

Supporting information

Strong Donor-Acceptor Couplings in a Special Pair-Antenna Model

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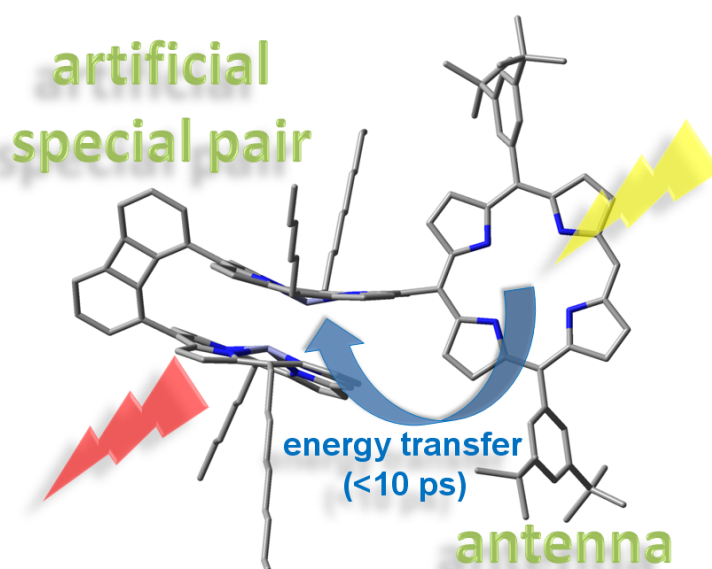
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General procedures

All known compounds (1,8-dibromobiphenylene(**2**)^{1,2,3,4}, 5,15-dinonylporphyrin⁵, 5,15-bis(3,5-di-*tert*-butylphenyl)porphyrin⁶ and 5-bromo-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrin(**8**)^{7,8} were synthesized as previously described.

The handling of all air/water sensitive materials was carried out using standard high vacuum techniques. Dried toluene was obtained by passing through alumina under N₂ in the solvent purification systems and then further dried over activated molecular sieves; extra dry DMF was purchased from Aldrich. Triethylamine and DCM were distilled from CaH₂; THF was distilled from sodium benzophenone ketyl. Unless specified otherwise all other solvents were used as commercially supplied. Where mixtures of solvents were used, ratios are reported by volume. Column chromatography was carried out on silica gel 60 at normal pressure. Size exclusion chromatography was carried out under gravity using cross-linked polystyrene Bio-Beads® SX-1 (200 – 400 mesh) in DCM.

UV-Vis spectra were recorded in solutions using Varian Cary 50 spectrophotometer (1 cm path length quartz cell). Emission and excitation spectra were measured by using a double monochromator Fluorolog FL-1039 instrument from HORIBA Jobin Yvon, equipped with TCSPC module for time-resolved measurements (interchangeable NanoLED pulsed laser-diodes as sources and TBX-04 photomultiplier tube as a detector were used). Emission quantum yields of the compounds were measured relative to the fluorescence of free-base tetraphenylporphyrin ($\phi_f=0.11$)⁹ in deoxygenated toluene. Sample concentrations were chosen to obtain an absorbance of 0.03 - 0.07, at least three measurements were performed for each sample. All the measurements were performed using deoxygenated (by Ar bubbling) freshly distilled tetrahydrofuran. Fluorescence lifetimes were obtained by deconvolution and distribution lifetime analysis.

Transient absorption measurements were performed with a home-built pump-probe setup. For measurements in the time range of 1-3 ns with a resolution of ~100 fs the output of a commercial titanium:sapphire amplifier (Coherent LIBRA HE, 3.5 mJ, 1 kHz, 100 fs) was split with one portion used to generate a 400 nm excitation pulse (second harmonic generation in a BBO crystal cut at $\theta = 29.2^\circ$) and another used to generate a white light probe using a home-built two-stage broadband (480-850 nm) non-collinear optical parametric amplifier (NOPA) for white light generation and amplification in the visible spectral range. The variable delay of up to ~3 ns between pump and probe was introduced by a broadband retroreflector mounted on a mechanical delay stage. Only reflective optics were used to guide the probe beam to the sample to minimize chirp. The excitation pulse was chopped at 500 Hz, while the white light pulses were dispersed onto a linear photodiode array which was read out at 1 kHz. Adjacent diode readings corresponding to the transmission of the sample after an excitation pulse and without an excitation pulse were used to calculate $\Delta T/T$.

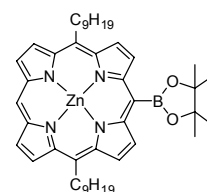
NMR spectra were recorded at room temperature using Bruker Avance 300 and Bruker Avance II 600 instruments with the chemical shifts reported as δ in ppm and coupling constants expressed in Hz. Accurate mass measurements (HRMS) were carried out using a Bruker microTOF-Q™ ESI-TOF mass spectrometer. MALDI-TOF mass spectrometry was carried out with a Bruker Ultraflex II MALDI-TOF mass spectrometer using dithranol as the matrix.

The electronic structure optimizations were calculated with the Gaussian 09(3) software, at the Université de Sherbrooke's Mammouth super computer, supported by the Réseau Québécois de Calcul de Haute Performance. The DFT(4-7) was calculated by the B3LYP(8-10) method with 3-21G* basis sets on all atoms(11-16). The TD-DFT(17-19) was calculated with the same method, but in this case a THF solvent model was also added(20). The UV-Vis spectrum was produced with the Gausssum software(24) with full-width at halfmaximum (fwhm) of 1000 cm⁻¹.^{10,11,12,13}

Experimental procedures

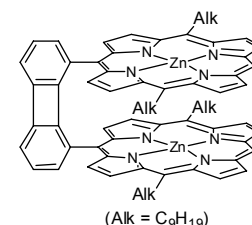
Zinc(II) 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10,20-dinonylporphyrin (3)

The solution of N-bromosuccinimide (0.044 g, 0.249 mmol) in chloroform (50 mL) was added to the solution of 5,15-dinonylporphyrin (0.14 g, 0.249 mmol) in chloroform (500 mL) at room temperature during a period of 5 min and the resulting mixture was stirred for 20 min before the reaction was quenched with acetone and solvent evaporated to dryness. The residue was dissolved in THF (100 mL), Zn(OAc)₂·2H₂O (0.545 g, 2.49 mmol) was added and the mixture was heated at reflux for 20 min. After cooling to room temperature water (100 mL) was added, the precipitate formed was filtered, washed at the filter with MeOH (200 mL) and dried in vacuum. The resulting solid material was mixed with PdCl₂(PPh₃)₂ (0.009 g, 0.0078 mmol) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.228 g, 32 mmol) in anhydrous 1,2-dichloroethane (10 mL) and distilled Et₃N (0.5 mL). The resulting mixture was heated at reflux 40 min under Ar. Allowed to cool, the mixture was diluted with dichloromethane, washed with water (1x20 mL), brine (1x20 mL), dried under Na₂SO₄ and evaporated in vacuum. Crude product was purified by column chromatography on silica gel, using hexanes-dichloromethane (1:1) as an eluent. Purple crystalline solid (0.120 g, 64% yield), m.p. > 300°C. **UV/vis** (THF) λ_{max} (log ε) 396 (4.64), 416 (5.69), 549 (4.17). **¹H NMR** (300 MHz, CD₂Cl₂, 25°C): δ 9.88 (d, *J* = 4.8 Hz, 2H), 9.74 (s, 1H), 9.58 (d, *J* = 4.8 Hz, 2H), 9.37 (d, *J* = 4.6 Hz, 2H), 9.14 (d, *J* = 4.6 Hz, 2H), 4.87-4.78 (m, 4H), 2.55-2.42 (m, 4H), 1.93 (s, 12H), 1.90-1.77 (m, 4H), 1.62-1.49 (m, 4H), 1.47-1.26 (m, 16H), 0.94-0.86 (m, 6H). **¹³C NMR** (75 MHz, CD₂Cl₂, 25°C) δ 153.12, 150.36, 149.97, 148.03, 133.41, 132.03, 129.65, 128.83, 120.27, 106.17, 85.75, 39.58, 35.84, 32.53, 31.27, 30.32, 30.01, 25.84, 23.29, 14.47. **ESI HRMS** *m/z* 749.40949; calcd for C₄₄H₅₉BN₄O₂Zn (MH⁺) 749.40534.



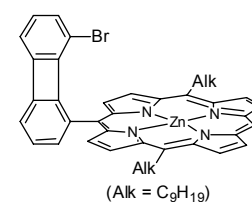
Zinc(II) 5-{8-[zinc(II)-10,20-dinonylporphyrin-5-yl]-biphenylene-1-yl}-10,20-dinonylporphyrin (4)

5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-10,20-dinonylporphyrin zinc(II) (0.05 g, 0.0665 mmol), 1,8-dibromobiphenylene (0.01 g, 0.0332 mmol), Cs₂CO₃ (0.043 g, 0.133 mmol), and Pd(PPh₃)₄ (0.0076 g, 0.0066 mmol) were dissolved in a mixture of dry DMF (2 mL) and dry toluene (4 mL). The solution was deoxygenated via bubbling Ar for 10 min and the resulting mixture was heated at 90 °C for 24 h under Ar. Allowed to cool, the mixture was quenched with water and extracted with CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄ and evaporated. Purification by column chromatography on silica gel, using hexanes-dichloromethane (2.5:1) supplied **4** as a brown crystalline solid (0.028 g, 60% yield), m.p. > 300°C. **UV/vis** (THF) λ_{max} (log ε) 406 (5.53), 450 (4.28), 560 (4.05), 599 (3.64). **¹H NMR** (300 MHz, d⁸-THF, 25°C): δ 9.25 (d, *J* = 5.9 Hz, 2H), 8.80 (d, *J* = 4.4 Hz, 4H), 8.65 (d, *J* = 4.6 Hz, 4H), 8.52 (d, *J* = 4.4 Hz, 4H), 8.25 (d, *J* = 4.6 Hz, 2H), 7.29-7.06 (m, 6H), 3.71-3.59 (m, 8H), 2.04-1.91 (m, 8H), 1.63-1.48 (m, 8H), 1.46-1.24 (m, 40H), 0.96-0.85 (m, 12H). **¹³C NMR** (75 MHz, d⁸-THF, 25°C): δ 155.43, 151.63, 149.08, 148.61, 148.27, 147.58, 137.40, 135.93, 131.21, 130.70, 127.72, 127.01, 126.90, 118.18, 116.61, 114.43, 104.70, 39.93, 35.30, 33.08, 31.57, 30.91, 23.76, 14.64. **ESI HRMS** *m/z* 1396.6560; calcd for C₈₈H₁₀₀N₄Zn₂ (M⁺) 1396.6648.



Zinc(II) 5-(8-Bromobiphenylene-1-yl)-10,20-dinonylporphyrin (5)

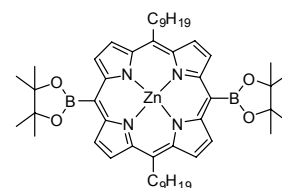
5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-10,20-dinonylporphyrin zinc(II) **3** (0.14 g, 0.186 mmol), 1,8-dibromobiphenylene (0.115 g, 0.372 mmol), Cs₂CO₃ (0.091 g, 0.28 mmol), and Pd(PPh₃)₄ (0.021 g, 0.0182 mmol) were dissolved in a mixture of dry DMF (4 mL) and dry toluene (8 mL). The solution was deoxygenated via bubbling Ar for 10 min and the resulting mixture was heated at 90 °C for 15 h under Ar. Allowed to cool, the mixture was quenched with water and extracted with CH₂Cl₂. The organic



layer was dried over anhydrous Na_2SO_4 and evaporated. Purification by column chromatography on silica gel, using hexanes-dichloromethane (3:1) supplied **5** as a purple crystalline solid (0.149 g, 94% yield), m.p. > 300°C. **UV/vis** (THF) λ_{max} (log ϵ) 422 (5.43), 554 (4.10), 598 (3.47). **^1H NMR** (300 MHz, CD_2Cl_2 , 25°C): δ 9.56 (s, 1H), 9.44 (d, $J = 4.8$ Hz, 2H), 9.24 (d, $J = 4.5$ Hz, 2H), 9.19 (d, $J = 4.7$ Hz, 2H), 8.97 (d, $J = 4.6$ Hz, 2H), 7.66 (d, $J = 8.2$ Hz, 1H), 7.23-7.15 (m, 1H), 7.03 (d, $J = 6.9$ Hz, 1H), 6.66 (d, $J = 6.7$ Hz, 1H), 6.43 (dd, $J_1 = 8.5$ Hz, $J_2 = 6.8$ Hz, 1H), 6.19 (d, $J = 8.6$ Hz, 1H), 4.75-4.65 (m, 4H), 2.44-2.30 (m, 4H), 1.76-1.64 (m, 4H), 1.48-1.36 (m, 4H), 1.31-1.11 (m, 16H), 0.83-0.73 (m, 6H). **^{13}C NMR** (75 MHz, CD_2Cl_2 , 25°C): δ 136.36, 134.48, 132.26, 132.11, 132.06, 130.55, 129.65, 129.46, 127.95, 120.79, 117.46, 116.73, 116.09, 110.73, 105.21, 39.65, 35.92, 32.52, 31.25, 30.34, 30.31, 29.99, 23.28, 14.47. **ESI HRMS** m/z 852.28104; calcd for $\text{C}_{50}\text{H}_{53}\text{BrN}_4\text{Zn}$ (M^+) 852.27396.

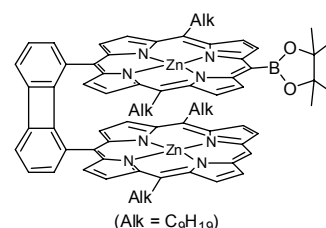
Zinc(II) 5,15-di-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10,20-dinonylporphyrin (**6**)

Obtained by the procedure described for **3**. Purple microcrystalline solid (72%), m.p. > 300°C. **UV/vis** (THF) λ_{max} (log ϵ) 400 (4.60), 420 (5.62), 534 (4.08), 573 (3.75), 602 (3.75). **^1H NMR** (300 MHz, CD_2Cl_2 , 25°C): δ 9.93 (d, $J = 4.8$ Hz, 4H), 9.70 (d, $J = 4.8$ Hz, 4H), 5.15-5.01 (m, 4H), 2.65-2.50 (m, 4H), 1.92-1.79 (m, 28H), 1.64-1.49 (m, 4H), 1.43-1.26 (m, 16H), 0.95-0.83 (m, 6H). **^{13}C NMR** (75 MHz, CD_2Cl_2 , 25°C): δ 152.83, 150.70, 133.85, 129.66, 120.97, 85.83, 39.65, 36.29, 32.50, 31.23, 30.36, 30.28, 29.98, 25.76, 23.27, 14.45. **ESI HRMS** m/z 875.48706; calcd for $\text{C}_{50}\text{H}_{70}\text{B}_2\text{N}_4\text{O}_4\text{Zn}$ (M^+) 875.49100.



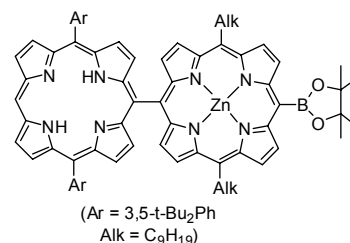
Zinc(II) 5-{8-[zinc(II)-10,20-dinonylporphyrin-5-yl]-biphenylene-1-yl}-15-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10,20-dinonylporphyrin (**7**)

Porphyrin **5** (0.07 g, 0.0818 mmol), 5,15-di-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10,20-dinonylporphyrin zinc (II) **6** (0.08 g, 0.0911 mmol), $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (0.005 g, 0.0158 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (0.002 g, 0.0017 mmol) were dissolved in dry DMF (5 mL). The solution was deoxygenated via bubbling Ar for 10 min and the resulting mixture was heated at 100 °C for 24 h under Ar. Allowed to cool, the mixture was quenched with water and extracted with CH_2Cl_2 . The organic layer was dried over anhydrous Na_2SO_4 and evaporated. Purification by column chromatography on silica gel, using hexanes-dichloromethane (content of CH_2Cl_2 was gradually increased from 30 to 50 vol%), supplied **7** as a purple crystalline solid (0.06 g, 48% yield), m.p. > 300°C. **UV/vis** (THF) λ_{max} (log ϵ) 407 (5.56), 561 (4.04), 602 (3.73). **^1H NMR** (300 MHz, CD_2Cl_2 , 25°C): δ 9.42 (d, $J = 4.7$ Hz, 2H), 9.23 (s, 1H), 8.84 (d, $J = 4.7$ Hz, 2H), 8.80 (d, $J = 4.5$ Hz, 2H), 8.71 (dd, $J_1 = 4.7$ Hz, $J_2 = 2.9$ Hz, 4H), 8.58 (t, $J = 4.7$ Hz, 2H), 7.36-7.10 (m, 6H), 4.00-3.78 (m, 8H), 2.14 (s, 12H), 2.07-1.93 (m, 8H), 1.72-1.59 (m, 8H), 1.52-1.24 (m, 40H), 0.94-0.85 (12H). **^{13}C NMR** (75 MHz, CD_2Cl_2 , 25°C): δ 155.52, 154.84, 151.91, 151.14, 151.11, 148.51, 148.41, 148.29, 148.25, 147.48, 146.81, 146.37, 136.50, 136.00, 134.42, 134.09, 132.62, 131.59, 130.98, 130.82, 127.94, 127.39, 127.29, 127.23, 126.73, 118.87, 118.61, 116.80, 115.68, 114.78, 104.96, 85.57, 39.26, 35.60, 35.48, 32.53, 31.24, 30.24, 30.01, 26.06, 23.30, 14.48. **ESI HRMS** m/z 1521.7373; calcd for $\text{C}_{94}\text{H}_{111}\text{BN}_8\text{O}_2\text{Zn}_2$ (M^+) 1521.7537.



