

Supporting Information

Acceleration of the Through Space S_1 Energy Transfer Rates in Cofacial Bisporphyrin Bio-Inspired Models by Virtue of Substituents Effect on the Förster J Integral and its Implication in the Antenna Effect in the Photosystems

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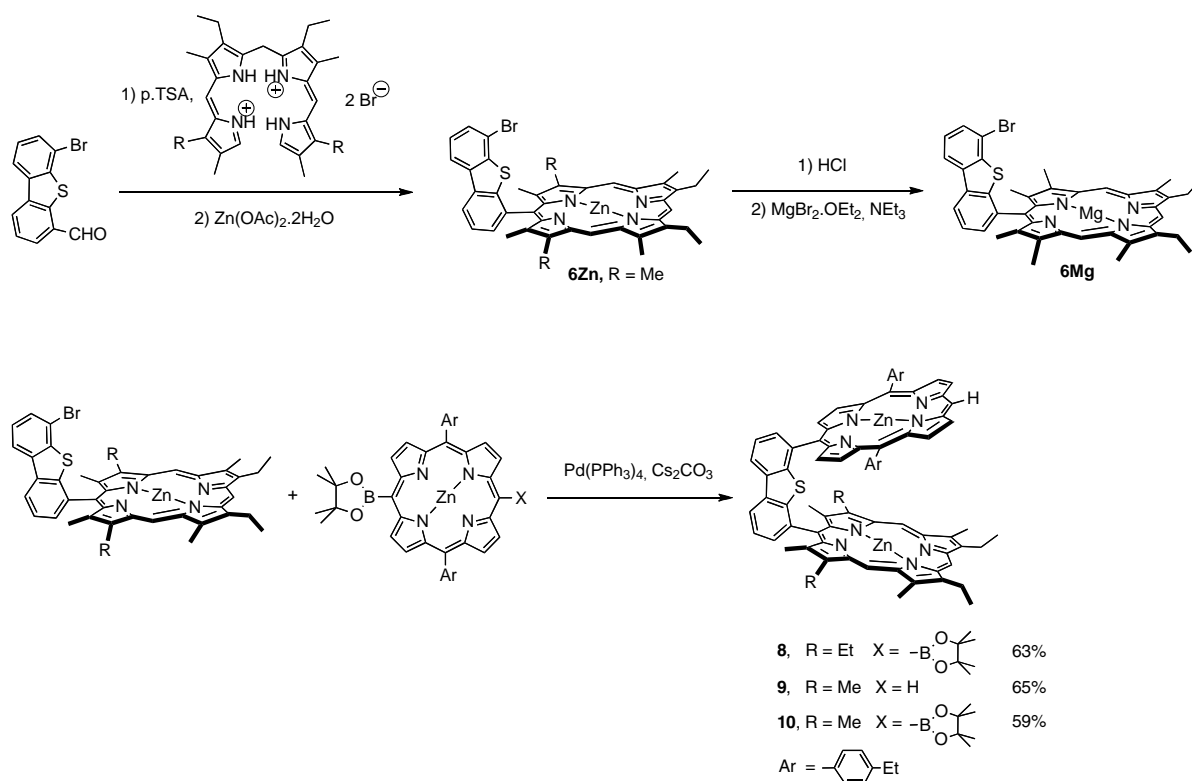
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1. Experimental Section

Instrumentation and Materials

10,20-bis(tolyl)-porphyrin **1** was synthesized according a similar procedure.¹ Synthesis of porphyrins **6Zn**, **8**, **9** and **10** is depicted in Scheme S 1 and will be described in due course elsewhere.²



Scheme S 1

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 nitrogen in the solvent purification systems and then further dried over activated molecular sieves; extra dry DMF was purchased from Aldrich. Triethylamine, dichloromethane and 1,2-dichloroethane were distilled from CaH₂; THF and toluene were distilled from sodium benzophenone ketyl. Unless specified otherwise all other solvents were used as commercially supplied. Silica gel (Merck; 70-120 mm) was used for column chromatography. Analytical

thin layer chromatography was performed using Merck 60 F254 silica gel (precoated sheets, 0.2 mm thick). Size exclusion chromatography was carried out under gravity using cross-linked polystyrene Bio-Beads® SX-1 (200 – 400 mesh) in DCM. Reactions were monitored by thin-layer chromatography, UV-vis spectroscopy, and MALDI/TOF mass spectrometry. ¹H NMR spectra were recorded on a Bruker Avance II 300 (300 MHz) or on a Bruker Avance DRX 500 (500 MHz) spectrometers at the “Plateforme d’Analyse Chimique et de Synthèse Moléculaire de l’Université de Bourgogne (PACSMUB)”); chemical shifts are expressed in ppm relative to chloroform (7.26 ppm), methylene chloride (5.30 ppm) or THF-d⁸ (1.73 and 3.58 ppm). UV-vis spectra were recorded on a Varian Cary 1 spectrophotometer. Mass spectra and accurate mass measurements (HR-MS) were obtained on a Bruker Daltonics Ultraflex II spectrometer in the MALDI/TOF reflectron mode using dithranol as a matrix. Both measurements were performed at the “Plateforme d’Analyse Chimique et de Synthèse Moléculaire de l’Université de Bourgogne (PACSMUB)”. For the photophysical measurements, UV-visible spectra were recorded on a Hewlett-Packard diode array model 8452A and the emission spectra were obtained using a double monochromator Fluorolog 2 instrument from Spex. The emission lifetimes were measured using a TimeMaster Model TM-3/2003 apparatus from PTI. The source was nitrogen laser with high-resolution dye laser (fwhm ~1600ps) and fluorescence lifetimes were obtained from deconvolution or distribution lifetimes analysis. Quantum yields measurements were performed in 2-MeTHF at 298K. The solvent used was passed over activated Aluminum oxide, neutral, Brockmann I, and then distilled over CaH₂ under inert atmosphere of Ar. Three different measurements (*i.e.* different solutions) were prepared for each photophysical datum. For 298K measurements samples were prepared under inert atmosphere (in a glove box, P_{O₂} < 15 ppm). The sample and standard concentrations were adjusted to obtain an absorbance of 0.05 or less. This absorbance was adjusted to be the same as much as possible for the standard and the sample for a measurement. Each absorbance value was measured five times for better accuracy in the

measurements of the quantum yields. The references used for quantum yield was Zn(TPP) (TPP = tetraphenylporphyrin; $\Phi = 0.033$).³

Syntheses

10,20-bis(tolyl)-15-mesitylporphyrin 2. MesLi was prepared by reaction of 2-bromomesitylene (0.78 mL, 5.1 mmol) with nBuLi (4.4 mL, 11.0 mmol) in diethyl ether (30 mL). The reaction mixture was stirred overnight at room temperature. The white precipitate was washed with Et₂O (10 mL) and dissolved in 15 mL of THF. The organolithium solution was added onto a solution of 250 mg of 10,20-bis(*p*-tolyl)-porphyrin **1** (0.51 mmol) in THF (100 mL). The greenish reaction mixture was stirred 1 hour at room temperature and hydrolysed by 2 mL of water in 5 mL of THF. After stirring for 15 min, a solution of 1.4 g of DDQ in methylene chloride (100 mL) was added and the reaction mixture was stirred for 1 hour, filtered through neutral alumina. The solvents were removed in vacuo and the residue was purified by chromatographic column on silica gel (CHCl₃/Petroleum Ether 1:2) affording the title compound as a purple solid (0.23 g, 45%). ¹H NMR (300.16 MHz, CDCl₃): δ 10.20 (s, 1H, meso), 9.32 (d, $J = 4.6$ Hz, 2H, β), 9.04 (d, $J = 4.6$ Hz, 2H, β), 8.90 (d, $J = 4.8$ Hz, 2H, β), 8.74 (d, $J = 4.7$ Hz, 2H, β), 8.14 (d, $J = 8.0$ Hz, 4H, Tol), 7.58 (d, $J = 8.0$ Hz, 4H, Tol), 7.29 (s, 2H, Mes), 2.72 (s, 6H, Mes), 2.64 (s, 3H, Mes), 1.84 (s, 6H, Tol) and -2.87 (s, 2H, NH) ppm. ESI HRMS : m/z 609.3005 calcd for C₄₃H₃₆N₄, 609.3012 (M⁺). UV-vis (THF) λ_{max} (log ϵ) = 411 (5.65), 507 (4.32), 541 (3.95), 584 (3.88), 640 (3.68) nm.

Zinc (II) 10,20-bis(tolyl)-15-mesitylporphyrin 2-Zn. 0.16 g of **2** (0.25 mmol) were suspended in 30 mL of CHCl₃ and 5 mL of methanol. Zn(OAc₂).2H₂O (0.55 g, 2.5 mmol) was added and the reaction mixture was stirred overnight. Water (20 mL) was added and phases were separated. The organic layer was washed with brine, dried over MgSO₄ and concentrated in vacuo. Washing with methanol afforded the title compound as a red purple solid (0.17 g, 96%). ¹H NMR (300.16 MHz, CDCl₃): δ 10.21 (s, 1H, meso), 9.37 (d, $J = 4.6$ Hz, 2H, β), 9.10 (d, $J = 4.5$ Hz, 2H, β), 8.97 (d, $J = 4.6$ Hz, 2H, β), 8.81 (d, $J = 4.6$ Hz, 2H, β),

8.14 (d, $J = 8.0$ Hz, 4H, Tol), 7.58 (d, $J = 7.9$ Hz, 4H, Tol), 7.28 (s, 2H, Mes), 2.73 (s, 6H, Mes), 2.64 (s, 3H, Mes) and 1.82 (s, 6H, Tol) ppm. ESI HRMS : m/z 693.1967 calcd for $C_{43}H_{36}N_4ZnNa$, 693.1928 ($M+Na^+$). UV-vis (THF) λ_{max} ($\log \epsilon$) = 418 (5.40), 550 (3.98), 590 (3.33).

5-Bromo-10,20-bis(tolyl)-15-mesitylporphyrin 3. To a solution of **2** (210 mg, 0.34 mmol) in CH_2Cl_2 (150 mL) and a drop of pyridine at 0 °C was added NBS (68 mg, 0.38 mmol). The reaction mixture was stirred 30 minutes and water (50 mL) was added. The organic layer was separated and washed with brine. After drying the organic phase over $MgSO_4$, the solution was concentrated in vacuo and passed through a short silica-gel column. The residue was recrystallized from $CH_2Cl_2/MeOH$ as a purple powder. (Yield: 0.22 g, 92%). 1H NMR (300.16 MHz, CD_2Cl_2): δ 9.65 (d, $J = 4.9$ Hz, 2H, β), 8.90 (d, $J = 4.9$ Hz, 2H, β), 8.77 (d, $J = 4.8$ Hz, 2H, β), 8.62 (d, $J = 4.8$ Hz, 2H, β), 8.06 (d, $J = 7.9$ Hz, 4H, Tol), 7.57 (d, $J = 7.9$ Hz, 4H, Tol), 7.27 (s, 2H, Mes), 2.69 (s, 6H, Mes), 2.59 (s, 3H, Mes), 1.80 (s, 6H, Tol) and -2.74 (s, 2H, NH) ppm. ESI HRMS : m/z 687.2084 calcd for $C_{43}H_{35}BrN_4$, 687.2117(M^+). UV-vis (THF) λ_{max} ($\log \epsilon$) = 418 (5.60), 517 (4.20), 549 (3.91), 597 (3.58), 654 (3.54) nm.

Zinc(II) 5-bromo-10,20-bis(tolyl)-15-mesitylporphyrin 4. 0.20 g of **3** (0.29 mmol) were suspended in 50 mL of $CHCl_3$ and 5 mL of methanol. $Zn(OAc_2) \cdot 2H_2O$ (0.32 g, 1.45 mmol) was added and the reaction mixture was stirred overnight. Water (20 mL) was added and phases were separated. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated in vacuo. Washing with methanol afforded the title compound as a red purple solid (0.21 g, 96%). 1H NMR (300.16 MHz, $CDCl_3$): δ 9.67 (d, $J = 4.9$ Hz, 2H, β), 8.95 (d, $J = 4.9$ Hz, 2H, β), 8.82 (d, $J = 4.8$ Hz, 2H, β), 8.68 (d, $J = 4.8$ Hz, 2H, β), 8.06 (d, $J = 7.9$ Hz, 4H, Tol), 7.53 (d, $J = 7.9$ Hz, 4H, Tol), 7.25 (s, 2H, Mes), 2.71 (s, 6H, Mes), 2.61 (s, 3H, Mes) and 1.81 (s, 6H, Tol). ESI HRMS : m/z 771.1015 calcd for $C_{43}H_{33}BrN_4NaZn$, 771.1072 ($M+Na^+$). UV-vis (CH_2Cl_2) λ_{max} ($\log \epsilon$) = 421 (5.37), 552 (3.96), 590 (3.30) nm.

Zinc(II) 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10,20-bis(tolyl),15-mesitylporphyrin 5. Under argon atmosphere, 50 mL of freshly distilled 1,2-dichloroethane were

added to a mixture of **4** (0.2 g, 0.3 mmol) and Pd(PPh₃)₂Cl₂ (6 mg, 0.009 mmol). Triethylamine (0.5 ml, 3.6 mmol) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.22 mL, 1.5 mmol) were added and the reaction mixture was stirred for 30 minutes at reflux. 20 mL of 30% aq. KCl was added to the reaction mixture. The organic layer was separated and washed with water (2 x 30 mL) and dried over anhydrous MgSO₄. The solvents were removed and the residue was separated with silica-gel column chromatography (CHCl₃). The second purple fraction was evaporated until dryness, washed with methanol and dried in vacuo affording a purple powder (180 mg, 78%). ¹H NMR (300.16 MHz, CD₂Cl₂): δ 9.87 (d, *J* = 4.7 Hz, 2H, β), 9.06 (d, *J* = 4.7 Hz, 2H, β), 8.99 (d, *J* = 4.6 Hz, 2H, β), 8.77 (d, *J* = 4.6 Hz, 2H, β), 8.09 (d, *J* = 7.9 Hz, 4H, Tol), 7.58 (d, *J* = 7.8 Hz, 4H, Tol), 7.28 (s, 2H, Mes), 2.71 (s, 6H, Mes), 2.60 (s, 3H, Mes), 1.84 (s, 12H, CH₃) and 1.80 (s, 6H, Tol) ppm. ESI HRMS : *m/z* 795.2952 calcd for C₄₉H₄₅BN₄O₂Zn, 795.2957 (M⁺). UV-vis (THF) λ_{max} (log ε) = 422 (5.78), 554 (4.36), 594 (3.60) nm.

