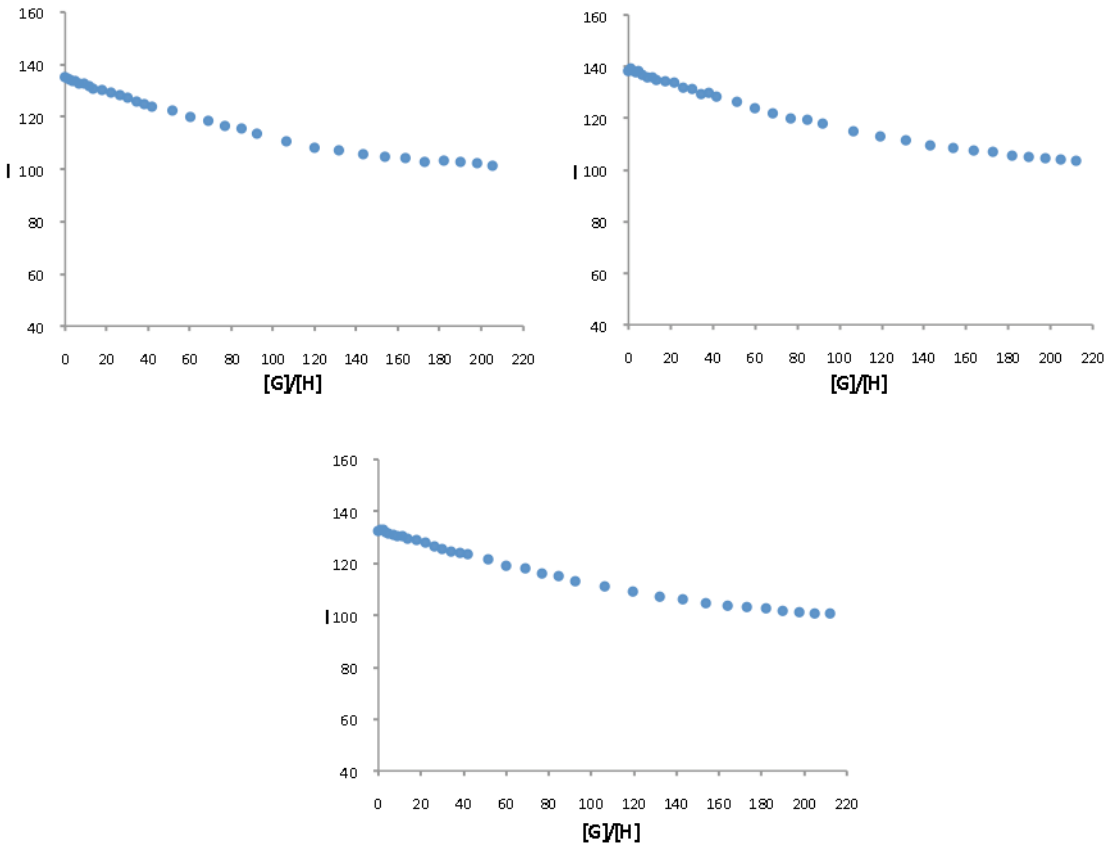

Figure 23. Fluorescence quenching of the *trans-cis-cis* metalloporphyrin trimer upon titration with C_{60}; excitation 428 nm, plots show the decrease in fluorescence intensity at an emission wavelength of 605 nm.

References:

[1] R. R. Srivastava, R. R. Singhaus, G. W. Kabalka, *J. Org. Chem.* **1999**, *64*, 8495-8500.

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[3] S.H.H. Zaida, R.S. Loewe, B.A. Clark, M.J. Jacob, J.S. Lindsey, *Org. Proc. Res. Dev.* **2006**, *10*, 304-314.

[4] K. A. Connors, *Binding Constants*, Wiley, New York, **1987**, pp. 141-160.