Zinc(II) 5-[10,20-Bis-(3,5-di-tert-butylphenyl)porphyrin-5-yl]-15-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10,20-dinonylporphyrin (**9**)

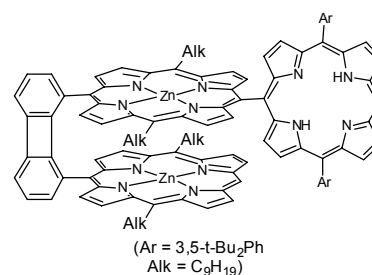
5-Bromo-10,20-bis(3,5-di-tert-butylphenyl)porphyrin (0.05 g, 0.0654 mmol), 5,15-di-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10,20-dinonylporphyrin zinc (II) (0.065 g, 0.0741 mmol), Cs_2CO_3 (0.042 g, 0.129 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (0.0075 g, 0.0157 mmol) were dissolved in a mixture of dry DMF (2 mL) and dry toluene (4 mL). The solution was deoxygenated via bubbling Ar for 10 min and the resulting mixture



was heated at 90 °C for 16 h under Ar. Allowed to cool, the mixture was quenched with water and extracted with CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄ and evaporated. Purification by column chromatography on silica gel, using hexanes-dichloromethane (2:1) supplied **9** as a brown crystalline solid (0.06 g, 64% yield), m.p. > 300°C. **UV/vis** (THF) λ_{\max} (log ϵ) 416 (5.64), 449 (5.45), 513 (4.81), 563 (4.77), 594 (4.42), 609 (4.34). **¹H NMR** (300 MHz, d⁸-THF, 25°C): δ 10.43 (s, 1H), 10.00 (d, J = 4.8 Hz, 2H), 9.69 (d, J = 4.8 Hz, 2H), 9.48 (d, J = 4.7 Hz, 2H), 9.25 (d, J = 4.7 Hz, 2H), 9.02 (d, J = 4.6 Hz, 2H), 8.57 (d, J = 4.8 Hz, 2H), 8.18 (d, J = 1.8 Hz, 4H), 8.02 (dd, J_1 = 4.8 Hz, J_2 = 2.5 Hz, 4H), 7.82 (t, J = 1.8 Hz, 2H), 5.11-5.00 (m, 4H), 2.62-2.51 (m, 4H), 1.92 (s, 12H), 1.87-1.76 (m, 4H), 1.48 (s, 36H), 1.38-1.20 (m, 20H), 0.84-0.77 (m, 6H). **¹³C NMR** (75 MHz, d⁸-THF, 25°C): δ 154.64, 154.50, 151.53, 150.92, 149.98, 142.25, 134.97, 134.36, 130.97, 130.66, 129.66, 128.95, 122.49, 122.09, 121.66, 121.03, 119.85, 106.22, 85.73, 40.39, 36.56, 35.85, 32.96, 32.14, 31.62, 30.93, 30.80, 30.47, 23.66, 14.54. **ESI HRMS** m/z 1434.8189; calcd for C₉₂H₁₁₁BN₈O₂Zn (M⁺) 1434.8324.

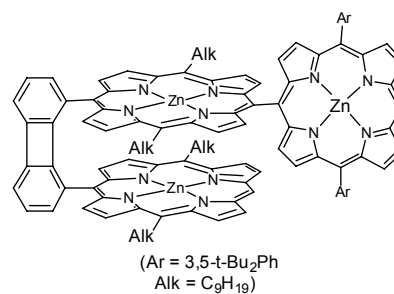
Zinc(II) 5-{8-[zinc(II)-10,20-dinonylporphyrin-5-yl]-biphenylene-1-yl}-[10,20-bis-(3,5-di-tert-butyl-phenyl)-porphyrin-5-yl]-10,20-dinonylporphyrin (1)

Porphyrin **7** (0.042 g, 0.0275 mmol), 5-bromo-10,20-bis(3,5-di-tert-butylphenyl)porphyrin (0.0105 g, 0.0137 mmol), Cs₂CO₃ (0.018 g, 0.0552 mmol) and Pd(PPh₃)₄ (0.003 g, 0.0026 mmol) were dissolved in a mixture of dry DMF (2 mL) and dry toluene (4 mL). The solution was deoxygenated by bubbling Ar for 10 min and the resulting mixture was heated at 100 °C for 7 h under Ar. Allowed to cool, the mixture was quenched with water and extracted with CH₂Cl₂. Separation of the target product from starting materials and by-products was performed by column chromatography on silica gel, using hexanes-dichloromethane (1:3), followed by preparative size exclusion chromatography (BioRad Bio-Beads SX-1 packed in CH₂Cl₂ in a 4 × 50 cm gravity-flow column; flow rate 4 mL min⁻¹). Brown crystalline solid (0.014 g, 50% yield), m.p. > 300°C. **UV/vis** (THF) λ_{\max} (log ϵ) 414 (5.61), 421 (5.60), 514 (4.59), 557 (4.37), 591 (4.32), 648 (3.85). **¹H NMR** (300 MHz, CD₂Cl₂, 25°C): δ 10.69 (d, J = 4.7 Hz, 1H), 10.41 (s, 1H), 9.74 (d, J = 4.7 Hz, 1H), 9.59 (d, J = 4.8 Hz, 1H), 9.43 (d, J = 4.6 Hz, 1H), 9.32 (d, J = 4.8 Hz, 1H), 9.26 (d, J = 4.7 Hz, 2H), 9.18 (s, 1H), 8.97 (d, J = 4.6 Hz, 1H), 8.84 (d, J = 4.8 Hz, 2H), 8.80 (d, J = 4.5 Hz, 2H), 8.67 (d, J = 4.5 Hz, 2H), 8.58 (d, J = 1.8 Hz, 2H), 8.53 (d, J = 4.8 Hz, 2H), 8.39 (d, J = 4.7 Hz, 2H), 8.05 (t, J = 1.8 Hz, 1H), 7.98 (d, J = 4.5 Hz, 2H), 7.95-7.89 (m, 2H), 7.84-7.79 (m, 4H), 7.58-7.40 (m, 3H), 7.23 (d, J = 6.4 Hz, 1H), 6.93 (dd, J_1 = 8.2 Hz, J_2 = 6.8 Hz, 1H), 6.54 (d, J = 7.9 Hz, 1H), 6.06 (d, J = 5.0 Hz, 1H), 3.97-3.70 (m, 4H), 3.61-3.40 (m, 2H), 3.29-3.09 (m, 2H), 2.09-1.83 (m, 8H), 1.75 (s, 18H), 1.70-1.55 (m, 8H), 1.53 (s, 18H), 1.48-1.20 (m, 42H), 0.90-0.79 (m, 12H), -2.32 (br. s, 2H). **ESI HRMS** m/z 2104.0605; calcd for C₁₃₆H₁₅₂N₁₂Zn₂ (M+Na⁺) 2104.0738.



Zinc(II) 5-{8-[zinc(II)-10,20-dinonylporphyrin-5-yl]-biphenylene-1-yl}-[zinc(II)-10,20-bis-(3,5-di-tert-butyl-phenyl)-porphyrin-5-yl]-10,20-dinonylporphyrin (1-Zn)

Porphyrin **1** (0.005 g, 0.0024 mmol) was dissolved in chloroform (4 mL) and the solution of Zn(OAc)₂·2H₂O (0.052 g, 0.24 mmol) in methanol (1 mL) was added under stirring. The mixture was stirred for 20 min at room temperature under Ar. Then the mixture was washed with water (1x10 mL), brine (1x10 mL), dried under Na₂SO₄ and evaporated in vacuum. The residue was dissolved in dichloromethane and filtered through a pad of silica gel (2x3 cm). Filtrate was evaporated to give the product as a brown crystalline solid (0.005 g, 97% yield), m.p. > 300°C. **UV/vis** (THF) λ_{\max} (log ϵ) 417 (5.51), 556 (4.56), 590 (4.31), 632 (3.88). **¹H NMR** (300 MHz, CD₂Cl₂, 25°C): δ 10.78 (d, J = 4.6 Hz, 1H), 10.45 (s, 1H), 9.82 (d, J = 4.6 Hz, 1H), 9.64 (d, J = 4.7 Hz, 1H), 9.49 (d, J = 4.5 Hz, 1H), 9.38 (d, J = 4.6 Hz, 1H), 9.27 (d, J = 4.7



Hz, 2H), 9.19 (s, 1H), 9.04 (d, $J = 4.5$ Hz, 1H), 8.85 (d, $J = 4.7$ Hz, 2H), 8.80 (d, $J = 4.5$ Hz, 2H), 8.67 (d, $J = 4.5$ Hz, 2H), 8.57 (d, $J = 1.8$ Hz, 2H), 8.52 (d, $J = 4.7$ Hz, 2H), 8.39 (d, $J = 4.7$ Hz, 2H), 8.04 (t, $J = 1.8$ Hz, 1H), 8.01 (d, $J = 4.8$ Hz, 1H), 7.98 (d, $J = 4.6$ Hz, 2H), 7.92 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.0$ Hz, 1H), 7.82 (d, $J = 1.9$ Hz, 2H), 7.79 (d, $J = 4.7$ Hz, 2H), 7.54 (t, $J = 1.8$ Hz, 1H), 7.45 (m, 2H), 7.22 (d, $J = 6.4$ Hz, 1H), 6.92 (dd, $J_1 = 8.2$ Hz, $J_2 = 6.8$ Hz, 1H), 6.54 (d, $J = 7.9$ Hz, 1H), 6.13 (d, $J = 4.8$ Hz, 1H), 3.97-3.70 (m, 4H), 3.60-3.42 (m, 2H), 3.29-3.11 (m, 2H), 2.1-1.84 (m, 8H), 1.75 (s, 18H), 1.68-1.54 (m, 8H), 1.51 (s, 18H), 1.47-1.18 (m, 42H), 0.89-0.80 (m, 12H). **ESI HRMS** m/z 1071.4910; calcd for $C_{136}H_{150}N_{12}Zn_3$ (M^{2+}) 1071.4985.

NMR and mass spectra

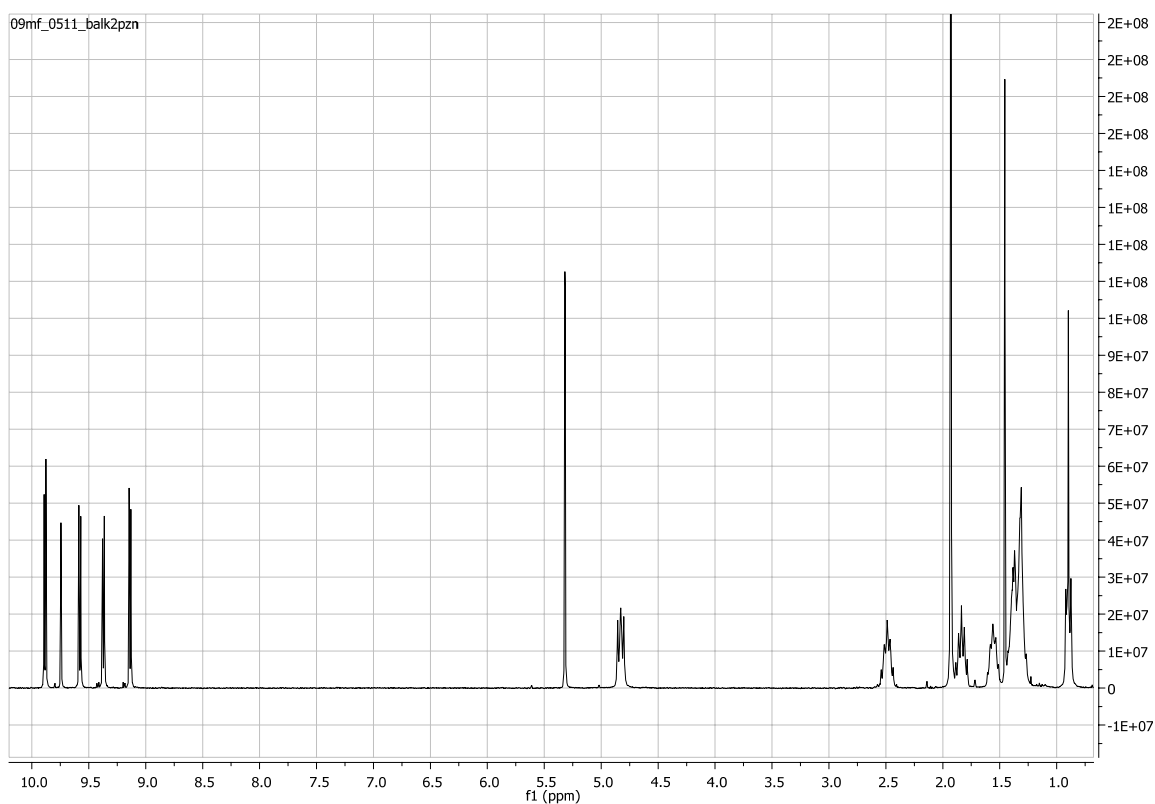


Figure S1. ^1H NMR spectrum of **3** (300 MHz, CD_2Cl_2 , 298 K).

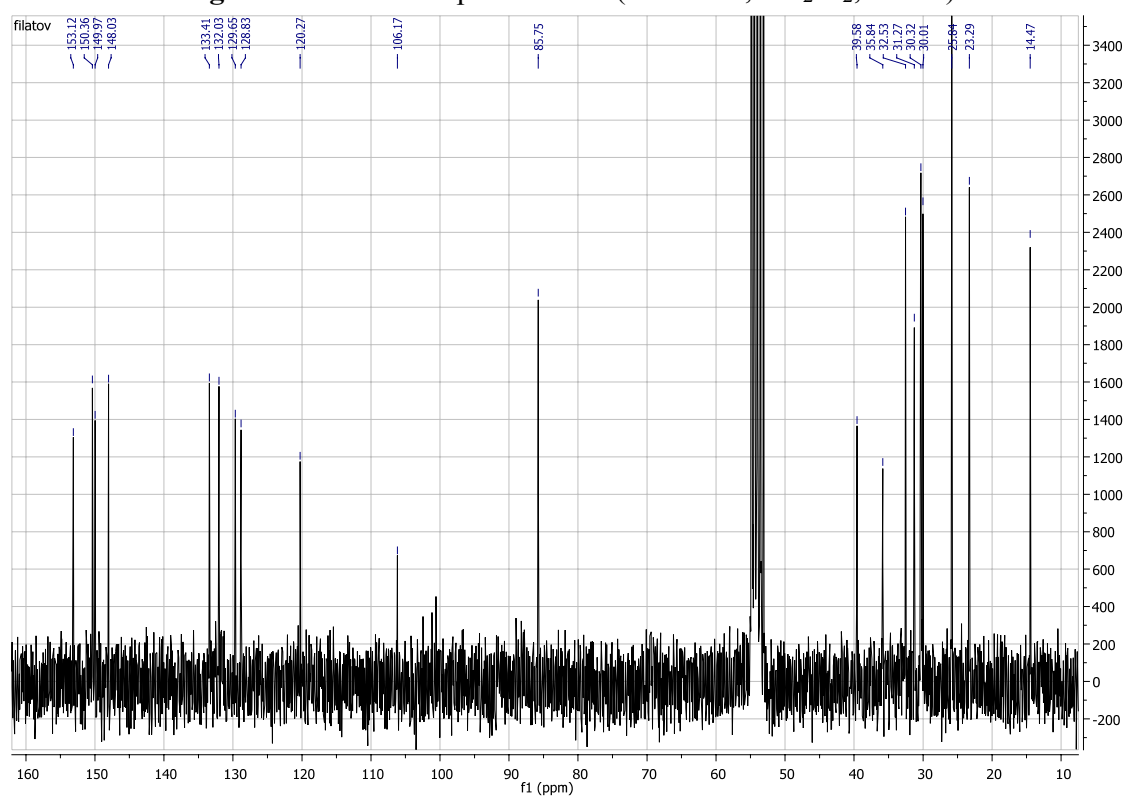


Figure S2. ^{13}C NMR spectrum of **3** (75 MHz, CDCl_3/TFA , 298 K).