Magnesium(II) 5-(4-(bromodibenzothien-6-yl))-(12,17-diethyl-2,3,7,8,13,18-hexamethyl)-porphyrin 6Mg

6Zn (29 mg, 0.038 mmol) was dissolved in 15 mL of dichloromethane and 15 mL of HCl solution (6M) were. The reaction mixture was vigorously stirred for 30 minutes and the aqueous layer was separated. The organic phase was washed with a NaHCO₃ solution (2 x 20 mL) and with brine (20 mL) and dried over MgSO₄. The solvent was removed in vacuo and the purple residue was dissolved in 20 mL of CH₂Cl₂. The solution was treated with 0.45 mL of NEt₃ (3.2 mmol) followed by MgBr₂.OEt₂ (0.40 g, 1.55 mmol). After stirring for 30 minutes, the metalation was complete based on absorption spectrum and the mixture was diluted with 20 mL of CH₂Cl₂, washed with 10% NaHCO₃ solution (2 x 20 mL) and dried over MgSO₄. The solvent was removed in vacuo and the compound was recrystallized in CH₂Cl₂/pentane yielding a reddish crystalline powder (13 mg; 45% yield). ¹H NMR (300.16 MHz, CDCl₃): δ 9.97 (br s, 2H, *meso*), 9.90 (br s, 1H, *meso*), 8.52 (d, *J* = 8.4 Hz, 1H, DPS), 8.34 (d, *J* = 7.8 Hz, 1H, DPS), 7.92 (br m, 2H, DPS), 7.53 (d, *J* = 7.5 Hz, 1H, DPS), 7.41 (t, *J*

= 8.2 Hz, 1H, DPS), 4.04 (br m, 4H, CH₂), 3.57 (s, 6H, Me), 3.42 (s, 6H, Me), 2.18 (s, 6H, Me) and 1.83 (br m, 6H, CH₃) ppm. ESI HRMS : m/z 755.1665 calcd for C₄₉H₄₅BN₄O₂ZnNa, 755.1668 (M+Na⁺). UV-vis (THF) λ_{max} (log ϵ) = 400 sh (4.64), 420 (5.34), 553 (4.11), 587 (3.70) nm.

Zinc(II) 5-{4-[zinc(II) (12,17-diethyl-2,3,7,8,13,18-hexamethyl)-porphyrin-5-yl]-dibenzothien-6-yl}-10,20-bis-tolyl-15-mesitylporphyrin 7Zn. Under an inert atmosphere, a mixture of zinc(II) 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10,20-bis(tolyl),15-mesitylporphyrin (56 mg, 0.07 mmol), zinc(II) 5-(4-(bromodibenzothien-6-yl))-(12,17-diethyl-2,3,7,8,13,18-hexamethyl)-porphyrin (070 mg, 0.09 mmol), cesium carbonate (0.06g, 0.18 mmol), Pd(PPh₃)₄ (8 mg, 0.007 mmol) in 15 mL of anhydrous toluene and 8 mL of DMF was stirred at 90 °C for 5 h. The reaction was quenched with an aqueous saturated NH₄Cl solution (20 mL). The organic layer was separated, extracted from aqueous phase. The combined organic fractions were washed with water (2 x 20 mL) and dried over MgSO₄. The solvent was evaporated and under vacuum and the residue was purified by silica gel (chloroform/petroleum ether 1:1) affording the title compound as a reddish purple solid (63 mg, 66%). ¹H NMR (300.16 MHz, CD₂Cl₂): δ 9.83 (s, 2H, *meso*), 9.69 (s, 1H, *meso*), 8.86 (d, J =8.2 Hz, 2H, DPS), 8.70 (d, J = 4.7 Hz, 2H, β), 8.66 (d, J = 4.6 Hz, 2H, β), 8.55 (d, J = 4.5 Hz, 2H, β), 8.41 (d, J = 4.6 Hz, 2H, β), 8.22 (dd, J = 7.3 Hz, J = 1.0 Hz, 1H, DPS), 8.03 (d, J = 7.5 Hz, 1H, DPS), 7.98 (d, J = 7.4 Hz, 1H, DPS), 7.94 (dd, J = 7.3 Hz, J = 1.5 Hz, 1H, DPS), 7.86 (d, J = 7.5 Hz, 2H, Tol), 7.63 (d, J = 7.6 Hz, 2H, Tol), 7.43 (m, 4H, Tol), 7.11 (s, 1H, Mes), 7.02 (s, 1H, Mes), 3.80 (q, J = 7.6 Hz, 4H, CH₂), 3.37 (s, 6H, CH₃), 3.31 (s, 6H, CH₃), 2.63 (s, 6H, CH₃), 2.46 (s, 3H, CH₃), 2.27 (s, 6H, CH₃), 1.62 (t, J = 7.6 Hz, 6H, CH₃) and 1.61 (s, 6H, CH₃) ppm. ESI HRMS : m/z 1362.4011 calcd for C₈₅H₇₀N₈SZn₂, 1362.4021(M⁺⁺). UV-vis (THF) λ_{max} (log ϵ) = 410 (5.65), 428 (5.52), 547 (4.35), 555 (4.36), 576 (4.15), 596 (3.73) nm.

5-{4-[(12,17-diethyl-2,3,7,8,13,18-hexamethyl)-porphyrin-5-yl]-dibenzothien-6-yl}-10,20-bis-tolyl-15-mesitylporphyrin 7. 10 mL of HCl solution (6M) were added onto a

solution of 25 mg of **7Zn** (0.18 mmol) in 30 mL of CH₂Cl₂. After vigorous stirring for 30 minutes the aqueous phase was withdrawn and a fresh 6M HCl solution (15 mL) was added. The green reaction mixture was stirred vigorously again for 30 minutes to ensure complete demetalation. The aqueous layer was separated and the organic phase was washed with a NaHCO₃ solution (2 x 25 mL) and washed with brine (2x 25mL). After drying over MgSO₄, the solvent was concentrated in vacuo and the residue was filtered through a SiO₂ pad eluting with CH₂Cl₂. Recrystallization in CH₂Cl₂/MeOH afforded a purple solid (20 mg, 90%). ¹H NMR (300.16 MHz, CDCl₃): δ 9.86 (s, 2H, *meso*), 9.69 (s, 1H, *meso*), 8.83 (m, 2H, DPS), 8.64 (d, *J* = 4.8 Hz, 2H, β), 8.60 (d, *J* = 4.8 Hz, 2H, β), 8.51 (d, *J* = 4.9 Hz, 2H, β), 8.37 (d, *J* = 4.9 Hz, 2H, β), 8.22 (d, *J* = 4.8 Hz, 1H, DPS), 8.02 (d, *J* = 8.1 Hz, 1H, DPS), 7.95-7.80 (m, 4H, 2 DPS + 2 Tol), 7.78 (d, *J* = 8.4 Hz, 2H, Tol), 7.44 (t, *J* = 6.6 Hz, 4H, Tol), 7.13 (s, 1H, Mes), 7.04 (s, 1H, Mes), 3.87 (q, *J* = 7.5 Hz, 4H, CH₂), 3.44 (s, 6H Me), 3.32 (s, 6H, Me), 2.66 (s, 6H, Me), 2.50 (s, 3H, Mes), 2.27 (s, 6H, Me), 1.70 (t, *J* = 7.5 Hz, 3H, CH₃), 1.69 (s, 3H, Me), 1.31 (s, 3H, CH₃), -3.11 (s, 2H, NH), -3.65 (s, 1H, NH) and -3.73 (s, 1H, NH) ppm.

ESI HRMS : *m/z* 1239.5787 calcd for C₈₅H₇₄N₈S, 1239.5829 (M+H⁺). UV-vis (THF) λ_{max} (log ε) = 400 (5.20), 420 (5.27), 510 (4.18), 547 (3.73), 590 (3.65), 627 (3.41), 649 (3.40) nm.

Magnesium(II) 5-{4-[magnesium(II) (12,17-diethyl-2,3,7,8,13,18-hexamethyl)-porphyrin-5-yl]-dibenzothien-6-yl}-10,20-bis-tolyl-15-mesitylporphyrin 7Mg. 15 mL of HCl solution (6M) were added onto a solution of 40 mg of **7Zn** (0.29 mmol) in 60 mL of CH₂Cl₂. After vigorous stirring for 30 minutes the aqueous phase was withdrawn and a fresh 6M HCl solution (15 mL) was added. The green reaction mixture was stirred vigorously again for 30 minutes. The aqueous layer was separated and the organic phase was washed with a NaHCO₃ solution and washed with brine. After drying over MgSO₄, the solvent was evaporated until dryness. The purple solid was redissolved in 50 mL of CH₂Cl₂ and the solution was treated with 0.6 mL of NEt₃ (4.3 mmol) followed by MgBr₂.OEt₂ (0.75 g, 2.9 mmol). After stirring during one hour the mixture was diluted with 20 mL of CH₂Cl₂, washed with 10% NaHCO₃ solution (2 x 20 mL) and dried over MgSO₄. The solvent was removed *in*

vacuo and the residue was purified by column chromatography on alumina eluting with CH_2Cl_2 and $\text{CH}_2\text{Cl}_2/\text{acetone}$ (5/1). The purple band was evaporated until dryness and the compound was recrystallized in $\text{CH}_2\text{Cl}_2/\text{methanol}$ as a purple solid (30 mg, 81%). ^1H NMR (300.16 MHz, CD_2Cl_2): δ 9.85 (s, 2H, *meso*), 9.75 (s, 1H, *meso*), 8.84 (m, 2H, DPS), 8.61 (d, $J = 4.1$ Hz, 2H, β), 8.58 (d, $J = 4.1$ Hz, 2H, β), 8.48 (d, $J = 4.0$ Hz, 2H, β), 8.32 (d, $J = 3.7$ Hz, 2H, β), 8.22 (m, 1H, DPS), 8.00 (m, 3H, DPS), 7.85 (d, $J = 6.4$ Hz, 2H, Tol), 7.69 (d, $J = 5.8$ Hz, 2H, Tol), 7.49 (d, $J = 7.0$ Hz, 2H, Tol), 7.43 (d, $J = 6.8$ Hz, 2H, Tol), 7.10 (s, 1H, Mes), 7.03 (s, 1H, Mes), 3.87 (q, $J = 7.5$ Hz, 4H, CH_2), 3.43 (s, 6H, CH_3), 3.34 (s, 6H, CH_3), 2.66 (s, 6H, CH_3), 2.47 (s, 3H, CH_3), 2.26 (s, 6H, CH_3), 1.68 (t, $J = 7.5$ Hz, 6H, CH_3), 1.57 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 0.66 (br s, coordinated H_2O) ppm. ESI HRMS : m/z 1282.5128 calcd for $\text{C}_{85}\text{H}_{70}\text{N}_8\text{SMg}_2$, 1282.5139 (M^{++}); 1300.5211, calcd for $\text{C}_{85}\text{H}_{70}\text{N}_8\text{SMg}_2\cdot\text{H}_2\text{O}$, 1300.5211 ($\text{M}+\text{H}_2\text{O}^+$); 1305.5245, calcd for $\text{C}_{85}\text{H}_{70}\text{N}_8\text{SMg}_2\text{Na}$, 1305.5037 ($\text{M}+\text{Na}^+$). UV-vis (THF) λ_{max} ($\log \epsilon$) = 412 sh (5.35), 418 (5.39), 434 (5.39), 556 (4.29), 570 (4.25), 583 (4.08), 615 (4.03) nm.

2. NMR and High Resolution Mass Spectra

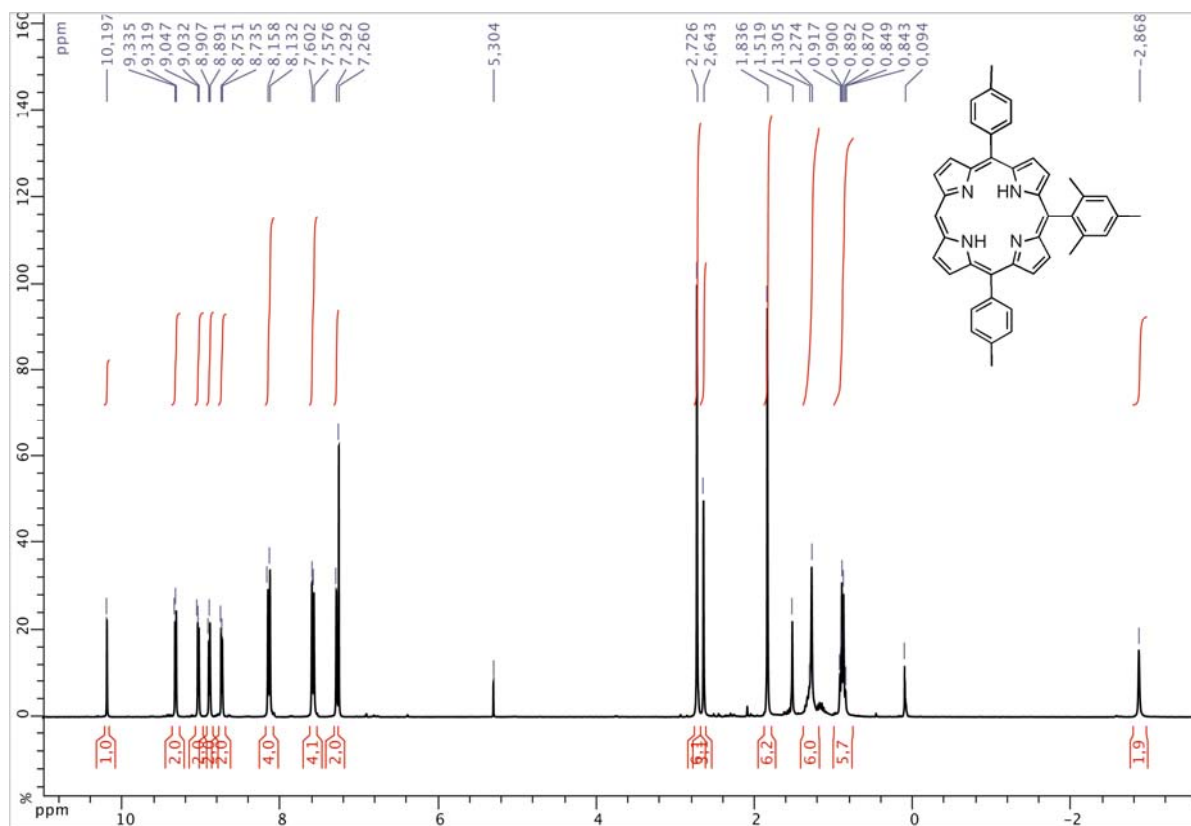


Figure S 1. ^1H NMR of 10,20-bis(tolyl)-15-mesitylporphyrin **2** (300 MHz, CDCl_3)