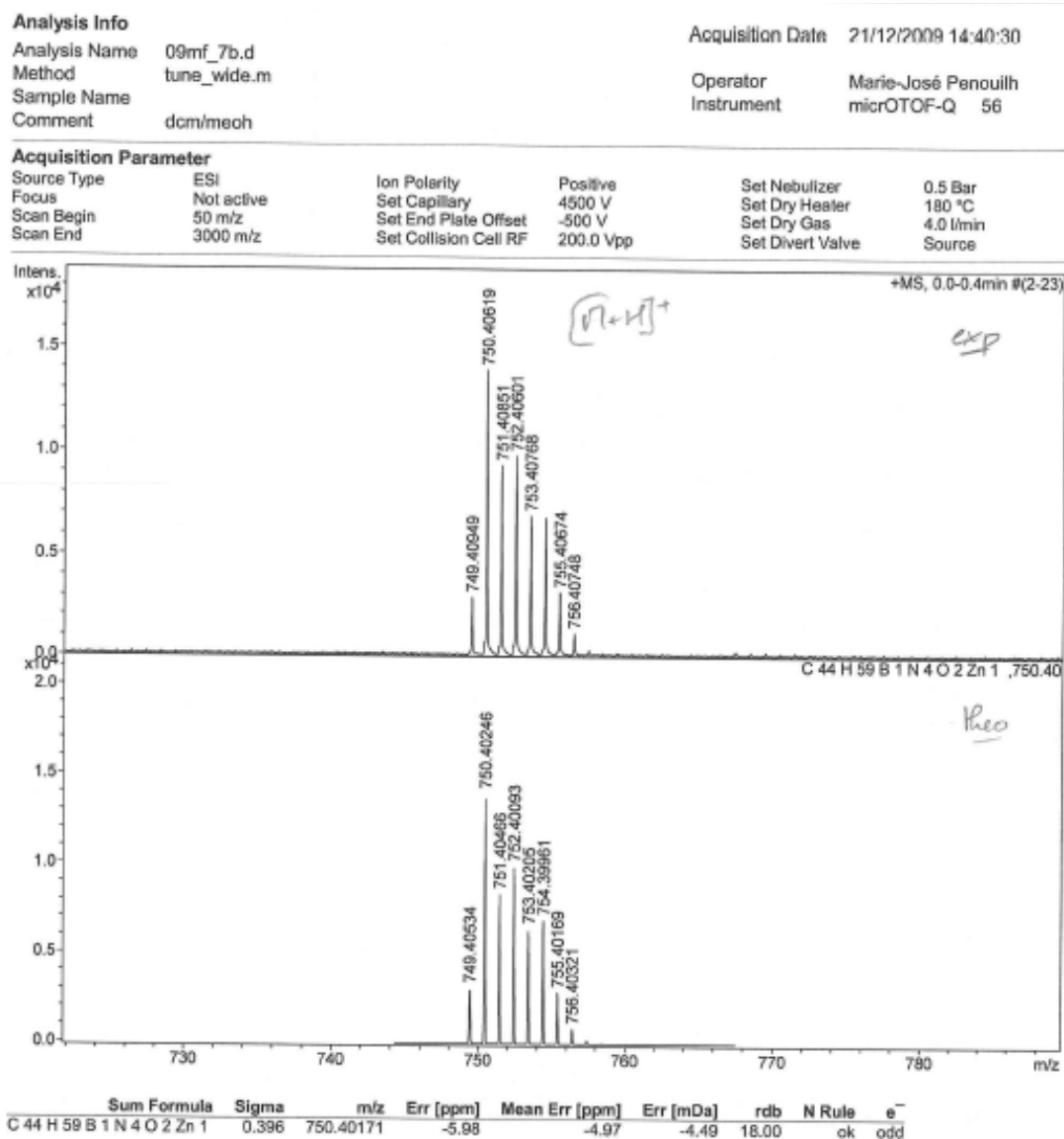


Figure S3. ESI HRMS spectrum of **3** (positive mode).

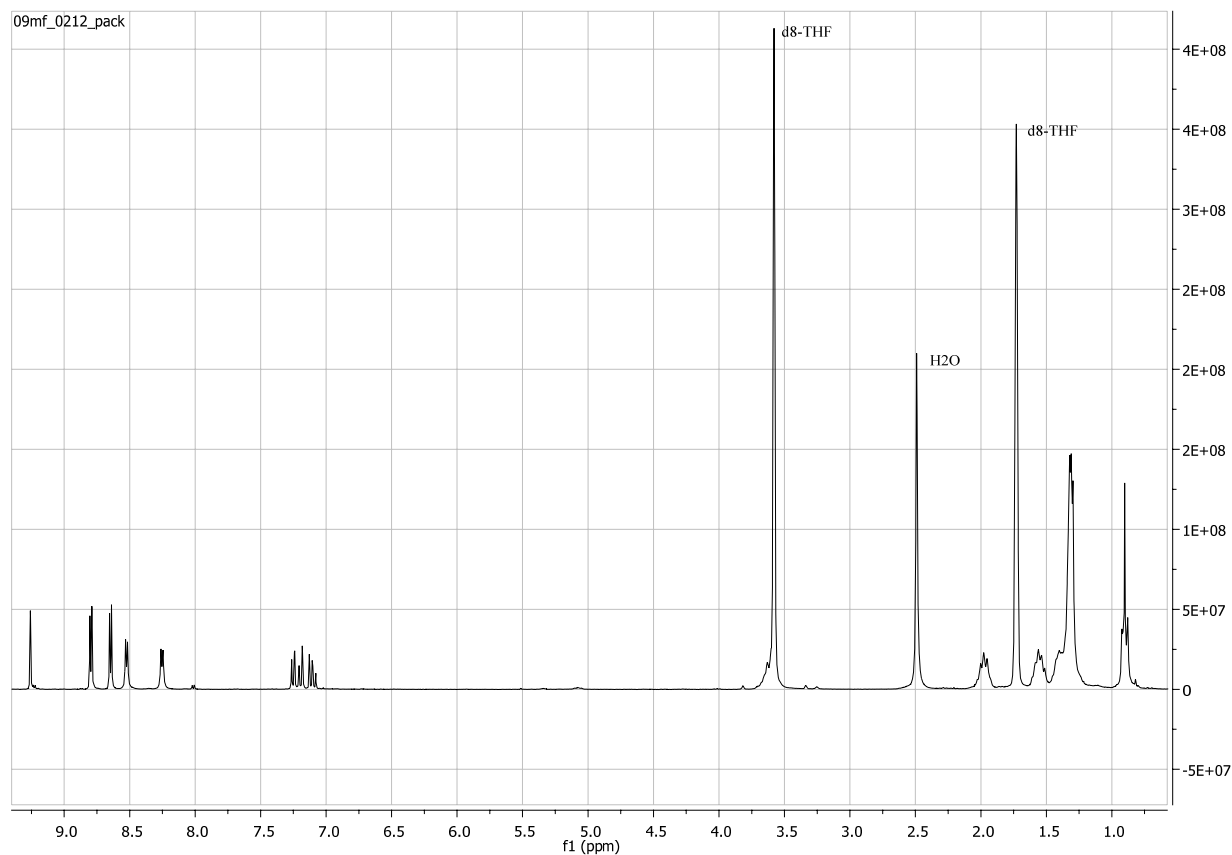


Figure S4. ^1H NMR spectrum of **4** (300 MHz, CD_2Cl_2 , 298 K).

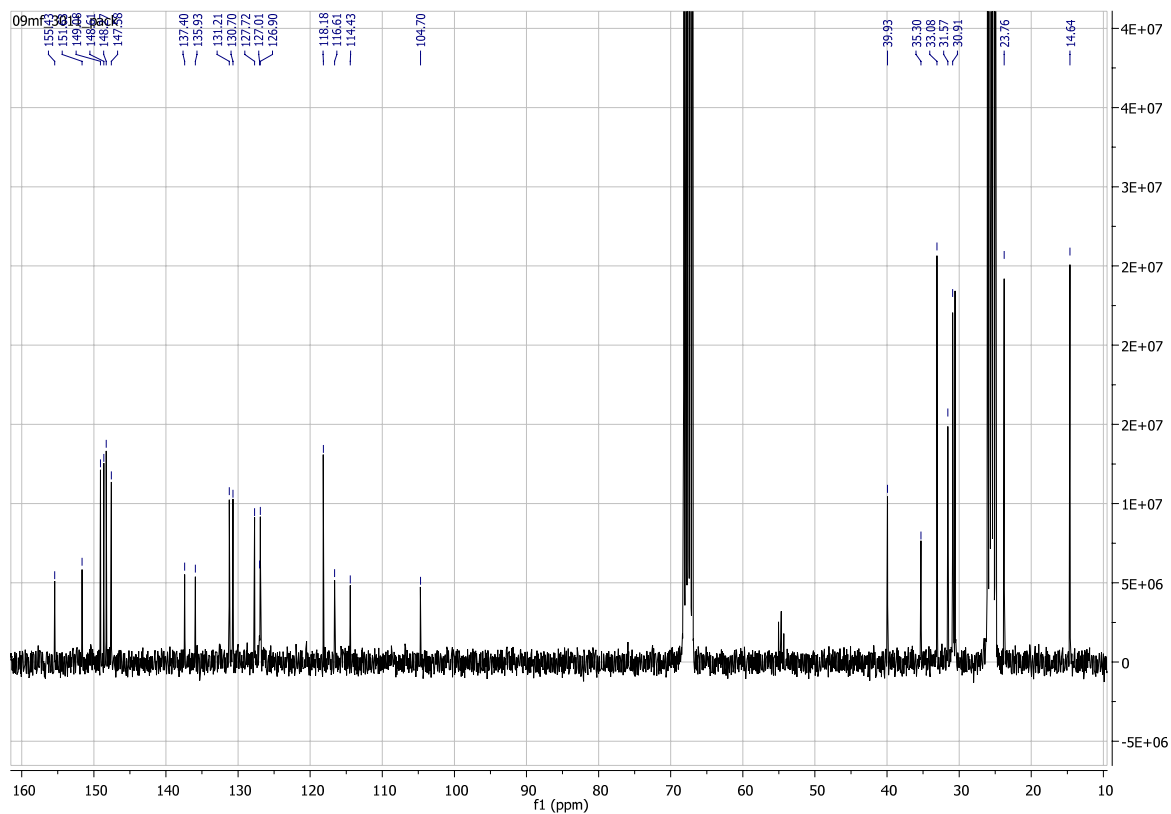


Figure S5. ^{13}C NMR spectrum of **4** (300 MHz, CD_2Cl_2 , 298 K).

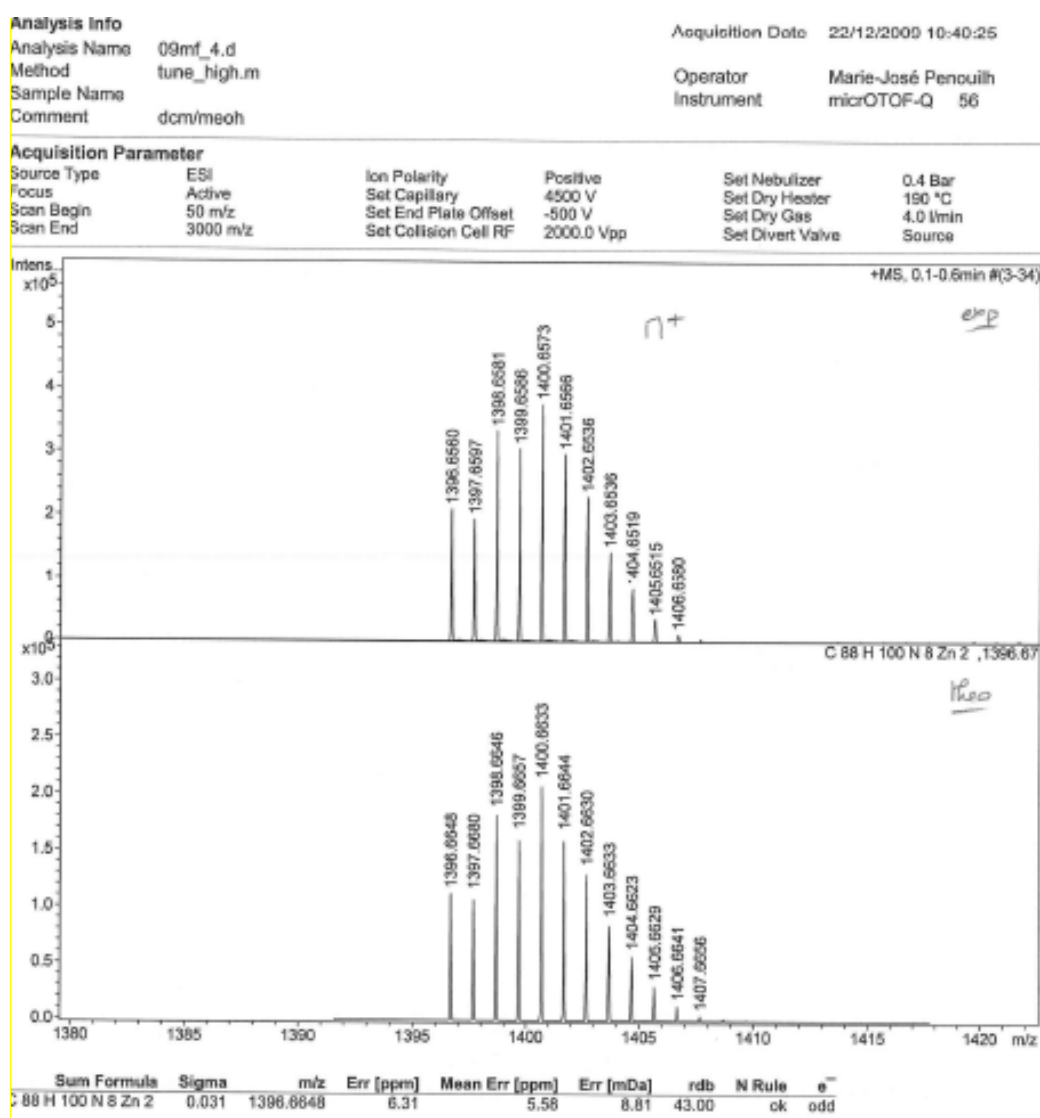


Figure S6. ESI HRMS spectrum of 4 (positive mode).

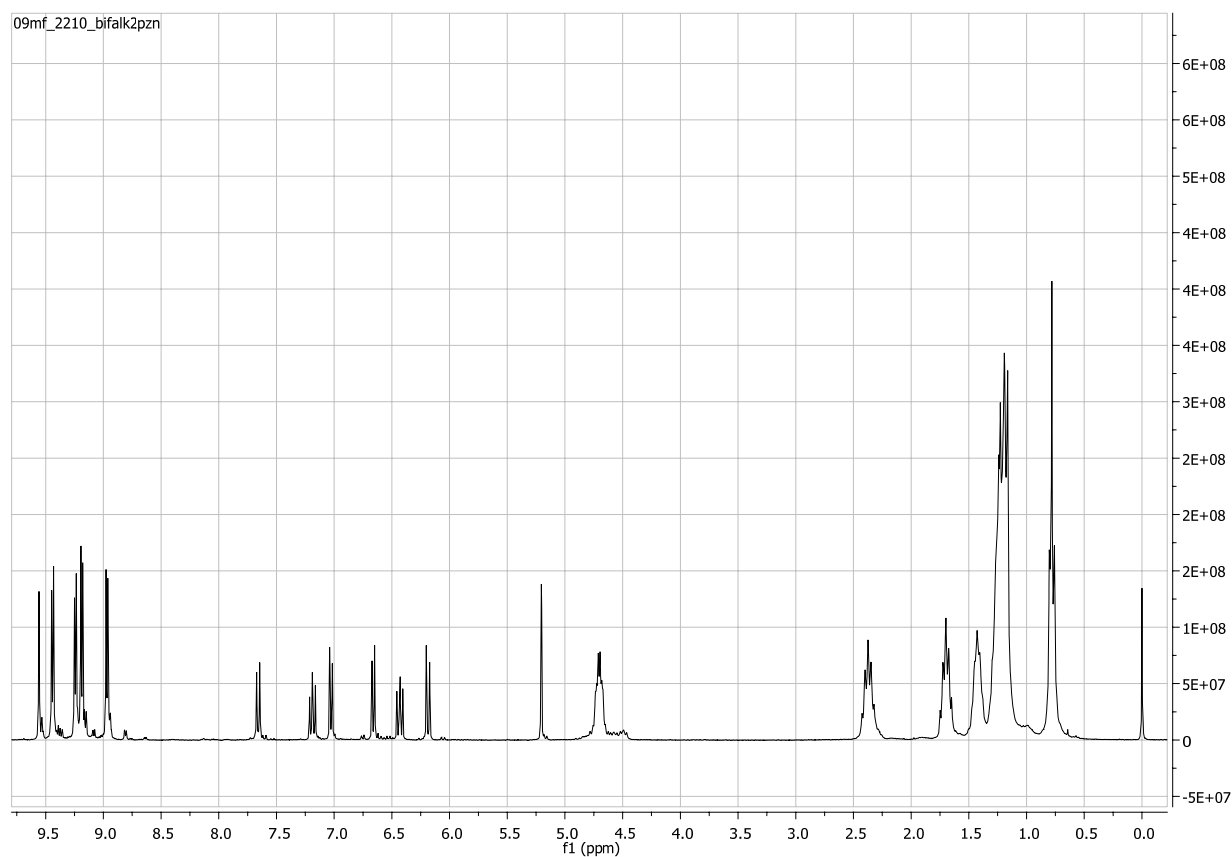


Figure S7. ^1H NMR spectrum of **5** (300 MHz, CD_2Cl_2 , 298 K).