Analysis Info

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 Method tune_wide_pos.m
 Sample Name
 Comment dcm/MeOH

Acquisition Date 1/24/2011 1:42:56 PM

Operator Marie-José Penouilh
 Instrument micrOTOF-Q 56

Acquisition Parameter

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Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

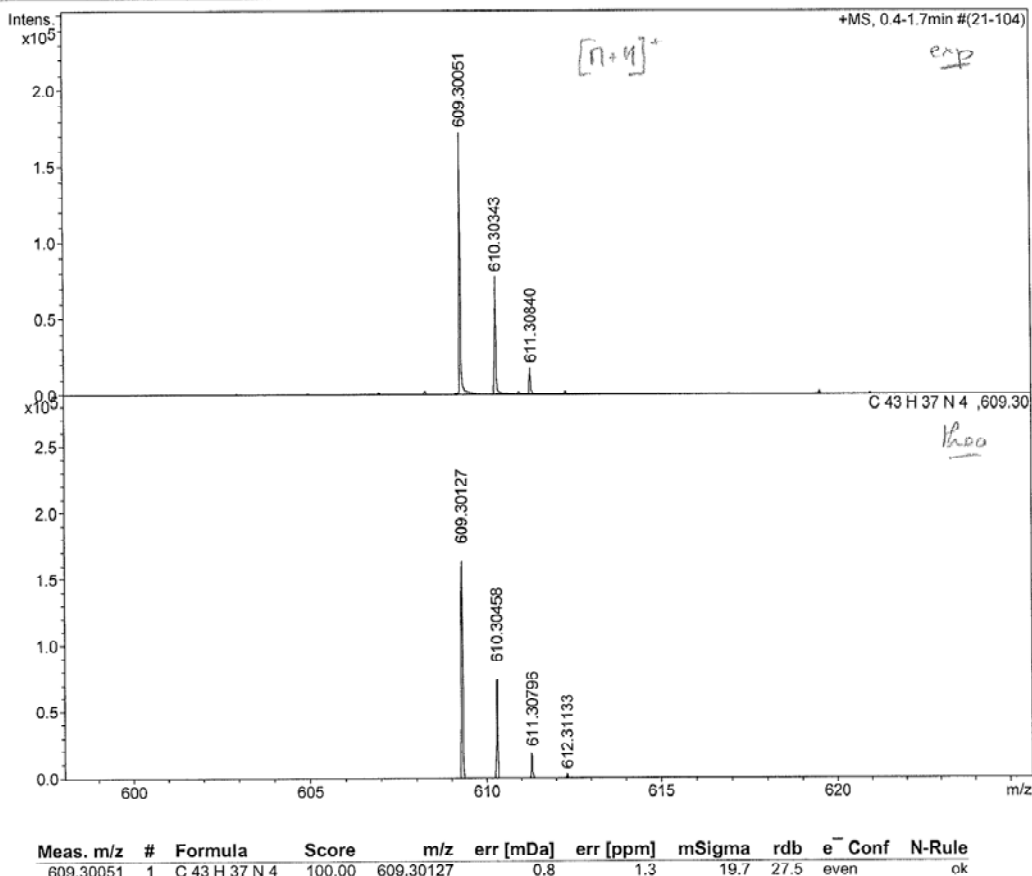


Figure S 2. ESI HRMS spectrum of 10,20-bis(tolyl)-15-mesitylporphyrin **2** (positive mode)

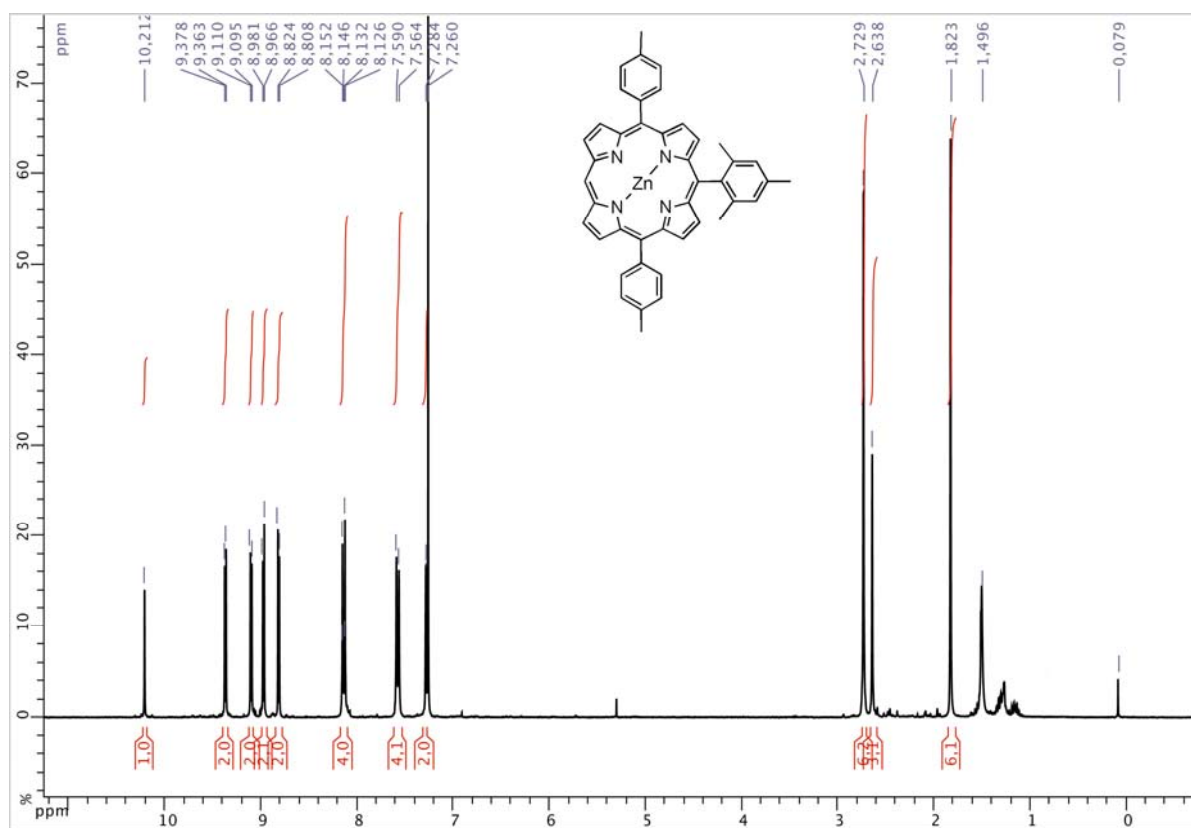


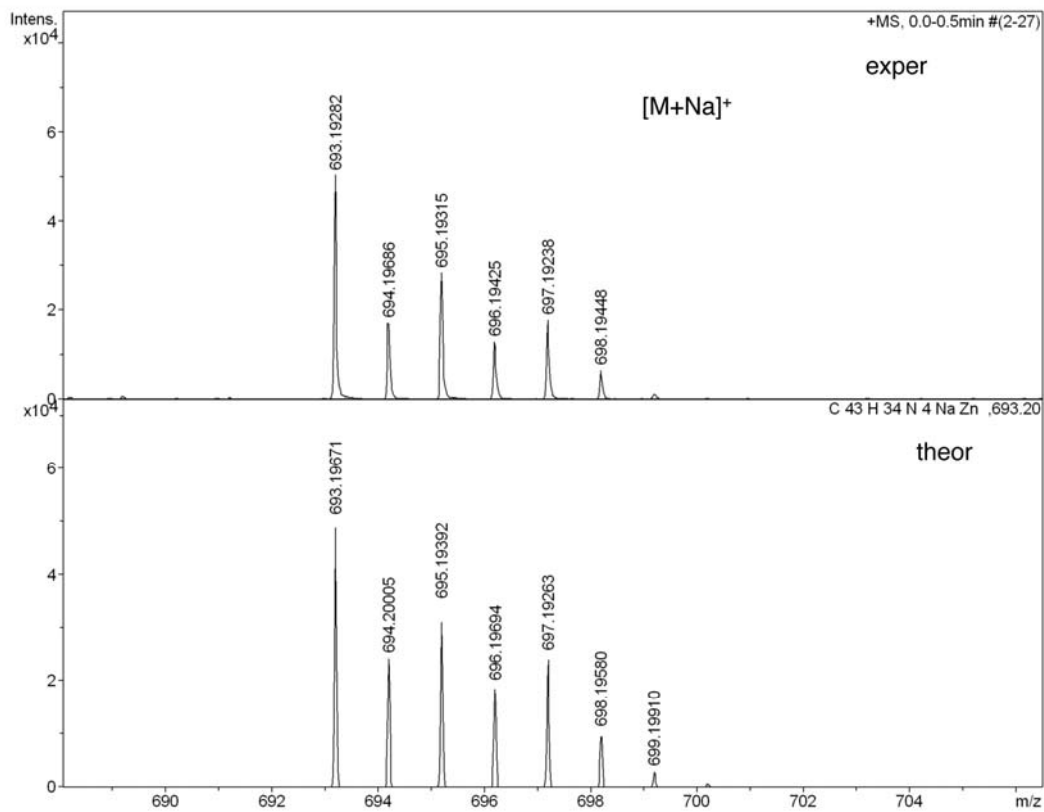
Figure S 3. ^1H NMR of zinc (II) 10,20-bis(tolyl)-15-mesitylporphyrin **2-Zn** (300 MHz, CDCl_3)

Analysis Info
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 Method tune_wide_pos.m
 Sample Name
 Comment dcm/MeOH

Acquisition Date 4/15/2011 11:04:06 AM
 Operator Marie-José Penouilh
 Instrument micrOTOF-Q 56

Acquisition Parameter

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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e ⁻ Conf	N-R rule
693.19282	1	C 43 H 34 N 4 Na Zn	100.00	693.19671	3.9	5.6	100.0	28.5	even	ok

Figure S 4. ESI HRMS spectrum of zinc (II) 10,20-bis(tolyl)-15-mesitylporphyrin **2-Zn** (positive mode)

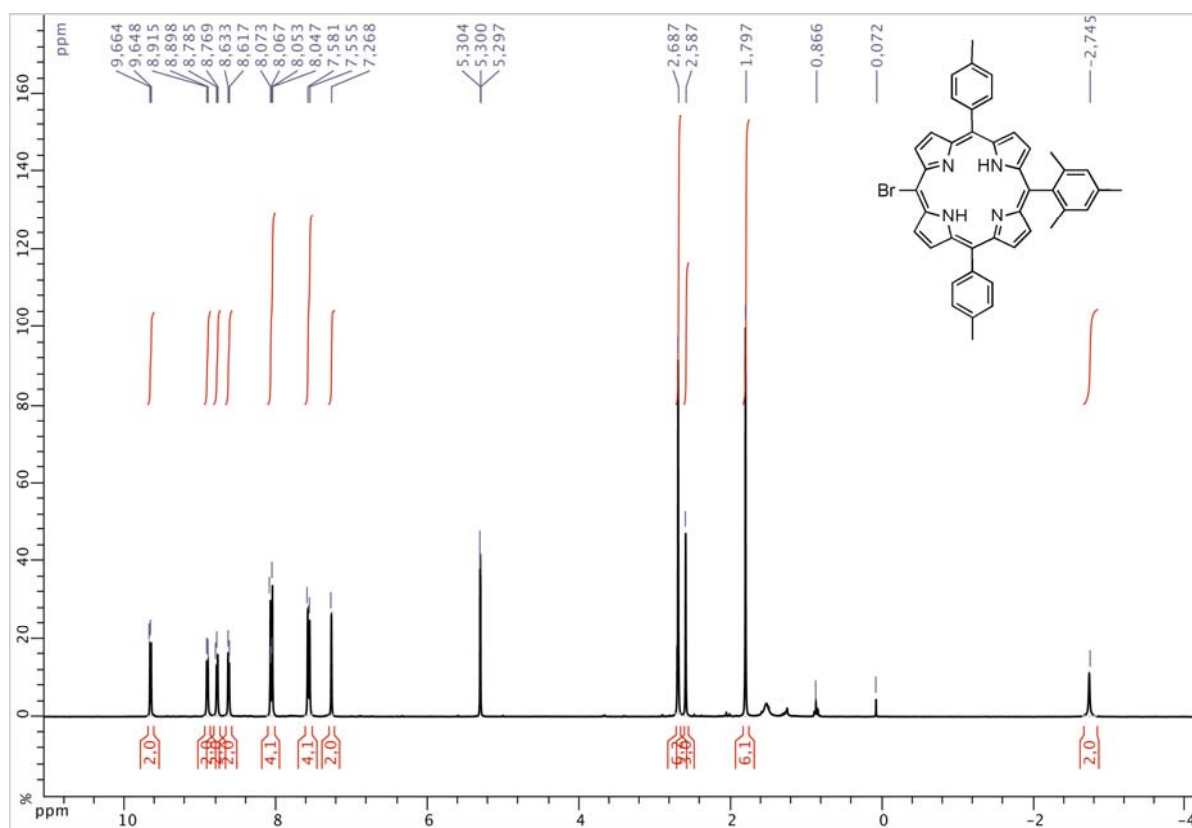


Figure S 5. ¹H NMR of 5-bromo-10,20-bis(tolyl)-15-mesitylporphyrin **3** (300 MHz, CD₂Cl₂)

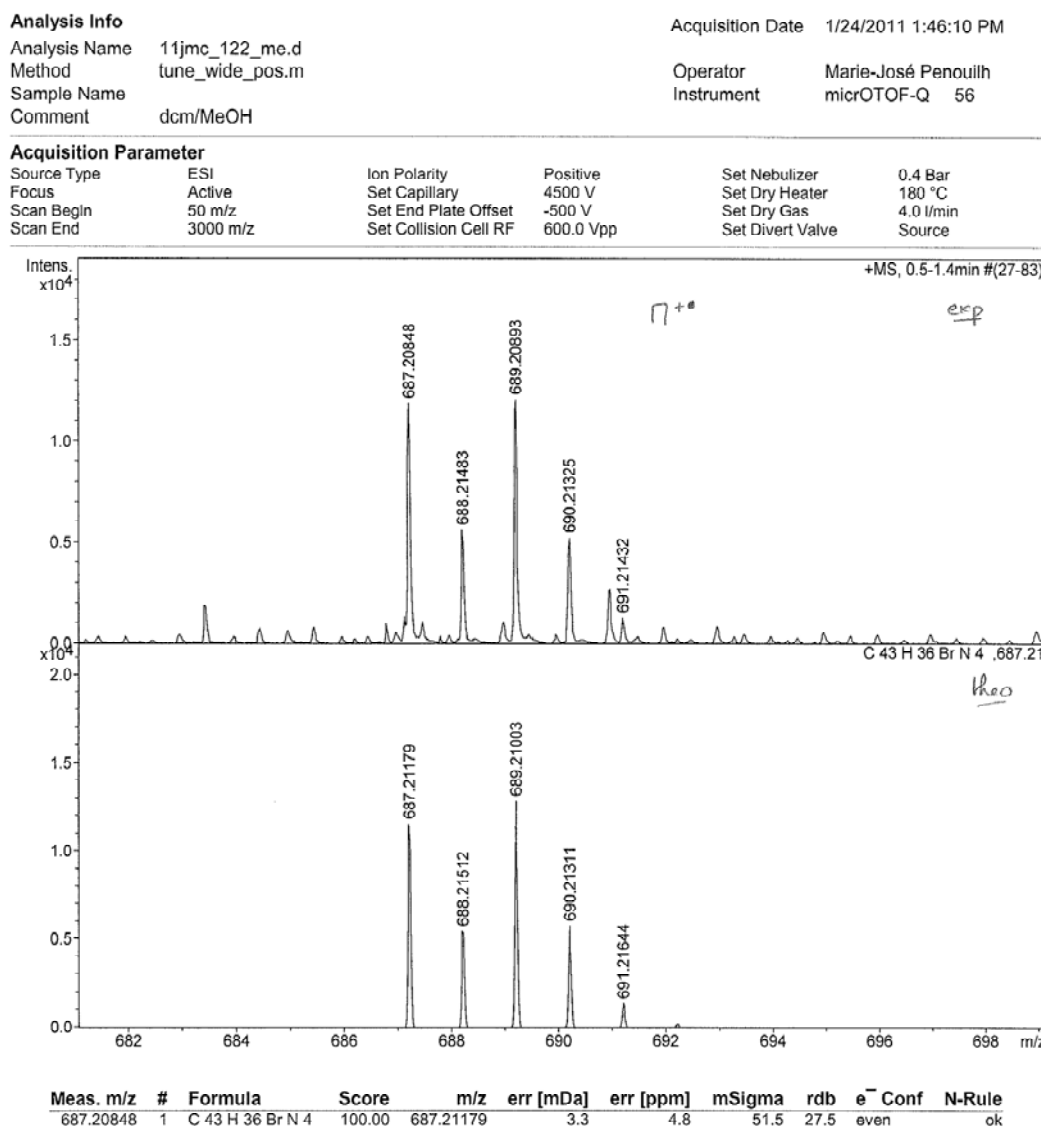


Figure S 6. ESI HMRS spectrum of 5-bromo-10,20-bis(tolyl)-15-mesitylporphyrin **3** (positive mode)

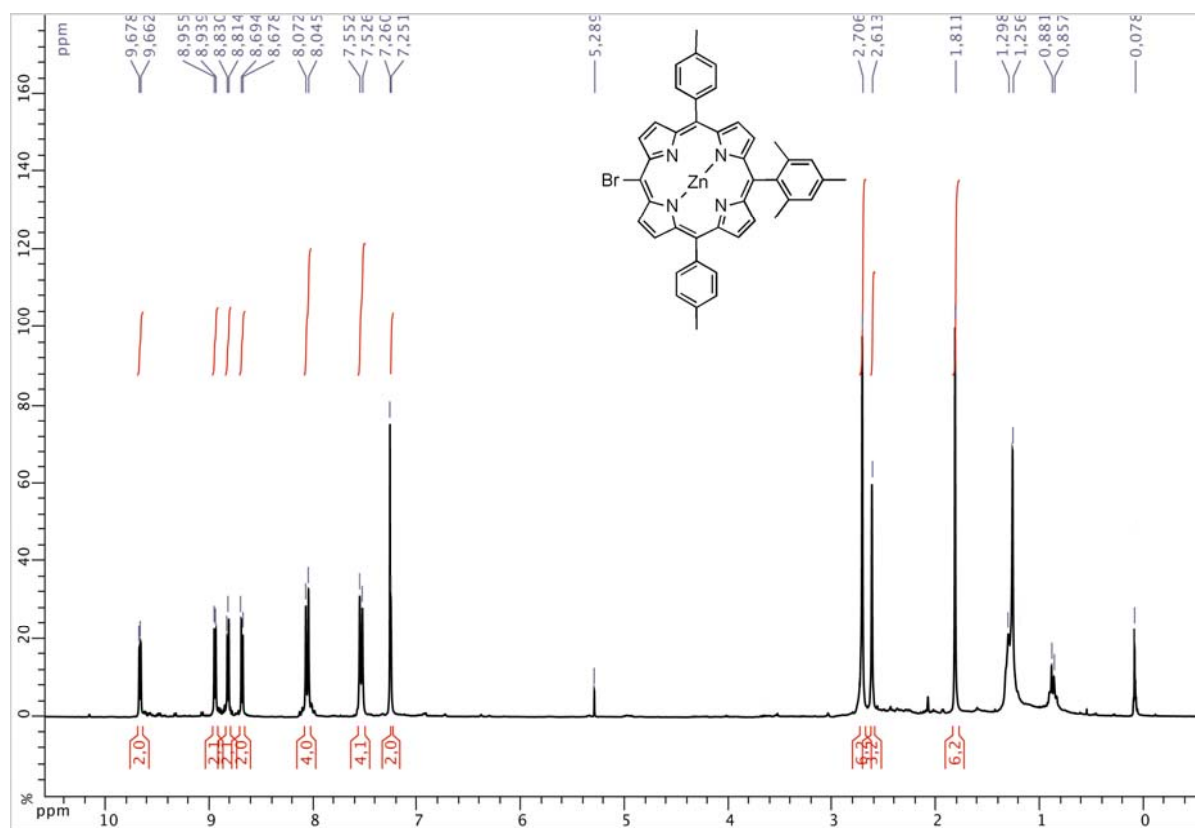


Figure S 7. ^1H NMR of zinc(II) 5-bromo-10,20-bis(tolyl)-15-mesitylporphyrin **4** (300 MHz, CDCl_3)

Analysis Info

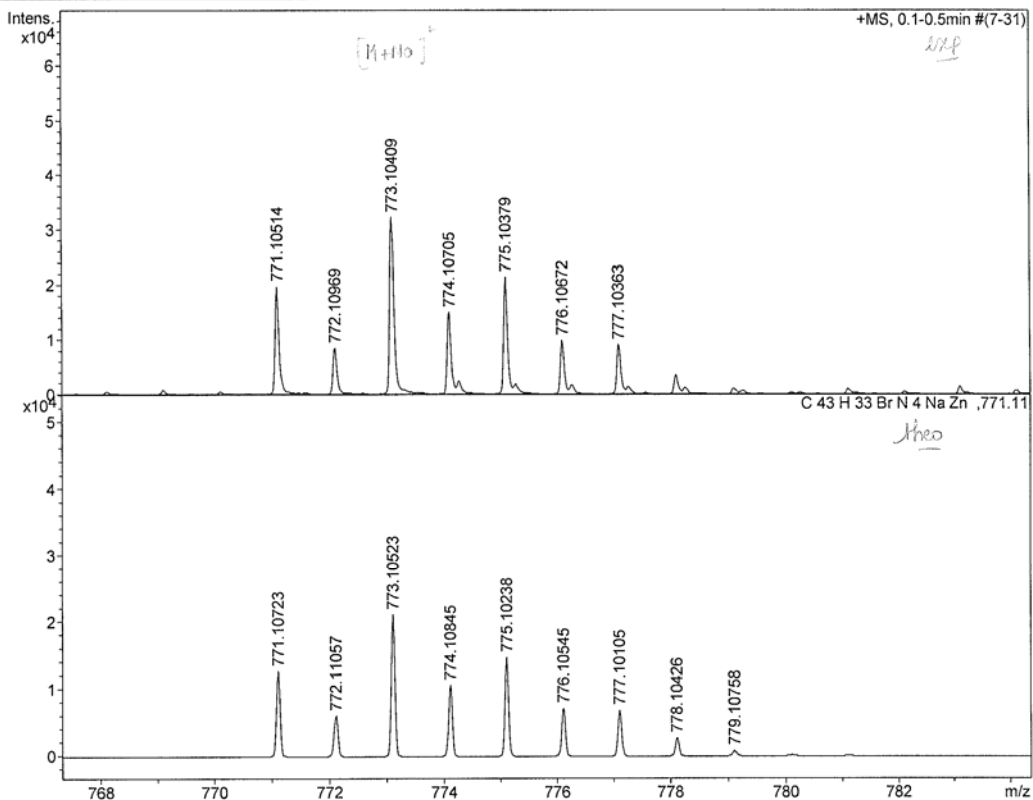
Analysis Name 11jmc_125_b_me.d
 Method tune_wide.m
 Sample Name
 Comment DCM/MeOH

Acquisition Date 2/4/2011 3:39:56 PM

Operator Fanny Chaux
 Instrument micrOTOF-Q 56

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Formula	Score	m/z	err [mD a]	err [pp m]	mSig ma	rdb	e ⁻ Conf	N-R ule
771.10514	1	C 43 H 33 Br N 4 Na Zn	100.00	771.10723	2.1	2.7	181.8	28.5	even	ok

Figure S 8. ESI HMRS spectrum of zinc(II) 5-bromo-10,20-bis(tolyl)-15-mesitylporphyrin **4** (positive mode)

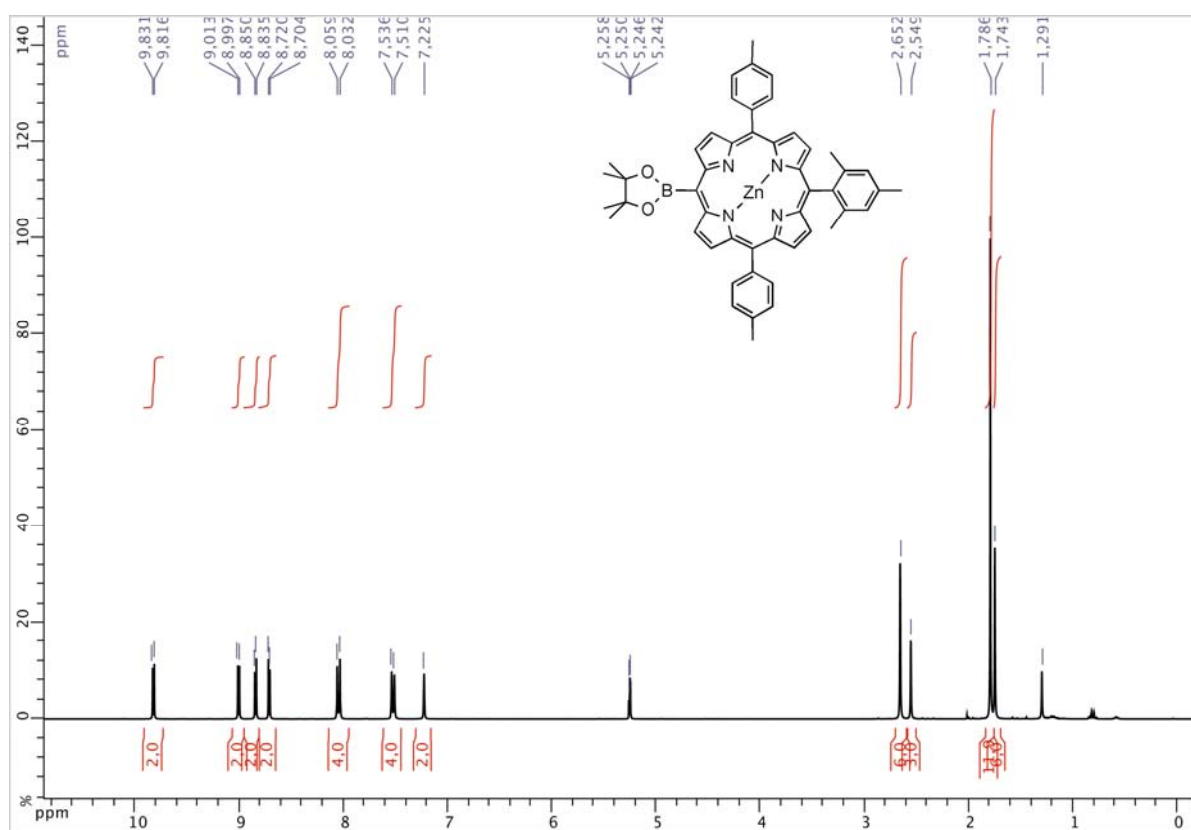


Figure S 9. ^1H NMR of zinc(II) 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10,20-bis(tolyl),15-mesitylporphyrin **5** (300 MHz, CD_2Cl_2)