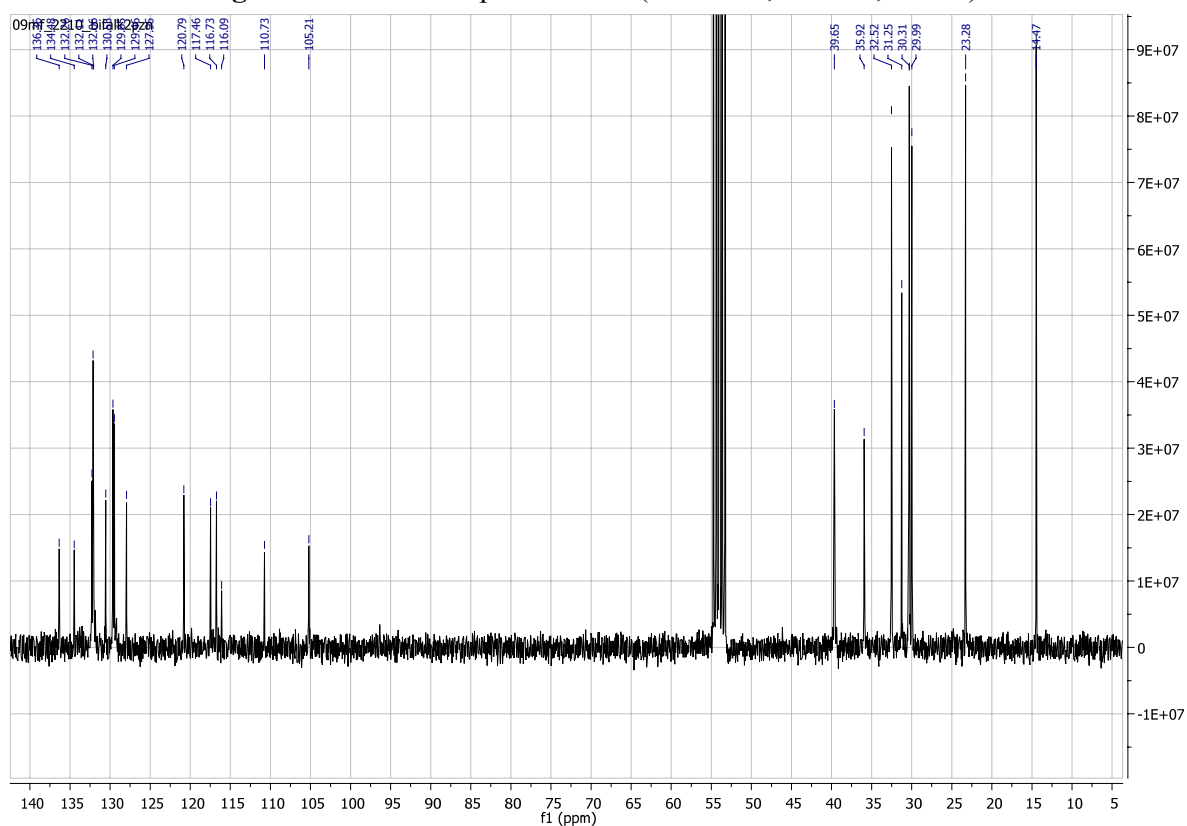


Figure S8. ^{13}C NMR spectrum of **5** (300 MHz, CD_2Cl_2 , 298 K).

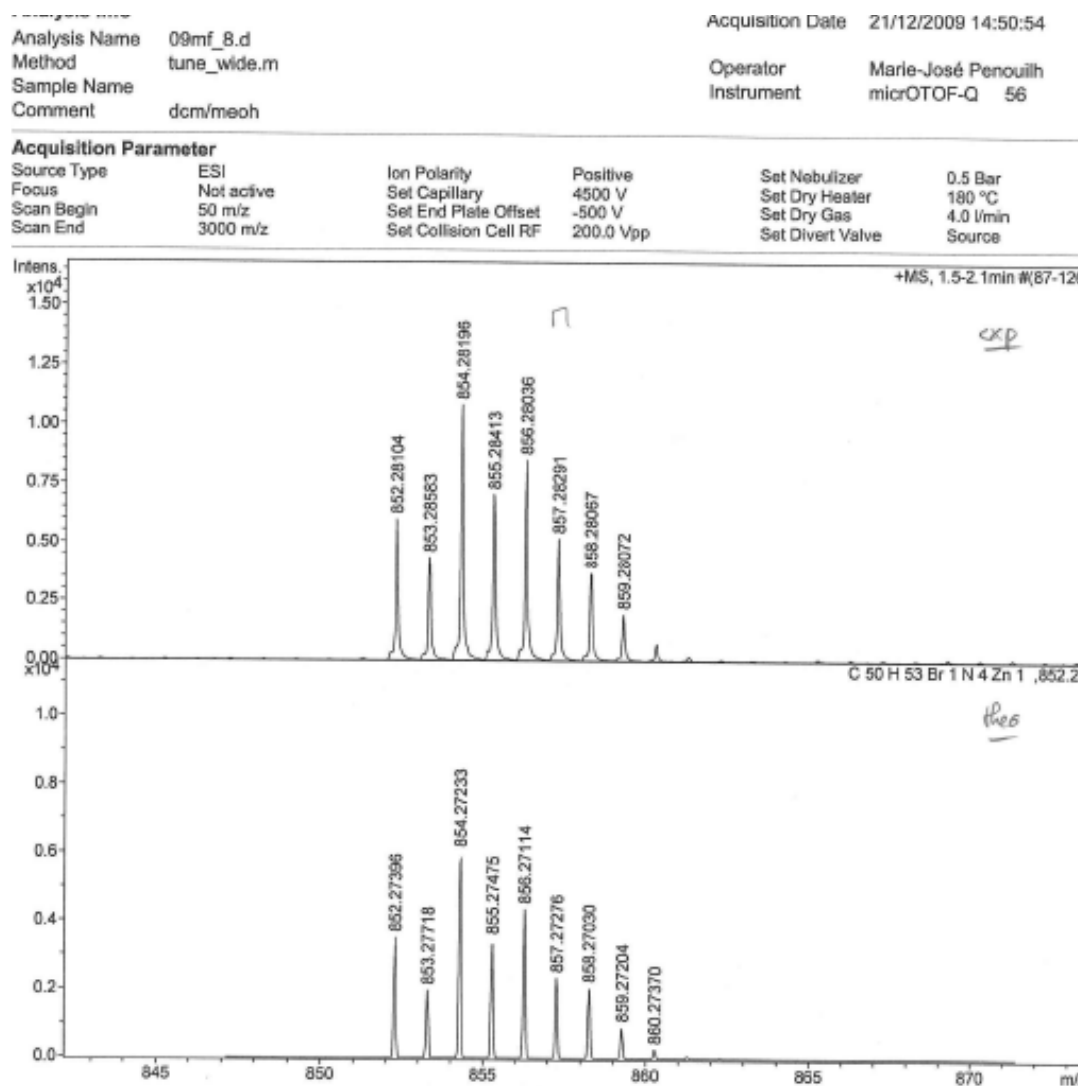


Figure S9. ESI HRMS spectrum of **5** (positive mode).

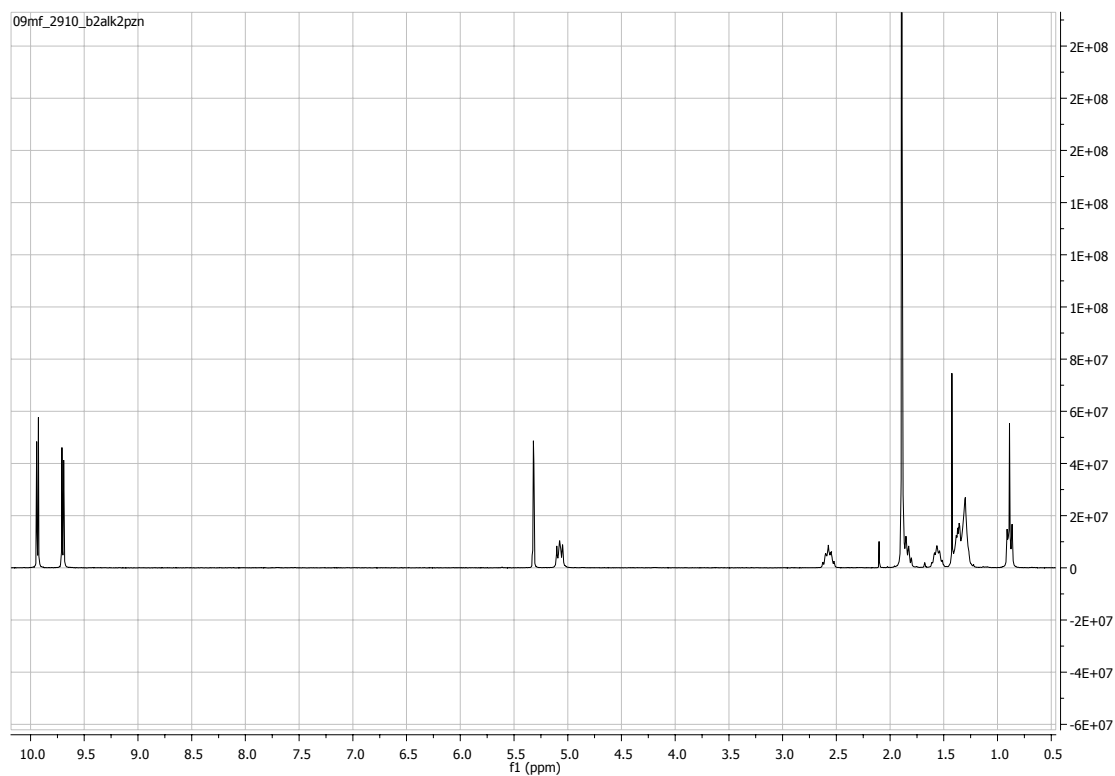


Figure S10. ^1H NMR spectrum of **6** (300 MHz, CD_2Cl_2 , 298 K).

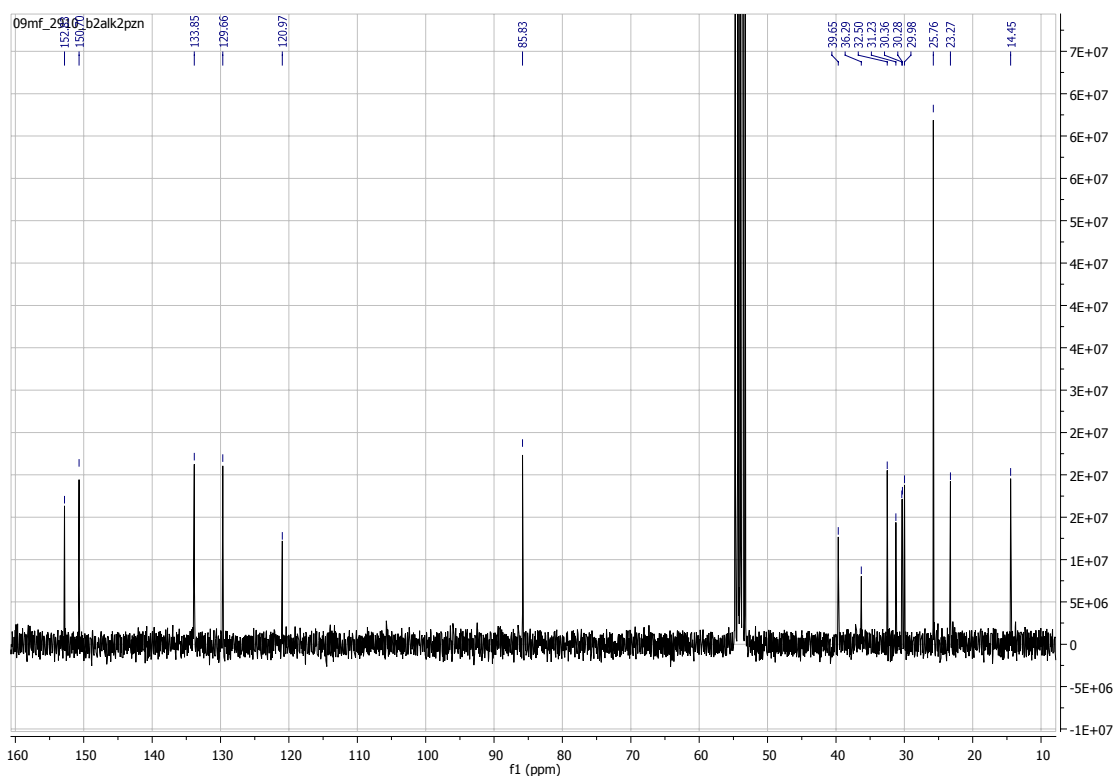


Figure S11. ^{13}C NMR spectrum of **6** (300 MHz, CD_2Cl_2 , 298 K).

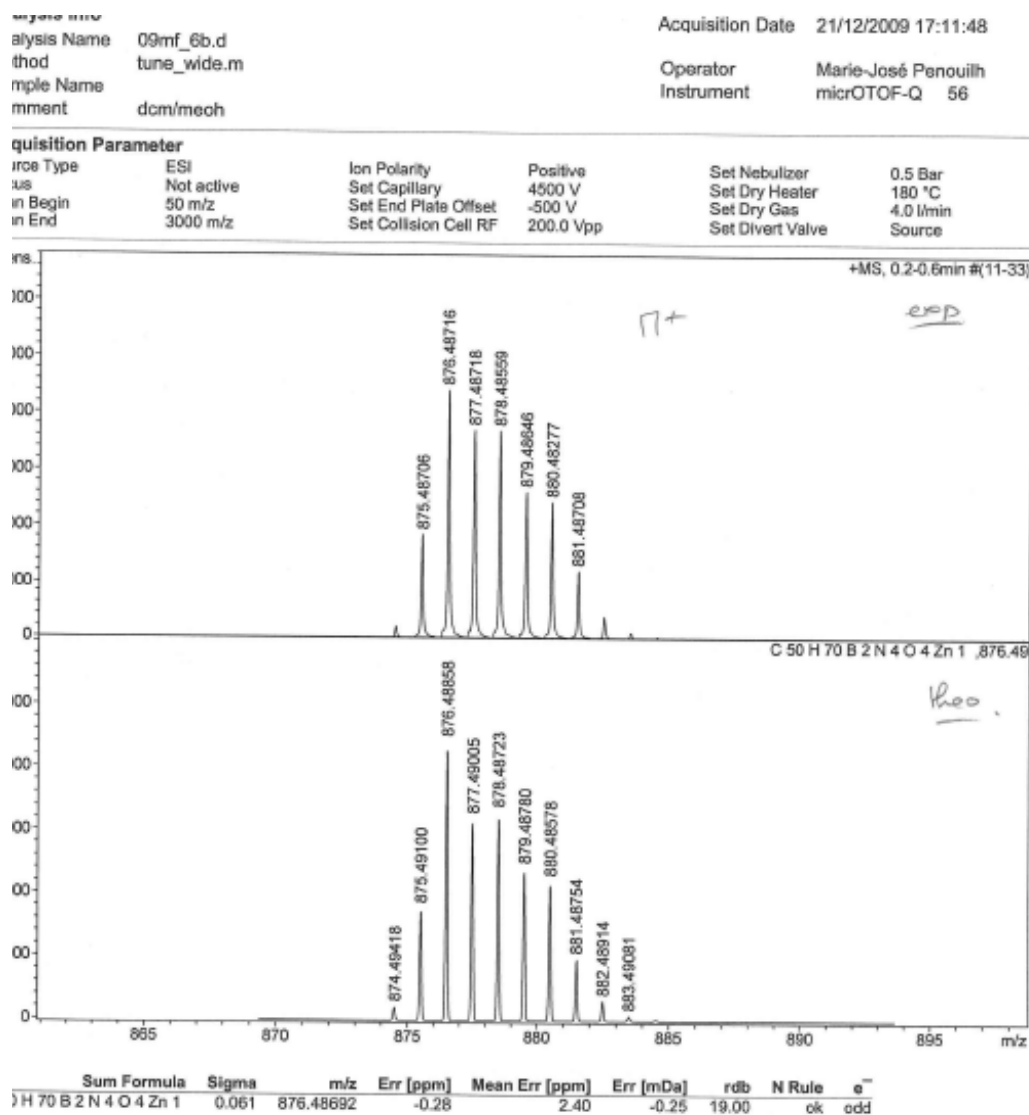


Figure S12. ESI HRMS spectrum of **6** (positive mode).

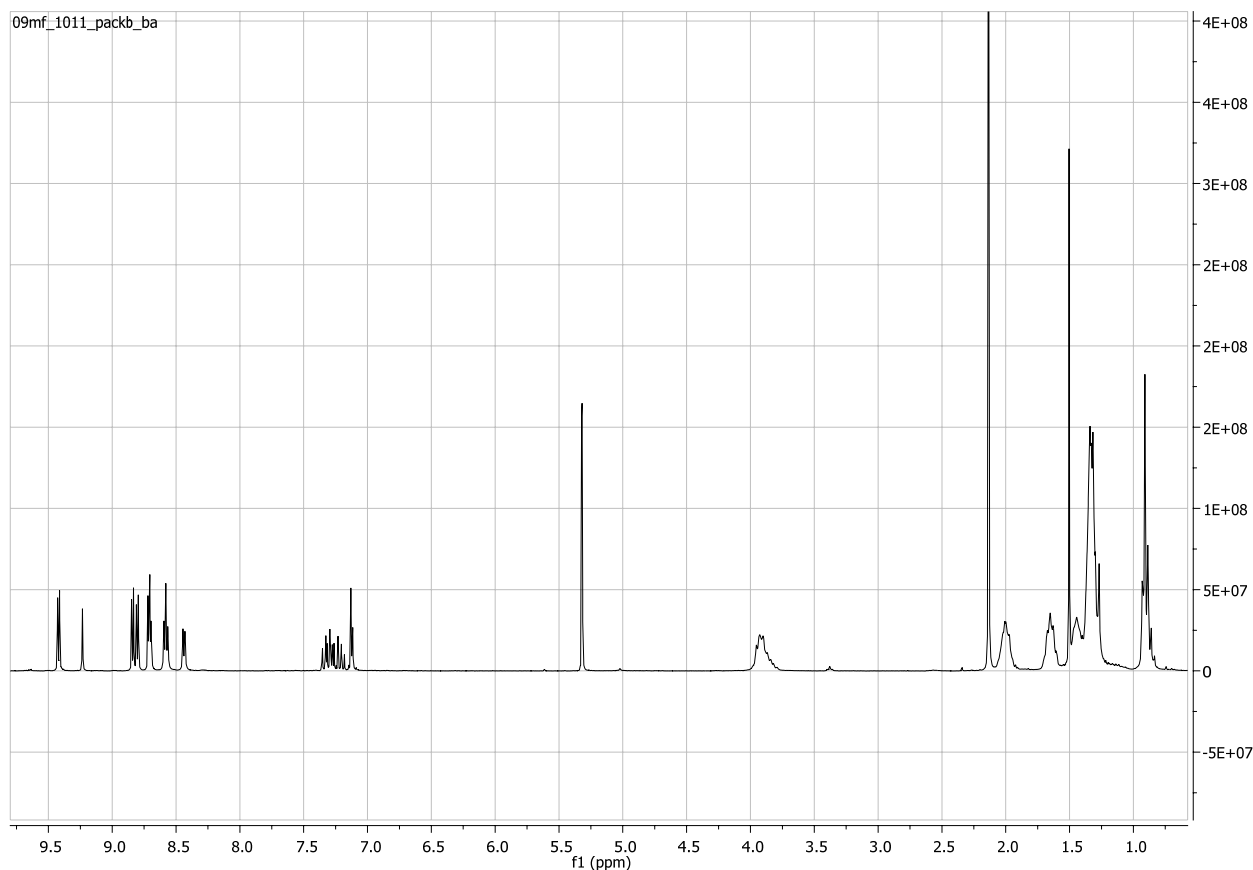


Figure S13. ^1H NMR spectrum of **7** (300 MHz, CD_2Cl_2 , 298 K).

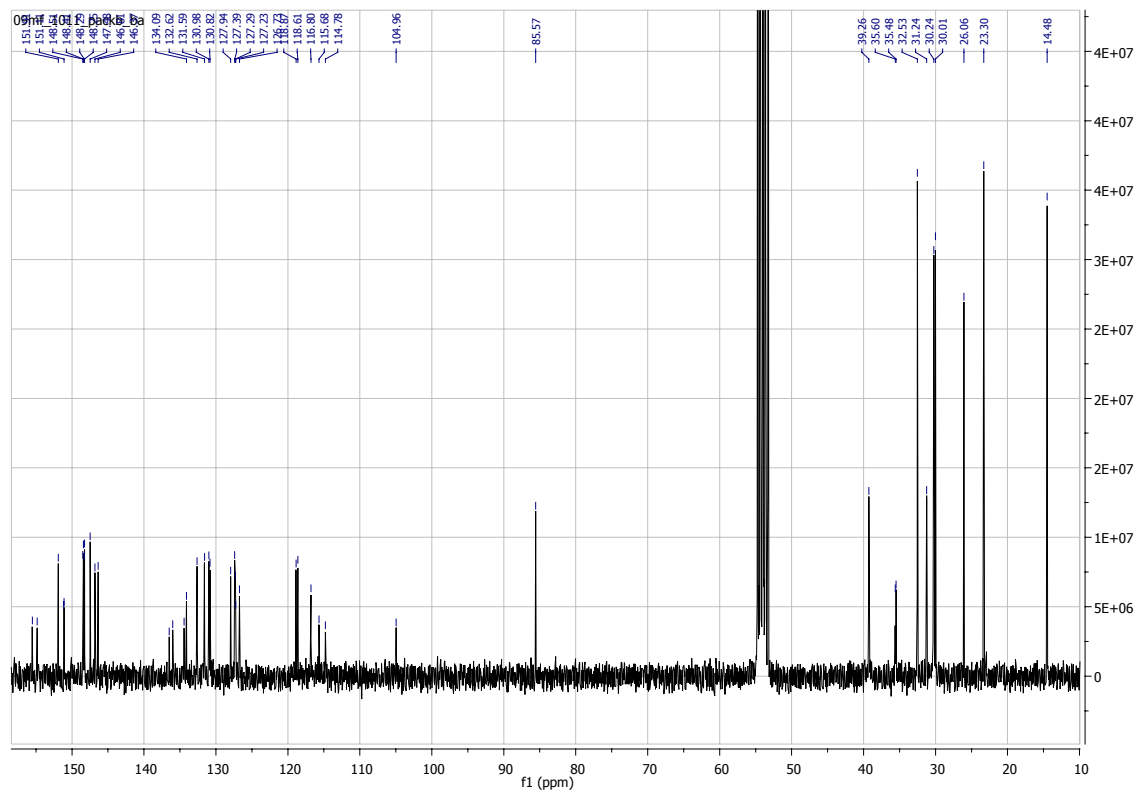


Figure S14. ^{13}C NMR spectrum of **7** (300 MHz, CD_2Cl_2 , 298 K).

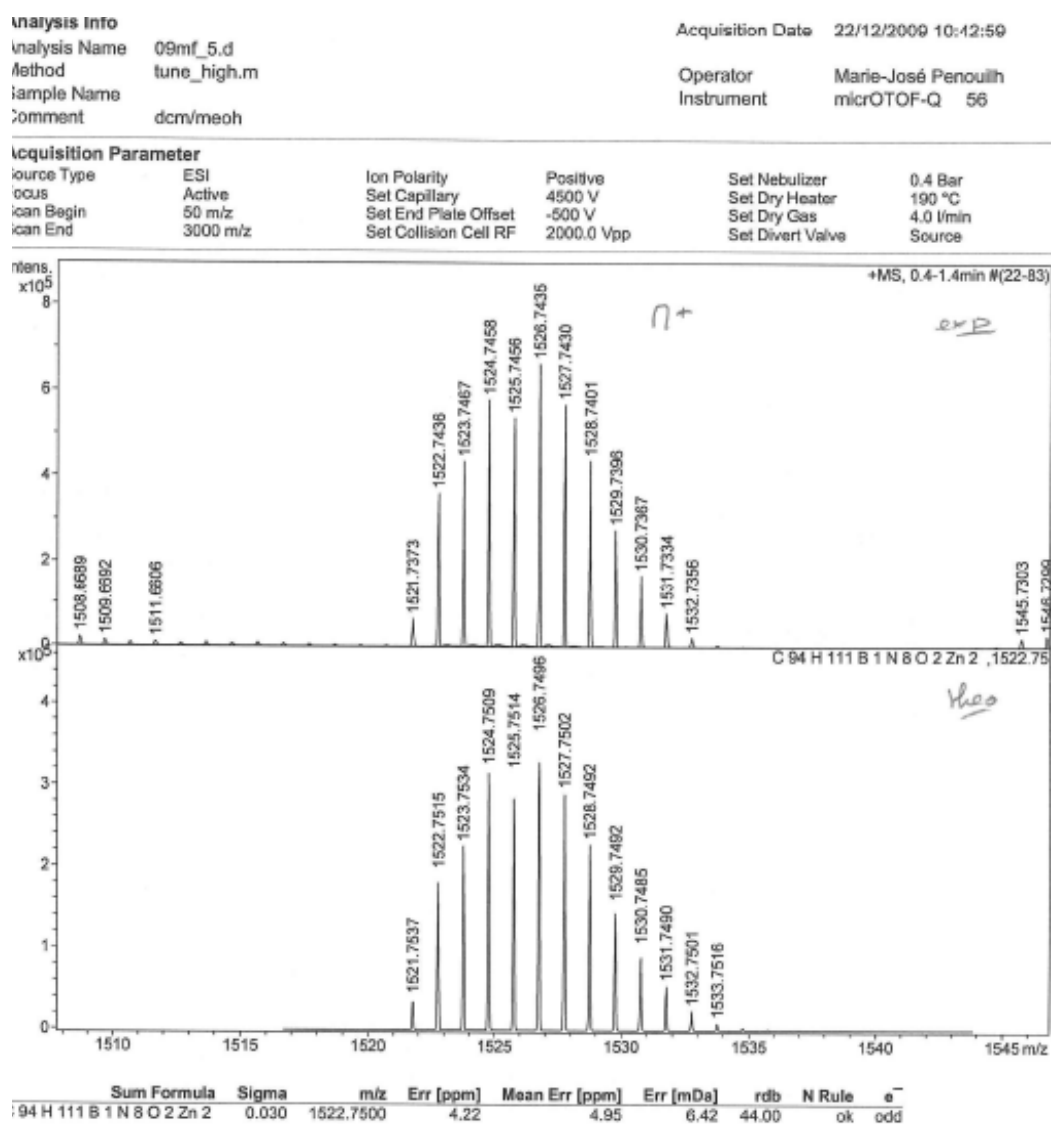


Figure S15. ESI HRMS spectrum of 7 (positive mode).

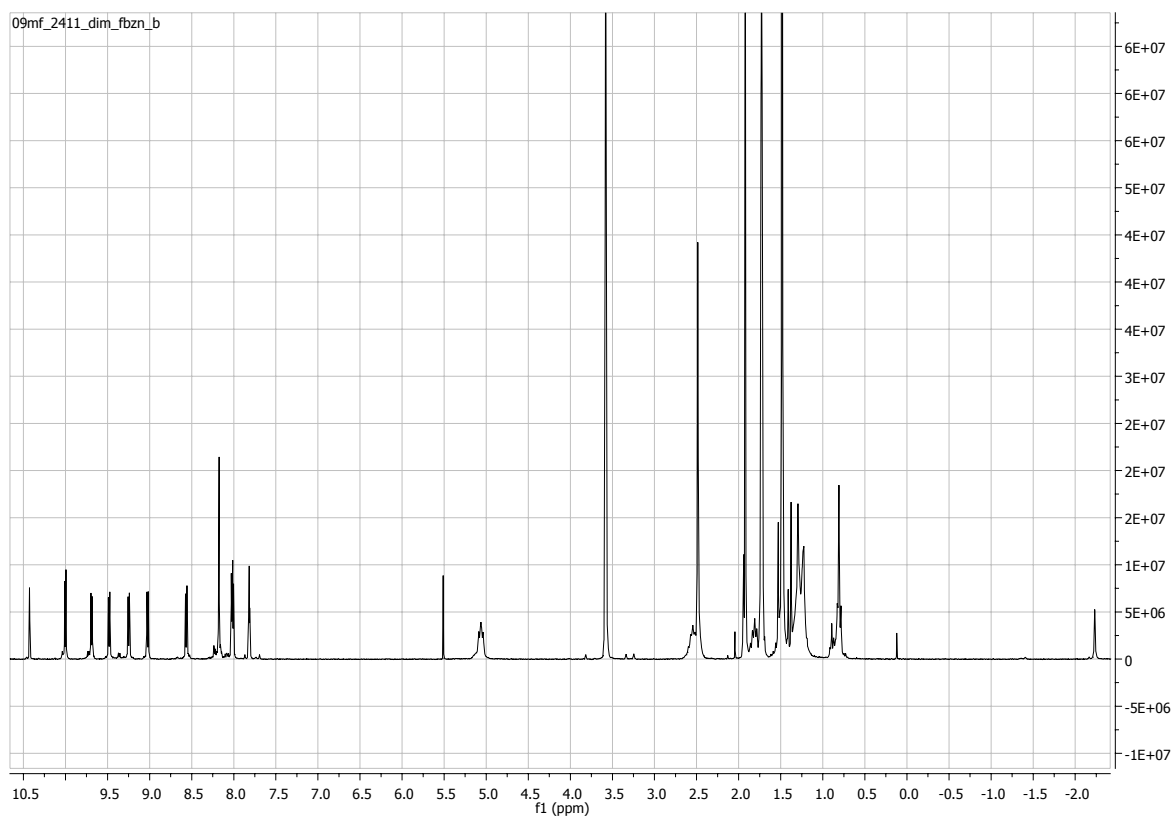


Figure S16. ^1H NMR spectrum of **9** (300 MHz, d^8 -THF, 298 K).

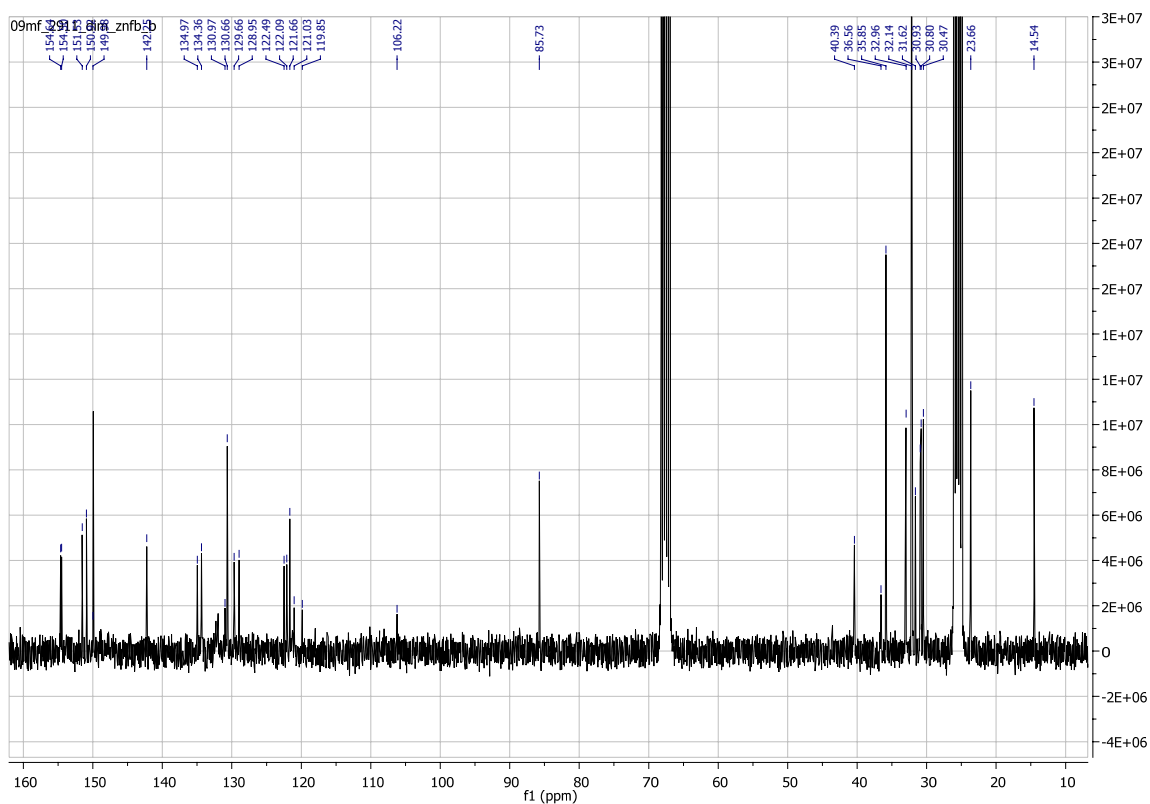


Figure S17. ^{13}C NMR spectrum of **9** (300 MHz, d^8 -THF, 298 K).

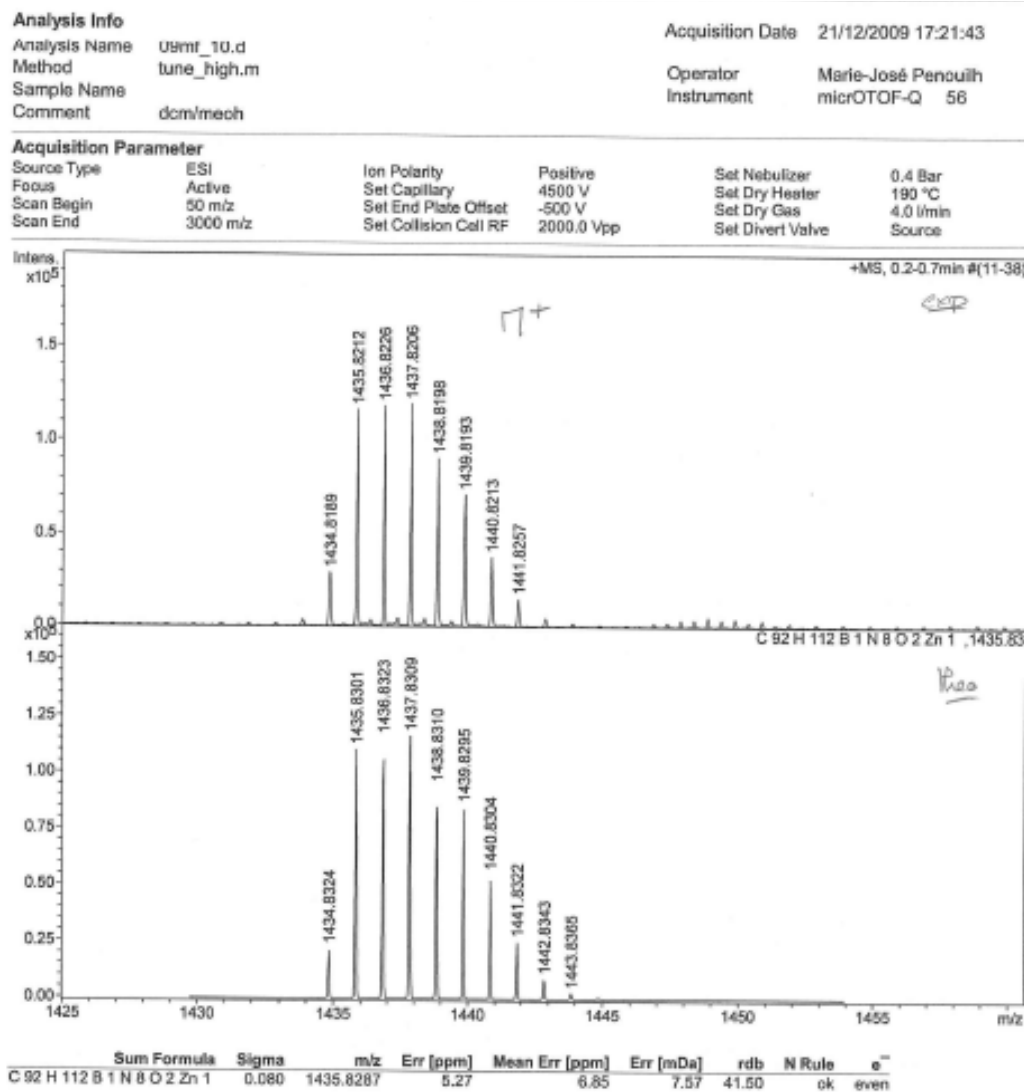


Figure S18. ESI HRMS spectrum of **9** (positive mode).