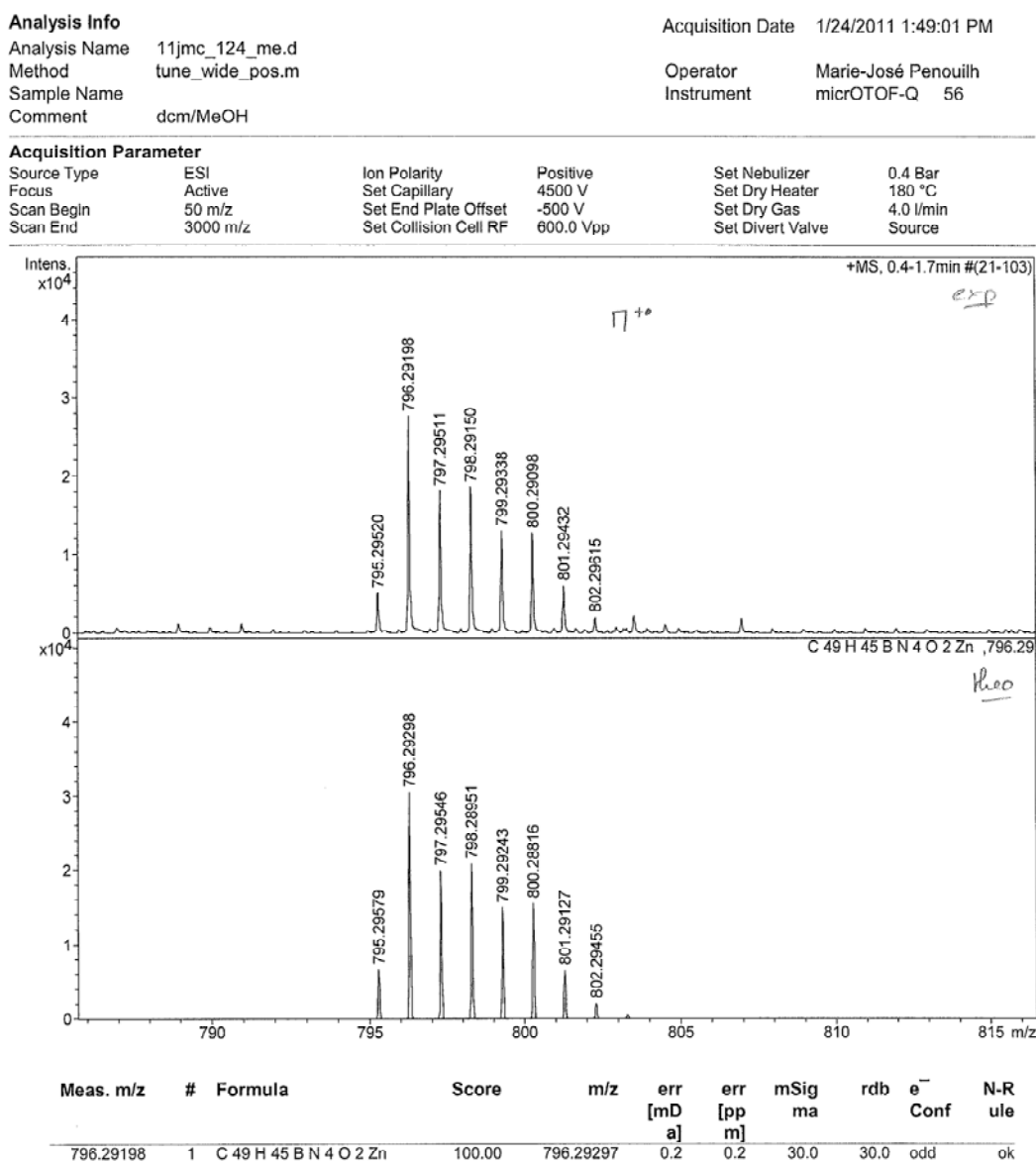


Figure S 10. ESI HMRS spectrum of zinc(II) 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10,20-bis(tolyl),15-mesitylporphyrin **5** (positive mode)

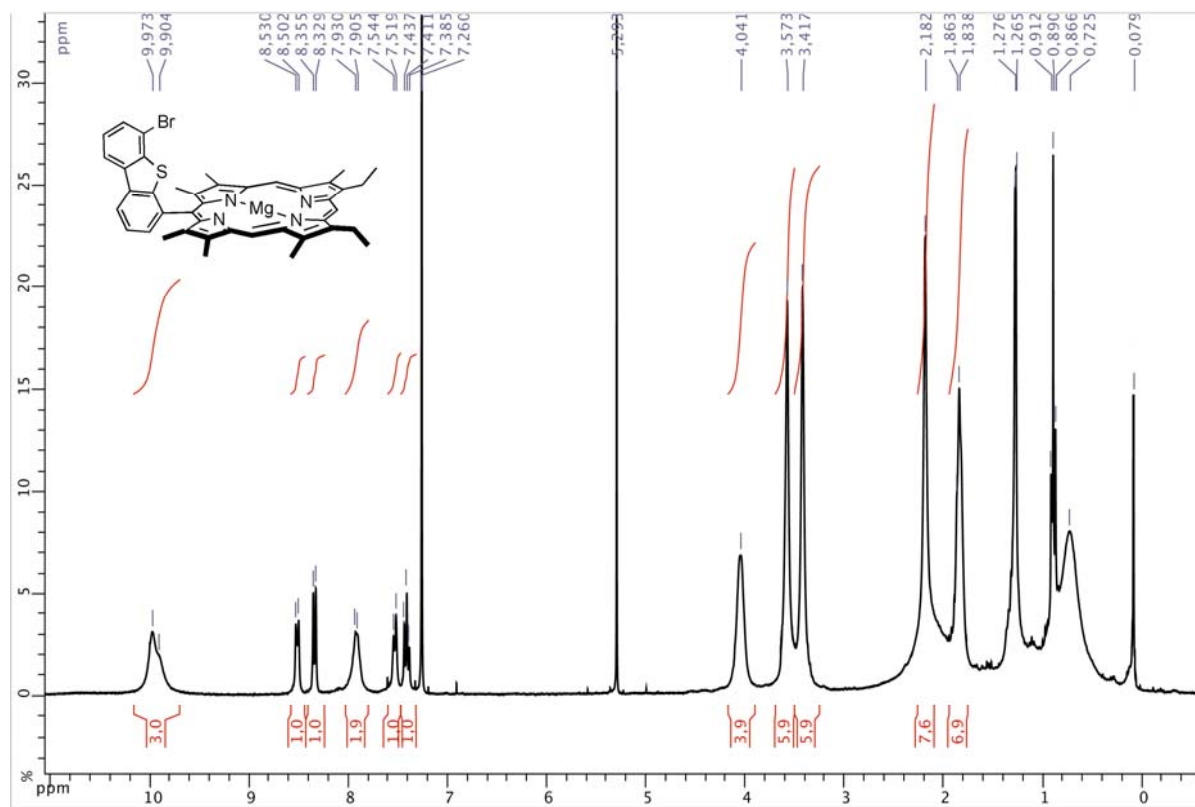


Figure S 11. ^1H NMR of magnesium(II) 5-(4-(bromodibenzothien-6-yl))-(12,17-diethyl-2,3,7,8,13,18-hexamethyl)-porphyrin **6Mg** (300 MHz, CDCl_3)

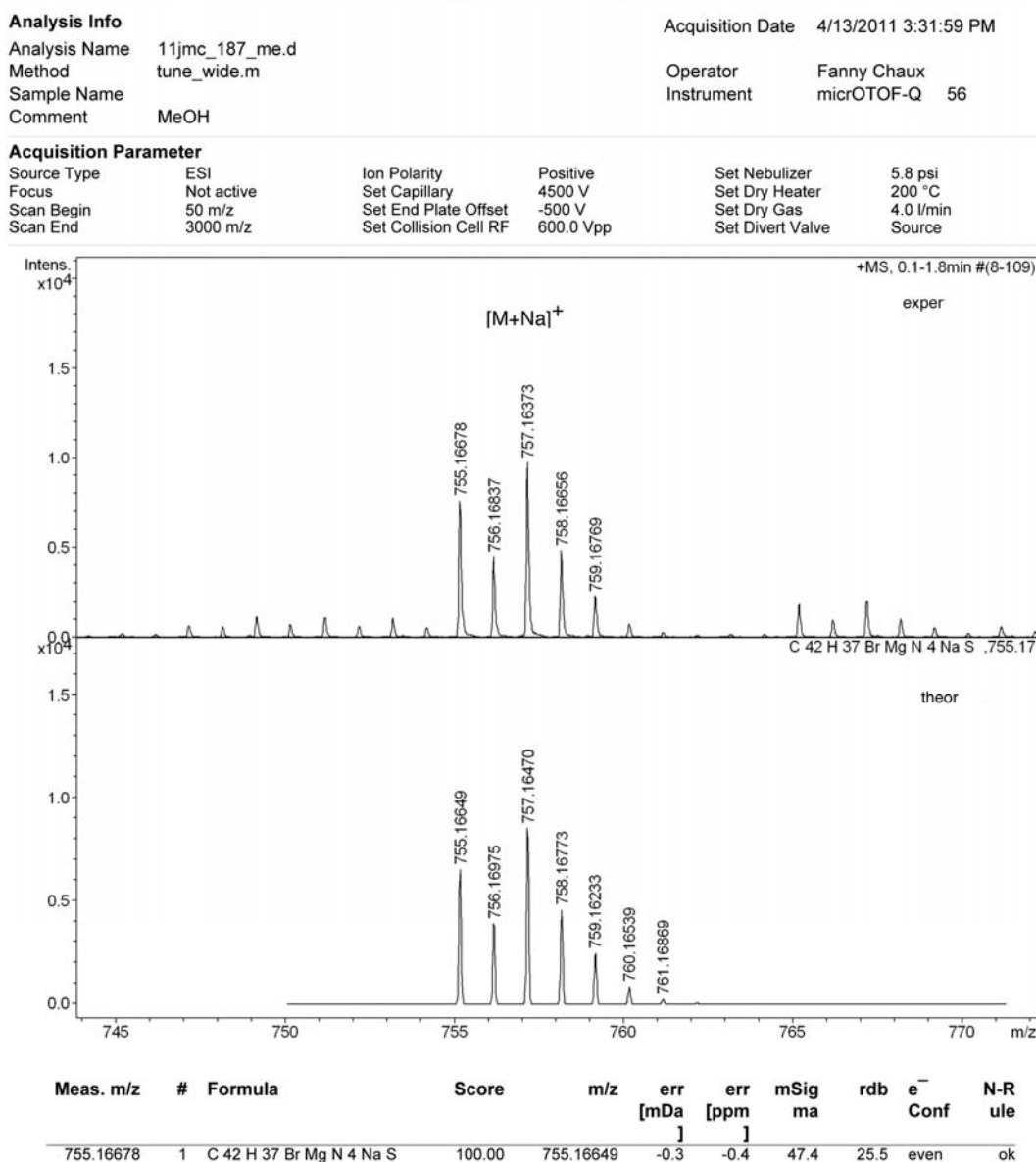


Figure S 12. ESI HRMS spectrum of magnesium(II) 5-(4-(bromodibenzothien-6-yl))-(12,17-diethyl-2,3,7,8,13,18-hexamethyl)-porphyrin **6Mg** (positive mode)

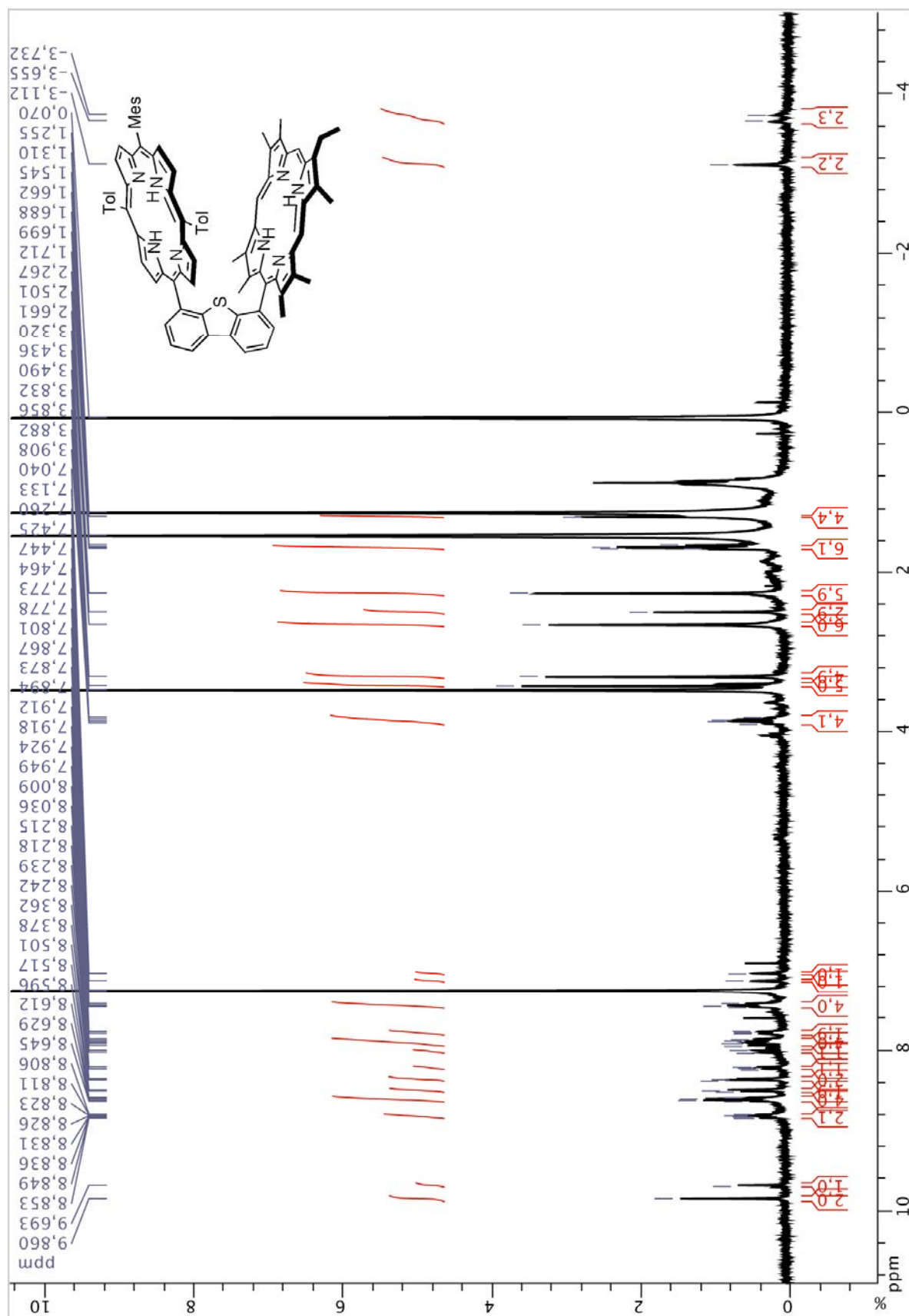


Figure S 13. ¹H NMR of 5-{4-[(12,17-diethyl-2,3,7,8,13,18-hexamethyl)-porphyrin-5-yl]-dibenzothien-6-yl}-10,20-bis-tolyl-15-mesitylporphyrin **7** (300 MHz, THF-d⁸)

Analysis Info		Acquisition Date	1/24/2011 10:41:10 AM
Analysis Name	11jmc_138_me.d	Operator	Fanny Chaux
Method	tune_high.m	Instrument	micrOTOF-Q 56
Sample Name			
Comment	DCM/MeOH		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	190 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	2000.0 Vpp	Set Divert Valve	Source