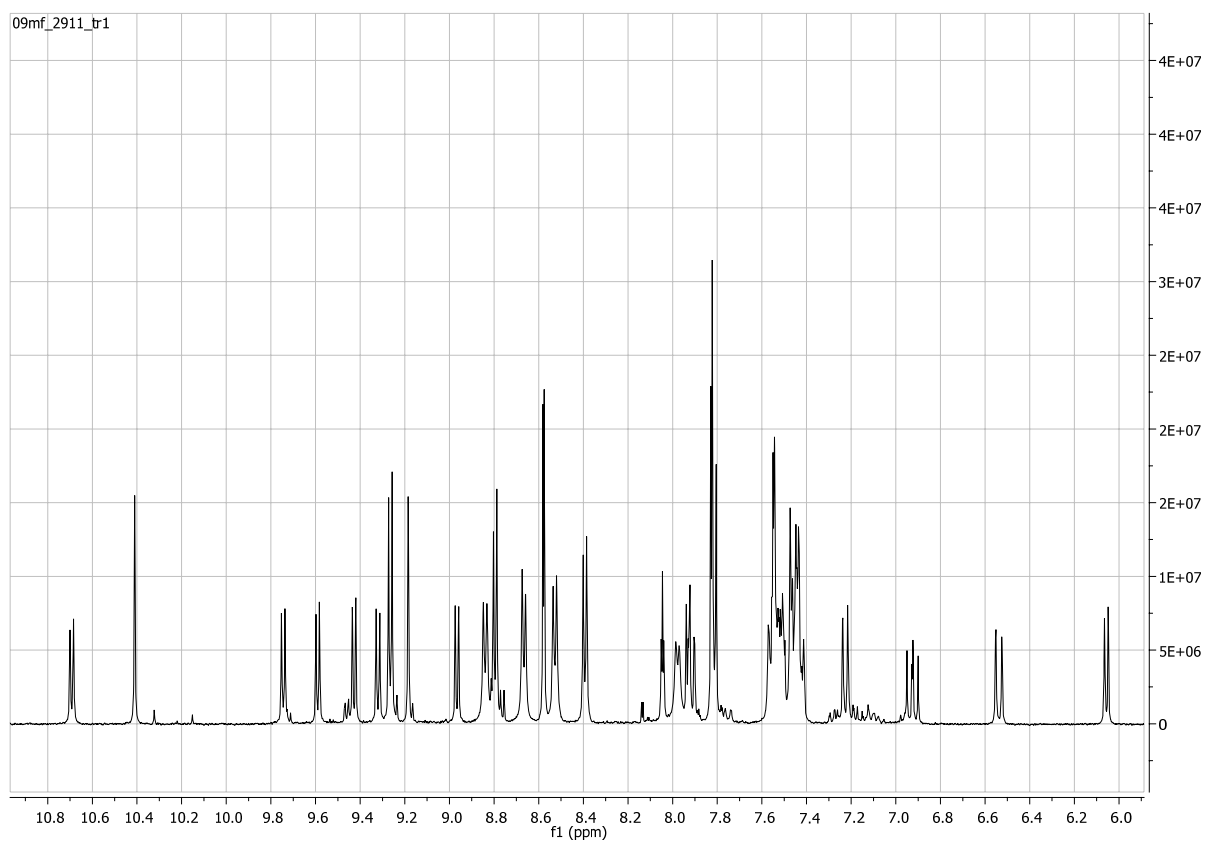
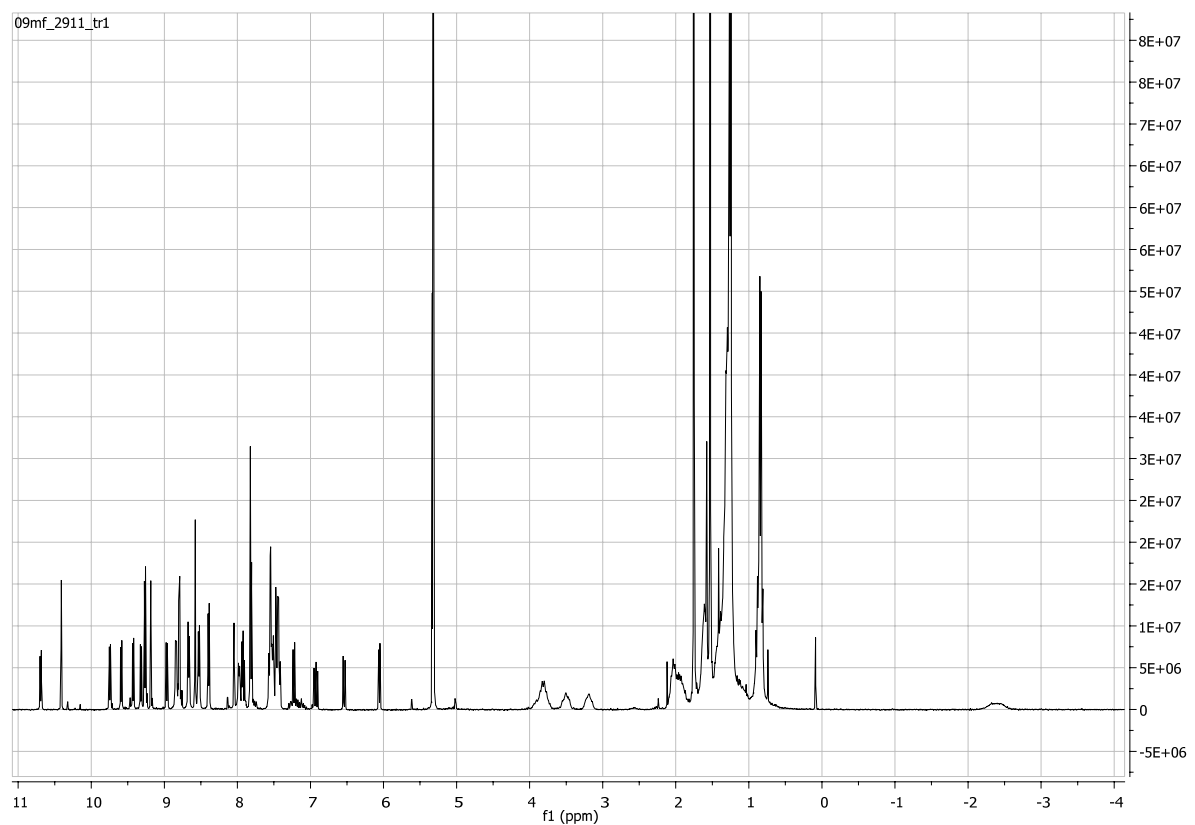


Figure S19. ¹H NMR spectrum of **1** (300 MHz, CD₂Cl₂, 298 K).

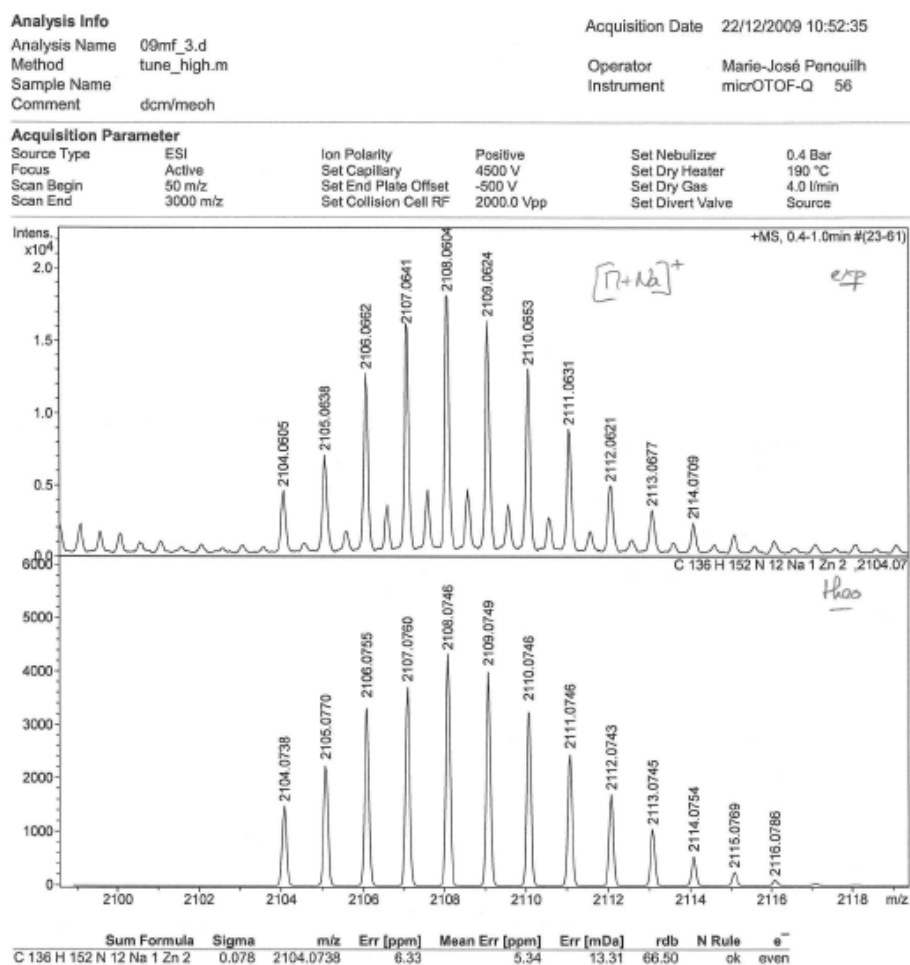


Figure S20. ESI HRMS spectrum of **1** (positive mode). Experimentally seen cluster of ions is a combination of $[M+H]^+$ and $[M+H]_2^{2+}$ clusters.

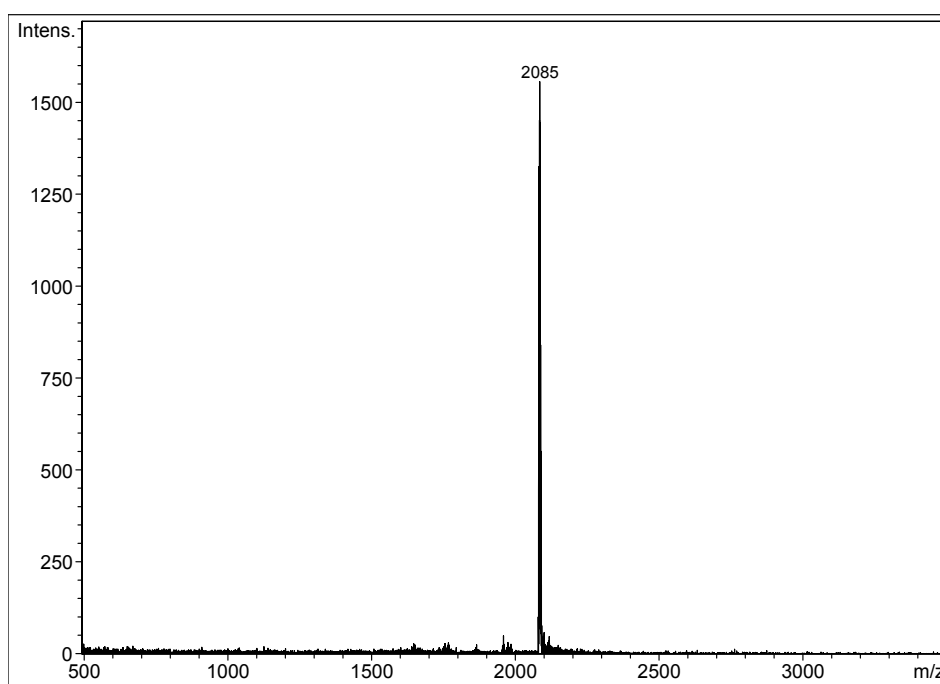


Figure S21. MALDI-TOF spectrum of **1** (positive mode).

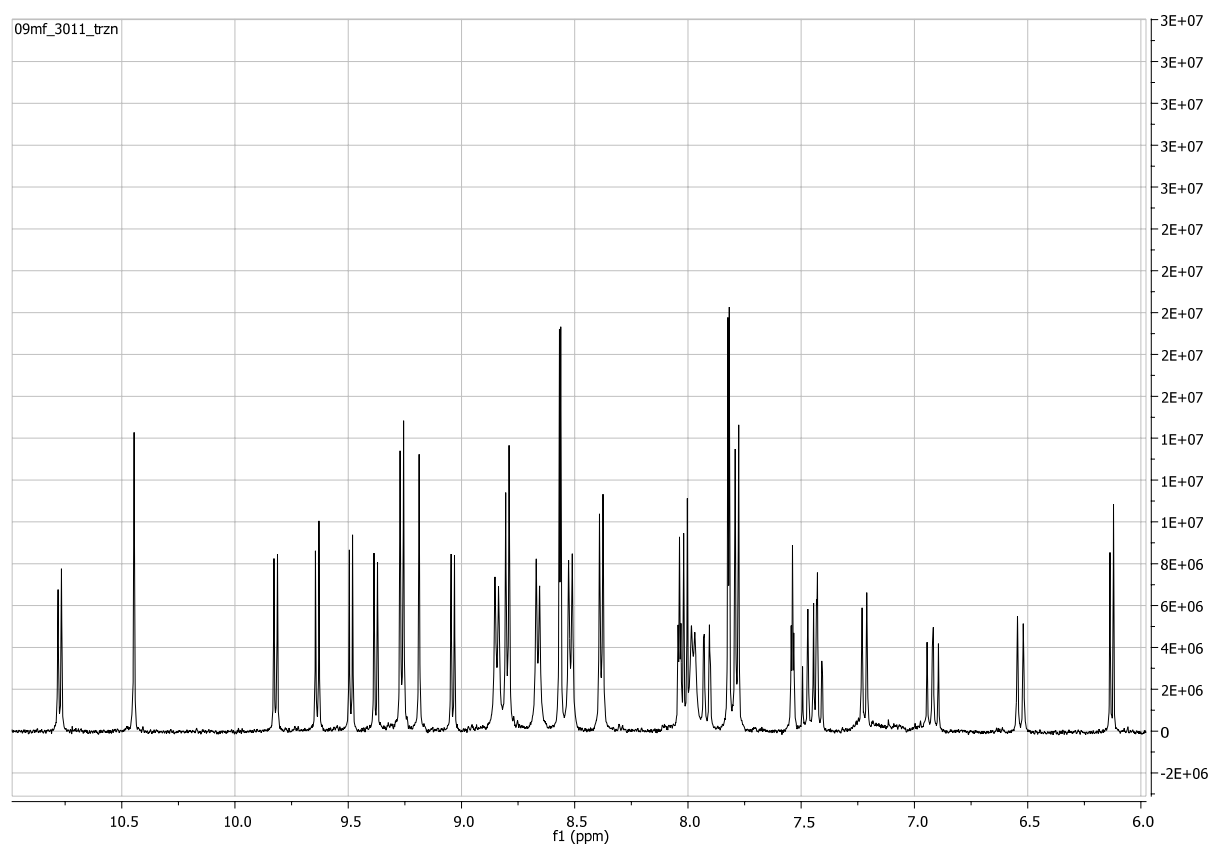
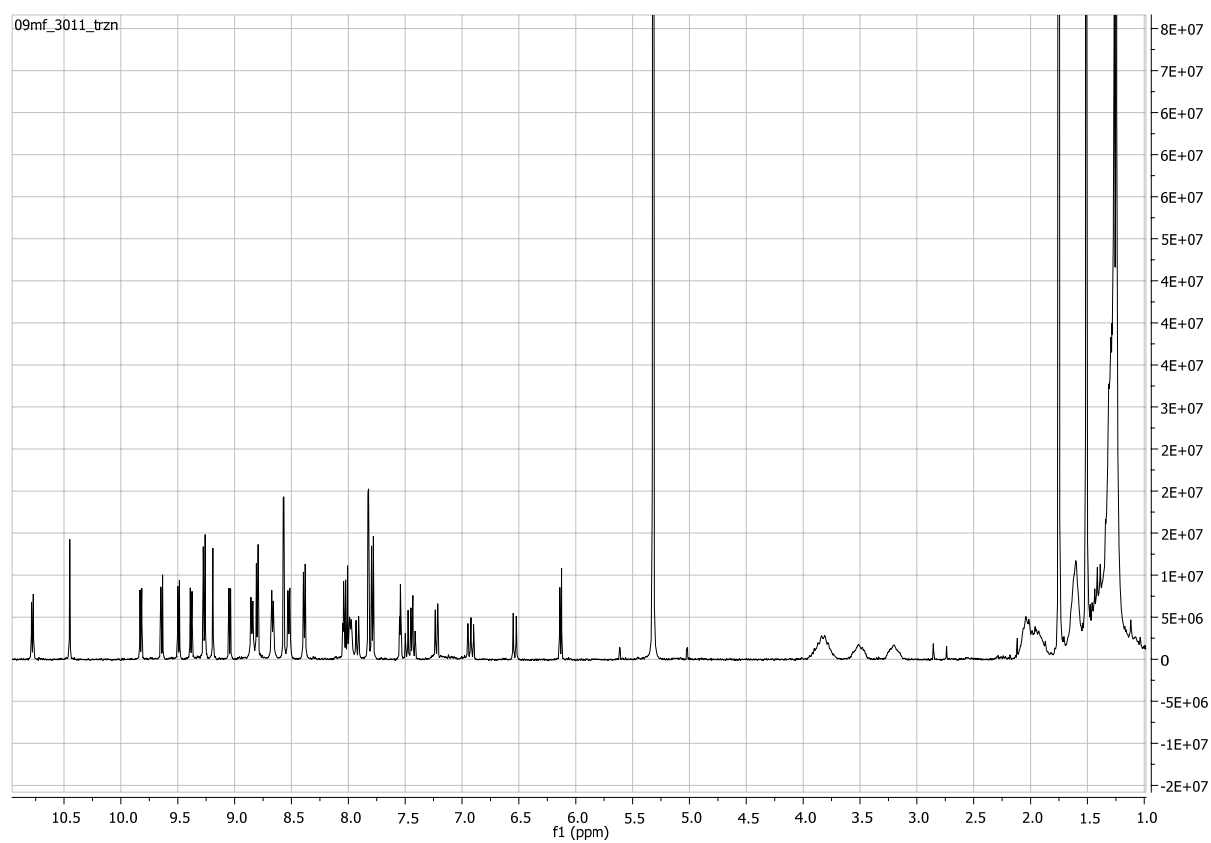


Figure S22. ¹H NMR spectrum of **1-Zn** (300 MHz, CD₂Cl₂, 298 K).

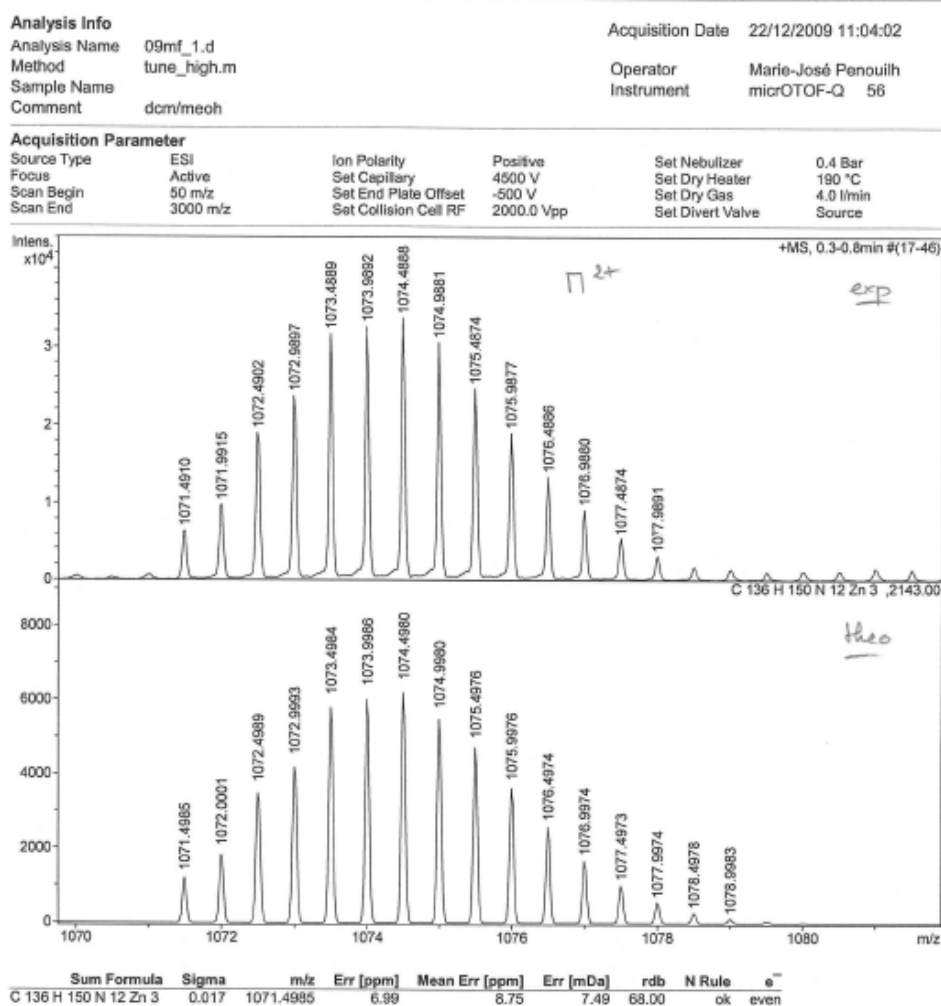


Figure S23. ESI HRMS spectrum of **1-Zn** (positive mode).

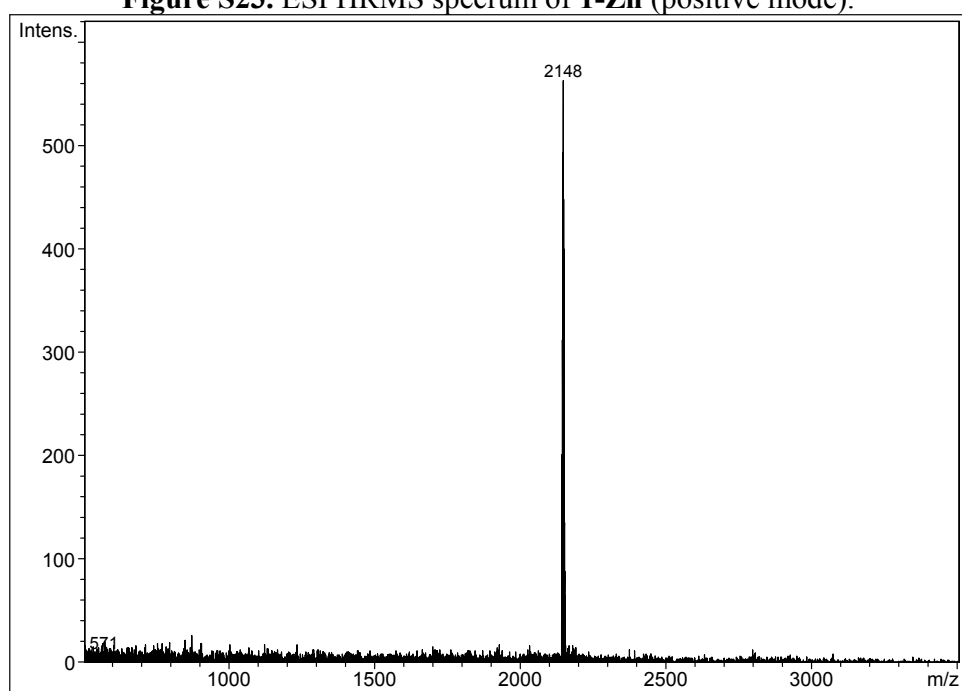


Figure S24. MALDI-TOF spectrum of **1-Zn** (positive mode).

Optical spectra

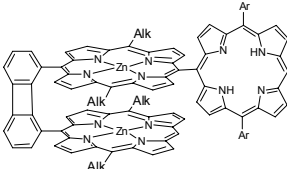
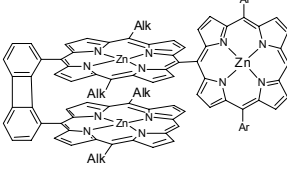
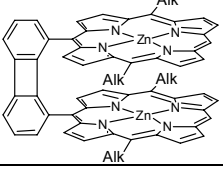
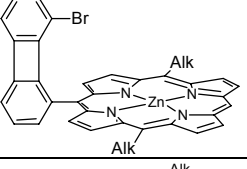
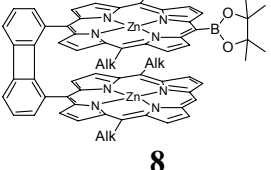
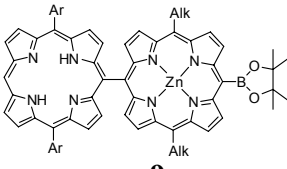
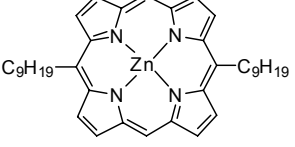
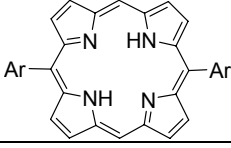
Porphyrin	Absorption	Fluorescence	Φ_F	τ_F , ns
	$\lambda_{\max}(\log \epsilon)$, nm	$\lambda_{\max}(\lambda_{\text{ex}})$, nm		
 1	414 (5.61)	716 (515)	0.047	2.27
	421 (5.60)			
	514 (4.59)			
	557 (4.37)			
	591 (4.32)			
	648 (3.85)			
 1-Zn	417 (5.51)	671 (555)	0.034	1.78
	556 (4.56)			
	590 (4.31)			
	632 (3.88)			
 4	406 (5.53)	667 (560)	0.016	1.95
	450 (4.28)			
	560 (4.05)			
	599 (3.64)			
 5	422 (5.43)	603, 648 (550)	0.021	2.1
	554 (4.10)			
	598 (3.47)			
 8	407 (5.56)	679 (560)	0.011	2.00
	561 (4.04)			
	602 (3.73)			
 9	416 (5.64)	661, 716 (560)	0.084	5.58
	449 (5.45)			
	513 (4.81)			
	563 (4.77)			
	594 (4.42)			
	609 (4.34)			
	392 (4.60)	589, 644 (550)	0.035	2.89
	411 (5.67)			
	547 (4.15)			
	407 (5.7)	635, 700 (535)	0.075	10.1
	502 (4.32)			
	535 (3.94)			
	576 (3.79)			

Table S1. Spectroscopic and photophysical data.

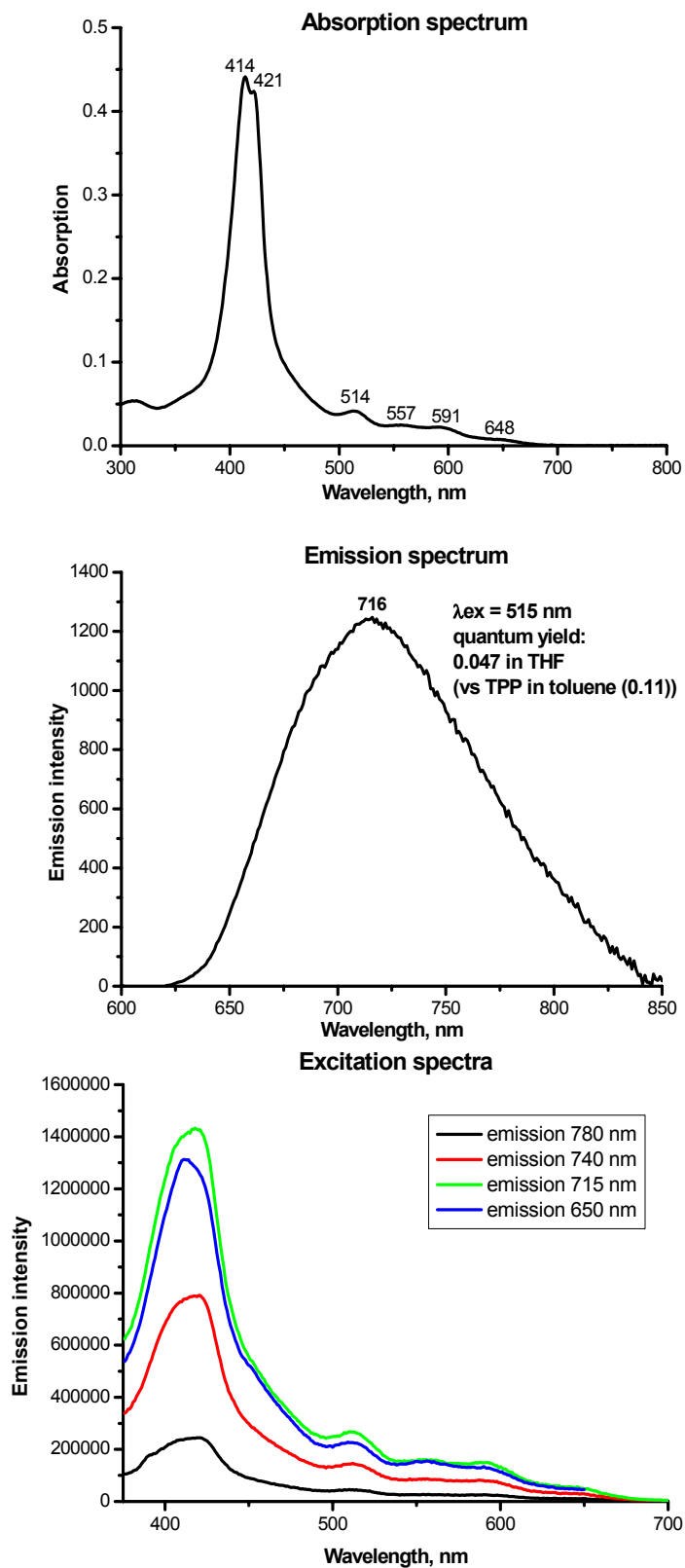


Figure S25. Optical spectra of trimer 1.

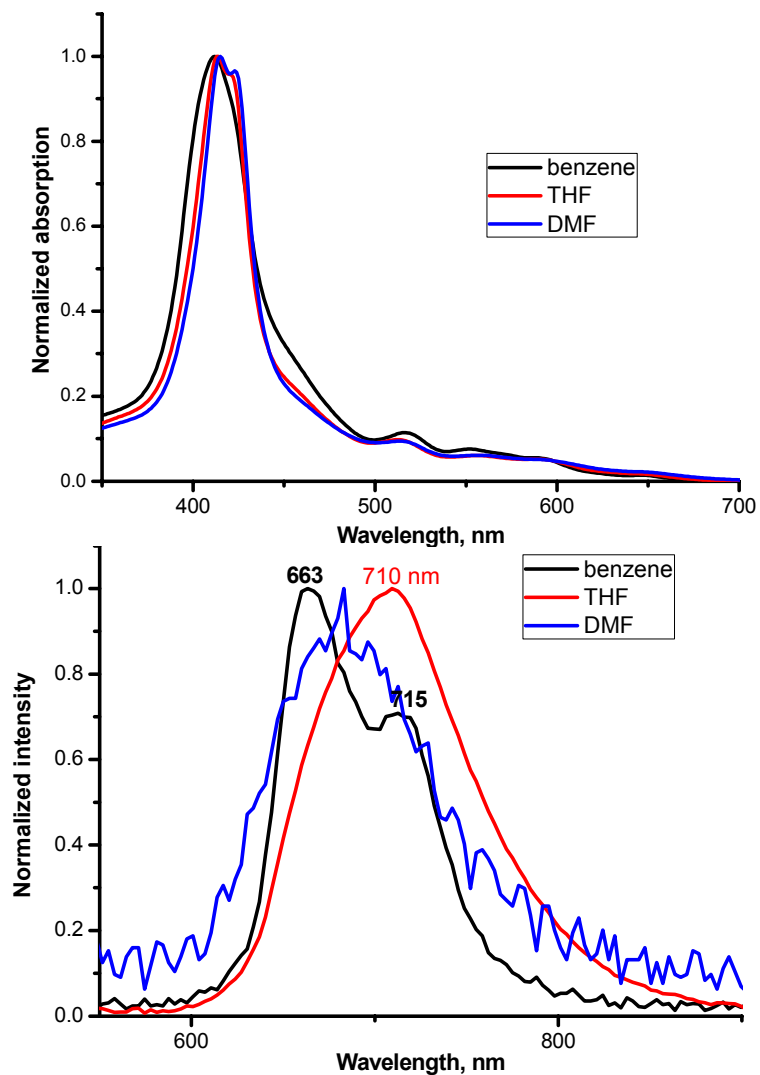


Figure S26. Normalized absorption and emission of trimer 1 in different solvents.

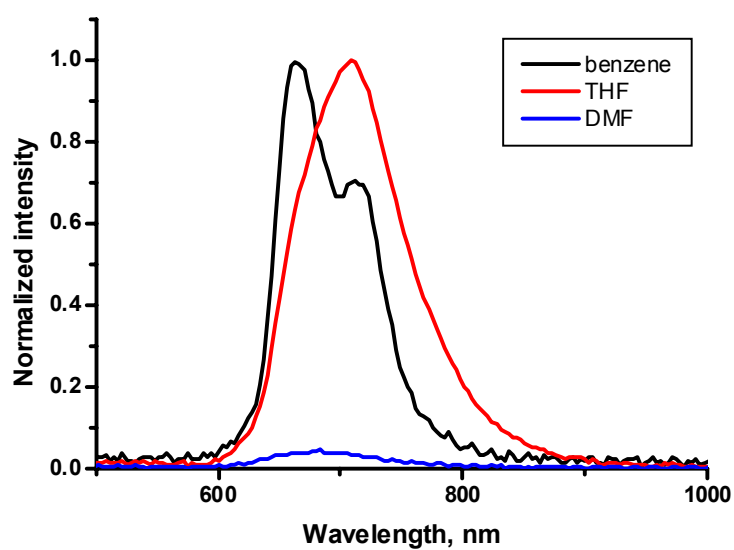


Figure S27. Relative intensities of emission of trimer 1 in different solvents.

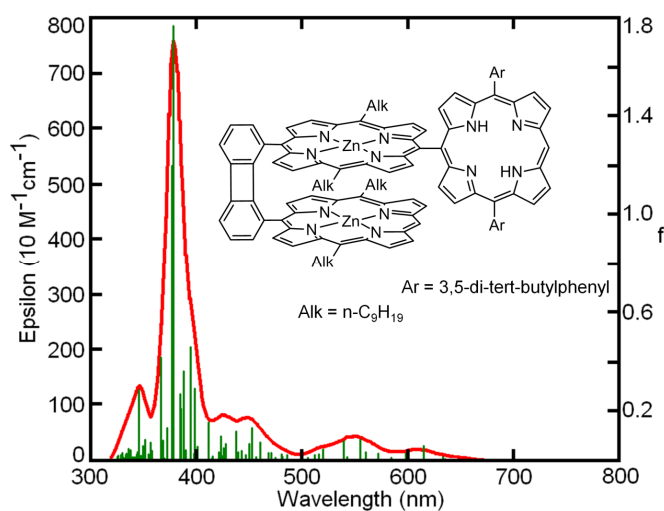


Figure S28. Calculated absorption spectrum of trimer **1**.