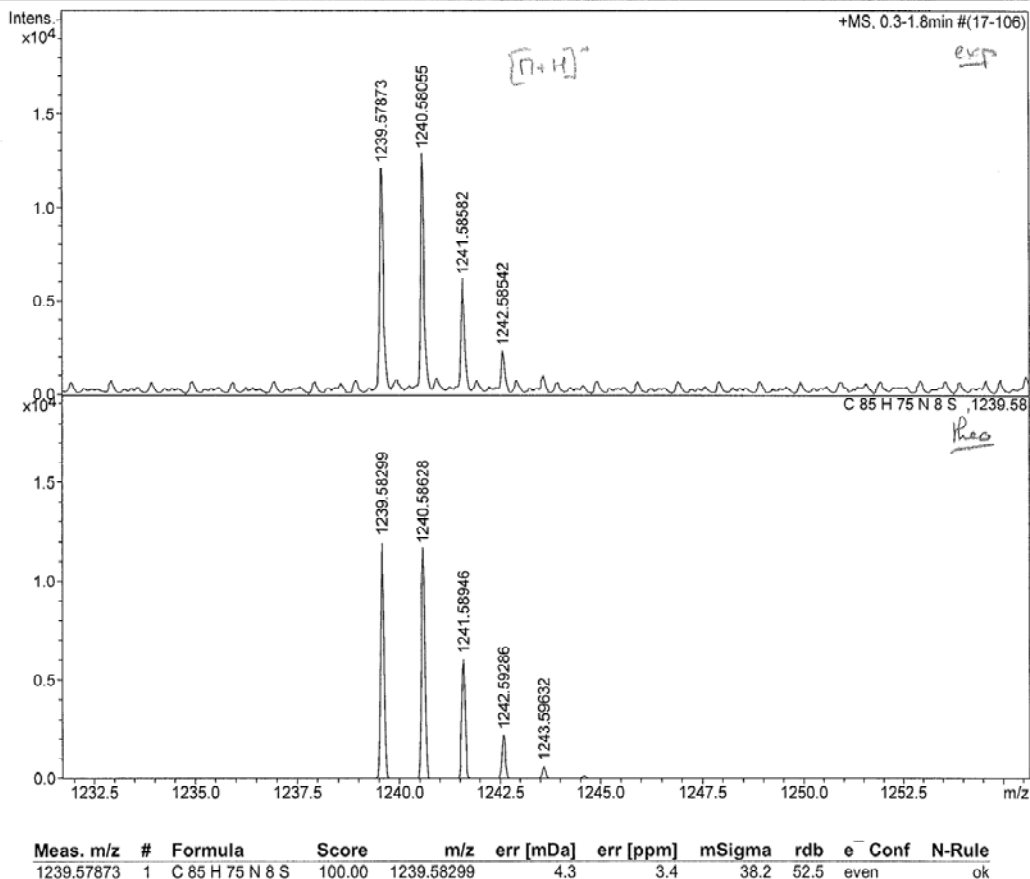


Figure S 14. ESI HMRS spectrum of 5-{4-[(12,17-diethyl-2,3,7,8,13,18-hexamethyl)-porphyrin-5-yl]-dibenzothien-6-yl}-10,20-bis-tolyl-15-mesitylporphyrin **7** (positive mode)

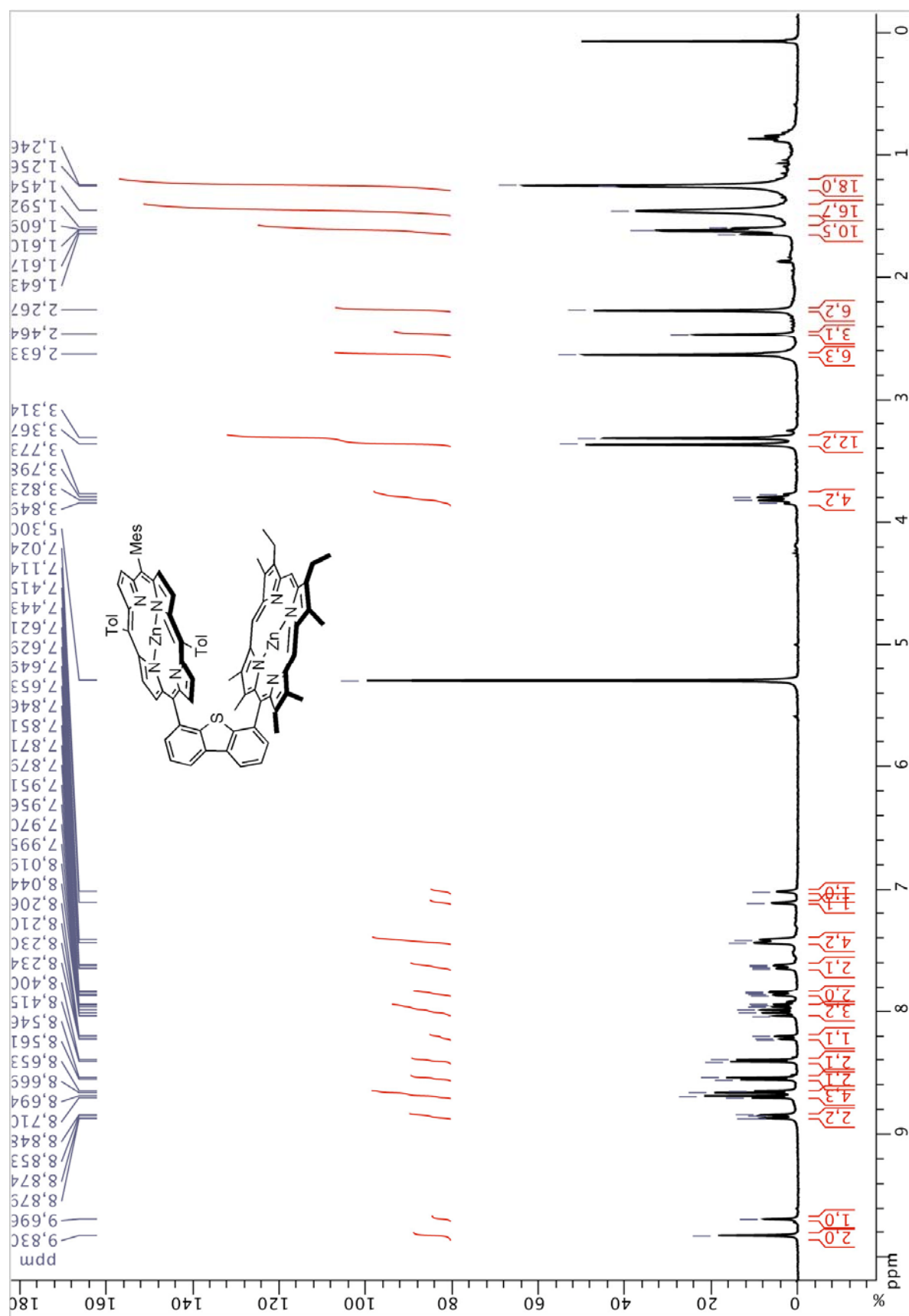


Figure S 15. ^1H NMR of zinc(II) 5-{4-[zinc(II) (12,17-diethyl-2,3,7,8,13,18-hexamethyl)-porphyrin-5-yl]-dibenzothien-6-yl}-10,20-bis-tolyl-15-mesitylporphyrin **7Zn** (300 MHz, CD_2Cl_2)

Analysis Info
 Analysis Name 11jmc_133_me.d
 Method tune_high.m
 Sample Name
 Comment DCM/MeOH

Acquisition Date 1/24/2011 9:53:33 AM
 Operator Fanny Chaux
 Instrument micrOTOF-Q 56

Acquisition Parameter

Source Type ESI
 Focus Active
 Scan Begin 50 m/z
 Scan End 3000 m/z

Ion Polarity Positive
 Set Capillary 4500 V
 Set End Plate Offset -500 V
 Set Collision Cell RF 2000.0 Vpp

Set Nebulizer 0.4 Bar
 Set Dry Heater 190 °C
 Set Dry Gas 4.0 l/min
 Set Divert Valve Source

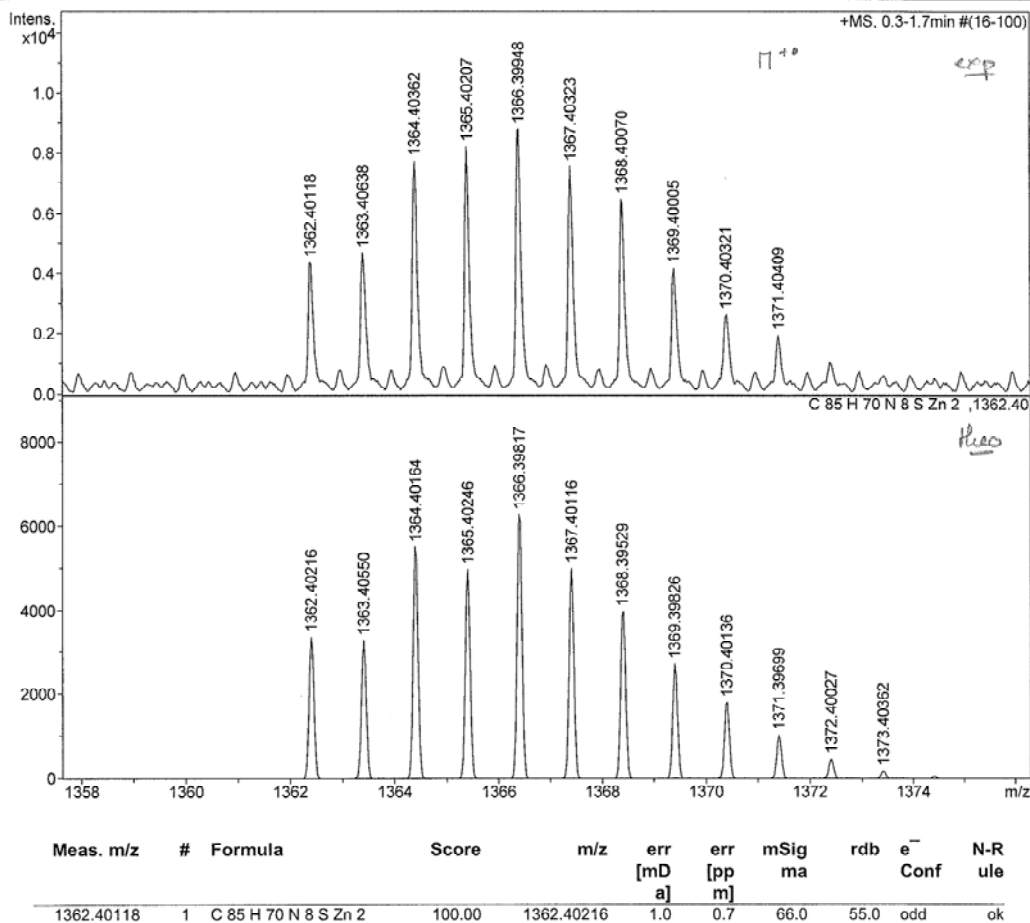


Figure S 16. ESI HMRS spectrum of zinc(II) 5-{4-[zinc(II) (12,17-diethyl-2,3,7,8,13,18-hexamethyl)-porphyrin-5-yl]-dibenzothien-6-yl}-10,20-bis-tolyl-15-mesitylporphyrin **7Zn** (positive mode)

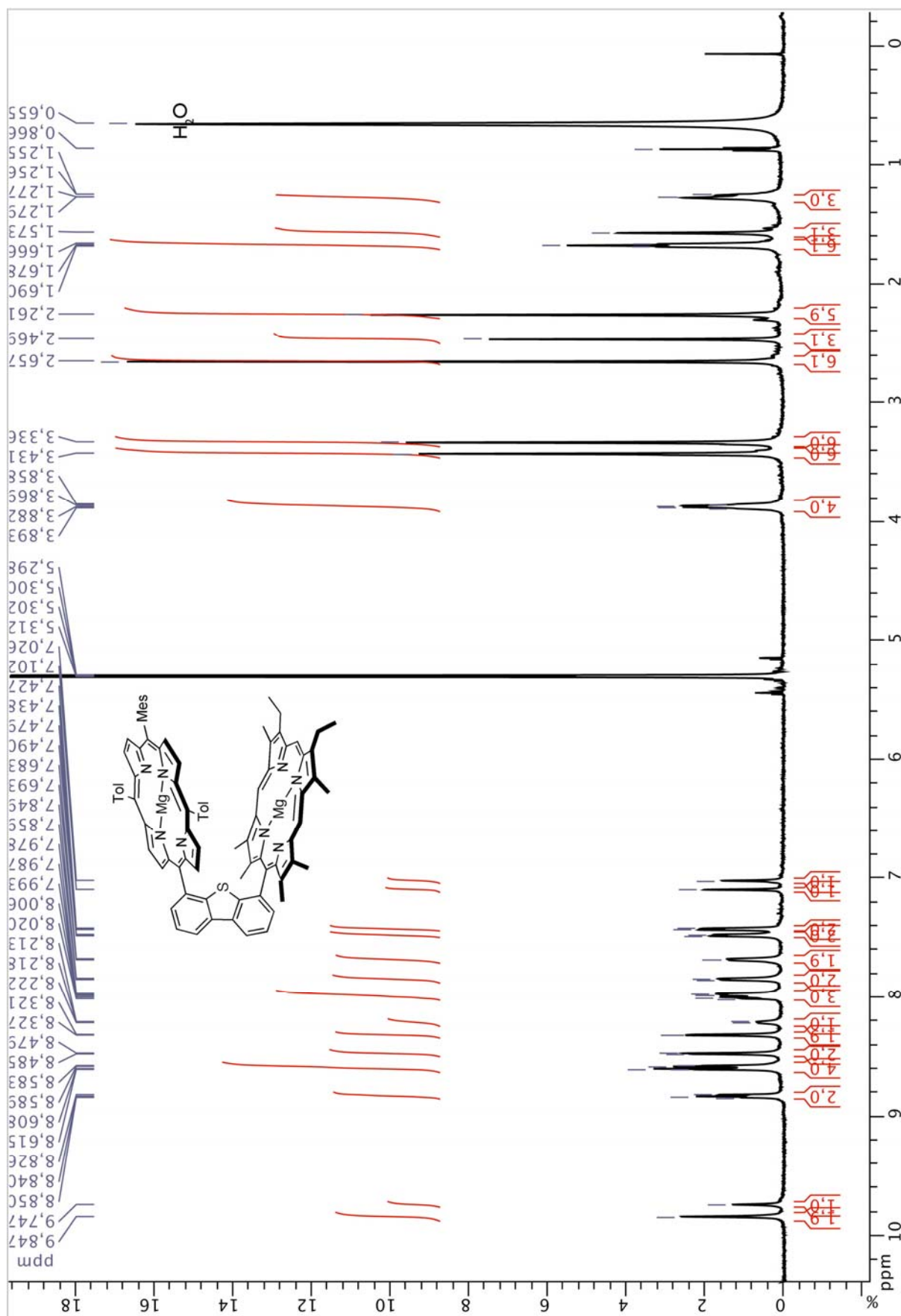
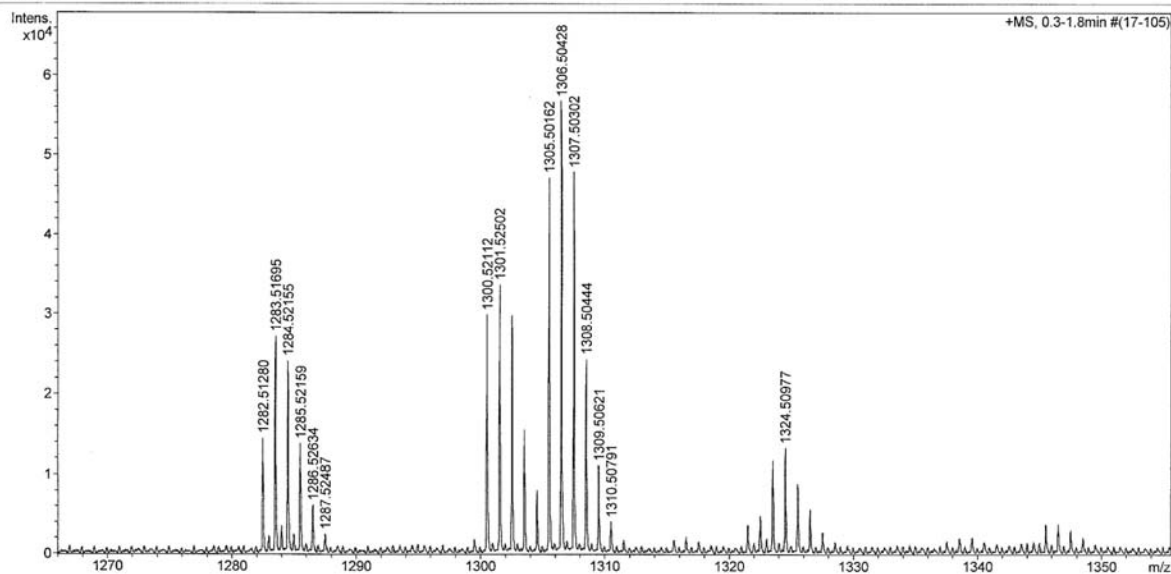