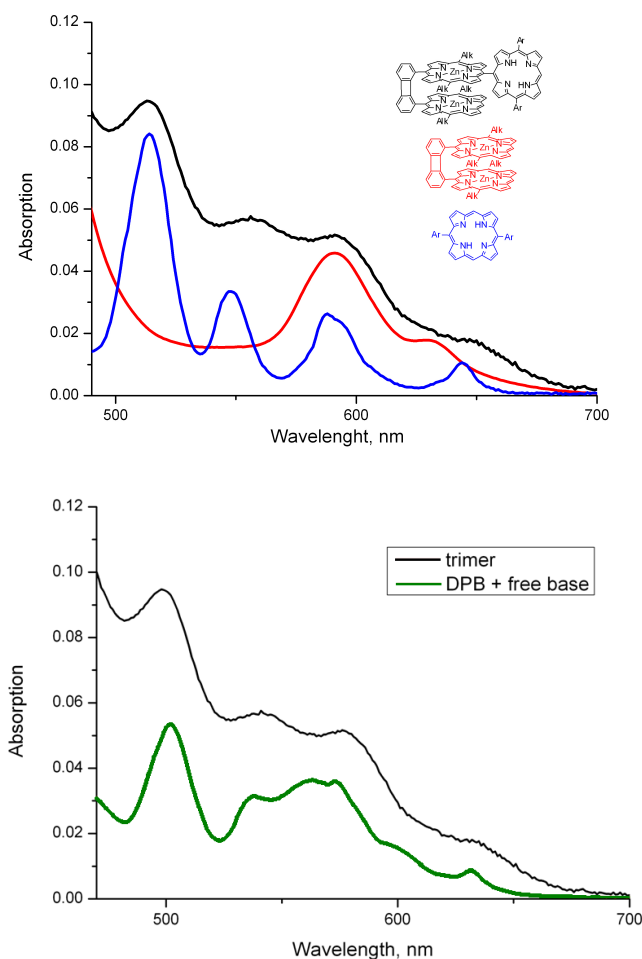


Figure S29. Comparison of the absorption spectra of trimer **1**, dimer **4** and 5,15-bis(3,5-di-tert-butylphenyl)porphyrin free base. The free base spectrum was shifted by 12 nm to the red to match the first band of **1**, the dimer spectrum was shifted by 31 nm to the red. Bottom: comparison of the curve generated by the sum of the blue and red spectra on top (in green) with the experimental spectrum of the trimer **1** (in black).

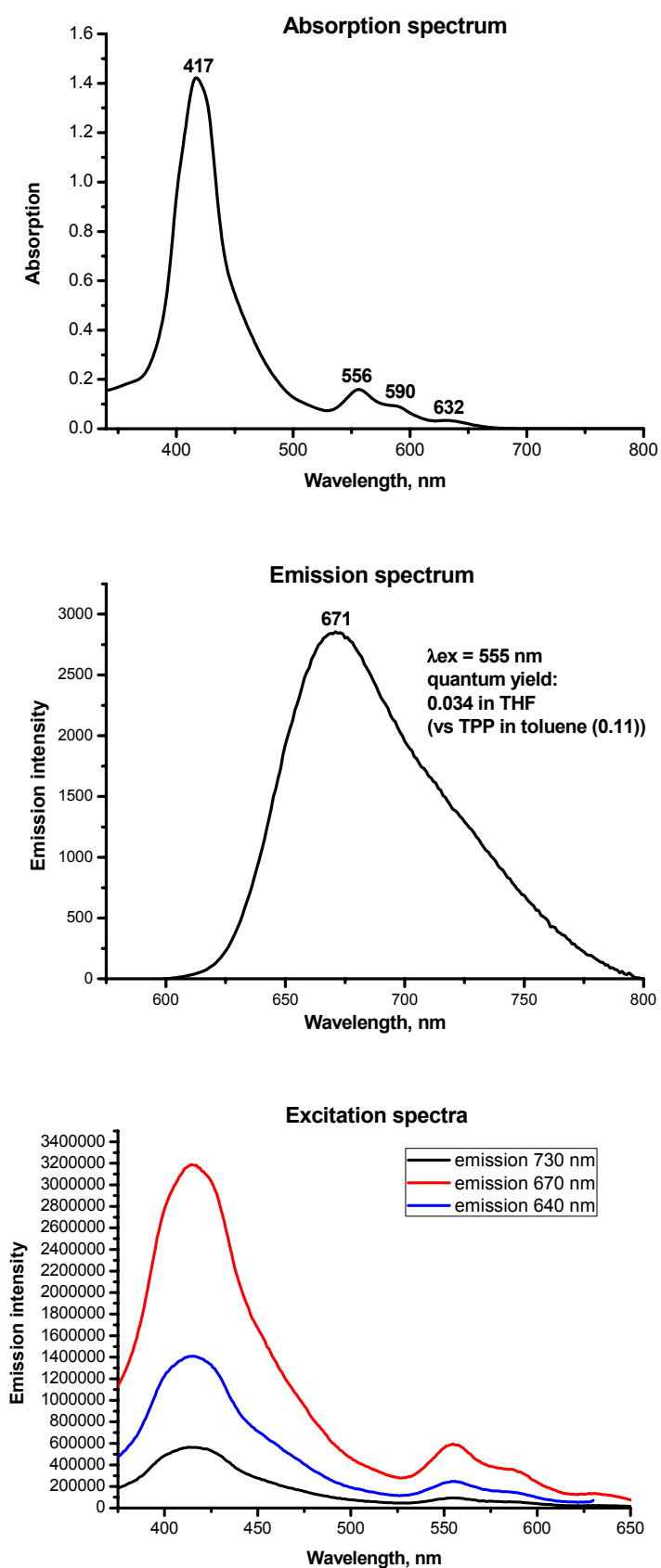


Figure 30. Optical spectra of trimer 1-Zn.

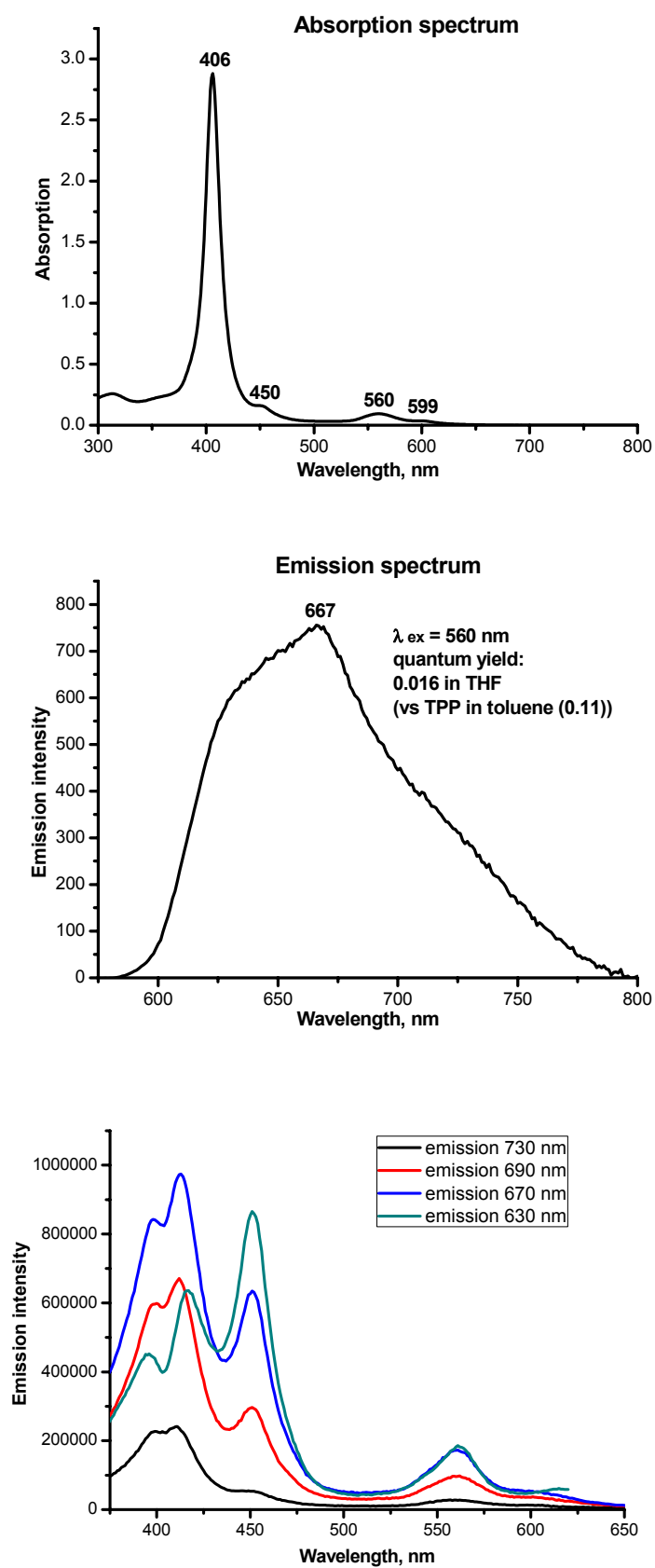


Figure 31. Optical spectra of face-to-face dimer 4.

DFT Calculations

No.	ν (cm ⁻¹)	λ (nm)	f	Major contributions (%)
1	15787.60544	633.4082796	0.0119	HOMO→LUMO (48), HOMO→L+2 (-43)
2	16268.31520	614.6918029	0.0593	HOMO→L+1 (59), HOMO→L+3 (-16)
3	16709.50352	598.4618267	0.0307	HOMO→LUMO (32), HOMO→L+1 (13), HOMO→L+2 (37)
4	17108.75072	584.4962127	0.0090	H-1→L+1 (-12), HOMO→L+1 (13), HOMO→L+3 (61)
5	17386.20736	575.1685686	0.0057	H-1→LUMO (18), H-1→L+2 (-13), HOMO→L+4 (40)
6	17493.47984	571.6415540	0.0287	H-1→LUMO (28), HOMO→L+4 (-27)
7	17861.27120	559.8705651	0.0321	H-2→LUMO (-18), H-2→L+1 (-11), H-1→L+2 (23)
8	18007.25856	555.3316162	0.0902	H-1→L+1 (39), HOMO→L+5 (-12)
9	18416.99104	542.9768619	0.0124	H-1→LUMO (13), H-1→L+1 (24), H-1→L+3 (26), HOMO→L+5 (12)
10	18544.42752	539.2455491	0.0923	H-2→LUMO (10), H-1→LUMO (12), H-1→L+2 (25), H-1→L+4 (-10)
11	18782.36272	532.4143799	0.0024	H-1→L+4 (63)
12	19217.09856	520.3699179	0.0466	H-3→L+3 (10), H-1→L+3 (26), HOMO→L+5 (-26)
13	19358.24656	516.5757120	0.0243	H-2→LUMO (-14), H-2→L+1 (39)
14	19522.78480	512.2220064	0.0196	H-3→L+2 (21), H-1→L+5 (11)
15	19764.75280	505.9511799	0.0081	H-7→L+3 (-14), H-6→LUMO (-12), H-6→L+2 (29)
16	19953.48784	501.1655145	0.0048	H-2→L+2 (42), H-2→L+3 (23)
17	20130.93104	496.7480133	0.0009	H-7→L+2 (-14), H-1→L+5 (23)
18	20597.12272	485.5047055	0.0195	H-6→L+3 (-12), H-3→LUMO (30)
19	20754.40192	481.8254960	0.0065	H-2→L+2 (-12), H-2→L+3 (44)
20	20770.53312	481.4512917	0.0233	H-6→L+2 (-11), H-4→L+2 (12)
21	21039.92416	475.2868843	0.0043	H-6→L+4 (11), H-4→L+3 (-13), H-3→L+4 (13)
22	21045.57008	475.1593785	0.0067	H-7→L+4 (-11), H-5→L+4 (-14), H-3→L+2 (16)
23	21224.62640	471.1508138	0.0293	H-3→LUMO (18), H-3→L+1 (-11), H-3→L+2 (10)
24	21357.70880	468.2150175	0.0290	H-3→L+1 (45), H-3→L+3 (20)
25	21732.75920	460.1348549	0.0745	H-6→L+4 (17), H-3→L+4 (-14)
26	21894.07120	456.7446551	0.0105	H-2→L+4 (57), H-2→L+5 (15)
27	22081.19312	452.8740791	0.1301	H-5→LUMO (12), H-4→LUMO (16)
28	22167.49504	451.1109614	0.0678	H-7→L+3 (13), H-6→L+3 (13)
29	22400.59088	446.4167956	0.0212	H-4→L+1 (36), H-4→L+3 (11)
30	22561.09632	443.2408717	0.0387	H-4→L+2 (15)

Table S2. Calculated positions, oscillator strengths (f), and major contributions of the 30 first electronic transitions of 1.

Transient absorption spectra

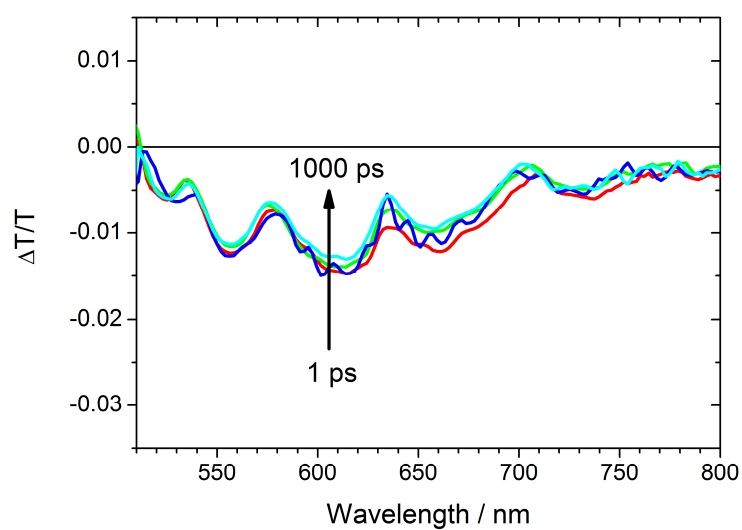


Figure 32: TA spectra of **12** (free-base porphyrin) in solution after 1 ps, 10 ps, 100 ps and 1000 ps. Note that there is virtually no decay of the signal on this time scale.

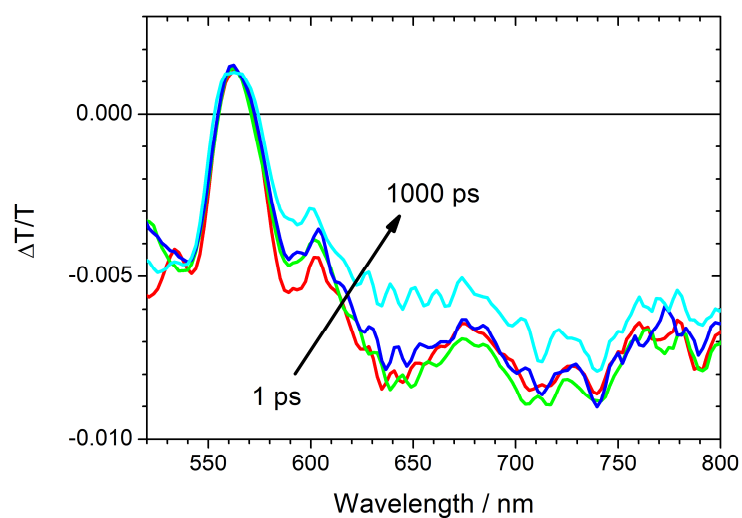


Figure 33: TA spectra of compound **4** at 1 ps, 10 ps, 100 ps and 1000 ps delay time after excitation at 400 nm.

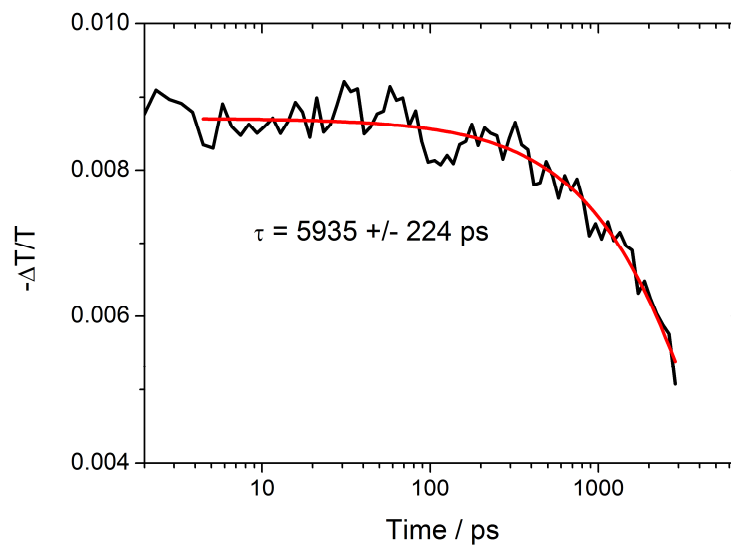


Figure 34: Decay of the photoinduced absorption of compound **4** integrated between 700 – 750 nm and fit to a single exponential decay yielding a life time of ~5.9 ns.

References

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