Figure S 17. ^1H NMR of magnesium(II) 5-{4-[magnesium(II) (12,17-diethyl-2,3,7,8,13,18-hexamethyl)-porphyrin-5-yl]-dibenzothiophen-6-yl}-10,20-bis-tolyl-15-mesitylporphyrin **7Mg** (300 MHz, CD_2Cl_2)

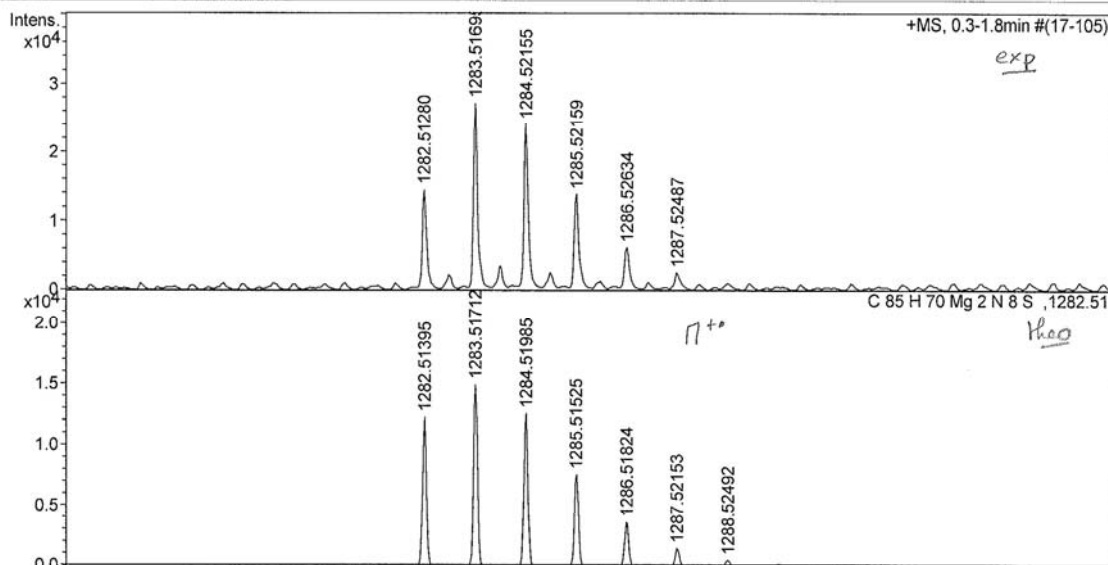
Analysis Info
 Analysis Name 11jmc_137_me.d
 Method tune_high.m
 Sample Name
 Comment DCM/MeOH
 Acquisition Date 1/24/2011 9:56:53 AM
 Operator Fanny Chaux
 Instrument micrOTOF-Q 56

Acquisition Parameter
 Source Type ESI Ion Polarity Positive Set Nebulizer 0.4 Bar
 Focus Active Set Capillary 4500 V Set Dry Heater 190 °C
 Scan Begin 50 m/z Set End Plate Offset -500 V Set Dry Gas 4.0 l/min
 Scan End 3000 m/z Set Collision Cell RF 2000.0 Vpp Set Divert Valve Source



Analysis Info
 Analysis Name 11jmc_137_me.d
 Method tune_high.m
 Sample Name
 Comment DCM/MeOH
 Acquisition Date 1/24/2011 9:56:53 AM
 Operator Fanny Chaux
 Instrument micrOTOF-Q 56

Acquisition Parameter
 Source Type ESI Ion Polarity Positive Set Nebulizer 0.4 Bar
 Focus Active Set Capillary 4500 V Set Dry Heater 190 °C
 Scan Begin 50 m/z Set End Plate Offset -500 V Set Dry Gas 4.0 l/min
 Scan End 3000 m/z Set Collision Cell RF 2000.0 Vpp Set Divert Valve Source



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSig	rdb	e ⁻ Conf	N-R rule
1282.51280	1	C 85 H 70 Mg 2 N 8 S	100.00	1282.51395	1.1	0.9	109.8	55.0	odd	ok

Figure S 18. ESI HMRS spectrum of magnesium(II) 5-{4-[magnesium(II) (12,17-diethyl-2,3,7,8,13,18-hexamethyl)-porphyrin-5-yl]-dibenzothien-6-yl}-10,20-bis-tolyl-15-mesityl-porphyrin **7Mg** (positive mode)

3. Optical Spectra

Cpds	λ_{\max} (nm)		donor	accept.	Δ	τ_{Fdonor}	k_{ET}
	298 K	77 K	$\lambda_{(0-0)}$	$\lambda_{(0-0)}$	(nm)	(ns)	(ns^{-1})
2	643, 711	637, 694, 707, 735	643	-	-	15.3	-
2-Zn	597, 645	590, 644, 765	597	-	-	2.41	-
6Zn	580, 634	576, 632, 702, 785	580	-	-	1.92	-
6Mg	590, 642	588, 639, 646, 698, 735, 820	590	-	-	8.5	-
7	629, 651, 720	622, 643, 688, 704, 715	629	651	22	0.28	3.49
7Zn	584, 603, 654	577, 601, 658, 703, 778	584	603	29	0.13	7.29
7Mg	590, 616, 668	588, 605, 616, 667, 677, 758	590	616	26	0.51	1.87
8	584, 606, 655	576, 603, 661, 770	584	606	22	0.08	15.29
9	591, 645	579, 596, 654, 709, 771	591	645	54	0.13	7.20
10	584, 607, 657	565, 593, 652, 693, 759	584	607	23	0.08	15.58
11 ⁴	629, 697	623, 689	629	-	-	18.0	-
11Zn ⁴	581, 636	583, 643, 720	581	-	-	1.95	-
12 ⁴	629, 696	623, 690	629	-	-	17.3	-
12Zn ⁴	580, 635	581, 639, 721	580	-	-	1.70	-

Table S 1. Luminescence data for mono- and bis-porphyrins (in 2-MeTHF, uncertainties of the λ_{\max} are ± 1 nm).

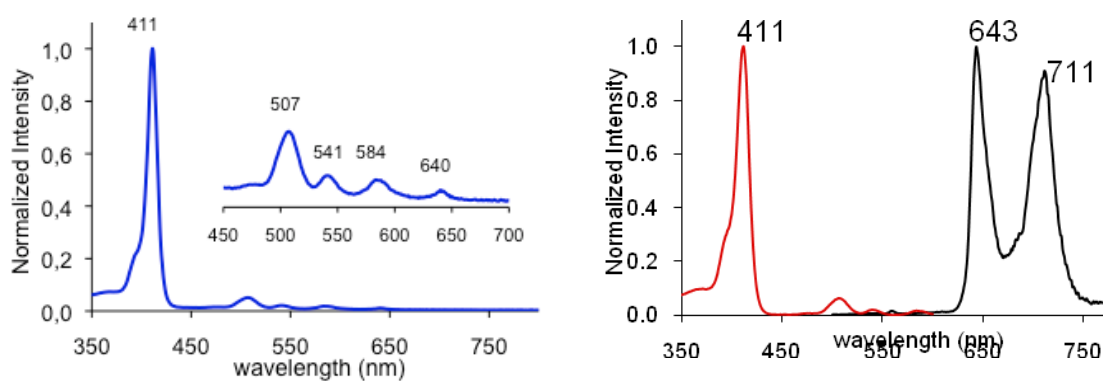


Figure S19. Optical spectra of **2** in 2-MeTHF (— absorption spectrum, — emission spectrum ($\lambda_{\text{exc}}=505$ nm), — excitation spectrum ($\lambda_{\text{emi}}=643$ nm))

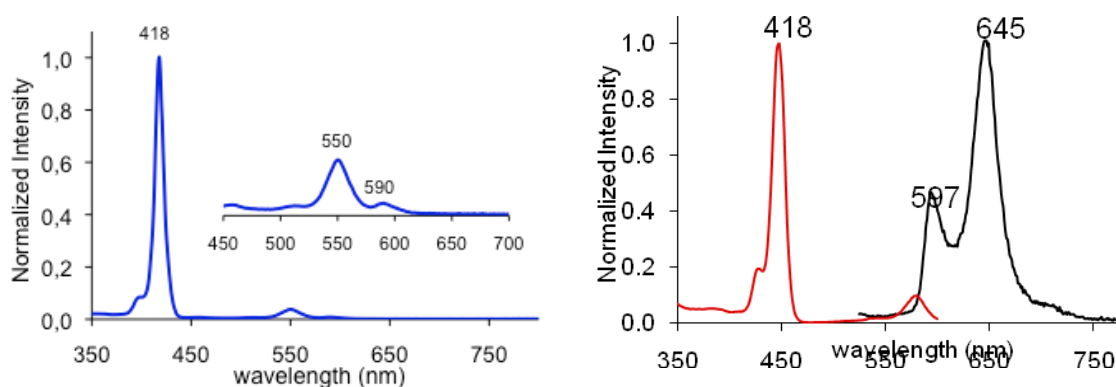


Figure S 20. Optical spectra of **2-Zn** in 2-MeTHF (— absorption spectrum, — emission spectrum ($\lambda_{\text{exc}}=505$ nm), — excitation spectrum ($\lambda_{\text{emi}}=645$ nm))

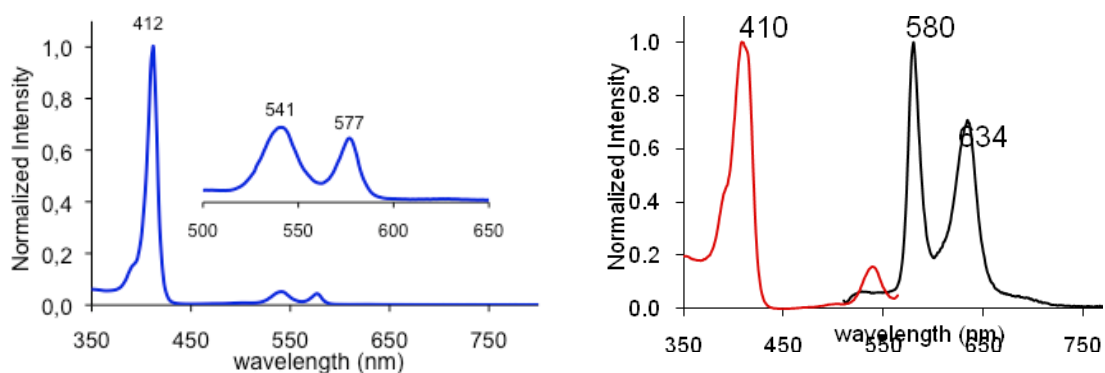


Figure S 21. Optical spectra of **6Zn** in 2-MeTHF (— absorption spectrum, — emission spectrum ($\lambda_{\text{exc}}=495$ nm), — excitation spectrum ($\lambda_{\text{emi}}=580$ nm))

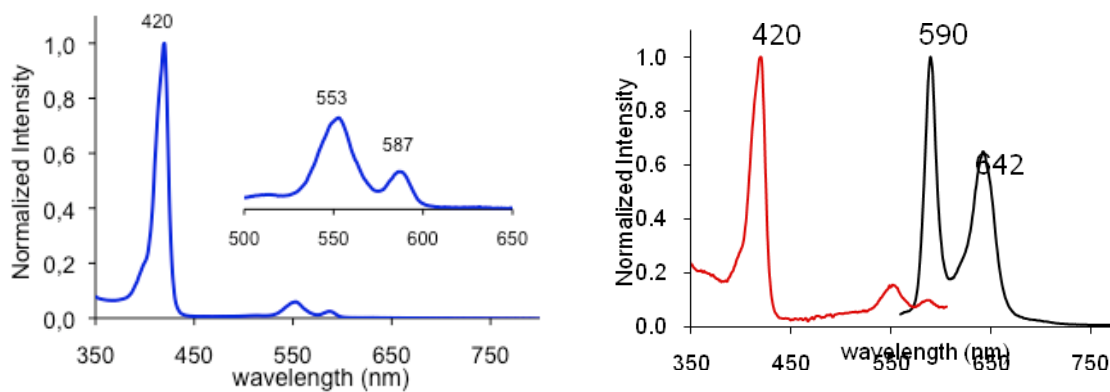


Figure S 22. Optical spectra of **6Mg** in 2-MeTHF (— absorption spectrum, — emission spectrum ($\lambda_{\text{exc}} = 545 \text{ nm}$), — excitation spectrum ($\lambda_{\text{emi}} = 640 \text{ nm}$))

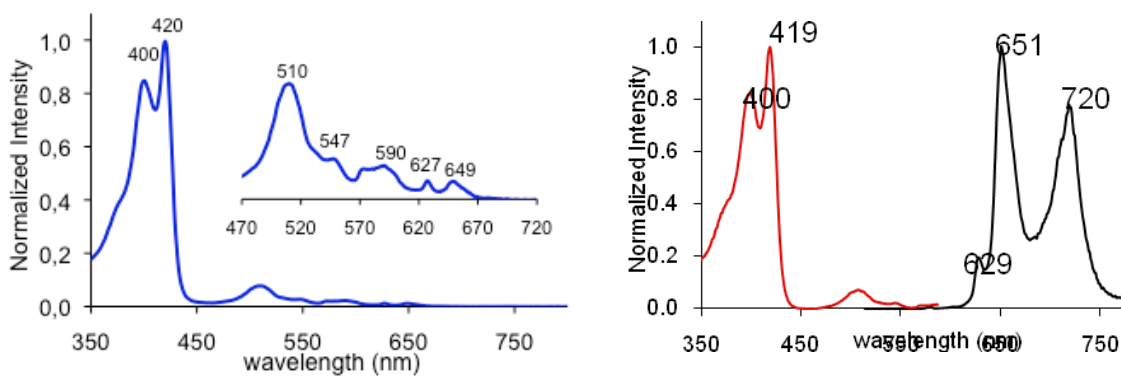


Figure S 23. Optical spectra of **7** in 2-MeTHF (— absorption spectrum, — emission spectrum ($\lambda_{\text{exc}} = 495 \text{ nm}$), — excitation spectrum ($\lambda_{\text{emi}} = 651 \text{ nm}$))

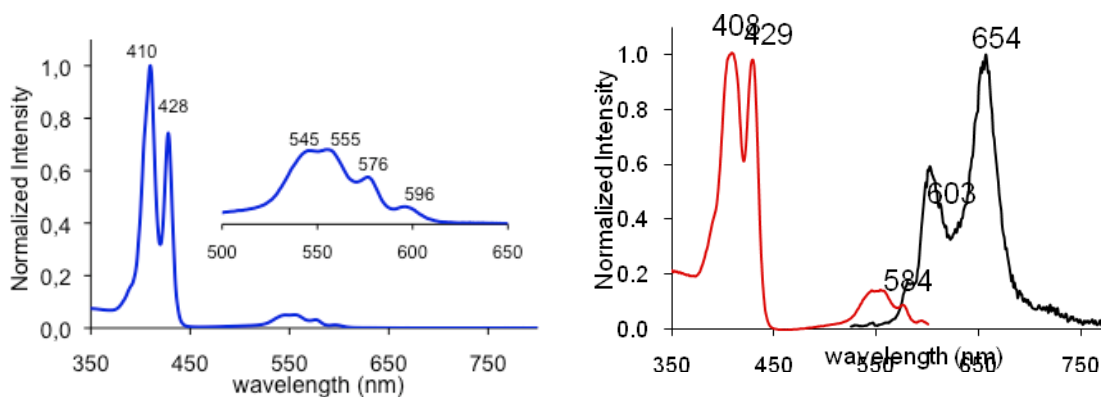


Figure Sv24. Optical spectra of **7Zn** in 2-MeTHF (— absorption spectrum, — emission spectrum ($\lambda_{\text{exc}} = 505 \text{ nm}$), — excitation spectrum ($\lambda_{\text{emi}} = 654 \text{ nm}$))

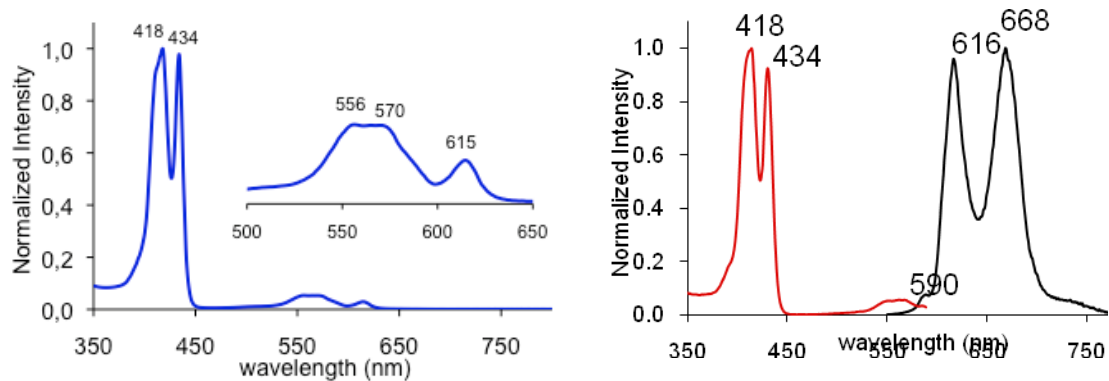


Figure S 25. Optical spectra of **7Mg** in 2-MeTHF (— absorption spectrum, — emission spectrum ($\lambda_{\text{exc}}=530$ nm), — excitation spectrum ($\lambda_{\text{emi}}=616$ nm))

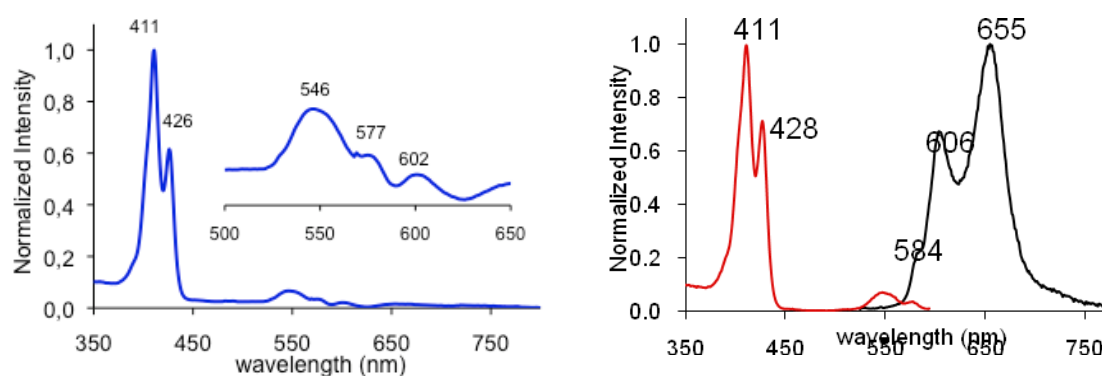


Figure S 19. Optical spectra of **8** in 2-MeTHF (— absorption spectrum, — emission spectrum ($\lambda_{\text{exc}}=505$ nm), — excitation spectrum ($\lambda_{\text{emi}}=655$ nm))

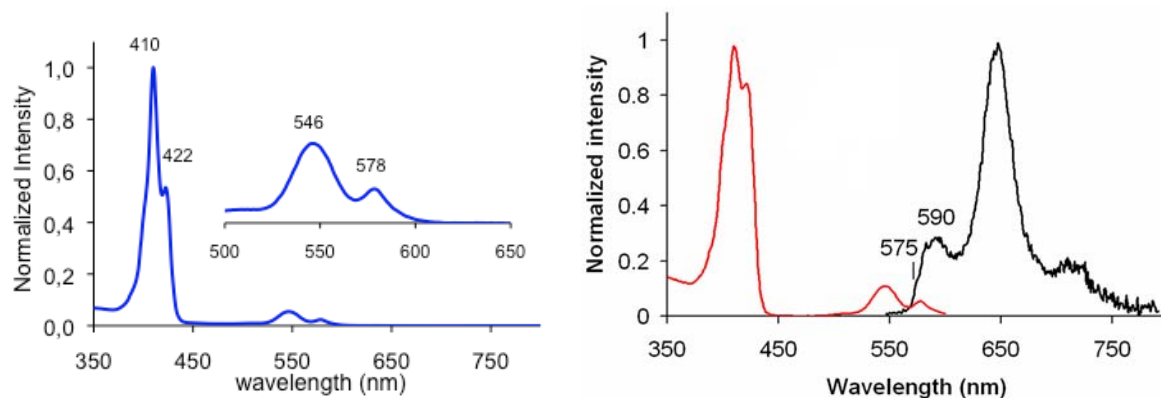


Figure S 27. Optical spectra of **9** in 2-MeTHF (— absorption spectrum, — emission spectrum ($\lambda_{\text{exc}}=525$ nm), — excitation spectrum ($\lambda_{\text{emi}}=645$ nm))

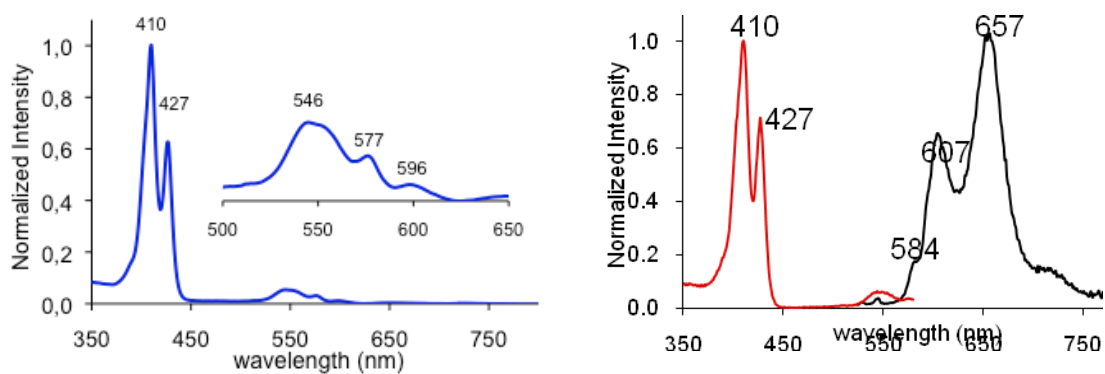


Figure S 28. Optical spectra of **10** in 2-MeTHF (— absorption spectrum, — emission spectrum ($\lambda_{\text{exc}}=505$ nm), — excitation spectrum ($\lambda_{\text{emi}}=655$ nm))

4. Comments on J/Δ relationship

In the singlet state, the Förster theory states that the rate for energy transfer, k_{ET} , is given by equation 1:⁵

$$k_{\text{ET}} = \frac{\Phi_{\text{F}}^{\circ}(\text{D})}{\tau_{\text{F}}^{\circ}(\text{D})} \kappa^2 \left(\frac{9000 (\ln 10)}{128 \pi^5 n^4 N_{\text{a}}} \right) \int_0^{\infty} F_{\text{D}}(\lambda) \varepsilon_{\text{A}}(\lambda) \lambda^4 d\lambda \quad (1)$$

where $\Phi_{\text{F}}^{\circ}/\tau_{\text{F}}^{\circ} = k_{\text{F}}^{\circ}$ is the radiative rate constant of the donor, κ^2 is the relative orientation factor of the transition moments of the donor vs acceptor, r is the donor-acceptor separation, n is the refractive index, N_{a} is the Avogadro's number, λ is the wavelength, F_{D} is the donor fluorescence intensity, ε_{A} is the absorptivity of the acceptor, and the integral represents the overlap between the two also called J . In Figure S , a qualitative relationship between J and the difference between the absorption and fluorescence maxima of the donor and acceptor, Δ , is obvious.

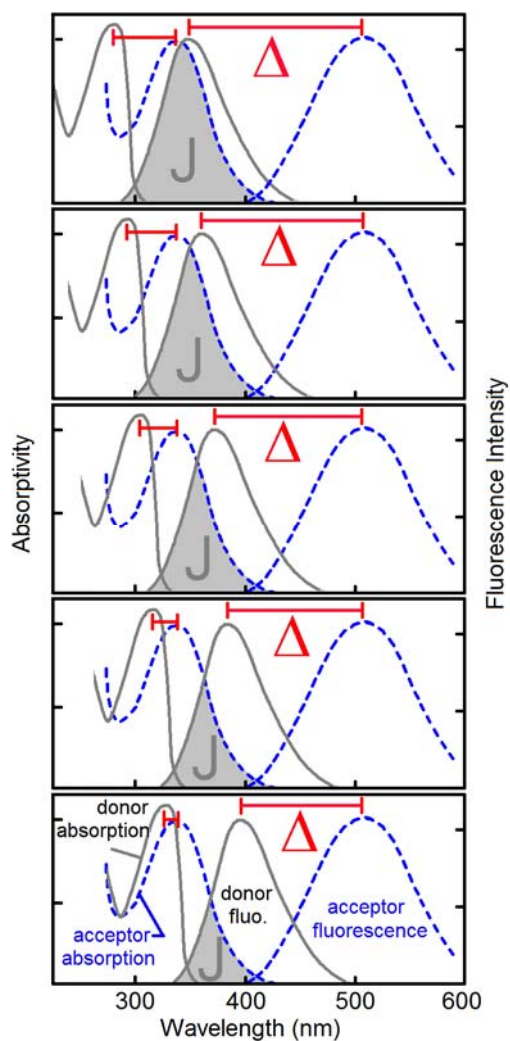


Figure S 29. Qualitative relationship between J and Δ .

5. References

1. L. Yu, K. Muthukumaran, I.V. Sazanovich, C. Kirmaier, E. Hindin, J.R. Diers, P.D. Boyle, D.F. Bocian, D. Holten and J. Lindsey, *Inorg. Chem.* 2003, **42**, 6629.
2. J.-M. Camus, R. Guillard, P.D. Harvey, paper in preparation.
3. G.D. Egorova, V.N. Knyukshto, K.N.; Solovev and M.P. Tsvirko, *Opt. Spektrosk.* 1980, **48**, 1101.
4. S. Faure, S. Stern, R. Guillard and P.D. Harvey, *J. Am. Chem. Soc.*, 2004, **126**, 1253.
5. T. Förster, *Ann. Phys.* 1948, **2**, 55.